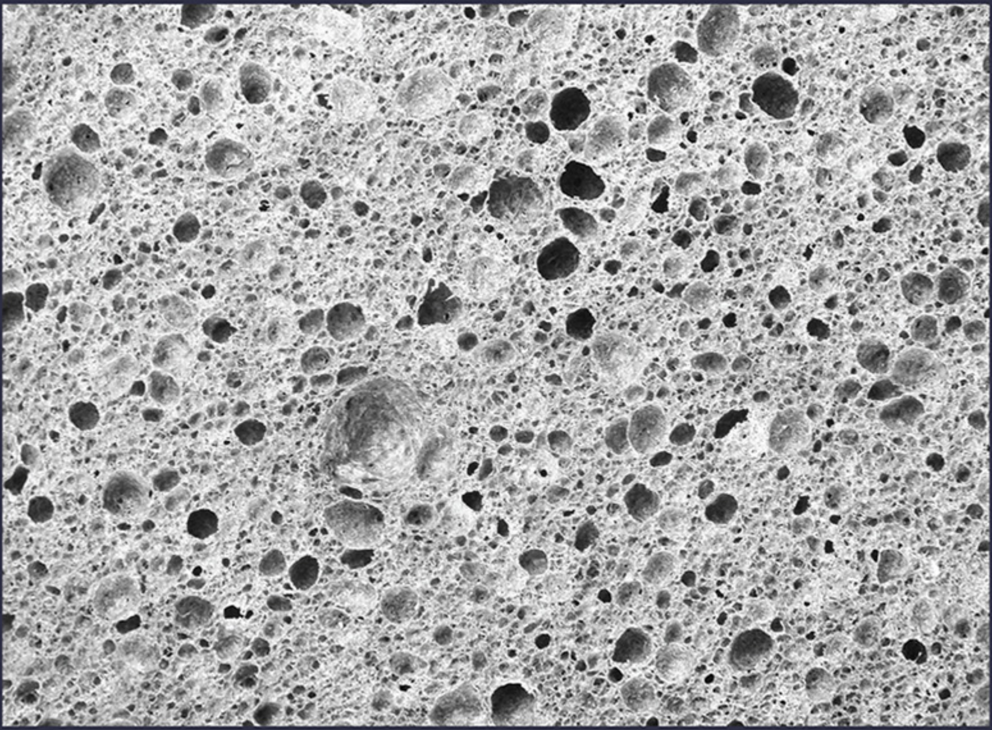
WOODHEAD PUBLISHING SERIES IN CIVIL AND STRUCTURAL ENGINEERING



INTEGRAL WATERPROOFING OF CONCRETE STRUCTURES

ADVANCED PROTECTION TECHNOLOGIES OF CONCRETE BY PORE BLOCKING AND LINING

ELSEVIER

MAHER AL-JABARI

Integral Waterproofing of Concrete Structures

Woodhead Publishing Series in Civil and
Structural Engineering

Integral Waterproofing of Concrete Structures

Advanced Protection Technologies of Concrete by Pore Blocking and Lining

Maher Al-Jabari

Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

ELSEVIER

WOODHEAD
PUBLISHING
An imprint of Elsevier

Woodhead Publishing is an imprint of Elsevier
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States
The Boulevard, Langford Lane, Kidlington, OX5 1GB, United Kingdom

Copyright © 2022 Elsevier Ltd. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

ISBN: 978-0-12-824354-1 (print)

ISBN: 978-0-12-824355-8 (online)

For information on all Woodhead Publishing publications
visit our website at https://www.elsevier.com/books-and-journals

Publisher: Matthew Deans
Acquisition Editor: Gwen Jones
Editorial Project Manager: Rachel Pomery
Production Project Manager: Kamesh Ramajogi
Cover Designer: Vicky Pearson

Typeset by MPS Limited, Chennai, India

ELSEVIER Book Aid International
Working together
to grow libraries in
developing countries
www.elsevier.com • www.bookaid.org

Contents

List of contributors

Maher Al-Jabari Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine; Chem-Crete Europe, Holic, Slovakia

Radi Al-Rashed International Chem-Crete Corporation, Richardson, TX, United States

Michael E. Ayers Global Pavement Consultants, Inc., Fithian, IL, United States

Doug Clement Construction Materials Testing, Des Moines, IA, United States

Maen Husein Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, AB, Canada

Xinbao Yu Civil Engineering Department, University of Texas at Arlington, Arlington, TX, United States

About the author

Maher Al-Jabari is a full professor of chemical and environmental engineering at Palestine Polytechnic University, Palestine, and an international expert in the fields of waterproofing of construction materials, hazardous waste, and wastewater treatment. Having achieved breakthroughs in protecting cementitious materials from environmental attacks and provided industrial durability solutions for concrete, Prof. Al-Jabari has been involved in international R&D projects in these fields, with a distinguished industrial record. Al-Jabari accomplished his industrial experience in International Chem-Crete Co., Richardson, TX, United States, starting as a director of manufacturing and then directing Chem-Crete R&D activities that led to patented crystallization waterproofing technology.

Preface

Water is the spirit, the aggressor, and the savior of concrete structures. Without water, concrete does not exist because the cement cannot harden into a paste that binds the concrete as a composite material. Then, water penetration and interaction with concrete motivate and activate most concrete attacks: Water is the transporter of many harmful materials and it establishes the medium for physical interactions and chemical and biochemical reactions threatening concrete integrity and durability. At the same time, water is the key actor for the functionality of various protection and waterproofing mechanisms that create shields for defending attacks. This is achieved through physical and chemical interactions of water with internally added waterproofing materials and the redesign of the pore structure of the cement paste. Consequently, water and concrete establish a unique triple helical relationship, the analysis of which requires a knowledge of concrete chemistry, structure, formulations, performance, and transport phenomena.

The fundamentals of these aspects are commonly established on a ground of civil engineering and are then extended deeply toward the chemical and material engineering fields. Basically, concrete technology is a subfield of material engineering as it combines its key aspects of structure, properties, processing, and performance. It is laid on the basics of chemical engineering when it comes to the kinetics of concrete reactions and the transport processes associated with concrete hardening and occur during its service life. In addition, the formulations, setting mechanisms, and protection actions of waterproofing materials are based on chemical technology. Overall, this field is an interdisciplinary topic. I have been inspired to write this book after establishing this understanding of the crosslinking of these engineering fields.

I chose to undergo the enjoyable endeavor of writing this book capitalizing on my solid industrial experience in the field of construction chemicals while coming from a chemical engineering academic background and having the opportunity to teach material science for many years. I have been involved in industrial activities for developing, formulating, manufacturing, and investigating the performance of patented internal waterproofing systems. During the development of my industrial career, I visualized the key aspects that can form the full engineering spectrum required for industrial and academic staff participating in this field. When I started my industrial career in this field, more than 20 years ago, minimal published materials existed in the scientific literature: most of the knowledge was spread in industrial guides, technical documents of the companies, and patents. Then, in the last few years, many scientific and engineering aspects of waterproofing technology have been published in research and review papers. This situation of scattered knowledge motivated me for writing a full integrated material in one book. In 4 of the 12 chapters, I invited five experts from civil and chemical engineering backgrounds to participate with me to enhance some topics. After making an extensive review of patents and publications in this filed, I realized that some waterproofing technologies are improperly presented. This could be partly related to the lack of a sufficient knowledge of some material formulations and mechanisms among some authors, most of the knowledge that I gained through my industrial career and R&D activities. I have established enjoyable communications with R&D staff members from some well-known waterproofing companies: I invited some of them to be involved with me in another two chapters, but these attempts were not finalized, possibly, for reasons of time availability or industrial competitions. During my writing, I had to manage the challenge of presenting and explaining waterproofing technologies while maintaining professional ethics of nondisclosing proprietary information.

I recognized the need for such a book for serving R&D staff in waterproofing companies and universities as well as civil engineers working in designing and implementing concrete projects. The book assists researchers and graduate students in establishing a sufficient background for their research problems. This piece of knowledge will be positively reflected in concrete projects during material selection, specifications, design, and characterization as well as in failure analysis. The industrial spread of durable concrete which endeavors the future of advancing concrete technology leads to foreseeing that civil, chemical, and/or material engineering syllabus will include more specialized courses in this field.

The book responds to the demand of R&D staff and project engineers for having an integrated engineering book: it takes the reader from introductory chapters on concrete chemistry, structure, durability problems, and mix designs into waterproofing technologies. In order to understand the waterproofing mechanisms, the fundamentals of hydro-interactions with cementitious surfaces (not commonly covered in concrete books) are established in another unique introductory chapter. Then, after two general chapters on waterproofing approaches and categorizations, a distinct chapter is devoted for each type of internal waterproofing systems. In order to complete the spectra, the final chapter is devoted to external barriers detailing integral waterproofing cementitious coatings and summarizing polymeric systems for comparative purposes.

List of abbreviations and symbols

A	the cross-sectional area perpendicular to the flow direction
AAR	alkali aggregate reactions
A_b	the total surface area of the porous materials in contact with the fluid
ACI	American Concrete Institute
ACR	alkali−carbonate reactions
AFt	ettringite crystals
A_p	the total cross-sectional area of pores
ASR	alkali − silica reactions
ASTM	American Society for Testing and Materials
BSE	Back-scattered Electron
BSEM	Back-scattered (mode scanning) Electron microscopy
C	the concentration of a component
C_1	the concentration of a component at side 1
C_2	the concentration of a component at side 2
c_i	the concentrations of adsorbate in the fluid phase
c_e	the equilibrium concentration of adsorbate in the fluid phase
c_p	the specific heat of concrete
C_3A	tricalcium aluminate $3CaO \cdot Al_2O_3$
C_4AF	calcium ferroaluminate $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
$C_6AS_3H_{32}$	ettringite
CC	cementitious coatings
CH	calcium hydroxides
CNFs	carbon nanofibers
CNTs	carbon nanotubes
C-S-H	calcium silicate hydrates
C_3S	tricalcium silicate $3CaO \cdot SiO_2$
C_2S	dicalcium silicate $2CaO \cdot SiO_2$
C/S	the ratio of calcium oxide to silicon oxide
D	the mass diffusivity
d_p	the size of particle
DP	dampproofing
$D(RH)$	the particle mobility diameter at a given RH
D_h	the diameter of the dry particle.
DOT	Departments of Transportations
DCE	dual-crystallization waterproofing engineered topical treatment
DCE_{HG}	the hygroscopic active ingredients in DCE
DCE_{HPL}	the hydrophilic active ingredients in DCE
DCE_{HPB}	the hydrophobic active ingredients in DCE
E	the activation energy of the reaction
EDS	Energy Dispersive Spectroscopy

EDX	Energy Dispersive X-ray
EPDM	ethylene propylene diene monomer
f_r	the roughness factor or the ratio of actual solid/liquid interface over the geometric surface
f	the friction factor of flow
$\boldsymbol{f_c}$	the compressive strength
$\boldsymbol{f_s}$	the fractional surface area of solid touching the water drop or the fractional contact of the solid/liquid
$\boldsymbol{f_t}$	the tensile strength
FTIR	Fourier-transform infrared
GGBFS	Ground granulated iron blast-furnace slag
GF(RH)	hygroscopic growth factor as a function of relative humidity (RH)
GPR	ground-penetrating radar
H	the mean curvature
HDPE	high density polyethylene
HPC	high-performance concrete
HVFA	high-volume fly ash
IL	limestone cements
IR	infrared
ISAT	Initial Surface Absorption Test
ITZ	interfacial transition zone
$i(t)$	the water absorption per unit surface area of a porous material
j	the number of pores per unit surface area of the bulk absorbent
J_i	the diffusional flux of component i
j_t	the total number of pores on the surface of the porous material
K	a constant
$\mathbf{k}$	the permeability coefficient, or simply the permeability
k'	an empirical constant
k_1	the adsorption (forward) rate constant
k_2	the desorption (backward) rate constant
$\mathbf{k_o}$	a preexponential empirical constant
k_c	the rate constant for the accumulation of water vapor in the hygroscopic material
K_F	the index of adsorption capacity (Freundlich adsorption coefficient)
K_L	the Langmuir adsorption equilibrium constant
$\mathbf{k_r}$	the coefficient of reaction rate
k_s	the swelling rate coefficient
$\mathbf{k_{th}}$	the thermal conductivity of concrete
L	the distance across which the pressure drops
LS	lithium silicate
$L(t)$	the penetration distance into the pore
MCE	multicrystallization enhancer
m_e	the droplet mass of the hygroscopic material at equilibrium
m_h	the dry mass of the hygroscopic material
MIC	microbiologically influenced corrosion
MID	microbiologically influenced deterioration
MIP	mercury intrusion porosimetry
MFS	magnesium fluorosilicate
MW	the molar mass of water

m_w	the mass of adsorbed water on a hygroscopic crystal
n	the adsorption (Freundlich) intensity
NPs	nanoparticles
OPC	ordinary Portland cement
P	the pressure
P_a	the pressure of air at the interface with water
PB	polymeric barriers
PCM	phase change materials
PLC	Portland limestone cement
PMCC	polymer-modified cementitious coatings
PMTS	poly-methyl triethoxy silane
PRA	permeability-reducing admixtures
PRAH	permeability-reducing admixture for hydrostatic conditions
PRAN	permeability-reducing admixture for nonhydrostatic conditions
PS	potassium silicate
PVC	polyvinyl chloride
P^v	the vapor pressure of water
P^{sat}	the saturation pressure of water
P_w	the pressure of the bulk water
q	the flow rate
Q	the rate of heat transfer
$\mathbf{q_i}$	the concentrations of adsorbate on the solid surface
$\dot{q}$	the rate of internal heat generation (or consumption) per unit volume
$\mathbf{q_e}$	the equilibrium concentration of adsorbate on the surface
q_m	the maximum adsorption capacity of the surface
r	the radius of the capillary or the pore
R	the universal gas constant
r_c	the reaction rate (or cement hydration rate)
R_d	the radius of curvature
Re	the Reynold number
RH	the relative humidity
S	the capillary sorption coefficient or the sorptivity
SAPs	superabsorbent polymers
SBS	styrene butadiene styrene
SCMs	supplementary cementitious materials
SEM	scanning electronic microscopy
SF	silica fume
SS	sodium silicate
TG	thermogravimetric
DTG	Derivative Thermogravimetry
ICP-AES	Inductive Coupled Plasma with Atomic Emission Spectroscopy
SRA	shrinkage-reducing admixtures
t	the time
T	the temperature
$\mathbf{T_1}$	the concrete temperature at location 1
$\mathbf{T_1}$	the concrete temperature at location 2
TEOS	tetraethyl orthosilicate
TOW	time of wetness (for the growth of organisms)
TPO	total pozzolan oxides

UV	ultra violet
V	the fluid velocity through a porous medium
$\mathbf{V_o}$	the superficial velocity of a fluid through a porous medium
V_p	the total volume of pores in a porous medium
V_b	the bulk volume of the porous material
VOC	volatile organic compounds
w_A	the work of adhesion
w/b	the water to binder ratio
w/c	water to cement ratio
w/cm	the water to cementitious material
WCA	the water contact angle
W_{cs}	the cumulative water absorption per unit area
W_e	the equilibrium swelling capacity of a gel
W_s	the mass fraction of water in a gel at a given time
WP	waterproofing
WR	water retention
XRD	X-ray diffraction
XRF	X-ray fluorescence
$\boldsymbol{\alpha}$	the degree of cement hydration
α_c	the thermal diffusivity of concrete
γ_{sa}	the surface/interfacial tension at the interface of solid − air
γ_{sw}	the surface/interfacial tension at the interface of solid − water
γ_{wa}	the surface/interfacial tension at the interface of the water − air
$\mathbf{\Delta H}$	the enthalpy changes of a reaction
$\mathbf{\Delta P}$	the pressure drop
ΔL	length of flow path.
ΔG_i	the change in Gibbs free energy at the interface
ε	the volume fraction of permeable empty space in a porous medium
θ	the contact angle between the liquid and the solid and the subscripts *a*, *w*, and s denote air, water, and solid phases.
θ_1	the contact angle between the liquid and a smooth surface of the solid sample
θ_2	the contact angle of the water−air interface
$\boldsymbol{\kappa}$	the hygroscopicity parameter
$\boldsymbol{\mu}$	the fluid dynamic viscosity
μ_i	the chemical potential of a component *i*
μ_v	the chemical potential of water in the atmosphere
$\mu_{w,h}$	the water activity/concentration in the hygroscopic material
ρ_c	the bulk density of concrete
$\boldsymbol{\rho_f}$	the fluid density
ρ_w	the density of water
ρ_h	the density of the dry hygroscopic material

Introduction to concrete chemistry

1

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

1.1 Introduction

Concrete is the most popular construction material, which has a widespread range of structural applications, under numerous environmental conditions and under various levels and types of mechanical loads. It is used in buildings, infrastructures, dams etc. Its suitability and durability require a set of mechanical, physical, and chemical characteristics in order to extend its service life. Concrete durability is defined according to Concrete Terminology by American Concrete Institute (ACI) [1], as "the ability of concrete to resist weathering action, chemical attack, abrasion, and other conditions of service." This performance is simply based on concrete chemistry. Concrete durability properties are determined by its chemical structure and porosity. These structural characteristics are determined by cement components and their reactions with water. Understanding concrete durability problems and solutions requires a sufficient knowledge about concrete chemistry.

The term concrete refers mainly to ordinary Portland cement (OPC) mixed with aggregates and traditional chemical admixtures. There are various types of admixtures and additives that are incorporated into the concrete mixture in order to improve its properties. The term modified or enhanced concrete is used to refer to concrete in which part of the cement is replaced by any kind of supplementary cementitious materials (SCMs), or any additional reactive materials. This chapter introduces the main cement components and the various types of concrete ingredients and it describes the cement hydration reactions and the associated thermal evolution processes. An introduction to cement composition and chemistry is provided for the purpose of establishing a common background for students, researchers, practicing engineers, production managers from various backgrounds of chemical, mechanical, and civil engineering. The chapter paves the road for the subsequent chapters on concrete structure, porosity, and transport processes that are involved with durability problems, and on the material selection and proportioning for watertight and durable concrete. In addition, it establishes the ground for understanding surface chemistry of concrete constituents and for describing the waterproofing technologies in the rest of the book chapters.

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00001-5

1.2 Concrete as a composite material

Composite materials are made by combining different constituent materials while maintaining different phases into a heterogeneous mixture, which has significantly different physical and/or chemical properties. When these phases are combined, they produce a material with uniform characteristics that are different from those of the individual constituents and phases. Concrete structure includes distinct phases of cement paste, aggregates, and air voids. Concrete structure may also include reinforcing steel bars. In typical concrete structures, the binding medium is formed from a combination of a hydraulic cement and water. According to ASTM C125−15b, Standard Definition of Terms Relating to Concrete and Concrete Aggregates [2], concrete is "a composite material that consists essentially of a binding medium within which are embedded particles or fragments of aggregate; in hydraulic cement concrete, the binder is formed from a mixture of hydraulic cement and water." According to ACI Concrete Terminology [1], concrete is a "mixture of hydraulic cement, aggregates, and water, with or without admixtures, fibers, or other cementitious materials."

Ordinary concrete is typically made by mixing OPC with water, in the presence of fine and coarse aggregates (e.g., sand and crushed rock particles). Cement is termed as a cementitious or hydraulic material that is composed of an inorganic material (or a mixture of inorganic materials) "that sets and hardens by chemical reaction with water and is capable of doing so under water" [2]. According to ACI Concrete Terminology [1], cement is "any of a number of materials that are capable of binding aggregate particles together." The paste is made of cement that hardens with water. Cement paste includes a hardened mixture of hydration products, bound and free water, and possibly other contents and unreacted cement. The paste volume fraction in concrete is about $25\% - 40\%$ [3].

Upon hardening, concrete forms a porous structure with a certain level of permeability for the flow of air and water. Porous concrete usually contains air voids that are unintentionally or intentionally incorporated in concrete structure for special applications [4]. The volume fraction of voids in the mixture of air-entrained concrete can be within the range of $4\%-8\%$ [3]. Cement mortars are made by mixing sand, cement, and water, excluding coarse aggregate while cement pastes are obtained by mixing cement and water.

From the perspective of material science, material structure may be described at various levels including macrostructure (e.g., by eye) and microstructure (magnified using a microscope), in addition to atomic and subatomic structures [5]. Here, the macrostructure and microstructure are discussed. At the macroscopic level, concrete structure is simply composed of two phases, which are aggregates dispersed in a matrix of the cement paste. For fully cured concrete, a possible inhomogeneity in the distribution of aggregates, paste, and voids can be ignored. A typical concrete structure of a plain concrete is shown in Fig. 1.1 [6]. The main phases of aggregates, cement paste, unreacted cement, and concrete pores are revealed.

At the microscopic level, the paste and aggregate phases are not homogeneous. The cement paste is weaker than aggregates [7]. More specifically, another paste phase with different structural characteristics exists at the interface between the aggregates and the bulk paste with a thickness in the range of 10−50 μm. It is

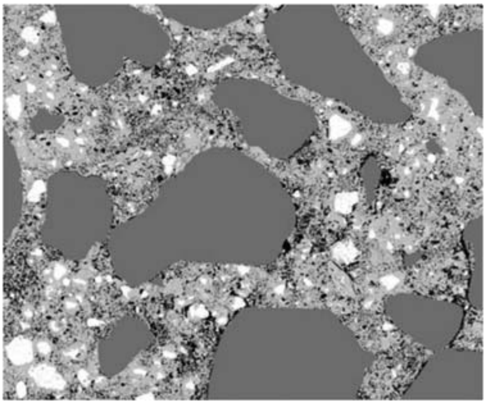


Figure 1.1 Structure of an OPC concrete at a water-to-cement (w/c) ratio of 0.5 and curing age of 7 days, revealing the various phases of aggregates, cement paste, and capillary pores (back-scattered electron images with a field of view of 1200 × 960 μm) [6].

generally weaker and more porous than either of the two distinct phases of aggregates and paste (see Chapter 2). In fact, every phase encloses other phases: the paste phase is heterogeneous with different phases including the solid paste, pores, microcracks, and air voids. Due to their natural structure, the aggregates themselves contain various types of mineral oxides and include microcracks and voids. On top of these phase descriptions, concrete structure may be maintained in a dynamic situation that changes with time, curing progress, chemical, and thermal environments including humidity and temperature. The concrete characteristics are the results of cumulative contributions of these major phases [8]. The concrete mixture and mix designs are discussed in Chapter 4. This chapter defines and describes the principal components of concrete and their main properties.

1.2.1 Concrete binder

Concrete hardens by a cementitious binder. According to ASTM C125−15b [2], the cementitious material is “an inorganic material or a mixture of inorganic materials that sets and develops strength by chemical reaction with water by formation of hydrates and is capable of doing so under water.” There are various natural and industrial materials that have cementing characteristics and can create bonding when mixed with water. These include Portland cements and SCMs. Portland cement is the most widely used hydraulic cements in concrete structures, which is based mainly on calcium silicate compounds. Other well-known types of cementing binders include fly ash, silica fume, slag cement, rice husk ash, and natural pozzolans (NPs), which are usually used in combination with Portland cement as a partial replacement of cement and thus termed as SCMs. The Portland cement is a fine material consisting of multicompounds and containing various mineral oxides, which are combined together through bonding created by thermal action, and then become reactive with water. As described in ACI CT-18 [1], ordinary Portland cement is the term used in the United Kingdom and elsewhere to designate the equivalent of American normal Portland cement or Type I cement; commonly abbreviated as OPC. More than one-third of the worldwide manufactured cements belongs to the OPC [9].

Portland cements are manufactured by a thermochemical processing at high temperature as shown schematically in Fig. 1.2. This is done in a kiln after mechanical operations of crushing, milling, and proportioning of natural raw materials of various mineral oxides. The raw materials include calcium carbonate ($CaCO_3$) obtained from limestone, as a source of calcium oxide (CaO), which represents 60%–67% of cement weight, and materials containing silicone oxide (SiO_2), such as sand or clay, which represents 17%–25% of cement weight [8]. Specific cement compositions are usually confirmed by using X-ray fluorescence analysis. For example, [10] reported that Type I cement used in their experimental work contained 65% and 20.5% for CaO and SiO_2, respectively. Also, [11] reported close values of 63.8% and 20.9% for CaO and SiO_2, respectively. Other important oxides include aluminum oxide (Al_2O_3), which comes from the raw materials (e.g., from clay) and represents 3%–8% of cement weight, and iron oxide (Fe_2O_3), which comes from the mechanical operation in steel machine, and represents 0.5%–6% of cement weight [8]. The cement usually includes other alkaline contents, which increases the alkalinity of concrete and impacts its durability. These minor constituents that are part of the raw materials include magnesia (MgO) at 0.1%–4% of cement weight, and soda and potash (Na_2O and K_2O) at 0.5%–1.3% of cement weight. In addition, other chemicals such as sulfur trioxide (SO_3) composing 1%–3% of cement weight are present, which comes from the combustion gases used for

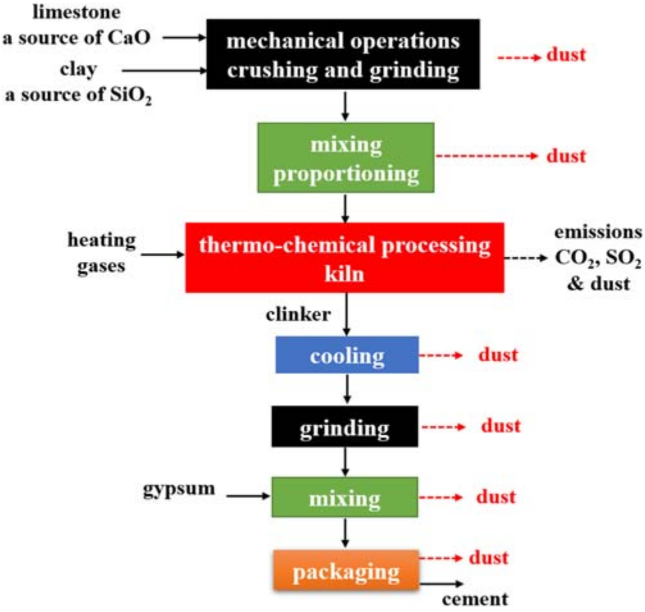


Figure 1.2 A block diagram of the cement manufacturing process.

heating the cement kiln. After the thermochemical processing, various silicate compounds are formed in the resulting clinker, obtained from the kiln. Then, the clinker is cooled, pulverized, and gypsum is added to it, for improving cement characteristics such as controlling its reactions with water (see Section 1.3).

Cement characteristics and chemical reactivity is governed by its particle size distribution, which is referred to as fineness [12]. Curves of size distribution (differential curves) for various types of cements are reported by [13]. The size of typical Portland cement powders ranges from 1 μm to 50 μm [14]. Nearly 95% of cement particles have sizes smaller than 45 μm and their average size is about 15 μm [12]. Liu et al. [10] reported a particle size of 13 mm for Type I cement by using a laser particle size analyzer. The particle size affects the reaction rate of cement hydration (see Section 1.3). Decreasing the particle size increases the surface area and thus increases the reaction rate of cement with water. The reaction rate then impacts the rate of heat evolution, which in turn has major impacts on concrete characteristics.

The Portland cement and its major silicate compounds are specified in ASTM C150 [15]. Various proportions of cement compounds can be used in various types of cements for obtaining different characteristics for different purposes and applications. According to ASTM C150 [15], there are five main types of cements (I − V): Type I is the most commonly used cement for general purposes. Similarly, type II is used for general purposes and when moderate sulfate resistance and moderate heat of reaction are required. Type III is used for applications requiring high early strength. Type IV is used for applications requiring low heat of hydration. Type V is used when a high sulfate resistance is required. Variations in cement compositions may occur in practical cases. The silicate compounds and typical compositions for types I, II and V are listed in Table 1.1, giving the chemical terminologies and the popular cement abbreviated notations. In these notations, C stands for calcium oxide (lime), S for silicone oxide (silica), A for alumina oxide, and F for iron oxide. The cement constituents include tricalcium silicate ($3CaO \cdot SiO_2$), abbreviated in cement notations as C_3S, dicalcium silicate ($2CaO \cdot SiO_2$), abbreviated as C_2S, tricalcium aluminate ($3CaO \cdot Al_2O_3$) abbreviated as C_3A, and tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) abbreviated as C_4AF. The specific gravities of the particles of C_3S, C_2S, C_3A, and C_4AF are 3.15, 3.28, 3.04, and 3.77, respectively [8]. The specific gravity of a typical mixture of OPC particles ranges from 3.10 to 3.25, and its average is about 3.15 [12]. The volume fraction of cement in a concrete mixture is within the range of 7%−15% [3].

The Portland cement also includes small fractions of uncombined lime, magnesia, gypsum, sulfates etc. Gypsum is added by 5% of cement weight. Limestone particles containing at least 70% of calcium carbonate may be also added to cement at 1%−3% [according to ASTM C150 [15]], not be more than 5.0% by mass. However, for economic and environmental purposes and other technical functions, new trends in the cement industry are currently shifting for the inclusion of a high percentage of calcium carbonate in the Portland limestone cements (IL cements). IL cements are being specified by some US departments of transportations [16]. Specific cement classifications include also white cement, air-entraining cement, pozzolanic cement, hydrophobic cement, quick-setting cement, rapid-hardening cement, low heat cement, sulfate-resisting cement, slag cement, high-alumina cement etc. Artioli and Bullard [9] provided a list of the main types of common and special cements summarizing the

Table 1.1 Constituents and compositions of Portland cements [27].

Constituent	**Structure**	**Abbreviation**	**Composition by mass %**	
			I	**V**
calcium oxide	CaO	C	63.7	64.3
silicon oxide	SiO_2	S	20.1	21.9
aluminum oxide	Al_2O_3	A	4.7	2.8
ferric oxide	Fe_2O_3	F	3.5	4.5
tricalcium silicate (Alite)	$3CaO \cdot SiO_2$	C_3S	53	64
dicalcium silicate (Belite)	$2CaO \cdot SiO_2$	C_2S	18	13
tricalcium aluminate (Celite)	$3CaO \cdot Al_2O_3$	C_3A	7	0
tetra-calcium aluminoferrite (Brownmillerite)	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	11	13
limestone			4.0	0.51
magnesium oxide	MgO		0.7	2.4
sulfur trioxide	SO_3		3.1	2.9
Equivalent alkalis as Na_2O			0.51	0.19

composition and the properties of each. Readers can refer to such a reference for more details, which are beyond the scope of this chapter.

Upon mixing with water, cement undergoes a series of hydration reactions producing various hydration products that create the binding property within the resulting cement paste. The resulting calcium silicate hydrates are stable in water, and they generate the adhesive or cementing characteristic. Reactivity with water and water stability of the hydration product are behind the term “hydraulic cement.” The following section discusses these reactions.

In general, tricalcium silicate and dicalcium silicates are the major contributors to the final strength of concrete. Tricalcium aluminate hydrates faster than tri and dicalcium silicates, and generates an initial large amount of heat that enhances the cement reactions; however, it makes no major contribution to concrete strength. Tetracalcium aluminoferrite is just added for cement manufacturing purposes (i.e., for lowering the required kiln temperature), rather than for concrete purposes. It is also the source of cement coloring (gray). Gypsum is added in order to control the cement initial reaction rates (setting time). In the modified concrete mixtures, part of the cement is replaced by SCMs, such as fly ash, which create binding through pozzolanic reactions (see Section 1.4).

1.2.2 Mixing water

Water is added to concrete mixture for several purposes: it creates its flowability characteristics for casting purposes, it provides one of the main reactants for cement hydration, and it establishes the medium for various chemical and physical activities during concrete curing. The main source of mixing water is batch water for which municipal tap water is usually accepted [6]. Other sources of water include free moisture content of aggregates and water from solutions of chemical admixtures, as well as ice, which might be used as part of the mixing water in hot climates [3]. There are attempts to consider adding water through other innovative methods. For example, water may be added to the concrete mix through a material that can store water temporarily without affecting the water balance of the cement paste and then releases it slowly as needed for further hydration reactions. This can be accomplished by using gels, superabsorbent polymers, or saturated lightweight aggregates [17].

Water quality is essential for obtaining the desired concrete characteristics. The presence of free ions and dissolved materials in water has several impacts on the characteristics of green and hardened concrete. Free ions alter the surface chemistry of the suspension of cement particles and thus change the characteristics of the fresh concrete mixture. For example, the uniform dispersion of cement particles is governed by the ionic strength of water, which impacts the surface charges of the cement particles and the colloidal stability of the suspension. Increasing the ionic strength increases the degree of flocculation of cement particles. The status of cement particles in suspension controls the followability and consistency of concrete mixture. The rate of cement hydration reaction is also affected by the cement flocculation and the chemical composition of water. These effects result in major impacts on the final strength of concrete. In addition, residual ions after concrete curing may create a deterioration environment for fully cured concrete, at later stages. For example, using salty water (such as seawater), which contains an appreciable amount of chlorides, leads to residuals of free chloride ions within concrete pores and causes various concrete durability problems including corrosion of steel reinforcement [18] (see Chapter 3). The possible use of seawater as a mixing water to batch concrete is linked to the case when there is no other choice and for unreinforced concrete [17]. The compressive strength of concrete prepared with seawater can decrease by about 20% compared to that made with fresh water. The same concern is mentioned when discussing the possibility of using treated wastewater from concrete making factories, as treated water discharge maintains some contents of ionic species or organic matter that impact the characteristics of concrete [3]. It is believed that such treated wastewater can be used only as a partial substitution of fresh water [17].

For these reasons, it is essential to use water within an acceptable range of dissolved materials [3]. Typical limits are set for water content of (1) sodium and potassium carbonates and bicarbonates, which have various effects on the setting times of concrete; (2) salts such as chlorides from seawater, which impacts the setting time of concrete and results in the corrosion of steel reinforcement from its residual in concrete pore [17]; and (3) sulfate content, which affects the durability of hardened concrete. In addition to these possible inorganic contents, the presence of other organic contents in mixing has other impacts on concrete characteristics. For example, low sugar content (sucrose) increases the time of cement setting, as it retards the cement hydration reactions. The presence of microorganisms such as algae makes water unacceptable for preparing concrete mixtures as they cause a noticeable reduction in concrete strength, as they cause a significant air entrapment in the concrete mixture.

The amount of water is added to meet a required water-to-cement (w/c) ratio, which is defined according to ASTM C125−15b [2] as "the ratio of the mass of water, excluding water absorbed by the aggregates, to the mass of Portland cement in a cementitious mixture, stated as a decimal." For cementitious mixtures containing a combination of Portland cement and SCMs or other binding constituents, the term water to cementitious material (w/cm) ratio or water to binder (w/b) ratio is used [2]. The w/c ratio is critical in concrete. Theoretically, the required amount of water can be determined from the minimum amount needed for full cement hydration, according to the stoichiometric of hydration reactions Section 1.3. Various relative amounts of water are needed for the hydration of the various cement compounds (see Table 1.1, as given in Section 1.3.1). Overall, an average of 23% of water by weight of cement is estimated for the chemical reactions of all compounds of Portland cement [3]. This amount is not sufficient to be set for specifying the minimum theoretical w/c ratio, as there are other water interactions with cementitious compounds. Thus in addition to such estimated chemical requirements, an additional amount of water is physically adsorbed within the porous structure of the produced hydration products, which composes about 15% of cement weight [3]. Consequently, a net of about 38% of water by cement weight is essential for the complete cement hydration reactions and saturation of the hydration products [3]. These estimates do not take into account unavoidable water evaporation due to the release of heat from the exothermic cement hydration [i.e., it is determined for the case of hydration in a sealed container [1]]. Typically, it is acceptable to state that a w/c of about 0.4 is needed for complete cement hydration and saturation [12,3]. However, there are always a faction of unreacted cement particles that do not undergo a complete hydration due to a lack of moisture accessibility and the long time period required for complete hydration. Hence, a lower w/c ratio may be used for high strength concrete, considering that a fraction of cement particles will not be reached for full reaction. In fact, a w/c ratio of 0.25 is specified for high performance concrete, considering that a portion of cement grain remains unhydrated in the core of cement particles [3]. On the other hand, higher w/c ratios are usually used for obtaining a required fluidity of concrete mixture and hence the w/c ratio can go up to 0.7 or higher.

The volume fraction of water in concrete mixture is usually within the range of 14%−21% [3]. Changing the volume of added water (i.e., changing w/c ratio) impacts the handling characteristics of fresh concrete, including the flowability and the coherence of the fresh mixture, and the structural and the mechanical properties of the cured concrete (see Chapter 4). The characteristics of fresh concrete are usually determined by the workability. Workability is related to the ease with which a concrete mixture can be handled, without segregation of concrete mixture. Thus it combines the characteristics of consistency (the degree of wetness of fresh concrete mixture) and cohesiveness (the ability of fresh concrete for finishing and compacting) [14]. According to ASTM C125−15b [2], workability of concrete is the "property of freshly mixed concrete that affects the ease with which it can be mixed, placed, consolidated, and struck off." Consistency is "the relative mobility or ability to flow" [2], and it is determined by measuring slump, using the standard cone test according to ASTM C143 [19]. Cohesiveness is usually determined through visual observation and experience [14].

The amount of water also impacts the stability of fresh concrete, which is related to the capacity of fresh concrete to hold water, otherwise bleeding occurs. According to ASTM C125−15b [2], "the autogenous flow of mixing water within, or its emergence from, a newly placed cementitious mixture caused by the settlement of the solid materials within the mass." The stability of fresh concrete is also related to the capacity of concrete mixture to hold coarse aggregates and thus preventing segregation [14]. As mentioned above, extra water is introduced to the mix from free moisture content of the aggregates. An estimate of such excess water for an ordinary concrete can be equivalent to altering the w/c ratio by 10%. This indeed can change the strength and durability of the fully cured concrete [17].

Concrete rigidity is developed gradually from the time of mixing. The change in the consistency of concrete mixture from fluid into rigid structure, as a result of initial reaction of cementitious compounds, is referred to as concrete setting [8]. The time of setting is "the elapsed time from the addition of mixing water to a cementitious mixture until the mixture reaches a specified degree of rigidity as measured by a specific procedure" [ASTM C125−15b [2]]. The initial setting and final setting times are determined according to ASTM C403/C403M [20], when the concrete exerts a penetration resistance of 500 psi (3.5 MPa) and 4000 psi (27.6 MPa), respectively. A loss of consistency of freshly mixed concrete with time occurs as a result of initial rapid reactions (see Section 1.3) [8]. These reactions are associated with an initial consumption of available water and a partial evaporation [14]. The loss of consistency, as an indication of loss of workability, can be measured by the loss of slump. The slump is totally lost by the final setting [8]. Workability retention is defined as a measure of how long the workability can be maintained after mixing. Its period varies with the type of concrete mixture or mix design (see Chapter 4) and may continue for a period of 1 − 2 hours [8]. Under normal conditions, during the first 30 minutes, the hydration of cement is minor, and thus the loss of workability is insignificant [14].

1.2.3 Aggregates

Aggregates are the granular mineral materials, which account for about 60%−75% of the net concrete volume (70%−85% by mass) [3]. In addition to the economic purpose, their addition to concrete mixture controls the characteristics of fresh concrete and the hardened properties and mixture proportions. The selection of aggregates is an important step in concrete mix design (see Chapter 4). Aggregates are classified into fine aggregates (e.g., sand) and coarse aggregates (e.g., natural gravels and crushed stone). Sands can be obtained from natural resources and from natural processes of friable sandstone disintegration and abrasion. Gravels are obtained from natural processes of rock disintegration and abrasion, or from processing of weakly bound conglomerate. Gravels compose about 50% of the coarse aggregates used in concrete in North America [3]; and most of the rest are crushed limestones. Limestone aggregates are produced industrially by crushing rocks. They are usually washed and screened to obtain the proper cleanliness and the required particle size range (grading). Other sources of aggregates in new concrete applications include industrial recycled materials and crushed recycled concrete.

Typical grading limits are set for aggregates that are usually specified as the percentage of material passing each sieve. The grading affects aggregate proportions in concrete mix design (see Chapter 4) and affects the workability, porosity, and other durability characteristics of concrete, as well as its economy [3]. According to ASTM C125−15b [2], the size of coarse aggregate is predominantly larger than 4.75 mm (i.e., retained on standard sieve No. 4) and generally within the range of 9.5−37.5 mm (3/8 in. and 11/2 in.) [3]. Fine aggregate are generally smaller than 4.75 mm but larger than 75 μm (i.e., passing standard sieve No. 4 and retained on standard sieve No. 200). The aggregates are categorized into (1) normal-density aggregates, which have a relative density in the range of 2.2−2.4; (2) high-density aggregates (heavyweight aggregates such as magnetite, limonite, iron, or steel aggregates), which have a relative density greater than 3.3; and (3) low-density aggregates (or lightweight aggregates such as volcanic cinders, diatomite, expanded clay, shale, perlite, or slag), which have a relative density in the range of 1.35−1.85 [2].

Aggregates must be strong and clean (free of absorbed chemicals). The main aggregate characteristics include bulk density, particle size and shape, size distribution (grading), porosity, moisture content, mechanical properties such as strength and abrasion resistance, chemical composition, and resistivity against reactions with concrete chemical conditions [14]. The types of aggregates and their properties control various concrete characteristics including its density, dimensional stability and durability, and elastic modulus. Shetty [3] provided a full list of characteristics and standard tests of aggregates. These include particle shape, surface texture and grading, compressive and flexural strengths, and other physical characteristics such as water absorption and surface moisture etc. They also include their resistances to chemical attack (e.g., sulfates), to mechanical attack (e.g., abrasion and degradation), and to thermal degradation (e.g., resistance to freezing and thawing). One of the most important durability effects of aggregates is their reactivity with the alkaline environment within concrete pores, through various deterioration chemical reactions (e.g., alkali aggregates reactions). From such a durability view, they are classified into reactive and nonreactive aggregates. These aspects are discussed in Chapter 3.

1.3 Cement hydration chemistry

In general, reaction engineering involves studying the reaction kinetics and the thermodynamics, in addition to the reaction stoichiometry, which specifies the proportions according to which the reaction occurs and the products are generated. The kinetics deals with the time-rate at which the reactants are converted into products. The reaction thermodynamics focus on the enthalpy changes (ΔH) or the heat evolution from the reactions. This section presents the types of chemical reactions, their stoichiometries, and the compositions of the produced hardened cement. The following subsection discusses the hydration kinetic and thermodynamic issues.

1.3.1 Stoichiometry of hydration reactions

Portland cement hardens after its mixing with water, through the hydration process, which involves a series of complex chemical and physical reactions and interactions between water and the silicate compounds listed in Table 1.1 [7]. The reactions proceed during the process of concrete curing and continue for a very long time. According to ASTM C125−15b [2], concrete curing is the "action taken to maintain moisture and temperature conditions in a freshly-placed cementitious mixture to allow hydraulic cement hydration and (if applicable) pozzolanic reactions to occur so that the potential properties of the mixture may develop." The two objectives of an efficient curing process include preventing the loss of moisture and controlling the temperature of concrete for a period sufficient to achieve a desired strength level. During the curing stage, various steps and mechanisms are involved, including the dissolution of the particles, surface reactions, gel formation, agglomeration, adsorption, evaporation, precipitation of new phases [9,21]. The chemical reactions vary in sequencing, reaction rate, the amount and rate of released exothermic heat, types of products and their contribution to concrete strength etc.

When the Portland cement is mixed with water, the gypsum particles are dissociated and their constituents are dissolved in water forming a solution in which the ions start to function within minutes. The hydration process is initiated by the rapid reaction of tricalcium aluminate with the gypsum in the presence of water to produce long crystals of ettringite, according to Eq. (1.1) [7]. Ettringite has no contribution to strength; however, this activity enhances the cement hydration reactions to start. The reaction of tricalcium aluminate is highly exothermal, thus it can cause rapid setting of the paste (or undesired flash set), with a fast loss of fluidity of the fresh concrete [9]. The heat of hydration of C_3A is reported to be about 324 cal/g and composes nearly about 65% of the total heat evolved within the first 3 days [8]. Without gypsum, C_3A hydrates very quickly and results in immediate concrete setting. Thus adding gypsum to cement is essential to control C_3A hydration.

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32} \qquad \Delta H = 300\ \mathrm{cal/g} \tag{1.1}$$

The first reaction generates sufficient heat to activate other reactions. Then, the tricalcium silicate (C_3S) is hydrated through an exothermic reaction according to Eq. (1.2) with a reaction enthalpy change of 120 cal/g [14]. It produces the hydrates of calcium silicate ($3CaO \cdot SiO_2 \cdot 3H_2O$) (also referred to as the C-S-H gel) that have a fibrous network structure. The C-S-H gel makes a major contribution to the initial and final strength of the cement paste. This reaction Eq. 1.2 also produces calcium hydroxide [$Ca(OH)_2$], which is also referred to as portlandite and abbreviated as CH. Calcium hydroxide is the undesired by-product that creates various concrete durability problems (see Chapter 3). The hydration of C_3S is relatively rapid and thus it contributes to the initial set of concrete and to its strength at early stages. When the original C_3S content in cement is high, a high early strength of concrete is obtained. The corresponding weights of the reaction stoichiometry involve that 100 g of C_3S reacts with 24 water to produce 75 g of C-S-H gel and 49 g of calcium hydroxide [3].

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad \Delta H_{C3S} = 120\ \mathrm{cal/g} \tag{1.2}$$

In general, the hydration reactions are usually given in approximate equations and the stoichiometric coefficients may be written differently in various literature. The typical simple equations for hydration reactions do not reflect the complexities of the actual reactions [3]. For example, 5.6H instead of 6H and 2.6CH instead of 3CH are given by [7]. Also, the chemical structures of the hydration products are not exactly defined. For example, the number of water molecules in the hydrates of ettringite may be between 30 and 32 [8] and the C/S ratio in calcium silicate hydrates (or C-S-H gel) may vary [8]. In fact, the length of the chain of C-S-H varies with the degree of polymerization and increases with curing age.

Then, the dicalcium silicate (C_2S) starts to hydrate through another exothermic reaction with water to form additional amounts of the calcium silicate hydrates (C-S-H gel) and additional amount of the undesired calcium hydroxide (CH), according to Eq. (1.3), with a reaction enthalpy change of 62 cal/g [14]. The corresponding weights of the reaction stoichiometry involve that 100 g of C_2S reacts with 21 water to produce 99 g of C-S-H gel and 22 g of calcium hydroxide [3]. Again, the stoichiometric coefficients are given as approximate values, for example, 3.6H instead of 4H and 0.6CH instead of 1H are given by [7]. The rate of hydration of dicalcium silicate (C_2S) Eq. 1.3 is lower than that of tricalcium silicate (C_3S) and it generates less thermal energy (i.e., $\Delta H_{C2S} < \Delta H_{C3S}$). Thus the hydration of C_2S contributes little to the early strength of concrete but it is essential for the long-term strength at a late concrete curing. The reaction's stoichiometries indicate that the products of the hydration reaction of C_3S Eq. 1.2 compose about 61% $C_3S_2H_3$ and 39% calcium hydroxide, whereas those of C_2S Eq. 1.3 compose about 82% $C_3S_2H_3$ and 18% calcium hydroxide. Consequently, tricalcium silicate (C_3S) produces more fraction of the undesired product, and less fraction of the desired product, than dicalcium silicate (C_2S).

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \quad \Delta H_{C2S} = 62\ \mathrm{cal/g} \tag{1.3}$$

Afterward, the tetracalcium aluminoferrite [$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or C_4AF (also referred to as ferrite)] undergoes the two reactions given in Eqs. (1.4) and (1.5). It hydrates rapidly but with a minor contribution to concrete strength as it has no cementing purposes. C_4AF reacts with the gypsum and water to form additional ettringite and calcium hydroxide according to Eq. (1.4). It further reacts with ettringite ($C_6AS_3H_{32}$), according to Eq. (1.5). The heat of hydration of the ferrite phase (C_4AF) is 102 cal/g, out of which nearly 68% is liberated in the first 3 days [8].

$$C_4AF + 3CSH_2 + 21\ H \rightarrow C_6AS_3H_{32} + FH_3 \tag{1.4}$$

$$C_4AF + C_6AS_3H_{32} + 7\ H \rightarrow 3C_4ASH_{12} + AH_3 \tag{1.5}$$

In addition to these reactions, and upon consuming all available gypsum in the first reaction Eq. 1.1, the unstable ettringite reacts with any available tricalcium aluminate to form the hydrates of the monosulfate aluminate crystals (C_4ASH_{18}) according to Eq. (1.6). The produced monosulfate aluminate hydrates are stable in a solution containing no sulfates, but it creates durability problems under certain conditions (as described in Chapter 3).

$$2C_3A + C_6AS_3H_{32} + 4\ H \rightarrow 3C_4ASH_{18} \tag{1.6}$$

For other types of cements, other reactions occur. For example, in rapid-hardening cement, the lime content is increased in order to increase the early stage strength of concrete, by absorbing CO_2 from the atmosphere to form $CaCO_3$ [22]. In addition, pozzolanic reactions are also involved when SCMs are added. These reactions are presented in Section 1.4.

In summary, the products of cement hydration process compose the hardened paste. The paste composition include the main binding and strengthening product of C-S-H gel (composing 50%–60% of the paste volume), the weak ettringite ($C_6AS_3H_{32}$) (composing 15%–20% of the paste volume), and the undesired calcium hydroxide (CH) (composing 20%–25% of the paste volume) [8]. In addition, 5%–8% of the paste volume are voids and pores. These include the capillary network and the entrapped and entrained air contents, which are described in detail in Chapter 2. The main hydration crystals of calcium silicate, calcium hydroxide, and ettringite, as well as the pores, are shown in Fig. 1.3.

The C-S-H gel binds the aggregates in cured concrete structure and provides concrete with the integrated and the strength characteristics. In fact, the cement hydration reactions do not accomplish full hydration and a fraction of cement particles remain anhydrate and dispersed within the microstructure of the hydrated cement pastes. For example, after a sufficiently long time of standard curing (typically 28-day curing), the paste structure is reported to include 85%–90% of hydration products while the remaining portion is unhydrated/unreacted cement grains [3].

There are discussions in the literature about the levels of similarities among the products of hydration reactions of C_3S and C_2S. It is now believed that the products of each of them turn out to be the same. The exact structure is not well-clarified and not well-defined [3,7], but it is typically described as a layered structure with a very high surface area in the order of $100 - 700\ m^2/g$ [14]. The reported morphology of C-S-H phase shows a poorly formed, thin, fibrous crystals interlocked into a

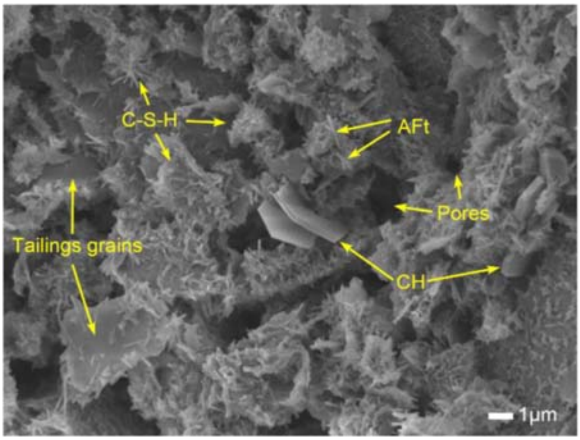


Figure 1.3 Scanning electron microscopy image of a cement paste at magnification of 5000 × , showing the main components of the hydration products including C-S-H gel, hexagonal plate calcium hydroxide (CH) crystals, and columnar ettringite (AFt) crystals [also shown in this image grains of tailings used as an additive in the used cement paste [23]].

fibrous fine structure forming a fluffy mass [3]. The bonding among the C-S-H structure is created through van der Waals forces. The typical distance between the crystalline layers is estimated to be about 1.8 nm (or within the range of 0.5–2.5 nm). The calcium silicate hydrates (C-S-H) are very fine colloidal, poorly crystalline material, which clusters into a gel. It is believed that the term gel might not be the suitable technical description of the C-S-H structure. The gel itself is porous, with an estimated porosity that can reach 28% [3].

The reaction by-product of calcium hydroxide (CH) precipitates from solution in empty pores, and crystallizes as large crystals of hexagonal plate-like shape [7], or hexagonal-prism morphology [14]. Their size is about two to three times larger than that of C-S-H particles, thus they have a lower surface area and their contribution to concrete strength is low (by van der Waals attractions) [8]. In addition, they are soluble in water; thus they create an alkaline pore solution of a high pH, which has an adverse effect on concrete durability (as discussed in Chapter 3), and it gets leached out making the concrete porous, particularly in hydraulic structures [8]. The presence of CH has the advantage of maintaining the alkalinity condition of concrete to a pH value close to 13, which hinders the corrosion of reinforcements (see Chapter 3). The crystals of ettringite ($C_6AS_3H_{32}$) are needles with a width of 0.25 μm and a length of up 10 μm, but they do not branch.

The specific gravities of the four main cement components ranges between 3 and 3.7, while that of the hydrates ranges between 1.8 and 2.5 [24]. The hydration products occupy a larger volume than that occupied initially by the cement particles forming the paste. However, the total absolute volume of cement hydration products is smaller than the combined initial volume of the anhydrous cement and water [13].

Hence, the cement hydration process is associated with a chemical shrinkage [24], which is detailed in Chapter 3, as one of the durability problems.

As it has been said earlier (see Section 1.2.2), according to the reaction stoichiometries, the full hydrations of C_3S and C_2S require 24% and 21% of water by weight of cement, respectively (with an average of 23% for the complete chemical reactions of Portland cement) [3]. These water requirements are simply for chemically combined water with hydrated cement (bound water). However, water is also physically adsorbed within the porous structure of C-S-H gel (gel water in gel pores), which composes about 15% cement weight [3]. Consequently, a net of about 38% of water by weight of cement is required for the complete cement hydration reactions and saturation of the C-S-H gel [3]. When more than 38% water is used, or when the cement hydration is not full for the 38% used water, the excess water will create capillary pores, the structure of which is detailed in Chapter 2.

1.3.2 Kinetics and heat of hydration reactions

Hydration kinetics is concerned with the reaction rate, which is dependent on the temperature (T), the chemical composition of the reactants, and the particle size [25]. The temperature dependency of the reaction rate is usually given by reaction coefficient (k_r) through the well-known Arrhenius equation, as given in Eq. (1.7).

$$k_r = k_o \exp\left(\frac{E}{RT}\right) \tag{1.7}$$

where k_o is a preexponential empirical constant, E is the activation energy of the reaction, R is the universal gas constant [25]. The dependency on the chemical composition is usually specified by the empirical order of reaction, with respect to the concentration reactants [25]. The cement hydration is dependent on particle size of cement as it is a heterogeneous chemical reaction involving liquid and solid phases. Such a dependency is governed by the availability of the reaction surface area that is in contact with water for hydration. The hydration kinetics can be followed, directly, by monitoring the concentrations of products or reactants with time, or indirectly, through measuring a consequence of the reaction. For cement hydration, the indirect method can be based on following the strength development, as concrete strength gain is the result obtained from the reaction progress. The concrete maturity is usually used to describe the extent of relative strength development of concrete with curing age. It is an indication of the progress of concrete curing as a relationship between concrete temperature, time, and strength gain. According to ASTM C125−15b [2], curing age is the number of days or hours of curing of a concrete mixture at a specified temperature required to produce a maturity equal to the maturity achieved by a given curing period at concrete temperatures different from the specified temperature. The hydration process continues with time over years, the length of which depends on the particle size and the surface area, the porosity of the paste and the surrounding conditions [9].

As commonly hypothesized for heterogeneous chemical reactions, the physical and chemical mechanisms involved in the cement hydration affect the rate at which the hydration process progresses. The review of Bullard et al. [21] for the mechanisms of cement hydration highlighted particle dispersion, ion dissolution, diffusion, particle agglomeration, phase changes, and chemical reactions. The hydration process starts by the dissolution or dissociation of the molecular structures from the surface of cement particles into solution in the concrete mixture. The release of heat of solution enthalpy results in a phase change for part of the water in the mixture. The diffusion of the soluble components within the pores of concrete mixture, or within the solid structure of particles, leads to various chemical and physical interactions. Surface − surface interactions between particles lead to particles' aggregation. The reactions between the soluble ions form ion complexes or lead to the adsorption of molecular complexes on the solid surfaces. For typical crystallization processes, the nucleation step is crucial when the hydration products precipitate homogeneously by self-association. Crystallization can also happen heterogeneously by adsorption on existing solid surfaces. The crystals grow with the progress of the hydration reactions through the attachment of the reaction products into the structure of paste compounds. Adsorption occurs through the accumulation of ions or other molecular units at solution/solid interfaces. Then, empty spaces in the paste are evolved due to combined actions of volume change of reactant and products and evaporation of mixing water. The existence of admixtures, additives, and other chemical contaminations interferes with these mechanisms. Each of these mechanisms occurs at a certain rate and releases a certain amount of heat at a different rate. The slowest step among these mechanisms controls the overall hydration rate and thus it is termed as the rate-controlling step. After the initial stage, it is believed that the hydration process is controlled by the diffusion of the reacting species through a mass transfer process [28]. The diffusion rate decreases with time, as the resulting C-S-H gel forms a barrier between water and unreacted cement, the thickness of which increases with time. Such a thickness can reach 4 μm, after 28 days of curing [3]. However, in transport phenomena analysis, a combined mass and heat transfer may provide a better perspective for following the hydration kinetics as the amount of heat released from the highly exothermic reactions is also an important parameter in governing the reaction rate. This means that diffusion and thermal conduction shall be both considered in analyzing the cement hydration kinetics. It is well-known that each cement compound reacts at a different rate and evolves different heat due to different values in reaction enthalpy changes (ΔH). The reaction rates and the enthalpies of reactions for the four constituents of cement are ranked in a descending order as follows: $C_3A > C_4AF > C_3S > C_2S$ [8]. The main cement constituent (C_3S) reacts at a rate faster than that of C_2S by more than five times [8]. The same descending order is almost given for the rate of dissolution of these compounds in water. Consequently, each constituent of the cement has its own kinetic behavior, as schematically illustrated in Fig. 1.4 [12]. It is not practical to study the individual chemical kinetics for each component contributing to the overall cement hydration [1].

In fact, the kinetic approaches for analyzing the cement hydration process include overall kinetics, particle kinetics, hybrid kinetics, and integrated kinetics [29]. The

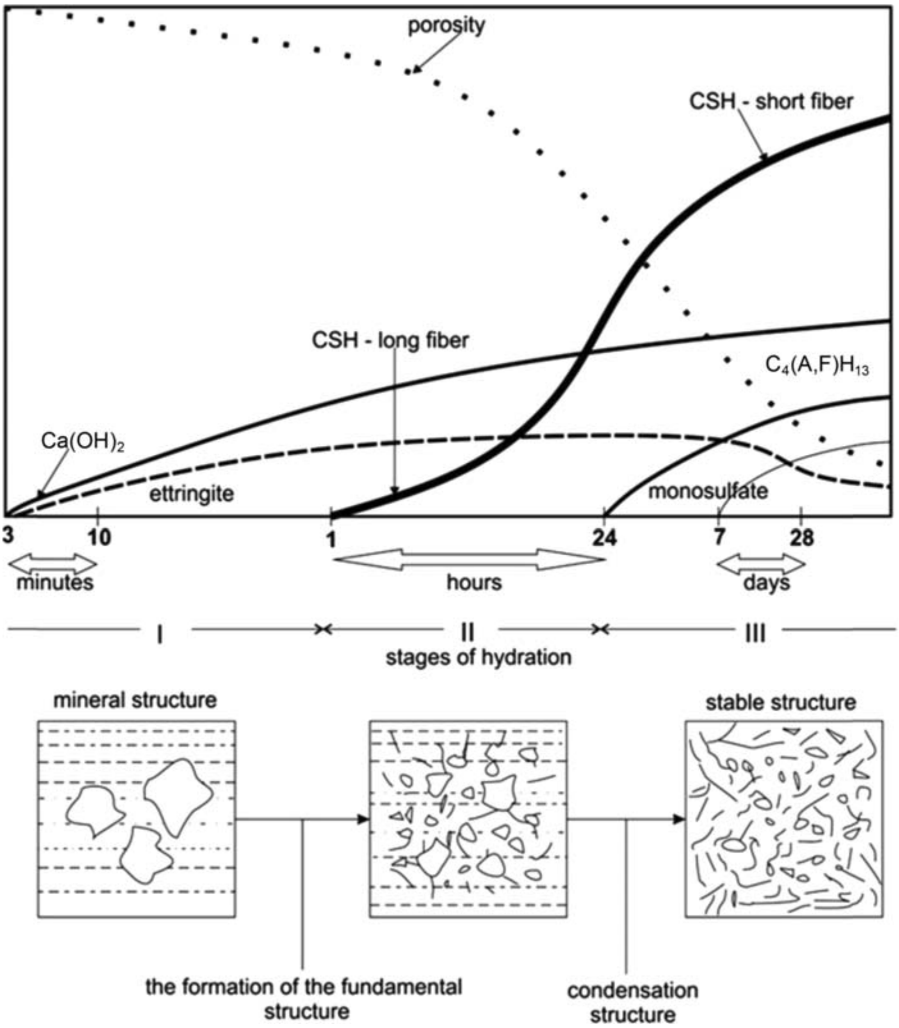


Figure 1.4 Kinetics of formation of the of hydration products [26].

overall hydration kinetics is the most practical approach, which uses the degree of hydration (α) as the time-dependent weight fraction of reacted cement [13]. It is defined as the ratio of the reacted amount of cement up to a certain time to the original amount of cement [7]. This is also linked to the rate of heat evolution as an indirect measurement of the hydration rate. The kinetics of hydration reactions (and the strength development of concrete) are controlled by the rate of heat evolved from the reactions.

From a thermodynamic perspective, the cement compounds react with water to acquire stable low-energy states. This thermodynamic process is associated with a release of thermal energy due to enthalpy change for the transformation [7]. When the released heat is not dissipated at the same rate at which it is being generated it causes a temperature change in the concrete mix. Such a temperature rise creates major concrete problems in mass concrete, as described in Chapter 4. There are various sources of heat release [9,31,28,32,11]: within the first few minutes from the moment of mixing cement with water, a fast heat evolution occurs, which represents the heat of solution of aluminates, sulfates, and possible other minerals [28]. Then, within a few hours, an additional amount of heat is evolved from the formation of ettringite through a highly exothermic reaction Eq. 1.1. This can also be associated with a possible minor thermal contribution from the enthalpy change of the dissolution of C_3S and from the enthalpy change of the early formation of C-S-H gel Eq. 1.2.

The major part of heat liberation results from the hydration of C_3S. It composes about 50% of the potential heat for full reaction of cement and is liberated within the first 3 days. Within about 3 months, about 90% of the thermal energy is released. The hydration of Type I cement generates a thermal energy in the range of 80−90 cal/g within 7 days [14]. It releases a net heat within a range of 90−100 cal/g within a standard concrete curing period of 28 days [14]. The rate of heat evolution is central for the indirect empirical determination of the hydration kinetics; and it is crucial in the analysis of mass concrete applications [1]. It is also important for concrete durability as the large temperature increase that occurs within the period of 1−3 days, followed by the subsequent cooling, results in shrinkage stresses and thus causes concrete cracking. The concrete tensile stress is a strong function of the heat of hydration of Portland cement [1].

Fig. 1.5 shows a schematic representation of the heat evolution curve from a typical cement hydration process [9,31,28,32,11]. Heat evolution curves can be presented in a differential and/or integral shape. The differential heat evolution curve reflects the overall cement reaction rate as a function of time and thus it can be utilized for indirect determination of the hydration kinetics. On the other hand, the integral form of the heat evolution curve gives the cumulative amount of heat released up to a certain time, which is in fact an indirect measure of the degree of hydration (α) [8]. Fig. 1.6, as described in the following section, compares these two types of thermal curves for practical cementitious materials. The characteristic shape of the curve shown in Fig. 1.5 is usually reported for different hydration processes of various cementitious binders. However, the quantitate behavior is largely dependent on the mix design, the cement composition and particle size, the use of admixture and other additives, w/c ratio, and the curing conditions (e.g., temperature and humidity) [21]. The rate of cement hydration increases with increasing the w/c ratio and with temperature [24].

Fig. 1.5 shows that after an initial quick heat evolution peak, a slow nearly steady rate of heat release occurs within the first hours, then the heat release is accelerated gradually until it reaches a maximum value within a few hours. Subsequently, heat release slows down for the rest of the hydration period. The major characteristic changes in the shape of the thermal curve in Fig. 1.5 reflect the various mechanisms and stages that are involved in the hydration process.

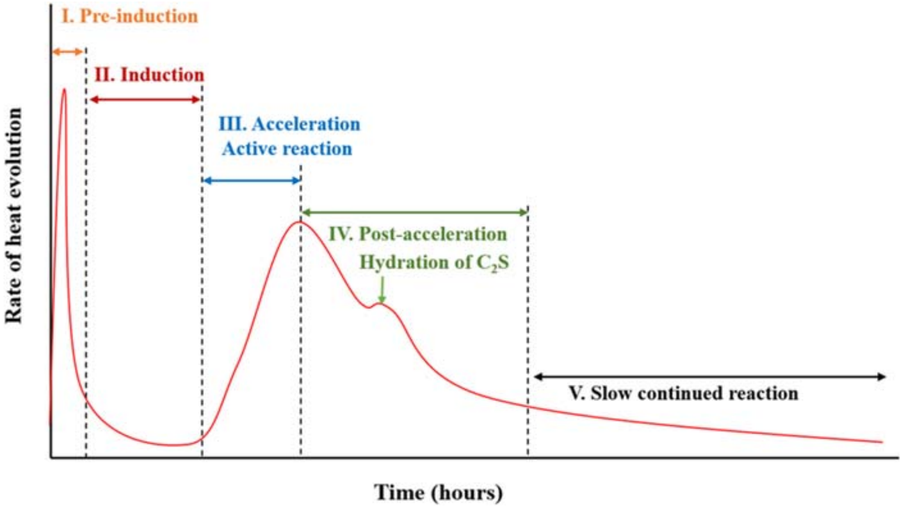


Figure 1.5 A schematic representation of the rate of heat evolution with time during the cement hydration stages.

Five stages are usually categorized in this analysis as shown schematically in Fig. 1.5 (I − V). It is also meaningful when interpreting these stages to notice the formations of the individual hydration products with curing age as shown in Fig. 1.4. These stages include:

I. *Pre-induction or initial stage*. It is represented by the first quick peak in the heat evolution curve, which is interpreted with several hypotheses for possible contributions in the involved rapid heat evolution. These include the following:

1. The heat evolution of wetting of the cement particles and the hydration of its free lime forming calcium hydroxide as given by Eq. (1.8) [11]. Some researchers indicated that such an enthalpy change of (CaO) hydration makes only a minor contribution.

$$CaO + H_2O \rightarrow Ca(OH)_2 + \Delta H_{CaO} \tag{1.8}$$

2. The hydration of calcium sulfate hemihydrate ($CaSO_4 0.0.5H_2O$) forming dihydrate gypsum, according to Eq. (1.9).

$$CaSO_4.0.5H_2O + 1.5H_2O \rightarrow CaSO_4.2H_2O + \Delta H_{gypsum} \tag{1.9}$$

3. The dissolution of calcium ions from the cement particles, as highlighted in the review of [21], which emphasized that both C_3S and C_3A dissolve congruently and rapidly within the first few seconds after wetting, according to Eqs. (1.10) and (1.11).

$$3CaO \cdot SiO_2 + 3H_2O \rightarrow 3\ Ca^{2+} + H_2SiO_4{}^{2-} + 4\ OH^- + \Delta H_{C3S-dis} \tag{1.10}$$

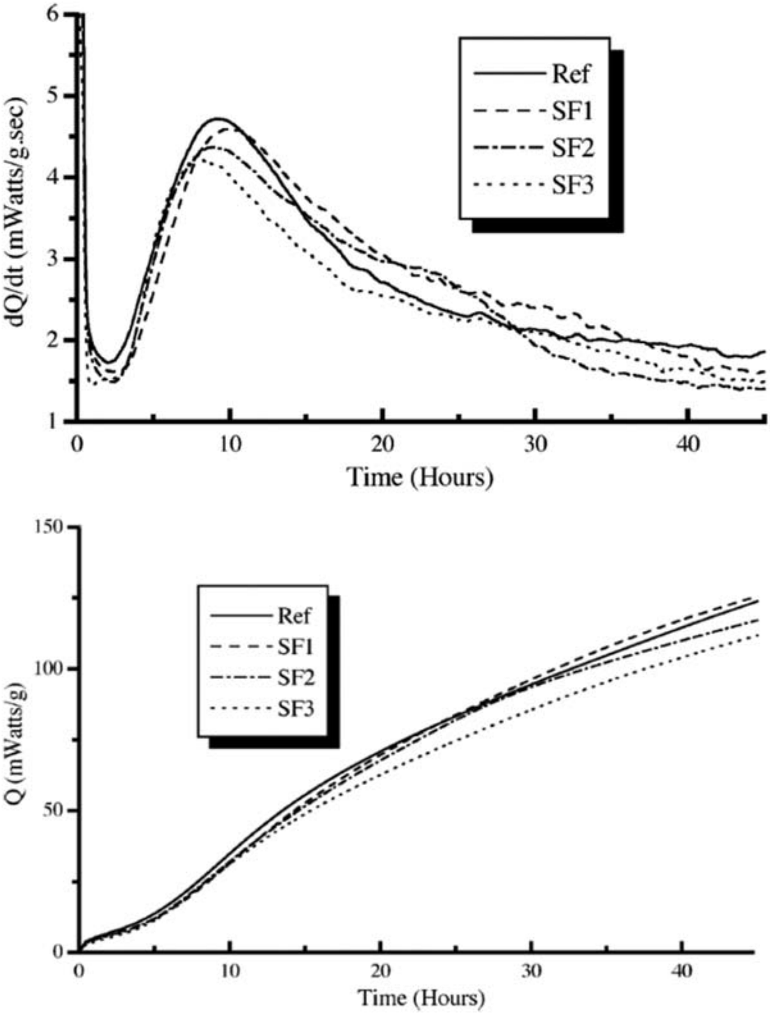


Figure 1.6 The rate of heat evolution of silica fume blended cements hydrated at 25°C (above) and the integral curves of heat of hydration for the same silica fume blended with normal Portland cements (below) at 10%, 20%, and 30% for SF1, SF2, and SF3, respectively, compared to unblended cement (Ref-specimen) [11].

$$3CaO \cdot Al_2O_3 + 2H_2O \rightarrow 3\ Ca^{2+} + 2\ AlO_2{}^{-} + 4\ OH^{-} + \Delta H_{C3A-dis} \tag{1.11}$$

The enthalpy of the congruent dissolution of C_3S ($\Delta H_{C3S\text{-}dis}$) is 138 kJ/mol, and that of C_3A ($\Delta H_{C3A\text{-}dis}$) is 248 kJ/mol [9] [see also the enthalpy of congruent dissolution in other references such as [21]].

4. The dissolution of the alkalinity content of the cement, which releases ions of K+, Na+ and OH−, and the formation of ettringite [according to reaction in Eq. (1.1)].

On the other hand, [11] did not detect ettringite within the first period of up to 4 hours from mixing.

II. *Induction period*. It is represented by a low and nearly constant rate of heat release, which occurs within the first hours (2–5 hours). This stage is interpreted by various hypotheses; however, the most obvious controlling mechanism is the formation of a protective layer on the C_3S particles that slows down its reaction. Therefore this period continues until such a layer is disintegrated and becomes permeable for the diffusional transfer of hydration reactants.

The workability period covers stage I and part of stage II and it lasts for 1 − 3 hours [8]. Within this dormant period, the initial concrete set occurs (within 60 minutes) [8]. The final concrete set occurs within the subsequent stage.

III. *Acceleration or active reaction stage* [8]. It is represented by the time period in which the rate of heat evolution increases with time until it reaches the major thermal peak within about 10 hours. This thermal rise is interpreted by the increase in the rate of C_3S hydration. This stage is associated with a remarkable loss of workability and it determines the rate of hardening and the final set, which occurs before the end of this stage (within a time period in the range of 3–5 hours) [8].

IV. *Postacceleration stage*. This stage involves the formation of hydration products and governs the rate of gain of early strength. It is represented by the time period in which the rate of heat release decreases gradually with time. This is interpreted by the decrease in the rate of the hydration reaction due to the decrease in the available reactants and to the depletion of very fine cement particles after they have been hydrated in the previous stage. This stage is controlled by the diffusion mechanism of reactants through the established layer of the hydration products. Bullard et al. [21] detailed the formation of the metastable barrier hypothesis and indicated that the growth morphology of C-S-H may be less porous and more resistant to diffusion. According to Bullard et al. [21], other factors are involved in this decrease such as the lack of space for the products and the lack of water for reaction. After a sufficient time, the hydration of C_2S starts to be substantial and its rate increases, thus its relative thermal contribution increases with time. This evolution of C_2S hydration may appear sometimes as a shoulder in the curve. However, as it has been said earlier (Section 1.3.1), the hydration of C_2S is less exothermic than that of C_3S; the hydration of C_2S is associated with nearly half of the enthalpy change of that for C_3S, as given by reactions in Eqs. (1.2) and (1.3).

V. *Slow continued reaction stage*. This stage involves the steady formation of hydration products and it governs the rate of late strength gain. It is represented by a slow and nearly constant rate of heat release for a very long period of time. This stage is mainly diffusion controlled. Within this period, most of the reduction in the concrete porosity and the increase in the strength occur.

Stages IV and V are the concrete hardening period [8]. Within the standard 28 days curing period, as a characteristic curing age of concrete, nearly 60%–65% of the hydration process is completed and 90% of the specified compressive strength is obtained [8]. Under certain conditions, the hydration reactions may proceed up to 5 years [8], or even for decades. Decreasing the w/c ratio increases the height of the major peak (stage III) [7]. Adding accelerating or retarding admixtures may shift the curve to left or right, respectively. Adding the mineral admixtures (or SCMs) as partial replacements of cement or other integral waterproofing materials decreases the height of the main peak and shifts its position to the right side due to their retarding effects.

1.4 Pozzolanic reactions

It is mentioned above that concrete mixtures may be incorporated with SCMs, which include pozzolans. Pozzolans are categorized as mineral admixtures, and their types and compositions are discussed in the following section on admixtures. According to ASTM C125−15b [2], a pozzolan is "a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of water, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties." ACI CT-18 terminology [1] gives a similar definition and refers to both natural and artificial pozzolans.

Reactive pozzolans are added to convert the undesired cement hydration by-product (CH) into a cementing material through a slow chemical reaction, termed as the pozzolanic reaction. The reactive silica in the pozzolans content converts the calcium hydroxide into binding material of hydrated calcium silicate, which has a similar binding characteristics as the C-S-H gel produced from the main cement hydration reactions Eqs. 1.2 and 1.3, but with differences in C/S ratio and in the precipitation pattern [8]. The general pozzolanic reaction can be written as given in Eq. (1.12). As in cement hydration reactions, the pozzolanic reaction releases heat (ΔH_R) and thus contributes to the temperature rise of concrete. However, it is usually less exothermic.

$$\text{Pozzolans} + \text{CH} + \text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \Delta\text{H}_\text{R} \tag{1.12}$$

In such a reaction, the acidic silanol sites on the solid surface of the pozzolan undergo an acid−base reaction with the alkalis and with available calcium hydroxide [11], as given by Eq. (1.13).

$$2\text{Si}_{(s)} - \text{OH} + \text{Ca(OH)}_2 \rightarrow \left(\text{Si}_{(s)} - \text{O}\right)_2\text{Ca} + 2\text{H}_2\text{O} \tag{1.13}$$

The most important advantage of this reaction is that it converts part of the problem-creating material (CH) into a solution-contributing product through creating more C-S-H gel. In addition, this approach of converting the problem into a solution occurs also in the ability of the product of the pozzolanic reaction to fill up large capillary space. This adds a direct positive effect on concrete integrity, as it improves the strength and reduces the concrete porosity. Overall, this approach has a major positive impact on concrete durability. The other nonpozzolanic mechanisms of the mineral admixtures are discussed in the following section.

From the perspectives of reaction kinetics and thermodynamics, this reaction is slow, thus the rate of heat release and strength development will be consequently slow. Fig. 1.6 shows the curves of heat liberation from the hydration of cement paste specimens prepared with various additions of silica fume, compared to a plain paste specimen (reference specimen). The general shape of the curves for heat evaluation with SCMs are similar to that for a typical cement hydration (as schematically shown in Fig. 1.5, and as given in Fig. 1.6 for the reference specimen. However, Fig. 1.6 has different quantitative behavior: concrete mixtures containing pozzolanic materials usually evolve less rates of heats of hydration compared to concrete mixtures with OPC, as they replace a considerable part of cement mass. In addition, the SMCs usually delay the time at which the major peak occurs, which is an indication of a retarding effect of pozzolanic materials. It was found by [33] that the kinetics of the pozzolanic reaction and the types of reaction products, for modified concrete with silica fume and kaolin, depend on the pozzolan and its lime content. Mostafa and Brown [11] confirmed experimentally that the hydrated silica are capable of reaction with the alkalis and $Ca(OH)_2$ during the induction period. Similar trends are usually obtained with other types of SCMs. In some cases, there is a kind of a shoulder for the curve, after the main hydration peak, which is interpreted by some researchers to be due to the pozzolanic reaction with the relatively high concentration of CH produced after the main hydration peak. The pozzolanic reaction is much slower than cement hydration [34]. It occurs at a late curing stage after the availability of sufficient CH content to react with. At early stages, only a small amount of cement is hydrated and thus the amount of CH is low.

Substituting part of the cement by SCMs (e.g., fly ash or slag) results in diluting the cementitious materials (mainly C_3S) in the concrete mixture. As described earlier, C_3S is the main contributor to the major hydration peak, then, both C_3S and C_2S contribute to the slow continuous reaction period. Although the pozzolanic reaction increases the heat evolution from the concrete mixture, the dilution effect decreases the net heat generation rate. This reduction in heat evolution is especially beneficial in concrete used for massive structures (i.e., mass concrete) [35]. The observed difference in the height of the peak-temperature (relative to 100% OPC) is related to two effects: (1) substitution of the pozzolanic materials (fly ash and slag) on the heat development; (2) dilution of main cement compounds (C_3S) with the addition of fly ash and slag.

1.5 Admixtures and pozzolanic materials

A wide range of organic and inorganic additives and admixtures are used in the construction industry for the purposes of controlling and manipulating various properties of fresh and cured concrete. It is worth mentioning that the terminologies used for material additions to concrete, include admixtures, additives, and enhancers. Although admixtures and additives may be used in intermingled manner, additives are more frequently used when a material is added to cement during the manufacturing of cement for improving its properties, while admixtures are added to a concrete mixture upon mixing for manipulating concrete characteristics. Eventually, both additions target to impact and control concrete properties. Concrete enhancers seem to be used in the concrete industry in relation to enhancing the integrity and waterproofing of concrete. The admixtures are categorized according to their chemical structure, composition, targeted purpose, function, and mechanism. They are added to concrete mixtures in the form of liquids, suspensions, or powders. The powdered mineral materials (e.g., fly ash, slag, and silica fume), which are added to concrete mixture, are termed SCMs and they belong originally to the group of admixtures. Thus they are categorized in principle as mineral admixtures. The mineral admixture term was deprecated in ASTM C125−15b [2], after a discussion note indicating that the term has been used to refer to different types of insoluble, finely divided materials, which are not useful to be grouped under a single term. Specific ASTM standards are available for these SCMs such as ASTM C618 [36], which specifies the use of fly ash and NPs in concrete and ASTM C989 [37] that provides the standard specification for ground granulated blast-furnace slag for use in concrete and mortars. Silica fumes are specified by ASTM C1240 [38].

This section is divided into two subsections describing SCMs and traditional standardized admixtures. Specific admixtures and enhancers that are added to concrete mixture for other purposes such as waterproofing are detailed in other chapters in this book.

1.5.1 Supplementary cementitious materials

SCMs are mineral oxides from natural and industrial sources (e.g., by-products of manufacturing). They include fly ash, silica fume, slag, rice husk ash, and NPs. According to ASTM C125−15b [2], SCM is “an inorganic material that contributes to the properties of a cementitious mixture through hydraulic or pozzolanic activity, or both.” The SCMs contain various types of reactive and nonreactive mineral oxides. These include the three main mineral oxides (i.e., SiO_2, Al_2O_3, and Fe_2O_3) in addition to calcium oxide (CaO), magnesium oxide (MgO), and sulfur oxide (SO_3). The total pozzolan oxides (TPO) are given by the summation of the percentages of SiO_2, Al_2O_3, and Fe_2O_3. From the perspective of chemical reactivity, the mechanisms of SCMs include pozzolanic activity and cementitious reactivity (referred to as latent hydraulic) [8]. The types of SCMs include materials that have both cementitious and pozzolanic activities such as fly ash class C, slags, and metakaolin. SCMs with only pozzolanic reactivity (with no hydraulic properties) include fly ash class F, silica fume, and NP. They require to be activated to undertake the pozzolanic activity through the presence of portlandite (CH). The pozzolanic reactions are different from the cement hydration as they are not capable of reacting with water without an alkaline activator (calcium ions) [34]. In addition to these reactive minerals, there is a third type of SCMs that include nonreactive or poorly reactive minerals. Materials of the third type (such as limestone powder) are added for filing purposes and for modifying the grindability of the clinker when added to cement. These SCMs are added to the concrete mixtures in large amounts, as partial replacements of the cement amount for (1) environmental purposes when they are recycled from industrial by-products, (2) economic purposes through reducing the cost of raw materials after replacing part of the required cement [39], and (3) quality purposes through their positive impacts on concrete characteristics. For example, they

Table 1.2 Sample compositions of fly ash, silica fume, slag, metakaolin, and natural pozzolan obtained from various sources.

Component/ material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Fly ash C [40]	39.5	16.3	6.67	22.77	4.10	4.3
Fly ash F [35]	56.3	34.2	3.2	1.2	–	0.26
Metakaolin—NP [1]	53	43	0.5	0.1	–	0.1
Calcined shale—NP [1]	50	20	8	8	–	0.4
Silica fume [41]	92–94	0.2–0.3	0.1–0.5	0.1–0.15	0.1–0.2	0.1
Slag	35	12	1	40	–	9

may improve the workability of fresh concrete due to their finely divided particles, and they enhance the concrete durability through reducing concrete porosity and consuming part of calcium hydroxide by pozzolanic reaction. Table 1.2 lists sample compositions of fly ash, silica fume, slag, metakaolin, and NP.

Fly ash is "a finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gases" [36]. The particle size of fly ash is close to that of cement particles (which has an average size of 15 μm). The particle size of fly ash has a range of $1-100$ μm, with a typical size under 20 μm [1]. Fig. 1.7 shows a scanning electron microscope micrograph of fly ash particles compared to Portland cement particles [42]. Fly ash is categorized into three main classes: C, F, and N. According to ASTM C618 [36], the total content of these pozzolan materials (TPO) must be more than 50% (see Table 1.2). Each class is produced from a certain combustion process. For example, fly ash C is normally produced from burning lignite or subbituminous coal. Fly ash F is normally produced from burning bituminous coal or from subbituminous coal. Fly ash N includes raw or calcined NPs such as diatomaceous earths, opaline cherts, shales, and volcanic ashes. Fly ash C is characterized with a high silica (SiO_2) content (above 35%), which is the main reactive material together in addition to alumina (Al_2O_3) and iron oxide (Fe_2O_3). In general, the mineral composition of fly ash C (oxides content) is close to the cement composition [40]. The main difference between fly ash C and F is the lime content and percentages of other oxides. Fly ash C contains high levels of lime (close to 25%), while fly ash F contains a much higher level of SiO_2 and a minor amount of CaO. The total mineral oxides other than CaO (i.e., SiO_2, Al_2O_3, and Fe_2O_3) are about 70% in classes F and N, while it is generally around 50% in class C. As said above, fly ash C has both the pozzolanic properties [reaction in Eq. (1.12)], and some cementitious properties (hydration with water), while Fly ash F has the pozzolanic properties only. Both of them include materials containing reactive silica and undergo the pozzolanic reaction according to Eq. (1.12).

The mechanisms of fly ash involve the reaction of the CH and gypsum from cement with the reactive silica and alumina to form additional C-S-H (with lower C/S ratio that that from cement hydration) and the monosulfate hydrate, respectively [8]. The

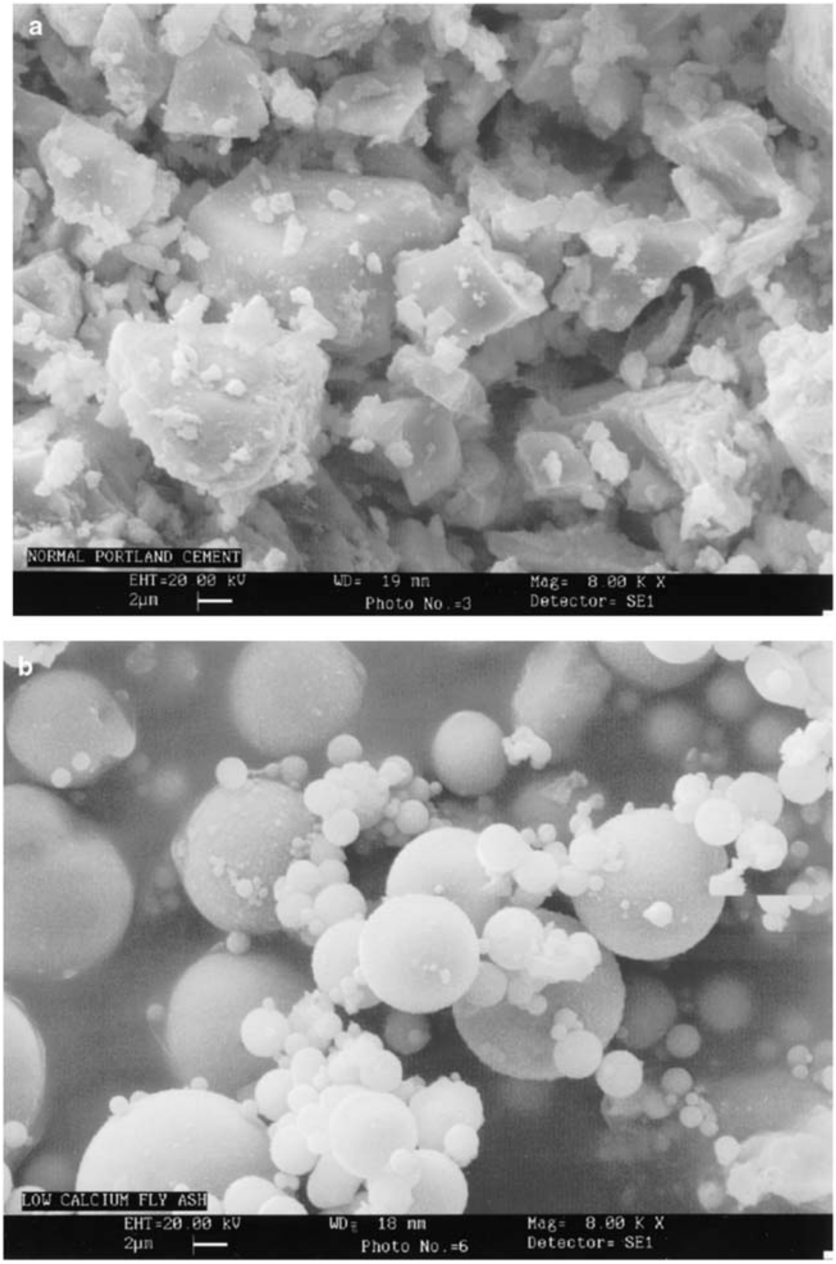


Figure 1.7 Scanning electron microscopy micrographs comparing particles of Portland cement. (A) Low-calcium fly ash. (B) At a magnification of 8000 × [42].

mechanism starts with the dissolution of reactive silica from fly ash into water solution forming silicic acid, as given by Eq. (1.14) [43]. Fly ash C involves the rapid hydration of free lime (CaO), which results in increasing the CH content. Sufficient amounts of free calcium ions and a high alkaline environment at a pH higher than 12 are needed to initiate and maintain the pozzolanic reaction of fly ash C Eq. 1.12. Thus the initial CH content in fresh concrete containing fly ash C is usually higher than that in ordinary concrete. But afterwards the CH content in concrete with fly ash C decreases through its consumption in the reaction of fly ash C with CH at higher rates [40]. Then, the pozzolanic reaction converts the soluble part of a silica-rich material (which has no cementing properties) to a calcium silicate hydrate with good cementing properties [40]. The pozzolanic reaction occurs between calcium hydroxide (CH), and silicic acid [H_4SiO_4 or $Si(OH)_4$], which is given by Eq. (1.15). It is believed that this reaction produces the same hydration products as cement [2].

$$SiO_{2-\text{solid}} + 2\,H_2O_{\text{liquid}} \rightarrow H_4SiO_{4-\text{aqueous}} \tag{1.14}$$

$$Ca(OH)_2 + H_4SiO_4 \rightarrow CaH_2SiO_4 \cdot 2\,H_2O \tag{1.15}$$

In addition to the above pozzolanic reaction(s), there are other cementitious reactions (as involved in cement hydration) for fly ash C, that is, between silica and lime (from fly ash C). Other pozzolanic reactions may be undergone by the other contents. The reactive noncrystalline alumina (Al_2O_3) reacts with gypsum and CH to form ettringite, then ettringite is converted to the monosulfate when gypsum is consumed from the fresh concrete [8]. However, iron oxide (Fe_2O_3) contributes little in these reactions, although it is included in the TPO [42].

The addition of fly ash to concrete mix as a partial replacement to cement has a noticeable impact on porosity, cement hydration, workability, and other durability problems such as alkali aggregate reaction (see Chapter 3). The addition of fly ash improves the fluidity or workability of fresh concrete [35], as its spherical particles act as lubricating agent and thus assists in improving the rheology of fresh paste [34]. This in turn reduces water demand of the mixtures [44]. Fly ash has a property of low heat for hydration, thus it has been used for mass concrete [35]. Fly ash has a retarding effect on cement hydration (mainly at high water/cementitious ratios) [43]. It has been reported that the addition of fly ash class C resulted in the same compressive strength as control concrete (without fly ash) [40]. Such a strength performance depends on the fly ash content of active silica [40]. Some reported experimental results indicated that when fly ash replaced cement (by 20%), the strength is slightly reduced in the first few days. Then, the strength of concrete with fly ash C is closer to the control concrete, and are almost identical after 49 days [40]. Other experimental results indicated that fly ash increases the compressive strength [45]. The compressive strength of fly ash mortar depends on the fly ash fineness (particle size) [44]. The addition of fly ash impacts the compressive strength through two mechanisms: (1) cementing action from the products of the above-mentioned reactions; (2) densifying effect through pore blocking by the insoluble nonreactive content of fly ash, which enhances concrete integrity. At early stages, the packing effect is more noticeable, while at late stages the pozzolanic reaction is more noticeable [44].

NPs that are classified by ASTM C618 [36] as fly ash class N include calcined clay, calcined shale, and metakaolin. They are used in dams, as they have the ability to control temperature rise in mass concrete and provide cementitious effect (hydration with water). They are also used to improve the concrete resistance to sulfate attack and reduce the alkali − silica reaction. Metakaolin is a kind of calcined clay that is produced by low temperature calcination of high purity kaolin clay, and grounded to an average particle size of about 1−2 μm [1]. It is very fine when compared with cement particles (which have an average size of 15 μm). Fig. 1.8 shows a scanning electron microscope micrograph of metakaolin particles [12]. Calcined shale usually contains an appreciable percentage of calcium oxide, which gives it the cementing property or hydraulic activity [12].

Silica fume (micro-silica) is defined in ASTM C1240 [38] as "a very fine pozzolanic material, composed mostly of amorphous silica produced by electric arc furnaces as a by-product of the production of elemental silicon or ferro-silicon alloys" (also known as condensed silica fume). It is essentially silicon dioxide and usually contains more than 85% of SiO_2 (see Table 1.2). It has an amorphous structure with extremely fine particles of less than 1 μm, and with an average size of about 0.1 μm, that is, it is very fine when compared with cement particles. Fig. 1.8 shows a scanning electron microscope micrograph of silica fume particles [46]. Silica fume is used in applications requiring a high strength and a very low permeability.

Ground granulated iron blast-furnace slag (slag cement) is a water-cooled nonmetallic hydraulic cement consisting essentially of silicates and aluminosilicates of calcium grounded to less than 45 μm [1]. Fig. 1.9 shows a scanning electron

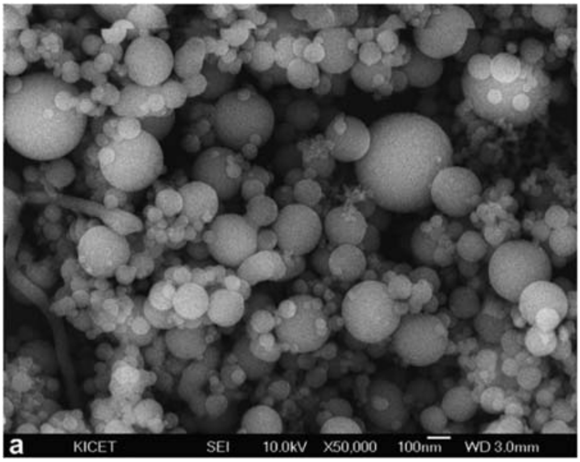


Figure 1.8 Scanning electron microscope micrograph of silica fume particles with average particle diameter of 0.1 mm [46].

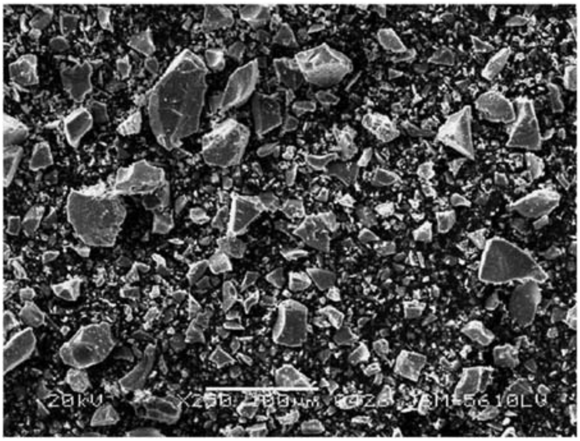


Figure 1.9 Scanning electron microscope micrograph of ground granulated iron blast-furnace slag particles at magnification of 2100 × [47].

microscope micrograph of slag particles [47]. It hydrates upon reacting with water and alkaline activator (CH), and sets similar to Portland cement. It is divided according to ASTM C989 [37] into grades 80, 100, and 120 for low, medium, and high activity index, respectively.

1.5.2 Chemical admixtures

According to ASTM C125−15b [2], an admixture is "a material other than water, aggregates, cementitious material, and fiber reinforcement that is used as an ingredient of a cementitious mixture to modify its freshly mixed, setting, or hardened properties and that is added to the batch before or during its mixing." ACI CT-18 [1] refers to admixture as chemical admixture and defines it as "a liquid, or dispersible powder, used as an ingredient in a cementitious mixture to improve its economy and/or properties in the plastic and/or hardened state." ACI published a report on chemical admixtures for concrete (ACI 212.3R) [48], with a definition of admixture similar to that in ASTM C125−15b [2].

The admixtures are added for improving concrete mixture economy and performance at various stages, starting from the moment of its mixing and continuing for long periods of its service life. Their performance is generally based on various physicochemical mechanisms related to surface interactions of nonhydrated or hydrated cement compounds. Understanding these mechanisms requires some background in the field of colloid chemistry and suspension stability. It requires recalling the concepts of water interactions with materials (see Chapter 5), including (1) hydrophobicity, which is an air-loving behavior (water-repelling) and (2) hydrophilicity, which is a characteristic of water attraction (water-loving). Within this context, surfactant admixtures are surface-active long chained organic molecules, which have hydrophilic and hydrophobic molecular ends. These chemicals can be adsorbed on the surface of cement particles and influence the surface tension of water. Their hydrophilic ends contain ionic groups such as carboxylic group (COO^-), which attract water molecules and maintain them in liquid phase, thus preventing their quick evaporation due to exothermic heat evaluation from cement hydration. On the other hand, the hydrophobic organic groups attract air and force air bubbles to be entrained in the concrete mixture. Other chemical admixtures dissociate to supply ions to mixing water, which then participate or interfere with the cement hydration reactions and other interactions at short or long time periods. For mineral admixtures and some enhancers, a chemical mechanism may also be involved through undergoing certain reactions with cement constituents or more frequently, with the hydration by-products of cement (e.g., see pozzolanic reactions as described in Section 1.3).

The purposes of using the chemical admixtures include any of the following or combinations of them:

1. Enhancing the properties of fresh concrete mixture to improve its flowability and to control its consistency. This purpose includes increasing slump, workability, pumpability, finishability, modifying rheology, and reducing settlement and segregation.
2. Controlling (extending it or decreasing) the time required for concrete setting. This is done according to the environmental conditions and project requirements, through manipulating and controlling the rate of cement hydration. These include retarding the hydration rate in hot climate or accelerating it in cold environments.
3. Reducing the required amount of water for certain targeted characteristics of fresh concrete, which then improves various characteristics of cured concrete as those indicated in purposes 4–6, below.
4. Enhancing the mechanical properties of cured concrete such as increasing compressive and flexural strength at all curing ages.
5. Reducing water penetration in concrete, for example by reducing its porosity through reducing w/c ratio or through pore blocking mechanism, or making its surface a water-repellent.
6. Enhancing concrete resistance against various types of aggressive environments including thermal, mechanical, chemical, and biological attacks (i.e., enhancing concrete durability).

In addition to achieving any of these targeted purposes, these admixtures may result in other desired or undesired effects on concrete properties. Admixtures that are formulated intentionally to target more than one purpose include, for example, water-reducing and accelerating admixtures (purposes 1 and 2), which reduce the quantity of mixing water required to produce concrete of a given consistency and accelerate the setting and early strength development of concrete. Then, it can have other purposes among the list of 4–6 as a consequence of reducing water requirement as will be detailed later in this book. The above explained mechanism of water retaining capacity of surfactant admixtures results also in improving the mixture homogeneity and thickening. Thus they reduce the availability of free water that may cause bleeding, and consequently, reduces the tendency for segregation.

ASTM C494 [49] includes standard specifications for seven types of the water-reducing and/or set-controlling chemical admixtures (A − G types). The chemical admixtures are classified in ACI 212.3R [48] into 13 groups. Some of the ACI groups can be considered as specific cases of other main groups. The following are the most commonly used admixtures:

1. *Air-entraining admixtures* such as organic salts of sulfonated hydrocarbons and sulfonated lignin, and fatty acids and their salts. They create microscopic air bubbles in concrete during mixing to improve the resistance of cured concrete against damage from cyclic temperature change under cycles of freezing and thawing, in the presence of deicing salts and other durability purposes. They also improve workability.
2. *Accelerating admixtures* such as sodium/calcium formate, sodium/calcium nitrite, calcium nitrate, aluminates, and silicates. They increase the rate of cement hydration and accelerate concrete setting, thus shortening the time of setting.
3. *Water-reducing and set-retarding admixtures* such as lignosulfonic acids and their salts, carboxylic acids, and carbohydrate-based compounds such as sugars. They are added to reduce the required amount of water for achieving a certain workability and for delaying the concrete setting by decreasing the rate of cement hydration. There are classified (according to ASTM C494/C494M) [49] into seven types (e.g., A, B, C . . ., etc.) according to the percentage reduction in water requirement and the type of setting control.
4. *Shrinkage-reducing admixtures* such as polyoxyalkylene alkyl ether and propylene glycol. They are added to reduce the drying shrinkage, which is one of the durability problems (see Chapter 3) and they achieve other purposes as described in Chapter 7.
5. *Corrosion-inhibiting admixtures* such as amine carboxylates aminoester organic emulsion, chromates, and phosphates. They are added to reduce the rate of steel corrosion due to chemical attack from soluble aggressive ions (e.g., chloride ions).
6. *Lithium admixtures* such as lithium nitrate, nitrite, carbonate, and hydroxide. They are added to reduce the lethal expansions from alkali − silica reactions (they are further discussed in Chapter 7).
7. *Permeability-reducing admixtures* such as crystallization materials that block the pores of concrete, and water-repelling materials that coat the surface of pores. They are used to reduce water penetration into concrete and to minimize water-related problems, as discussed in the coming chapters of this book.
8. Other miscellaneous admixtures such as polymeric materials used for increasing bonding, pigments for coloring concrete, and fungicidal, insecticidal materials (e.g., copper compounds) for inhibiting the growth of harmful microorganisms.

In addition to these chemical and mineral admixtures, there are other additives for improving other nonconventional characteristics of concrete, such as thermal properties. Additives of these kinds include phase change materials (PCM) such as paraffins and other materials that impact the thermal characteristics of concrete. PCM and other additives have noticeable effects on the thermal conductivity, heat capacity, and the thermal diffusivity of concrete. These additives are recently applied in the field of energy savings in buildings through improving concrete insulation characteristics and for durability purposes such as improving concrete resistance against thermal stresses. Some of these additives are further discussed in Chapter 2.

1.6 Durability problems related to concrete chemistry

The concrete physicochemical behavior is associated with various damaging problems that reduce its service life. As said earlier, concrete durability is the ability of a material to resist weathering action, chemical attack, abrasion, and other conditions of service. Concrete durability problems are caused by the surrounding conditions that are chemically reactive or physically interactive with concrete. These problems are better discussed after the analysis of concrete microstructure, permeability, and other transport properties for the migration of aggressive materials through concrete, as detailed in the next chapter. Meanwhile, this chapter is concluded with highlights on the relationship between the presented concrete chemistry and the associated concrete structural problems. Then Chapter 3 details concrete durability problems based on the required background in Chapter 2.

As described above, the hydration of cement results in empty spaces between the products and the addition of some admixtures create air voids, both of which make the concrete a porous material. Such a concrete porosity is directly related to concrete permeability for liquids and gases, and its diffusivity of various components, which are described by well-known transport equations as analyzed in Chapter 2. The reactivity of aggressive materials with the mineral compounds of cement paste and aggregates are the main causes of concrete problems. For example, the soluble alkaline content of concrete controls the pH of the solution within the pores of concrete. This in turn governs the types of deteriorating reactions that may occur within concrete structure. Under high alkaline conditions, chemical reactions with aggregates may occur, while under less alkaline conditions (due to acidic environment), other reactions may occur such as corrosion reactions with reinforcing steel bars and carbonation reactions with lime. The alkalinity of pore solution is governed by the alkaline materials, which come from the by-product of cement hydration (CH), as described above, and from the cement basic content (e.g., MgO, K_2O, and Na_2O, as listed in Table 1.1. The source of acidity can be from solubilization of carbon dioxide from air, or from other chemical contaminants that are carried with water penetration in concrete. These reactions are detailed in Chapter 3.

Based on this introduction, Table 1.3 summarizes parameters of concrete chemistry in relation to its durability problems. The cement composition is the first

Table 1.3 The main parameters of concrete chemistry and their relationships to its durability.

Parameter	Durability effects
Concrete structure as a composite material	There are various reactive phases that interact with the environmental exposure conditions, which may create disintegration and discontinuity of phases.
Concrete binder	The types of cements and their additives impact the hydration products and their stability. The cement is a source of harmful alkaline materials, which have destructive reactions with concrete. Also, the cement content of SO_3 impacts expansion and drying shrinkage.
Mixing water	The chemical content (e.g., salts and chloride ions) can be a source of deterioration reactions of concrete and reinforcing steel bars.

(*Continued*)

Table 1.3 (Continued)

Parameter	**Durability effects**
Aggregates	The types of aggregates and their reactivity with alkaline materials can lead to their deterioration and weakness through alkali aggregate reactions.
Cement hydration chemistry	Various concrete problems are associated with the degree of the hydration reactions, the types of the hydration products, and the resulting degree of concrete porosity and other transport properties.
Heat of hydration and kinetics	The rate of hydration reaction governs the rate of heat evolution and thus controls the level of temperature rise and the evaporation rate of water, which in turn impact the level of concrete cracking and shrinkage damage.
Pozzolanic reactions	They consume part of the harmful calcium hydroxide and thus reduce its aggressive damaging reactions in concrete. They also reduce concrete permeability for aggressive materials.
Mineral admixtures	They have important impacts on concrete problems as explained in Chapter 2.
Chemical admixtures	They have various impacts on controlling concrete damaging problems, for example, reducing water content, results in less porous and less permeable pores, and thus more resistant concrete for chemical attack. Also, air-entraining admixtures create more voids to accommodate the expansion of water upon freezing.

important parameter, as it dictates the types of cement hydration products and their stability, and it specifies the contents of alkaline materials and sulfur trioxide. The quality of mixing water affects the severity and reactivity of the water environment and the residual contaminants in concrete pores. The type and chemical composition of the aggregates determine their porosity and their reactivity with alkaline materials, through alkali aggregate reactions. The addition of chemical admixtures impacts the integrity of concrete and the void content, which then controls the penetration and the expansion of water upon freezing. The reactions and pore blocking effects of the SCMs and the pozzolanic materials play major roles in controlling concrete permeability and thus enhancing its durability, as detailed later in this book.

References

[1] ACI. (2018). *CT-18 concrete terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[2] ASTM. (2003). *C125 − 15b Standard terminology relating to concrete and concrete aggregates. Annual Book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

[3] Shetty, M. (2005). *Concrete technology theory and practice* (pp. 420−453). S. Chand & Company Ltd.

[4] Chindaprasirt, P., et al. (2008). Cement paste characteristics and porous concrete properties. *Construction and Building Materials*, *22*(5), 894−901.

[5] Callister, W. D., & Rethwisch, D. G. (2011). *Materials science and engineering* (Vol. 5). New York: John Wiley & Sons.

[6] Wong, H., et al. (2011). Effect of entrained air voids on the microstructure and mass transport properties of concrete. *Cement and Concrete Research*, *41*(10), 1067−1077.

[7] Ye, G. (2003). Experimental study and numerical simulation of the development of the microstructure and permeability of cementitious materials. Master of Engineering thesis, University of Technology, TU, Delft. Delft, The Netherlands.

[8] Bapat, J. D. (2012). *Mineral admixtures in cement and concrete*. CRC Press.

[9] Artioli, G., & Bullard, J. W. (2013). Cement hydration: The role of adsorption and crystal growth. *Crystal research and technology*, *48*(10), 903−918.

[10] Liu, F., Sun, Z., & Qi, C. (2015). Raman spectroscopy study on the hydration behaviors of Portland cement pastes during setting. *Journal of Materials in Civil Engineering*, *27* (8), 04014223.

[11] Mostafa, N., & Brown, P. (2005). Heat of hydration of high reactive pozzolans in blended cements: Isothermal conduction calorimetry. *Thermochimica Aacta*, *435*(2), 162−167.

[12] Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C. (2002). *Design and control of concrete mixtures* (Vol. 5420). Skokie, IL: Portland Cement Association.

[13] Pang, X., et al. (2013). A comparison study of Portland cement hydration kinetics as measured by chemical shrinkage and isothermal calorimetry. *Cement and Concrete Composites*, *39*, 23−32.

[14] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. New York, USA: McGraw-Hill Education.

[15] ASTM. (2017). *C150/C150M-17, Standard specification for Portland cement. Annual book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

[16] Garcia, J.E., et al., *Laboratory and Outdoor Exposure Site Evaluations of Portland Limestone Cements (Report No. FHWA/TX-18/0-6858-1)*. 2019, The University of Texas at Austin: Austin, USA.

[17] Aïtcin, P. C. (2016). 5—Water and its role on concrete performance. In P.-C. Aïtcin, & R. J. Flatt (Eds.), *Science and technology of concrete admixtures* (pp. 75−86). Woodhead Publishing.

[18] Kaushik, S., & Islam, S. (1995). Suitability of sea water for mixing structural concrete exposed to a marine environment. *Cement and Concrete Composites*, *17*(3), 177−185.

[19] ASTM. (2020). *C143/C143M-20, Standard test method for slump of hydraulic-cement concrete. Annual book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

[20] ASTM. (2016). *C403/C403M-16, Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance. Annual book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

[21] Bullard, J. W., et al. (2011). Mechanisms of cement hydration. *Cement and Concrete Research*, *41*(12), 1208−1223.

[22] Dunuweera, S., & Rajapakse, R. (2018). Cement types, composition, uses and advantages of nanocement, environmental impact on cement production, and possible solutions. *Advances in Materials Science and Engineering*.

[23] Sun, X., & Hou, Y. (2020). Experimental investigation of the macroscopic behavior and microstructure property evolution of hardened cement consolidated tailings. *Minerals*, *10*(1), 6.

[24] Mounanga, P., et al. (2004). Predicting Ca (OH)2 content and chemical shrinkage of hydrating cement pastes using analytical approach. *Cement and Concrete Research*, *34* (2), 255−265.

[25] Fogler, H. S. (2010). *Essentials of chemical reaction engineering*. Pearson Education.

[26] Franus, W., R. Panek, and M. Wdowin. *SEM Investigation of Microstructures in Hydration Products of Portland Cement. in 2nd International Multidisciplinary Microscopy and Microanalysis Congress*. 2015. Cham: Springer International Publishing.

[27] Fu, T., Montes, F., Suraneni, P., Youngblood, J., & Weiss, J. (2017). The influence of cellulose nanocrystals on the hydration and flexural strength of portland cement pastes. *Polymers*, *9*(9), p. 424.

[28] Livesey, P., Donnelly, A., & Tomlinson, C. (1991). Measurement of the heat of hydration of cement. *Cement and Concrete Composites*, *13*(3), 177−185.

[29] Van Breugel, K. (2004). Modelling of cement-based systems—The alchemy of cement chemistry. *Cement and Concrete Research*, *34*(9), 1661−1668.

[30] Tennis, P. D., & Jennings, H. M. (2000). A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes. *Cement and Concrete Research*, *30*(6), 855−863.

[31] Knapen, E., & Van Gemert, D. (2009). Cement hydration and microstructure formation in the presence of water-soluble polymers. *Cement and Concrete Research*, *39*(1), 6−13.

[32] Marchon, D., & Flatt, R. J. (2016). 8—Mechanisms of cement hydration. In P.-C. Aïtcin, & R. J. Flatt (Eds.), *Science and Technology of Concrete Admixtures* (pp. 129−145). Woodhead Publishing.

[33] Mostafa, N., et al. (2001). Characterization and evaluation of the pozzolanic activity of Egyptian industrial by-products: I: Silica fume and dealuminated kaolin. *Cement and Concrete Research*, *31*(3), 467−474.

[34] Zeng, Q., et al. (2012). Determination of cement hydration and pozzolanic reaction extents for fly-ash cement pastes. *Construction and Building Materials*, *27*(1), 560−569.

[35] Sakai, E., et al. (2005). Hydration of fly ash cement. *Cement and Concrete Research*, *35*(6), 1135−1140.

[36] ASTM. (1985). *C618: Specification for fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete*. *Annual book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

[37] ASTM. (1999). *C989: Standard specification for ground granulated blast-furnace slag for use in concrete and mortars*. *Annual book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

[38] ASTM. (2004). *C1240-05: Standard specification for silica fume used in cementitious mixtures*. Annual book of ASTM Standards. West Conshohocken, PA, USA: American Society for Testing and Materials Standard Practice, Philadelphia, Pennsylvania, USA.

[39] Zhang, Y., & Zhang, M. (2014). Transport properties in unsaturated cement-based materials—A review. *Construction and Building Materials*, *72*, 367−379.

[40] Papadakis, V. G. (2000). Effect of fly ash on Portland cement systems: Part II. High-calcium fly ash. *Cement and Concrete Research*, *30*(10), 1647−1654.

[41] Malhotra, V. M. (1989). Fly ash, silica fume, slag, and natural pozzolans in concrete. In: 3. *International Conference on fly ash, silica fume, slag, and natural pozzolans in concrete*. American Concrete Institute: Trondheim, Norway.

[42] Papadakis, V. G. (1999). Effect of fly ash on Portland cement systems: Part I. Low-calcium fly ash. *Cement and Concrete Research*, *29*(11), 1727−1736.

[43] Langan, B., Weng, K., & Ward, M. (2002). Effect of silica fume and fly ash on heat of hydration of Portland cement. *Cement and Concrete Research*, *32*(7), 1045−1051.

[44] Tangpagasit, J., et al. (2005). Packing effect and pozzolanic reaction of fly ash in mortar. *Cement and Concrete Research*, *35*(6), 1145−1151.

[45] Saha, A. K., et al. (2018). The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials*, *171*, 743−758.

[46] Jo, B.-W., et al. (2007). *Characteristics of cement mortar with nano-*SiO_2 *particles*. *Construction and Building Materials*, *21*(6), 1351−1355.

[47] Wan, H., Shui, Z., & Lin, Z. (2004). Analysis of geometric characteristics of GGBS particles and their influences on cement properties. *Cement and Concrete Research*, *34* (1), 133−137.

[48] ACI. (1999). *Committee 212. ACI 212.3R-91 chemical admixtures for concrete*. Farmington Hills, MI, USA. American Concrete Institute

[49] ASTM. (2004). *C494: Standard specification for chemical admixtures for concrete. Annual book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

Concrete porosity and transport processes

2

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

2.1 Introduction

The penetration of water and harmful materials cause various types of concrete attacks and reduces its durability. The permeability of concrete is based on its porosity and both of them govern its durability. In order to establish the required background for understanding the mechanisms of water-related problems and analyzing the technologies of waterproofing and durability solutions, structural analysis is essential. For this purpose, this chapter discusses the structure and the types of pores and air voids and describes the main transport processes in concrete. In chemical engineering literature, the transport processes involve fluid flow, heat transfer, and mass transfer, which are governed by well-established laws that relate the transport rate to a specific driving force for each transport process. These driving forces include pressure, concentration, and temperature gradients. The associated transport characteristics of permeability, diffusivity, and conductivity and the general governing equations of fluid flow, heat transfer, and mass transfer are presented and analyzed.

Concrete microstructure depends on many parameters such as the amount and the type of the binder and its particle size distribution, material selection and proportioning, cement hydration temperature, humidity conditions, and the curing age [1]. In addition, it can be controlled by the addition of admixtures and enhancers. Most of these parameters are discussed in Chapter 1. The topics of material selection and proportioning are discussed in Chapter 4, while the durability problems are described in Chapter 3.

2.2 Concrete structure and porosity

In this section, the structures of pores and voids are analyzed as an introduction to the subsequent sections and to the book topics. The impact of pore and void structures on concrete mechanical and transport properties are discussed. For concrete in service, the microstructure involves cracks resulting from concrete durability problems and degradation mechanisms, as detailed in Chapter 3.

Concrete porosity is related to the macrostructure of the two main phases of aggregate particles and cement paste. The aggregates usually include two types (e.g., sand and crushed limestone). In fact, the aggregates and paste phases are

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00002-7

composed of several phases. At the microscopic level, these phases are themselves porous. The coarse aggregates contain voids and microcracks. The paste phase is heterogeneous and it is composed of a solid cementitious matrix, pores, and microcracks. Variations in the density and porosity within the paste may occur. In fact, there is an additional paste phase, labeled as an interfacial transition zone (ITZ) between the aggregates and the bulk of the paste. The ITZ phase between the aggregates and the bulk paste has a thickness with the range of 10−50 μm and has different characteristics and porosity than those of the bulk cement phase. It is weak and less dense than the bulk paste. The capillary porosity is higher near the surface of the aggregates because of wall effect [2]. The sizes of pores and voids vary from phase to phase, and from concrete type to another, and changes with concrete curing age and w/c ratio.

The evolution of the paste microstructure is commonly investigated through experimental and modeling approaches [1]. The mechanism of pores formation within the paste is attributed to both colloidal behavior and hydration mechanism. The porosity is created by chemical contraction of the unfilled space in the concrete mixture during cement hydration when water is consumed by the hydration reactions or evaporated due to the exothermic heat release [3]. The porosity is strongly affected by the water to cement (w/c) ratio. Increasing the water content in the fresh concrete mixture increases paste porosity. As indicated in Chapter 1, a w/c of about 0.38 is required for the reaction of full cement hydration and for supplying the required physically adsorbed water within the gel pores. When more water content is used, the extra water will create more capillary pores.

In fresh concrete, the cement particles exist in water suspension, and they attract each other through the colloidal forces. Thus they assemble into agglomerations, which entrap water within their networks. Part of such an entrapped water is utilized in the hydration of cement. Subsequently, the entrapped water phase becomes concentrated with dissolved materials giving rise to concentration gradients within the water phase. In addition, part of the water evaporates as a result of the heat evolution from the exothermic cement hydration reactions creating a space filled with humid air. Air humidity changes with temperature as well as with the phase change of water and the mass transfer between liquid and air at variable evaporation/condensation rates. These variations lead to changes in the porosity coupled with strength development as concrete matures.

The total volume of concrete remains essentially constant during the curing process. However, changes in internal volumes occur when part of the water volume in the fresh concrete is consumed by the cement hydration reactions and another part is evaporated. Pores and voids are then formed at relatively high temperature and low relative humidity [4]. As indicated in Chapter 1 the specific gravities of the four main cement components (the silicates) are in the range of 3−3.7, while, the specific gravities of the resulting hydrates range between 1.8 and 2.5 [5]. Thus the volume of the total hydration products is larger than the volume of cement (by a factor of 2.3) [2]. Chemical shrinkage is the reduction in net volume of cementitious paste that occurs during hydration because the reaction products occupy less volume than originally occupied by the water and unreacted cementitious materials (ASTM C125−15b) [6]. For example, the hydration of tricalcium silicate is associated with a chemical shrinkage of 54.5 mm^3/g C_3S and that of dicalcium silicate is 200 mm^3/g C_2S [5]. The density of concrete is strongly dependent on its porosity.

Concrete pore structure includes permeable and impermeable pores. They occupy about 5%−6% of the paste volume. The total concrete porosity is defined as the total volume fraction of all pores. It includes the effective porosity plus the so-called ink-bottle porosity and isolated pores. The effective porosity takes into account the effective flow channel in the pore structure and it composes about 20% − 50% of the total porosity [1]. Fig. 2.1 shows the effect of curing age and w/c ratio on porosity [7]. A larger fraction of irregular pores with complex structure exists at early age and for mixtures with high w/c ratio [1]. The total porosity of a cementitious mixture decreases with curing age and with decreasing w/c ratio. A similar trend is reported for the effective porosity, which governs the water permeability. Then, the pore size decreases by increasing curing time and/or decreasing w/c ratio [8].

There are several definitions of density in relation to the pore structure. Relative density (specific gravity) is the ratio of the density of material to the density of distilled water at the same stated temperature (or assumed to be 23°C [73.5°F]). Absolute density is the mass per unit volume of a material. Apparent density is the mass of the solid material divided by the volume of solid material plus impermeable pores [6]. Skeleton density is defined as the mass of the solid material divided by the volume of solid material only (without the volume of pores) [1]. Oven-dry and saturated-surface-dry densities are defined when permeable concrete pores are included in the volume, in order to specify the moisture condition of the pores when measuring the mass of concrete. The concrete density can be decreased by

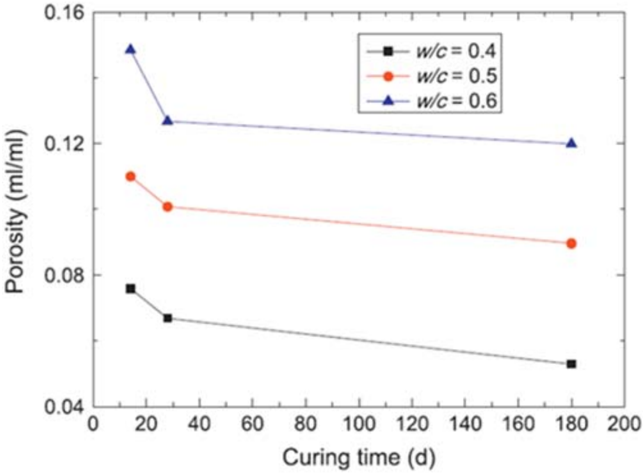


Figure 2.1 Effect of curing age on porosity of cement mortar for various water/cement (w/c) ratios [7].

consolidation (the process of increasing the density of a fresh cementitious mixture in a form, mold, or container by reducing the volume of voids) [6].

Concrete is characterized by a heterogeneous pore structure with a wide range of pore size distribution, as illustrated in Fig. 2.2. The pore structure is complex and largely dependent on the hydration process and the w/c ratio. The pore size ranges from less than 1 nm to 1 μm (beyond what is plotted in Fig. 2.2, and the variation can reach up to six orders of magnitude [1]. The interfacial transition zone between the aggregates and the cement paste (ITZ) is more porous and it contains cracks resulting from shrinkage [4]. The pores are classified into gel and capillary pores as shown schematically in Fig. 2.3. The cementitious matrix occupied by the hydration products encloses fine pores that exist within the C − S − H crystals or gel (named gel pores). The hydration crystals are surrounded by larger capillary pores that form connected networks. Air voids are formed by the entrapped and entrained air [1]. Table 2.1 lists the characteristics of these various types of pores and voids. Fig. 2.4 shows a typical backscattered electron imaging image of concrete containing entrained air, revealing the aggregates, the paste matrix, the air voids, and the capillary pores [9].

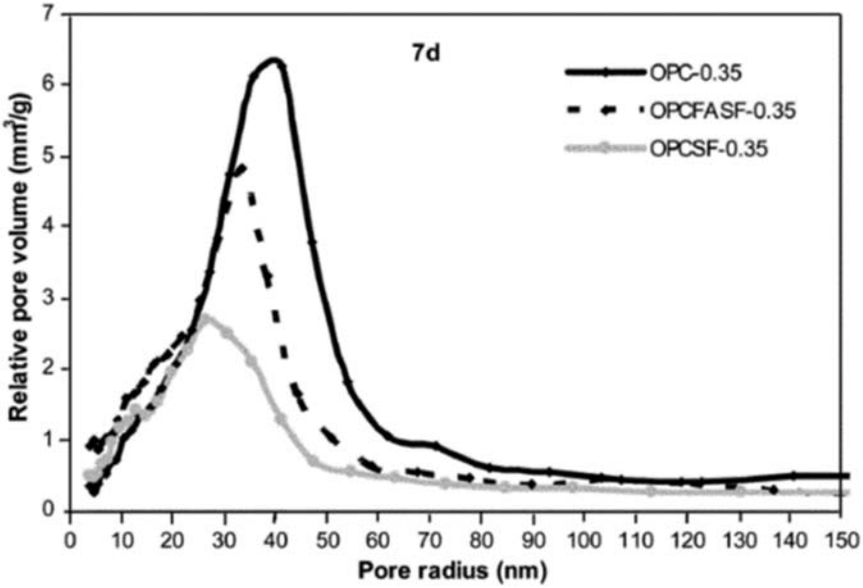


Figure 2.2 Relative pore volume for 0.35 concrete mixtures at 7 days comparing cases with concrete made of ordinary Portland cement and with 8% cement replacement by silica fume (containing 94.9% SiO_2) and ternary binder where 4% and 22% of the cement were replaced by silica fume and fly ash (containing 52%, 27%, 4.7%, and 8.6% for SiO_2, Al_2O_3, CaO, and Fe_2O_3, respectively) [8].

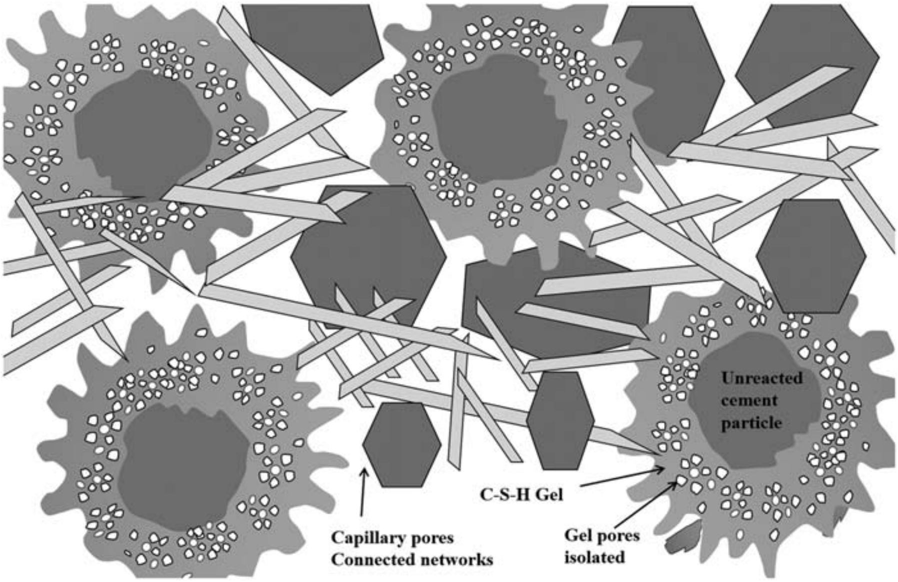


Figure 2.3 Schematic representation of a cement paste, showing gel pores and capillary networks.

The capillary porosity is controlled by the degree of hydration. As the hydration process proceeds, the total porosity of cement paste decreases (see Fig. 2.1) and the volume of large pores decreases significantly [8]. In addition to its impact on minimizing the total porosities (as illustrated in Fig. 2.1), the w/c ratio has a higher effect on refining the pore structure than curing time (i.e., shifting the peak of Fig. 2.2) [8]. Reducing the size of cement particles increases the fraction of smaller pores. On the other hand, increasing the cement flocculation increases the pore size.

Controlling the pore size and distribution along with their connectivity is an essential parameter for controlling the concrete transport properties and durability properties such as shrinkage [8] (see Table 2.1). In fact, the pore size distribution is more important in analyzing concrete porous structure than considering just a nominal pore size. The connectivity of the pores is dependent on the degree of cement hydration [11]. The fine pores may result in two opposing impacts on concrete characteristics: on one hand, they improve the mechanical performance and thus enhance the durability. On the other hand, they increase self-desiccation shrinkage, which is caused by the high capillary depression.

Concrete made of ordinary portland cement is more porous and contains larger pores than concrete modified with the addition of mineral admixtures or supplementary cementitious materials (SCMs). The use of pozzolanic materials, such as fly ash and silica fume (SF), decreases the total porosity and refines the pore structure

Table 2.1 Characteristics of various types of pores and voids in cementitious pastes.

Type	Description	Size	Occurrence	Impacts
Gel pores	Interlayer micropores	< 0.5 nm	Within hydration layers	Shrinkage, creep
	Micropores	0.5−3 nm	Within hydration layers	Shrinkage, creep
Capillary pores	Small capillaries	3−10 nm	Within hydration layers	Shrinkage to 50% relative humidity (RH)
	Medium capillary	10−50 nm	Between C-S-H crystals	Strength, permeability, shrinkage at high humidity
	Large capillaries (macropores)	50 nm−0.5 µm (or < 3 µm) [10]	Between C-S-H crystals	Strength, permeability
Entrained air voids	Nearly spherical voids—macropores [8]	10−1000 µm (1 mm) [6] (or > 3 µm) [10]	Intentionally added through admixtures	Durability—resistance to freezing and thawing
Entrapped air voids	Irregular macropores [8]	≥ 1 mm	Unintentionally created from bad mixing and handling of fresh mixtures	—

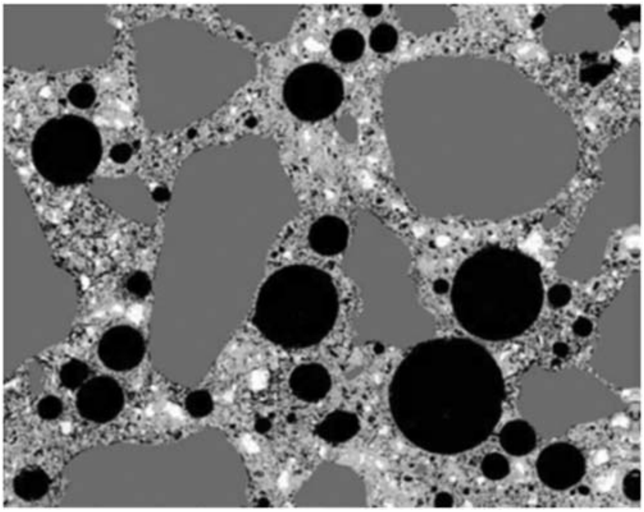


Figure 2.4 Backscattered electron imaging (BSE) image of a control concrete (A). Concrete containing entrained air (B). Images were obtained at 100 × magnification (field of view: 1200 × 960 μm) and segmented to reveal the aggregates, the paste matrix, the air voids, and the capillary pores [9].

by reducing the volume of large pores [8] (see Fig. 2.2). The achievable level of refinement of these pores depends on the type, proportion, and fineness of the pozzolanic materials incorporated [8]. It was reported that the incorporation of pozzolanic materials reduces the average pore size significantly and it increases the amount of pores smaller than 15 nm [8]. The pozzolanic reaction (see Chapter 1) results in more $C-S-H$ gel formation and consumes part of the calcium hydroxide; thus it contributes greatly in refining the pore structure of concrete by subdividing the large pores into fine ones.

Fly ash has a noticeable impact on the pores structure and the porosity of modified concrete. It has been experimentally found that concrete specimens with fly ash of high lime content (Class C) had a higher micropore content, a lower total porosity, and a denser and a finer microstructure than control specimens [12]. The hydration of fly ash consumes part of the cement hydration by-product, $Ca(OH)_2$ (portlandite), and thus it fills the already-formed pores with its own hydration products. This helps in achieving a more compact pore structure [13]. These effects are attributed to two main reasons: (1) reducing the thickness of the ITZ between the aggregates and the cement paste, and (2) refining the pore size of the cement matrix by the products of the pozzolanic reaction and by filling effect of the unreacted fine SCMs particles [14]. On the other hand, when fly ash (with low lime content, e.g., class F) is added as a partial cement replacement, the porosity increases in proportion with the amount replaced [15]. When portland cement is partially replaced by SF or slag, the structure of $C-S-H$ crystals are changed from fibrillar to foil-like. Such a structural modification results in a less connected capillary pores [16]. Adding SF was found to be more effective for these purposes than the curing age. It refines the pore structure over time and increases both the volume fraction of pores and their surface area.

Pore structure has been used extensively for the prediction of various concrete properties [8]. The concrete porosity and pore structure impact many properties including strength, permeability, diffusivity, shrinkage, and durability. The fine pores (gel pores) are believed to have no influence or just a little impact on the mechanical properties or permeability of concrete [16], but are related to creep and shrinkage (see Table 2.1). However, the larger pores (e.g., capillary pores) impact the strength and permeability properties significantly [8]. Meddah and Tagnit-Hamou [8] reported that the finer the capillary network, the higher the capillary stress induced.

2.3 Structure of entrapped and entrained air voids

An air void is a space within a cementitious mixture that is filled with air. According to ACI concrete terminology [17] and ASTM C125−15b [6], the air content is “the volume of air voids in cement paste, mortar, or concrete, exclusive of pore space in aggregate particles, usually expressed as a percentage of total volume of the paste, mortar, or concrete.” Air voids are generated intentionally or unintentionally. These macro voids include entrapped air voids and entrained air voids, with a size ranging from 50 μm to 1 mm (or above) and with a volume percentage in the range of 3%−6% [16]. Intentionally formed air voids are generated by the addition of suitable surfactants formulated in air entraining admixtures, for manipulating some concrete characteristics (durability). Usually, air entraining admixtures are added at dosages to achieve a volume fraction of voids within the range of 4%−8% [18]. The dosage is conditioned by the maximum size of aggregates and the severity of the exposure conditions. In dry concrete, these voids are filled with air. According to ASTM C125−15b [6], entrained air voids are spherical or nearly so with a typical size between 10 μm and 1 mm [9]. According to ACI concrete terminology [17], air entrainment is “the incorporation of air in the form of microscopic bubbles [typically smaller than 1 mm (0.04 in.)] during the mixing of either concrete or mortar.” It is used mainly for the purpose of increasing concrete resistance against cycles of freezing and thawing (see Chapter 3). Concrete may contain up to 2% by volume of entrapped air voids that are unintentionally entrapped during the mixing and handling of the fresh mixture and because of incomplete compaction [9]. Extended mixing time of fresh concrete increases air contents. The entrapped air voids are irregular and larger than the entrained air voids; their size is 1 mm or larger. However, the experimental observations of Rashed and Williamson [19] did not reveal visible differences between the entrapped and the entrained air voids.

Concrete durability is governed by the sizes of air voids as well as the spacing between them. According to ACI concrete terminology [17], the spacing factor is “an index related to the maximum distance of any point in a cement paste or in the cement paste fraction of mortar or concrete from the periphery of an air void." Increasing air content increases void availability and enhances their distribution among the paste structure, and thus decreases the spacing factor [9]. For good performance against damage from cycles of freezing and thawing and scaling, the spacing factor should be smaller than a critical distance (about 200–250 μm) [9].

The characteristics of air voids (their percentage, size, and size distribution) have various effects on the properties of fresh concrete and on the properties of cured concrete including microstructure, strength, and durability [16]. As introduced in Chapter 1, the air entraining agents act as surfactants, thus they increase the workability of fresh concrete, improve its consistency, and reduce the bleeding and segregation tendency [19]. Wong et al. [9] found that the air voids had a noticeable impact on concrete microstructure, as they disrupted the packing of cement and increased the heterogeneity of the microstructure and porosity distribution. They found that the interface at the air voids (within thickness of about 30 μm from the void boundary) is similar to the aggregate-paste ITZ. They observed a relatively big hexagonal crystal of calcium hydroxide in the water-filled space around the air voids in pastes with SF [19]. On the other hand, Wong et al. [9] reported less calcium hydroxide deposited at the air void – paste interface than at the aggregate – paste interface. These structural alterations from the presence of air voids are associated with a decrease in the compressive strength. Commonly, a 1% increase in air content results in about 5% decrease in the compressive strength of concrete. With vibration of fresh concrete, the air void content can be reduced [20], and the compressive strength can be increased.

Some applications require porous concrete, or pervious concrete, which contains continuous intentionally incorporated large voids [20]. Pervious concrete is defined as a "hydraulic-cement concrete proportioned with sufficient, distributed, interconnected macroscopic voids that allow water to flow through the material under the action of gravity alone" [ASTM C125–15b [6]]. According to ACI concrete terminology [17], pervious concrete is "concrete containing little, if any, fine aggregate that results in sufficient voids to allow air and water to pass easily from the surface to underlying layers." This type of concrete is commonly used in pervious pavement, which is defined as "a pavement comprising material with sufficient continuous voids to allow water to pass from the surface to the underlying layers" [17]. In such cases, concrete high porosity is a required characteristic rather than a cause for durability problems (e.g., for environmental purposes: to allow the infiltration of rainwater into ground).

2.4 Concrete permeability

In concrete applications, there are various types of potential fluid flow and mass transfer fluxes. These include liquid and vapor penetration, gas permeabilities, and diffusivities of ions and gases. From the perspective of transport phenomena, the mechanisms of these phenomena are related. This section deals with water permeability. Concrete porosity and permeability are strongly dependent [1]; however, they refer to different characteristics. As described in the previous section, porosity is a structural criterion that indicates how much of a concrete is an open space through pores and voids, which is characterized by both the pore size and size distribution as well as on the connectivity of the pores [11,20]. Concrete porosity creates the channels or pathways for fluid flow. However, permeability is an intrinsic property that specifies the rate of fluid flow into concrete [3]. In particular terms, water permeability is an indication of the ease with which water can be transported through concrete under a pressure difference. The permeability of concrete is defined as "the movement of water due to a pressure gradient, such as water in contact with a concrete structure installed underground" [17].

In fact, moisture exists in the cement paste in various phases and forms. Thus water penetration in concrete is not limited to flow under a pressure difference. Water penetration mechanisms include capillary absorption (or sorptivity) in addition to flow permeability. According to ACI concrete terminology [17], permeability is "the ability of a given concrete to permit liquids or gases to pass through." On the other hand, penetrability is "a general term related to the ease of fluid penetration into concrete, which may occur by permeation, absorption, diffusion, or a combination thereof" [1]. Capillary absorption (or wicking) [17] "is the movement of water through the small pores in concrete in the absence of an externally applied hydraulic head." It is only driven by the surface chemistry of pores and their interaction with water (see Chapter 5). According to ACI concrete terminology [17], capillary action, or capillary suction (also termed capillary rise or capillarity) "is the movement of a liquid in the interstices of concrete, soil, or other finely porous material due to surface tension." It is characterized by the capillary water absorption coefficient [21]. This mechanism can create a water penetration velocity in the order of 10^{-6} m/s, which is very high, compared to a typical water permeability coefficient in concrete. That is why some researchers believe that the long-term durability is controlled by capillary absorption.

Moreover, not all water in concrete participates in the penetration process, as water exerts various types and amounts of surface forces on pores and cementitious compounds, and it exists in gel pores and capillary pores. The strongest interaction occurs with the chemically bound water that forms an integral part of the structure within the hydrated cement particles. Such a water form cannot be detached from concrete without destructive thermochemical actions, such as decomposing upon heating the concrete to high temperatures. ACI concrete terminology [17] defines nonevaporable water as "the water that is chemically bonded during cement hydration." The second water form is the adsorbed water onto the internal surfaces of the paste, which is physically attached to the concrete internal surfaces by the hydrogen bonding. The adsorbed water is held in pores within the $C-S-H$ structure (in gel pores); thus it is not flowable. The bonding forces of adsorbed water molecules decrease largely with increasing distance from the solid surface. The water adsorption layer can extend up to six molecular levels of water, that is, to about 1.5 nm [3]. However, a considerable part of the weakly adsorbed water can be desorbed and released back into the bulk free moisture through a mass transfer process, under strong drying conditions. This can happen when the internal percent relative humidity decreases below 30% [3]. As a consequence, the C − S − H structure shrinks considerably. The removal of such an adsorbed water is responsible for the shrinkage of the paste upon drying. The third water form is the bulk water, which is free from the aforementioned attractive forces to the concrete surface, and can fill voids larger than 5 nm. Free moisture is "a moisture having essentially the properties of pure water in bulk" [17]. This bulk water can be transported through concrete, and is the only type that is related to the water permeability phenomenon. In this section, the focus is on water transport under pressure, while Chapter 5, "Physical and chemical interactions of water with surfaces and particles" discusses the other forms of water interactions.

The concrete permeability is exponentially dependent on the porosity, which is characterized by both the size distribution of the pores and their connectivity [11,20]. Fig. 2.5 shows experimentally obtained relationship between permeability and total porosity on a semilog scale [22]. Fig. 2.5 confirms that there is an exponential increase in concrete permeability with increasing the percentage of porosity in cement paste. In fact, pore connectivity and tortuosity are more crucial in water transport than just capillary porosity [1]. From the perspective of water absorbance and penetrability, concrete pores are classified according to ASTM C125−15b [6] into two types: impermeable pores that are not filled with water when the concrete is submerged for a prescribed time period, and permeable pores that become filled with water when the specimen is submerged for that time period. The volume of permeable pores increases with increasing the w/c ratio or with increasing the age of concrete. According to ASTM C125−15b [6], "absorption is the process by which a liquid is drawn into and tends to fill permeable pores in a porous solid body; also, the increase in mass of a porous solid body resulting from the penetration of a liquid into its permeable pores."

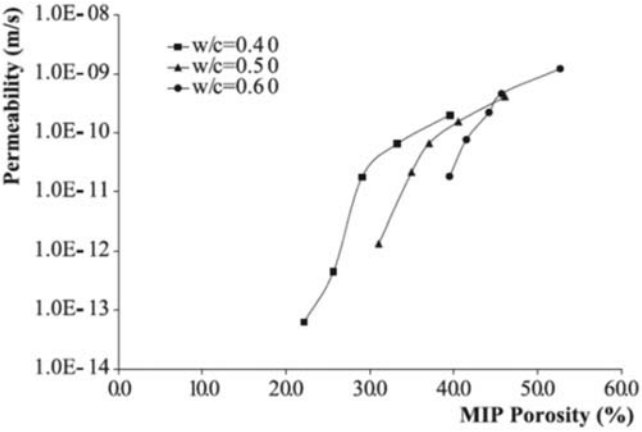


Figure 2.5 Relationship between permeability and total porosity measured by the method of mercury intrusion porosimetry [22].

Only capillary pores (see Table 2.1 and Fig. 2.3) are responsible for water permeability in concrete [1]. According to ACI concrete terminology [17], capillary pores are "microscopic channels within hydrated paste that will draw liquid water due to surface tension." As listed in Table 2.1, capillary pores include large capillaries that contain free water and have sizes in the range of 50 nm to 0.5 μm. The removal of water from these large capillary pores does not cause a volume change or shrinkage. However, water in the intermediate capillaries of 10−50 nm sizes is held by capillary tension. Thus its removal may add to shrinkage problems that are caused also by the removal of the adsorbed water as explained above.

As concrete porosity changes with the concrete age and the w/c ratio, its permeability is also dependent on the curing age and the w/c ratio [1]. Fig. 2.6 shows that the concrete permeability decreases with curing age. This is attributed to the changes in the microstructure, and the reduced porosity with age as shown in Fig. 2.1 and as discussed above [1]. Similarly, the permeability increases with increasing w/c ratio.

Fig. 2.7 shows a schematic comparison of the kinetic changes in porosity, permeability, and strength, associated with the change in the rate of heat evolution accompanying cement hydration reactions during curing. As the process of cement hydration evolves, both the porosity and the permeability decrease, while the compressive strength increases. The measure reduction in permeability is associated with the formation of C − S − H gel produced from the cement hydration reactions. It is accompanied with the process of strength development.

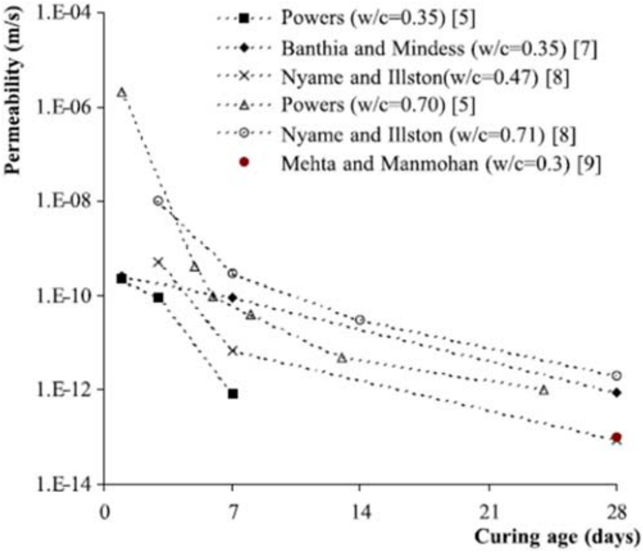


Figure 2.6 Comparison of permeability values reported by different authors as function of curing age [22].

The permeability of water containing dissolved materials (e.g., calcium hydroxide) is different from the permeability of pure water. This is due to the interactions of the dissolved ions with the mineral compounds on the walls of pores in the cement paste [3]. In addition, soluble compounds usually affect the hydraulic characteristics of water such as viscosity and density and thus impacts its permeability.

The previous discussion is related to the permeability of cement paste. The aggregates are also porous, and their porosity depends on their natural structure and strength. The aggregates are usually stronger than cement paste, and their porosity is lower than that of the typical cement paste, and it rarely exceeds 10% [3]. On the other hand, the aggregates have a larger capillary size ($> 10\,\mu$m). This is much higher than the typical size range of the capillary pores in cement pastes, which is mainly in the range of 10−100 nm [3] (see Table 2.1). In addition, the ITZ between the cement paste and the aggregates is more porous [4]. Thus the permeability of a concrete containing aggregates can be higher by an order of magnitude than the permeability of the corresponding cement paste [3]. When the aggregates are added to a cement paste, the permeability increases considerably; this effect increases with increasing the size of the aggregates [3]. This effect also results from the microcracks that occur in the ITZ between the aggregate and the cement paste [3].

In addition, the air voids may contribute to concrete permeability [11], although researchers commonly believe that air voids can make little to no contribution to the bulk fluid flow through concrete. In fact, the effect of voids of entrained air on permeability depends on the level of water content in these voids. Air voids can be filled with water only at a very slow rate compared to that for the capillary pores [11]. The air voids reduce water absorption by capillary suction in concrete (see Chapter 5) due to their low suction capacity (due to their large size) compared to that of the capillary pores (much finer) [11]. The structure of air voids may be altered by pressure variations or by the long-term diffusion and convection fluxes,

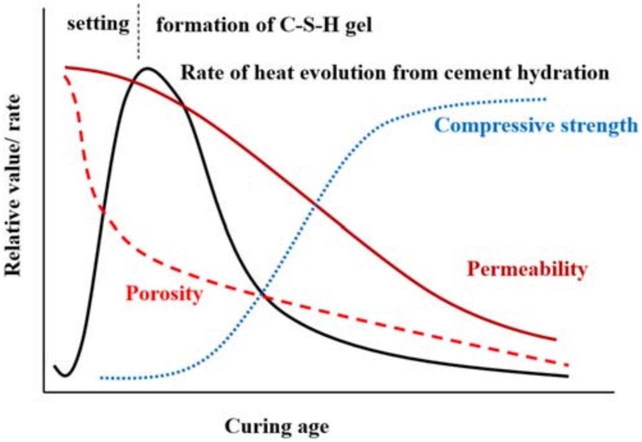


Figure 2.7 Trends in the kinetic change of concrete properties with curing age compared to the rate of heat evolution from the cement hydration reactions.

when concrete is subjected to continuous water exposure. Consequently, the air voids may achieve saturation with sufficient time [11]. Furthermore, some researchers suggested that air entrainment can reduce the concrete permeability, owing to the improved workability of fresh concrete [9]. Although voids of entrained air appear to be isolated, they can be interconnected through the network of the capillary pores that are scattered and much smaller in size [9]. Air entrainment in concrete may increase permeability by intersecting internal capillaries that can provide ingress for water. However, the porosity near the interface of air void − paste is roughly 2−3 times larger than that of the bulk paste [1].

Concrete permeability is also related to other transport properties governing other forms of transport processes, such as gas permeability and mass and diffusion fluxes. These transport properties are discussed in Section 2.5.

2.4.1 Effect of pressure on the rate of water permeation

Water permeation in concrete is a process of flow through a porous medium, as schematically illustrated in Fig. 2.8. It is essential to differentiate between the rate of water permeation (flow rate), and the permeability, which is a property of the concrete. Permeability is the coefficient that relates the flow rate with the pressure drop and it refers to the rate at which water is transmitted through a saturated specimen of concrete under an externally maintained hydraulic gradient [23]. Water permeation is governed by the well-known fluid flow equations, as presented in Section 2.6.

In general, the governing equations relate the permeation flow rate with the pressure drop across the concrete. The type of the relationship between the pressure drop and the flow rate depends on the degree of particle packing and sizes (the porosity and the pore size), length of flow path, fluid viscosity, and fluid density. Such a dependence is specified by the permeability as a property of concrete. In general, the general equation for obtaining the pressure drop in packed beds has two terms accounting for the two-flow regime of laminar and turbulent behaviors [24], as detailed in Section 2.6. In both flow regimes, the rate of water permeation is dependent on the hydrostatic pressure of water, with a linear form for laminar

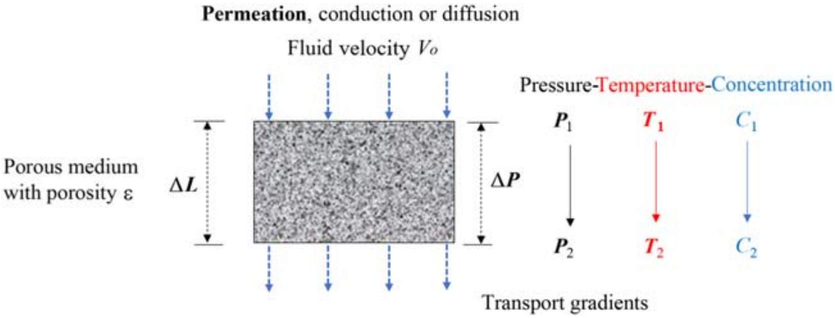


Figure 2.8 Schematic illustration of transport processes through porous media.

flow and a nonlinear form for the turbulent flow. For most typical concrete applications, the porosity is small and the flow is very slow, thus a laminar flow condition exists. The flow rate of water permeation is then linearly proportional to the pressure drop. Thus concrete applications under high hydrostatic pressures exhibit larger water penetration rates than those under just wetting conditions only. Such a pressure dependence is essential when discussing the various waterproofing systems, especially those that cannot resist a high pressure (see Chapters 6 and 7). In fact, the hydrostatic pressure is the parameter used to distinguish between the two categories of waterproofing and dampproofing, as detailed in Chapter 6.

The existence of cracks in concrete creates more channels and more connections for flow paths. Thus they increase the permeability substantially [25]; hence, they increase the rate of permeation for the same applied pressure drop. The permeability increases with increasing the width of the cracks. These cracks cause a continuous increase in permeability with service time as they endure further concrete deterioration (see Chapter 3). The increase in the deterioration increases permeability, which then increases porosity, and undergoes the-so-called chain reaction, as detailed in Chapter 3.

2.5 Transport characteristics of concrete

The transport processes in concrete include (1) bulk motion of fluid, which is governed by fluid viscosity, (2) molecular diffusion, which is governed by the molecular motion of the diffusing species within the medium (or sometimes the ionic mobility), and (3) thermal conduction, which is driven with the molecular energy (e.g., atomic vibrations), as in the case of mass diffusion. In addition, the mobility of soluble ions in water (such as chloride ions) creates another related concrete characteristic of electrical conductivity. In fact, concrete electrical conductivity is used in some experiments as an indirect indication of chloride ion penetration (which is a diffusion process). The governing equations and models for these transport processes are presented in the following section. In addition to the aforementioned internal processes, heat and mass transfer processes occur at the surface of concrete by convection to the surrounding air. These external transport processes are driven by the differences in concentrations and temperatures between the concrete surface and the surrounding air and are correlated by the convection coefficients. However, the surface convection transport mechanism is not a material characteristic, thus it will not be detailed here. In this section, the related transport properties including air permeability, diffusivity, electrical and thermal conductivities are discussed. These transport properties govern various mass and heat transfer processes, which drive the mechanisms of concrete durability problems. The detailed mechanisms of concrete durability issues are discussed in Chapter 3, "Concrete durability problems: Physicochemical and transport mechanisms". The physical mechanisms of these transport characteristics are linked to that of water permeability already discussed in the previous section, which provides the basis for analyzing these properties.

The physical concepts of air permeability are similar to those of water permeability. Mass transfer of soluble components and ions (e.g., chloride ions) within a concrete substrate is driven by the concentration difference between two regions and it is dependent on its mass diffusivity (or molecular diffusion coefficient). According to ACI concrete terminology [17], “diffusion is the movement of species (ions, gas, or vapor) from an area of higher concentration to an area of lower concentration independent of the bulk motion of a fluid.” Heat transfer is driven by the difference in temperature and it is dependent on its thermal diffusivity (or thermal conductivity). According to ACI concrete terminology [17], thermal diffusivity is defined as "an index of the ease which a material undergoes temperature change.” In general, these transport characteristics have a similar general qualitative dependence on concrete parameters. It is worth mentioning that in the field of chemical engineering, there is a well-known analogy between various transport processes of fluid, heat, and mass transport [26]. Such an analogy guides researchers toward obtaining general correlations for predicting system behaviors or transport properties of similar processes. For example, the analogy between the thermal and mass diffusivities leads to similarity in the form of correlations for the dimensionless transport numbers (e.g., Nusselt number and Sherwood number), which are used in determining the heat or the mass transfer coefficients at the surface of concrete subjected to wind movement. Interested readers can refer to chemical engineering books on heat and mass transfer for further details. These mathematical analogies assist in establishing transport equations for a certain system (e.g., mass transfer) from a known equation for other similar systems (e.g., heat transfer). The mass transfer model may be transformed into a heat transfer model by replacing the mass diffusivity with the thermal diffusivity. In fact, water permeability is sometimes termed as hydraulic conductivity in analogy with the thermal conductivity. For all these reasons, mass transport tests are increasingly used for obtaining indicators of concrete performance and durability [9].

In general, the impacts of various concrete parameters on permeability can be considered as controlling parameters for the other transport characteristics. Fig. 2.9 shows that the diffusion coefficients of oxygen and carbon dioxide increase exponentially with increasing the porosity of cement paste [27]. This is similar to the dependence of water permeability on the porosity as discussed above (see Fig. 2.5). There are several theories correlating the porosity and pore structure parameters with either diffusivity or permeability. Wong et al. [9] investigated various diffusivities and transport properties including oxygen diffusion, oxygen permeability, water absorption, and electrical conduction. However, there are noticeable differences that must be considered in the interactions of the transported components with cementitious compounds. For example, the physical interactions of water with pores render the mechanism of water permeability different from that of air permeability. Furthermore, the permeation of gases (low viscosity) is faster than that of liquids. In other cases, some diffusing species may be physically or chemically reactive with the concrete constituents and thus they undergo a unique transport

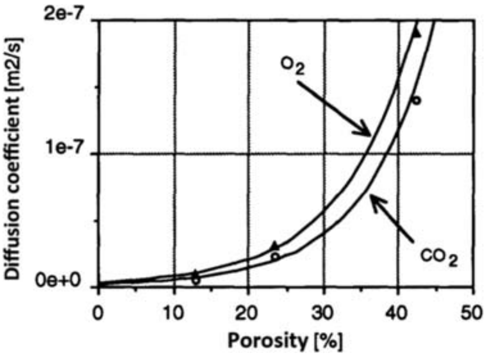


Figure 2.9 Influence of the porosity of hardened cement paste on the effective diffusivities of CO_2 and O_2 at 55% RH [27].

behavior. For example, the diffusion of water vapor within air in concrete voids involves various interactions and equilibration mechanisms and thus it is not similar to the diffusion of noninteractive material (e.g., nitrogen).

The moisture content of concrete and its distribution are crucial parameters that govern the transport properties. In general, transport properties such as ionic diffusivity and gas permeability in partially saturated concrete are largely dependent on moisture content [28]. The transport properties of concrete changes with repeated cycles of narrowing and widening of pores, due to the physicochemical interactions between water and the mineral compounds in the cement paste [3]. Details are available in the review of Zhang and Zhang [28] on the diffusivity of chloride ions and gas permeability in unsaturated concrete, mortars, and modified concrete using SCMs. As indicated in Section 2.4, practical concrete structures are usually unsaturated and possibly at a low level of water saturation. Thus only a thin layer of water is attached to the wall of pores, which may provide an insufficient medium for ions for mass transport by diffusion [28]. Furthermore, decreasing the moisture content results in disconnection of water-filled path within the concrete pores, and thus decreases the diffusion of ions (e.g., chloride ions). This is clearly indicated in Fig. 2.10, as the diffusivity of chloride ions in cement paste increases with the degree of saturation. Fig. 2.10 also shows that the ionic diffusivity increases with increasing the w/c ratio in the paste, as demonstrated in Section 2.4 for the increase of water permeability with w/c ratio. However, chloride binding is an important parameter related to the diffusivity of chloride ions. Chloride ions can be captured physically by adsorption on the hydration products such as C−S−H gel and calcium mono-sulfoaluminate. Such chemisorption interactions immobilize part of the chloride ions by binding to the cementitious surfaces. This process also affects the pore structure of the paste and accordingly affects the diffusion rate and the free concentration of chloride ions [28]. Thus the governing equations for mass transfer of chloride ions through concrete might not be given simply by a simple diffusional term, but also includes a reaction (sink) term as well (see Section 2.6).

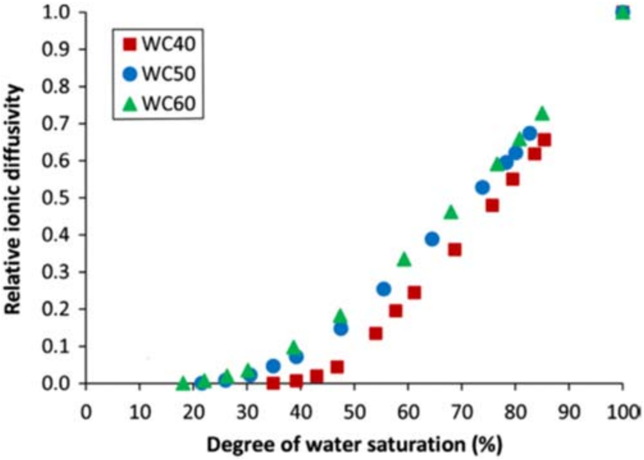


Figure 2.10 Relative chloride ionic diffusivity versus water content for cement pastes with w/c ratios (in the diagram referred to as WC) of 0.4, 0.5, and 0.6.

The impact of water saturation on gas permeability has an opposite trend of that for ionic diffusivity. Decreasing moisture content in concrete allows more space for the bulk flow of gases, that is, creates more open channels for gas phase permeation. Fig. 2.11 shows that the gas permeability increases with increasing concrete dryness [28]. For partially saturated concrete, the water phase occupies the volume of small pores only, while the gas phase occupies the large voids. Fig. 2.11 shows that the gas permeability approaches zero when the degree of water saturation exceeds 80%. This characteristic behavior is essential for the so-called concrete breathing, a process that is essential for the release of humidity through air permeability in concrete (in order to control biodegradation, see Chapter3). However, an increase in gas permeability contributes to the problem of radon gas penetration in buildings, which is one of the public health problems in residential applications. Various models are available for predicting other transport properties in unsaturated concrete such as chloride ion diffusion [e.g., Saetta's model [28]]. Fig. 2.11 also shows that the gas permeability increases (slightly) with increasing the water to binder (w/b) ratio in the paste. This is similar to increasing water permeability and ionic diffusivity with increasing w/c ratio.

Different values of local transport properties are usually obtained for the paste and the ITZ between the aggregates and the bulk of the paste. The estimated diffusion coefficient of chloride in the ITZ is larger than that within the bulk of the paste by a factor in the range of $1.5 - 2.8$ [28]. This is due to the fact that the ITZ has a higher porosity than the bulk paste. A similar difference is also reported for water permeability in the ITZ and in the bulk of the paste as described in Section 2.4.

As explained in Section 2.4, permeability may be affected by presence of the air voids in concrete. Measurements of transport properties of concrete containing entrained air voids revealed major differences from those of concrete without air

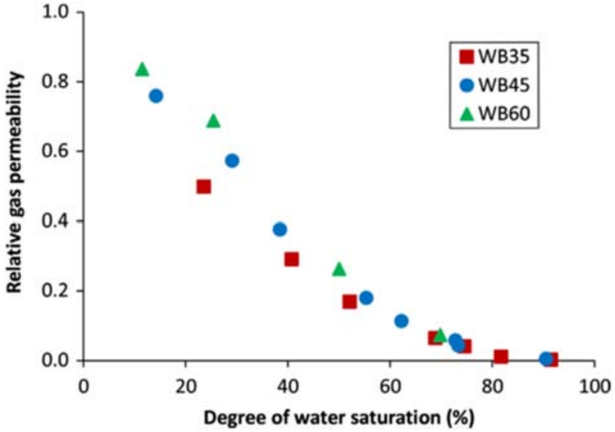


Figure 2.11 Gas permeability in partially saturated cement mortars as a function of degree of saturation for mortars with various water to binder (w/b) ratios indicated in the figure as WB (modified by [28] after [29]).

entrainment [11]. In fact, the reported differences in the diffusivity and permeability can reach up to two orders of magnitude, and for sorptivity and conductivity up to one order of magnitude. As in the case of the effect of air voids on water permeability of concrete, there is a similar debate on the effect of the entrained air voids on the other transport properties. The entrained air voids can increase or decrease the transport properties, depending on the moisture state of these voids and the transport mechanism (e.g., mass transfer, fluid flow of vapor, or liquid phases). Breugel [11] found that the presence of entrained air voids enhanced air permeability and gas diffusivity, regardless of the w/c ratio, curing age, or conditioning regime. Wong et al. [9] found that the diffusivity and the permeability increased up to a factor in the range of 2—3 for concrete with high air contents. Such a level of increase was equivalent to that obtained when the w/c ratio was increased from 0.35 to 0.50. Similarly, the effect of entrained air voids on electrical conductivity was governed by the moisture condition of air voids as it governs the availability of a continuous solution phase for the diffusional process of ions [9]. Concrete is electrically conductive under the existence of ions in the pore solution [11]. Some authors believe that the electrical conductivity of concrete decreases with increasing air content. The effect is interpreted by bearing in mind that the air voids create nonconductive barriers and decrease the cross-sectional area available for the ionic penetration. In this case, air voids act in a similar manner as the aggregates do in reducing water permeability. However, there is still a debate in the literature pertaining to the inconsistent trends for the effect of air entrainment on electrical resistivity and the penetration of chloride ion in concrete.

The values of the different transport properties in concrete can be decreased through optimizing material selection and proportioning (see Chapter 4). For example, this can be achieved through the addition of SCMs and chemical admixtures as well as reducing the w/c ratio. The effect of adding air entrainment admixtures and changing w/c ratio on transport properties has been demonstrated in the discussion above. However, the effects of SCMs need further discussion. It has been demonstrated that adding SF, blast furnace slag, or fly ash decreases the diffusivity of chloride ion through the modified concrete [28]. In particular, it has been reported that adding SF and calcined clay to concrete mixture can increase the resistance of concrete for chloride ion penetration to a level of electrical conductivity less than 1000 coulomb, as required by ASTM C 1202 (rapid chloride permeability) [30]. In a similar fashion, the addition of SF, fly ash, calcined shale, or slag enhances concrete resistance against chemical attacks by sulfates or seawater [30]. The densifying effect of SF has been reported not only for the bulk of the cement paste phase, but also for the microstructure of the ITZ. SFs have a positive effect of reducing concrete diffusivity and permeability. This is accomplished through producing less diffusible and less permeable pozzolanic $C-S-H$ gel than the conventional $C-S-H$ gel. SF also reduces the overall capillary porosity (a combined property of the bulk paste and the ITZ) for a fixed degree of cement hydration [2].

2.5.1 *Thermal characteristics of concrete*

The thermal properties of concrete have been investigated widely in recent publications for applications related to energy savings in buildings, in addition to minimizing concrete damage due to freezing and thawing cycles [31]. The thermal conductivity governs the rate of heat dissipation from concrete during curing. The thermal characteristics of a concrete structure subjected to cyclic changes of surrounding temperatures governs its durability. They govern the heat transfer rate at which concrete losses the heat gained during thawing cycle when it is subjected to freezing conditions. Concrete resistance to freezing and thawing cycles is dependent on the specific heat as a thermodynamic characteristic that reflects how much thermal energy can be stored in concrete. Both characteristics (thermal conductivity and specific heat) are related together through thermal diffusivity, which is a property defined in analogy with mass diffusivity, as given by Eq. (2.1):

$$\alpha_c = \frac{\mathrm{k}_{th}}{\rho_c \mathrm{c}_\mathrm{p}} \tag{2.1}$$

where α_c is the thermal diffusivity of concrete, k_{th} is the thermal conductivity of concrete, ρ_c is the concrete bulk density, and c_p is the specific heat of concrete. The thermal conductivity and diffusivity also control the rate of heat transfer for dissipating the thermal energy from the exothermic cement hydration process (see Chapter 1). It receives particular attention in mass concrete, as a large amount of thermal energy is liberated (see Chapter 4). The thermal applications in concrete are usually under more than one thermal mechanism. For example, a heat source or sink may be encountered from the cement hydration in fresh concrete or from the inclusion of phase change materials (PCMs) for energy storage. In some analysis effective properties are used taking into account some of these effects (e.g., the use of PCMs) [32].

The mechanism of thermal conduction is driven by the atomic and molecular energies. The collisions of vibrating atoms and molecules transfer part of their energy to the adjacent molecules. Such a random motion is also the basic mechanism for diffusional mass transfer. In thermal conductors such as metals, the mechanism of conduction is driven by the transfer of electrons within the materials, in a similar fashion as that for electrical conductivity. The thermal conductivity of normal strength concrete is usually within the range of 1.4−3.6 W/m°C [33]. Compared to other construction materials, concrete has a moderate thermal conductivity. For example, it is higher than that of insulating materials, such as wood, while it is lower than that of metallic conductors.

Asadi et al. [31] provided a detailed review on the thermal conductivity of concrete, enhanced with various types of additions, such as crushed recycled glass, mineral admixtures (fly ash, SF, and blast furnace slag), mineral wool, bottom ash from coal combustion in power plants, vegetable fibers, and wood shavings. In addition to these minerals and agricultural wastes, other studies focused on the addition of PCMs, which have the capability of storing heat (by its absorption as a latent heat upon melting), then releasing it again upon freezing. In building applications, the use of PCMs in concrete walls does not only reduce energy cost, but it also flattens the fluctuation of indoor temperature and consequently improves the thermal comfort [34]. In concrete pavement applications, the use of PCMs enhances concrete resistance against damage due to cycles of freezing and thawing and assists in minimizing ice bonding with concrete [35].

As in the case of previously described transport properties, the thermal conductivity is dependent on concrete structure, porosity, and permeability. Particularly, the controlling parameters include concrete mix design, w/c ratio, curing age, temperature, humidity, amounts and proportions of fine and coarse aggregates, and types and dosages of admixtures [31]. Again, w/c ratio has a major impact on thermal conductivity. The thermal conductivity of concrete decreases with (1) increasing the w/c ratio, (2) decreasing cement content [36], (3) decreasing the proportions of the coarse aggregate, or (4) through the use of lightweight aggregates benefiting from their high porosity. Also, the use of admixtures is very influential on thermal conductivity [31]. For example, adding SCMs as partial replacements of Portland cement decreases the thermal conductivity of concrete and mortar [36], in a similar fashion to their effect on permeability. In addition, the thermal conductivity of concrete is dependent on the degree of water saturation [31], as indicated above for the dependence of mass diffusivity. The thermal conductivity of saturated concrete is greater than that of dry concrete [31]. However, in most of the reported experimental works, the thermal conductivity of cement-based materials was measured using oven-dry or saturated specimens. In practical applications, the thermal conductivity of concrete changes during service due to changing the degree of saturation associated with the changes in wetting and drying conditions. The thermal conductivity of concrete increases exponentially with increasing its bulk density [31]. Fig. 2.12

shows an exponential empirical correlation between the thermal conductivity and the density of concrete obtained by Asadi et al. [31] based on 185 groups of previously reported experimental data. There are other several linear and nonlinear correlations for the relationship between thermal conductivity of concrete and density, for several types of additions [31].

There are several materials that can be used as PCMs for enhancing concrete thermal resistance. These include organic and inorganic compounds and eutectic mixtures. The selected PCMs for a specific thermal application must satisfy various physical and chemical requirements, such as cycling and chemical stability, reversible and high heat of fusion, with a relatively low melting temperature and high specific heat, so that it gains more thermal energy with small volume and within a small temperature difference. It is also required to meet safety and environmental requirements (nonhazardous and nonflammable). Examples of investigated PCMs include paraffin waxes, polyglycol, salt hydrates such as sodium and potassium acetates, fatty acids such as palmitic and stearic acid, and other stearate compounds such as isopropyl, butyl, vinyl, and methyl-12 hydroxy stearates, and eutectic organic and nonorganic compounds [37,38]. Coupled systems including paraffin wax and stearic acid have been shown by [39] to be efficient and stable for 1500 thermal cycles. Fatty acids, myristic acid, and palmitic acid were found to have the greatest stability [40]. PCMs are applied to concrete structure by various techniques, such incorporation through pipes filled with PCM, impregnation in lightweight aggregates or using microcapsules with PCM, or filling the surface voids through PCM absorption [32]. For example, Farnam et al. [35] used a coupled system of methyl laureate and paraffin oil in concrete pavement by two methods (embedded in a tube system or incorporated in lightweight aggregate). The sizes of incorporated particles of PCMs are in the range of millimeters to micrometers. Adding encapsulated PCMs to the concrete mixture at the time of batching [41,42] is more suitable than other methods [43]. PCMs have been added at a wide range of percentages of the total volume of concrete. When PCMs are added to fresh concrete, they impact its properties of fresh concrete [e.g., decreasing the workability [44]]. They also alter the properties of hardened concrete, for example, their addition decreases the concrete density [36], decreases the compressive strength by a percentage in the range of $30\% - 50\%$ [32], and decreases the thermal conductivity by a percentage in the range of $20\%-50\%$ [45]. On the other hand, their addition increases the specific heat of concrete [41].

2.6 Fundamentals of transport processes in concrete

In the previous sections, water permeability and other transport properties in concrete are introduced and discussed, from the perspective of concrete structure and porosity. In this section, the basic laws and transport equations that govern the fluid flow and mass and heat transfer processes in concrete are presented.

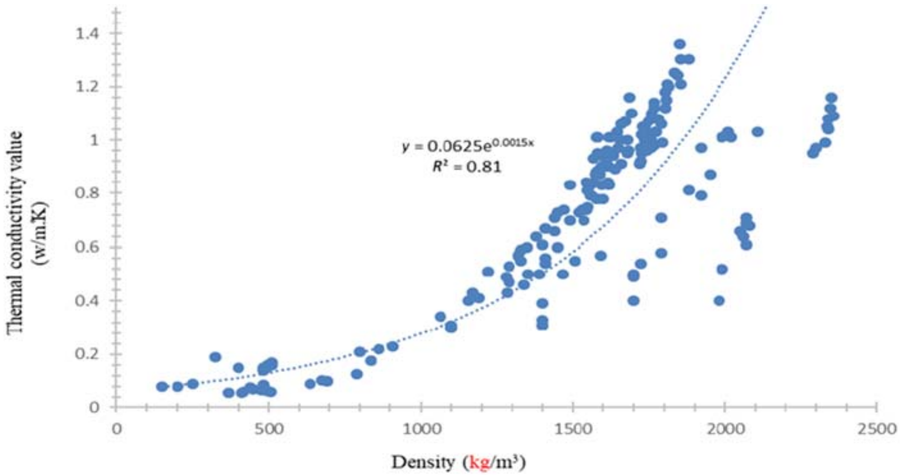


Figure 2.12 Empirical correlation between the thermal conductivity and the density of concrete, as suggested by Asadi et al. [31] based on 185 groups of previous reported experimental data.

2.6.1 Fluid flow through concrete

Bulk water is transported through concrete by the mechanism of flow through a porous medium, which is governed by the fluid flow equations through packed beds, as covered in books of transport phenomena [24]. The flow rate (or fluid velocity) is related to the pressure drop (ΔP), or the hydraulic gradient, across the porous medium, see Fig. 2.8. Usually a superficial velocity (V_o) is defined as the volumetric flow rate divided by the area perpendicular to the flow (including porous and solid parts of the area). The type of the relationship between the pressure drop and the flow rate depends on the type of flow regime. Theoretically, such a flow is dealt with as a flow past a large number of submerged objects, having a diameter (d_p). The Reynold number (Re) is defined for porous medium, according to its modified form, as given by Eq. (2.2):

$$Re = \frac{\rho_f d_p \mathrm{V}}{\mu(1-\varepsilon)} \tag{2.2}$$

Where V is the fluid velocity, ρ_f is the fluid density, μ is its dynamic viscosity, d_p is the size of particle in the bed, and ε is the volume fraction of permeable empty space (i.e., porosity). For a continuous flow of water, a pressure drop is created by the frictional forces (which are pronounced in the laminar flow regime) and by inertia forces (which are pronounced in the turbulent flow regime). The general pressure drop equation in packed beds has the two terms accounting for the two types of forces (or the two types of flow regimes), given by the well-known Ergon equation for the full range of flow regimes [24], as given by Eq. (2.3):

$$\Delta P = \frac{K\mu\Delta L\mathrm{V}(1-\varepsilon)^2}{{d_p}^2\varepsilon^3} + \frac{1.75\rho_f\Delta L V^2(1-\varepsilon)}{d_p\varepsilon^3} \tag{2.3}$$

Where ΔL is length of flow path and K is a constant with a theoretical value of 72, while it has an empirical value of 150, which is used in the subsequent analysis [24]. The first term in Eq. (2.3) accounts for the laminar effects, while the second one accounts for the turbulent effects. This equation is sometimes written in terms of friction factor (f) in analogy to the flow through pipes, as as given by Eq. (2.4) [46], as follows:

$$f = \frac{\Delta P\, d_p \quad \varepsilon^3}{\rho_f V^2 \Delta L(1-\varepsilon)} = \frac{150}{Re} + 1.75 \tag{2.4}$$

Ergon equation has been used by some researchers for flow through highly porous concrete [e.g., pervious concrete [46]]. Eq. (2.3) indicates that the flow rate of water permeation is largely dependent on the pressure drop for the two flow regimes. Thus concrete applications under high hydrostatic pressures may exhibit larger water penetration rates than those under just wetting conditions. For most typical concrete applications, the porosity is relatively small and the flow is very slow, and thus only the first laminar term is considered. In such a case, the well-known equation of Blake-Kozeny is obtained, which is given by Eq. (2.5).

$$\Delta P = \frac{150\mu\Delta L\mathrm{V}(1-\varepsilon)^2}{{d_p}^2\varepsilon^3} \tag{2.5}$$

This equation has the best validity for cases with $\varepsilon < 0.5$ and $Re < 1.0$. These conditions are applicable for water penetration through concrete. Eq. (2.5) provides a linear relationship between the flow rate and the pressure drop. Such a linearity is also given by another well-known equation for laminar flow, given by Darcy's law. Darcy's law is widely used in civil engineering for capillary permeability of cement pastes and for flow through soil, as given by Eq. (2.6):

$$q = \frac{k}{\mu} A \frac{\Delta P}{\Delta L} \tag{2.6}$$

where q is the flow rate, A is the cross-sectional perpendicular to the flow direction, and k is the permeability coefficient, or simply the permeability [3], which is a characteristic parameter for the flow of water through concrete. It is also referred to as the hydraulic conductivity of saturated concrete [46] in analogy with the thermal conductivity (k_{th}). According to ACI concrete terminology [17], the "coefficient of permeability to water is the rate of discharge of water under laminar flow conditions through a unit cross-sectional area of a porous medium under a unit hydraulic gradient and standard temperature conditions, usually 20°C (68°F)." The value of the permeability (or the hydraulic conductivity) is usually obtained experimentally by a constant head or a falling head permeameter method [25] (see Chapter 7 for standard testing methods). Its physical meaning can be realized by comparing Eqs. (2.5) and (2.6), then the hydraulic conductivity can be expressed as given by Eq. (2.7) [46]:

$$k = k' \frac{{d_p}^2 \varepsilon^3}{(1-\varepsilon)^2} \tag{2.7}$$

Where k' is an empirical constant. Eq. (2.7) indicates that the permeability is strongly dependent on the porosity and the particle size, or in another meaning the pore size and the length of flow path. Montes and Haselbach [46] found that when the porosity was less than 15%, a limited hydraulic conductivity was obtained.

This analysis is applicable for water saturation conditions in the concrete pores, and for estimating the so-called saturated hydraulic conductivity. In fact, the permeability varies with moisture content in concrete, as described in Section 2.4. In general, the degree of moisture saturation is a key parameter in controlling the transport properties of concrete [28]. From a thermodynamic perspective, the degree of saturation of concrete is linear with the relative humidity [28]. Thus the permeability coefficient is dependent on the relative humidity. Concrete structures are usually unsaturated, in service conditions, but exist at a low saturation level, where a thin layer of water is attached to the walls of pores [28]. In such cases, the unsaturated hydraulic conductivity is specified and found to be a function of the degree of saturation of concrete [46]. The unsaturated hydraulic conductivity, over a wide range of water content, can be calculated through an empirical model of Van Genuchten. The model is based on desorption isotherms to obtain the relative permeabilities of water and gas [28].

Furthermore, concrete is usually under an unsteady state of water penetration conditions, in which the permeation flow changes with time. This is also the case in experiments for determining the concrete permeability by the falling head permeameter. The unsteady state continuity equation is used to model the flow of water and gas in concrete. In such a case, a simplified differential form of the relationship between the flow rate and the pressure drop is usually used [25]. Based on Eq. (2.6), the differential form is given by Eq. (2.8)

$$\frac{dq}{dt} = -\frac{k}{\mu}\frac{A}{\Delta L}\frac{dP}{dt} \tag{2.8}$$

where t is the time.

This analysis above is also valid for gas permeability, as a bulk flow through concrete (which is distinguished from gas diffusion). The above-mentioned governing equations are valid for gas permeation. However, as the properties of fluid (viscosity and density) are different, then different characteristic behavior and different values of gas permeability are obtained [28]. In general, the values of permeabilities of concrete for gases or water vapor are lower than water permeability [3]. Other water transport mechanisms such as capillary actions are considered in describing the vertical water transport in concrete, resulting from water rising in capillaries [47]. Capillary action is detailed in Chapter 5.

2.6.2 Mass transfer through concrete

Mass transfer through a concrete substrate occurs for the case of water-soluble components in liquid phase such as chloride ions penetration and for gases in the air phase such as the diffusion of carbon dioxide or radon gas penetration [48]. Such processes are different from fluid flow from the perspective of the driving force for the transport mechanism and the governing variables. For example, chloride ions are transported through water filled concrete capillaries under the effect of concentration difference. While fluid flows from a region of high pressure to a region of low pressure, mass transfer occurs from a region of high concentration to a region of low concentration (see Fig. 2.8). In fact, there are two mechanisms for mass transport processes: diffusion and advection [49]. Diffusion is the net transport due to random motion of molecules or atoms. Advection is the mass transfer of a component carried by a moving fluid, as a result of the bulk motion of the carrying fluid. The diffusional flux is estimated using Fick's law [24]. The rate of mass transfer of a diffusing species is related to its concentration gradient and the mass diffusivity (or diffusion coefficient). For one-dimensional mass transfer in the x-direction Fig. 2.8, Fick's first law is written as given by Eq. (2.9) [27]:

$$J_i = D\frac{dC}{dx} \tag{2.9}$$

Where J_i is the diffusional flux, D is the mass diffusivity of the transported component in concrete, and C is its concentration. In a porous medium, like concrete, the gas diffuses through the pores of the material, and thus an effective diffusion coefficient may be used in Fick's first law [27]. For steady state diffusion in a concrete slab separated by a distance ΔL, and having concentrations C_1 and C_2 at the two sides Fig. 2.8,), the diffusional flux is given by Eq. (2.10):

$$J_i = D\frac{C_1 - C_2}{\Delta L} \tag{2.10}$$

For water soluble materials, mass transfer by advection occurs through concrete, when a bulk flow condition is created, for example, by water permeation as a result of pressure difference between two sides of a concrete substrate [50]. A pressure difference is encountered with radon penetration in basements of buildings, from concrete side next to soil region to indoor region. However, advection mechanism in gas phase within concrete structures is believed to be negligible compared to diffusion, as no flow conditions or minor permeation of bulk air occurs through pores. Advection mass transfer becomes more significant when cracks are created in concrete [51].

In practical situations of concrete, the concentration changes with time, and thus unsteady state mass transfer processes occur. Mass transfer may be associated with consumption or generation of a reactive component and/or with an adsorbing/desorbing material. In such cases, the governing partial differential equation is obtained through performing a shell material balance [26]. When diffusion, advection, reaction, and unsteady state terms are included, the general modeling equation for mass transfer in concrete applications is given by Eq. (2.11):

$$D\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right)+V\left(\frac{\partial C}{\partial x}+\frac{\partial C}{\partial y}+\frac{\partial C}{\partial z}\right)+r_c=\frac{\partial C}{\partial t} \tag{2.11}$$

Where r_c is the reaction term, x, y and z are the Cartesian coordinates, and V is the fluid velocity. The relative importance of each term in Eq. (2.11) depends on the physical system and the mechanisms involved in the application. For example, for mass balance in fresh concrete the reaction term r_c is a very important term when modeling the diffusion of water vapor at early stages, as the cement hydration term (r_c) is high and involves water as a reacting species. This r_c term is also important when Eq. (2.11) is used for mass balance of humidity changes in air in cured concrete in which water can be removed or added to air phase through adsorption or evaporation. It also accounts for the interactions of chloride ions with cementitious compounds through the chloride binding mechanism, that is, the formation of complex salts such as Friedel's salt or Kuzel's salt and the physical adsorption of chloride ions on $\mathrm{C-S-H}$ gel [52]. In many cases, the advection terms (e.g., $V\frac{\partial C}{\partial x}$) are negligible. For mass transfer of nonreacting soluble material, with negligible advection, Eq. (2.11) simplifies to Fick's second law for unsteady state diffusion, as given by Eq. (2.12):

$$D\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right)=\frac{\partial C}{\partial t} \tag{2.12}$$

Eq. (2.12) can be used for modeling the penetration of chloride ions in concrete, with an implicit assumption that chloride ions are not consumed through reactions with cementitious materials (i.e., no chloride binding) [52]. In fact, the interactions of chloride ions are accounted for through the use of an "apparent diffusion coefficient," by including the binding effects in a modified D term [52]. Furthermore, a two-dimensional form for unsteady state diffusion is obtained by neglecting the z-diffusional term. For example, such a simplification was used by [53] for obtaining a mathematical expression for the two-dimensional concentration profiles of chloride ions in concrete. For large slabs and walls (for positions far from the edges of the slabs), Fick's second law is given by the simplest form of one-dimensional diffusion equation as given by Eq. (2.13). Eq. (2.13) was used by many researchers for modeling the penetration of chloride ions. However, the two-dimensional form becomes more important for obtaining better results of chloride ions concentration at concrete edges.

Similarly, [54] used the one-dimensional diffusion equation [Eq. (2.13)] to model moisture diffusion.

$$D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \tag{2.13}$$

In the aforementioned equations, the diffusion coefficient is assumed to be constant, thus it is taken out of the derivative terms. In some practical concrete applications, the diffusion coefficient may change with position in the concrete due to changes in the level of water saturation or changes of other parameters (as described in Section 2.5). For example, Fig. 2.10 shows that the diffusion coefficient of a soluble component (e.g., ions) decreases considerably with increasing humidity. In such cases, the forms of these equations become more complicated, as the diffusivity (D) term must be inserted within the derivative terms. Solving such unsteady state [Eqs. (2.11−2.13)] for a particular concrete system, requires the knowledge of the boundary conditions (e.g., the concentrations at the concrete surfaces) and the initial condition within concrete. Solutions can be obtained numerically using the finite element methods and through certain softwares. For simplified cases (one and two-dimensional cases), solutions in the form of error functions are readily available. Such ready solutions were used in some concrete applications [53].

2.6.3 Heat transfer through concrete

Heat transfer through concrete occurs as a result of temperature difference, according to Fourier's law of conduction [24]. For simple applications, with a one-dimensional heat transfer in the x-direction, the rate of heat transfer is given by Eq. (2.14):

$$Q = k_{\mathrm{th}} A \frac{dT}{dx} \tag{2.14}$$

where Q is the rate of heat transfer, A is the cross-sectional area normal to the heat transfer direction, k_{th} is the thermal conductivity of concrete as defined in Eq. (2.1), and T is the temperature. For steady state one-dimensional conduction, the rate of heat transfer between two locations in concrete separated by a distance ΔL, at temperatures T_1 and T_2, is given by Eq. (2.15):

$$\frac{Q}{A} = k_{\mathrm{th}} \frac{T_1 - T_2}{\Delta L} \tag{2.15}$$

However, heat transfer in concrete is usually an unsteady state process, and occurs in more than one dimension. In such cases, the governing heat balance equation, in the Cartesian coordinates, used to model concrete applications is given by Eq. (2.16):

$$k_{\mathrm{th}}\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}\right)+V\left(\frac{\partial T}{\partial x}+\frac{\partial T}{\partial y}+\frac{\partial T}{\partial z}\right)+\dot{q}=\rho_c c_p\frac{\partial T}{\partial t} \tag{2.16}$$

where $\dot{q}$ the rate of internal heat generation (or consumption) per unit volume, ρ is the concrete bulk density, and c_p is the specific heat of concrete, as defined for Eq. (2.1). Such an equation may be used for the thermal modeling of a concrete structure during a curing process. When the thermal diffusivity (α_c) [defined by Eq. (2.1)] is used in Eq. (2.16), the mathematical form of Eq. (2.16) becomes identical to that of the general mass transfer equation [Eq. (2.11)] (when C is replaced with T, r_c is replaced with $\dot{q}/\rho_c c_p$, and D is replaced with α_c). This is the basic concept behind the similarity in modeling transport processes as mentioned in Section 2.5. For typical concrete applications, heat is transferred only by conduction, Eq. (2.16) simplifies to the form given by Eq. (2.17):

$$k_{\mathrm{th}}\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}\right)+\dot{q}=\rho_c c_p\frac{\partial T}{\partial t} \tag{2.17}$$

Eq. (2.17) is used for estimating the maximum temperature and the temperature differences within mass concrete applications, in which a high rate of heat is evolved from the exothermic cement hydration reaction $\dot{q}$, as used in the analysis of [55]. Such a model is essential for controlling mass concrete applications (see Chapter 4). However, for one-dimensional unsteady state heat conduction, Eq. (2.17) is simplified to the form given by Eq. (2.18):

$$k_{\mathrm{th}}\frac{\partial^2 T}{\partial x^2}+\dot{q}=\rho_c c_p\frac{\partial T}{\partial t} \tag{2.18}$$

Eq. (2.18) is used in analyzing the thermal conduction process through concrete walls or slabs containing PCMs [31] (see Section 2.5.1). In such a case, the source/sink term ($\dot{q}$) is determined by the latent heat of the PCM and its amount. Alternatively, the effective thermal properties of PCMs-modified concrete can be used in the Fourier's second law, instead of keeping the thermal source/sink term ($\dot{q}$) [32]. For typical one-dimensional unsteady state heat conduction in concrete walls or slabs [32], the simplest form given in Eq. (2.19) can be used [32].

$$k_{\mathrm{th}}\frac{\partial^2 T}{\partial x^2}=\rho_c c_p\frac{\partial T}{\partial t} \tag{2.19}$$

In a similar fashion as for mass transfer equations, solving the unsteady state thermal balance equations [Eqs. (2.16–2.19)] requires the specifications of the appropriate boundary and initial conditions [55]. These equations are usually solved for a particular concrete system (such as mass concrete) using the finite element methods [55,56], for obtaining the temperature profiles, the maximum concrete temperature, and the maximum internal temperature difference. For simplified cases of one and two-dimensional conduction without a heat source/sink term, solutions in the form of error functions similar to those obtained for diffusion equations are readily available [24].

References

[1] Ye, G. (2003). Experimental study and numerical simulation of the development of the microstructure and permeability of cementitious materials. Master of Engineering thesis, University of Technology, TU, Delft. Delft, The Netherlands.

[2] Song, H. W., et al. (2007). An estimation of the diffusivity of silica fume concrete. *Building and Environment*, *42*(3), 1358–1367.

[3] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. New York, USA: McGraw-Hill Education.

[4] Sharma, A., et al. (2020). Characterization of paste microstructure for durability properties of concrete. *Construction and Building Materials*, *248*, 118570.

[5] Mounanga, P., et al. (2004). *Predicting Ca $(OH)_2$ content and chemical shrinkage of hydrating cement pastes using analytical approach. Cement and Concrete Research*, *34* (2), 255–265.

[6] ASTM. (2003). *C125 – 15b Standard terminology relating to concrete and concrete aggregates*. Annual Book of ASTM Standards, West Conshohocken, PA, USA.

[7] Chen, X., & Wu, S. (2013). Influence of water-to-cement ratio and curing period on pore structure of cement mortar. *Construction and Building Materials*, *38*, 804–812.

[8] Meddah, M. S., & Tagnit-Hamou, A. (2009). Pore structure of concrete with mineral admixtures and its effect on self-desiccation shrinkage. *ACI Materials Journal*, *106*(3), 241.

[9] Wong, H., et al. (2011). Effect of entrained air voids on the microstructure and mass transport properties of concrete. *Cement and Concrete Research*, *41*(10), 1067–1077.

[10] ACI. (2008). *Committee 201, AC I 201.2R-08 Guide to Durable Concrete in 2008*. Farmington Hills, MI, USA: American Concrete Institute.

[11] Van Breugel, K. (2004). Modelling of cement-based systems—The alchemy of cement chemistry. *Cement and Concrete Research*, *34*(9), 1661–1668.

[12] Papadakis, V. G. (2000). Effect of fly ash on Portland cement systems: Part II. High-calcium fly ash. *Cement and Concrete Research*, *30*(10), 1647–1654.

[13] Zeng, Q., et al. (2012). Determination of cement hydration and pozzolanic reaction extents for fly-ash cement pastes. *Construction and Building Materials*, *27*(1), 560–569.

[14] Saha, A. K., et al. (2018). The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials*, *171*, 743–758.

[15] Papadakis, V. G. (1999). Effect of fly ash on Portland cement systems: Part I. Low-calcium fly ash. *Cement and Concrete Research*, *29*(11), 1727–1736.

[16] Bapat, J. D. (2012). *Mineral admixtures in cement and concrete*. Boca Raton, FL, USA: CRC Press.

[17] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[18] Shetty, M. (2005). *Concrete technology theory and practice*. New Delhi, India: S. Chand and Company LTD.

[19] Rashed, A. I., & Williamson, R. B. (1991). Microstructure of entrained air voids in concrete, Part I. *Journal of Materials Research*, *6*(9), 2004–2012.

[20] Chindaprasirt, P., et al. (2008). Cement paste characteristics and porous concrete properties. *Construction and Building Materials*, *22*(5), 894−901.

[21] Lu, J., Wang, K., & Qu, M.-L. (2020). Experimental determination on the capillary water absorption coefficient of porous building materials: A comparison between the intermittent and continuous absorption tests. *Journal of Building Engineering*, *28*, 101091.

[22] Ye, G. (2005). Percolation of capillary pores in hardening cement pastes. *Cement and Concrete Research*, *35*(1), 167−176.

[23] ACI. (1999). *Committee 212, ACI 212.3R-91 Chemical Admixtures for Concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[24] Geankoplis, C. J. (2003). *Transport processes and separation process principles: (includes unit operations)*. Prentice Hall, Professional Technical Reference.

[25] Wang, K., et al. (1997). Permeability study of cracked concrete. *Cement and Concrete Research*, *27*(3), 381.

[26] Bird, R. B. (2002). Transport phenomena. *Applied Mechanics Reviews*, *55*(1), R1−R4.

[27] Houst, Y. F., & Wittmann, F. H. (1994). *Influence of porosity and water content on the diffusivity of CO_2 and O_2 through hydrated cement paste*. *Cement and Concrete Research*, *24*(6), 1165−1176.

[28] Zhang, Y., & Zhang, M. (2014). Transport properties in unsaturated cement-based materials—A review. *Construction and Building Materials*, *72*, 367−379.

[29] Zhang, M., Ye, G., & van Breugel, K. (2012). Modeling of ionic diffusivity in non-saturated cement-based materials using lattice Boltzmann method. *Cement and Concrete Research*, *42*(11), 1524−1533.

[30] Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C. (2002). *Design and control of concrete mixtures* (Vol. 5420). Skokie, IL: Portland Cement Association.

[31] Asadi, I., et al. (2018). Thermal conductivity of concrete—A review. *Journal of Building Engineering*, *20*, 81−93.

[32] Šavija, B. (2018). Smart crack control in concrete through use of phase change materials (PCMs): A review. *Materials*, *11*(5), 654.

[33] Bažant, Z. P., Kaplan, M. F., & Bazant, Z. P. (1996). *Concrete at high temperatures: material properties and mathematical models*. Harlow, England: Longman Group Limited.

[34] Latha, P., Darshana, Y., & Venugopal, V. (2015). Role of building material in thermal comfort in tropical climates—A review. *Journal of Building Engineering*, *3*, 104−113.

[35] Farnam, Y., et al. (2016). Evaluating the use of phase change materials in concrete pavement to melt ice and snow. *Journal of Materials in Civil Engineering*, *28*(4), 04015161.

[36] Demirboğa, R., & Gül, R. (2003). Thermal conductivity and compressive strength of expanded perlite aggregate concrete with mineral admixtures. *Energy and Buildings*, *35*(11), 1155−1159.

[37] Baetens, R., Jelle, B. P., & Gustavsen, A. (2010). Phase change materials for building applications: A state-of-the-art review. *Energy and Buildings*, *42*(9), 1361−1368.

[38] Zalba, B., et al. (2003). Review on thermal energy storage with phase change: Materials, heat transfer analysis and applications. *Applied Thermal Engineering*, *23*(3), 251−283.

[39] Sharma, A., Sharma, S., & Buddhi, D. (2002). Accelerated thermal cycle test of acetamide, stearic acid and paraffin wax for solar thermal latent heat storage applications. *Energy Conversion and Management*, *43*(14), 1923−1930.

[40] Sarı, A., & Kaygusuz, K. (2003). Some fatty acids used for latent heat storage: Thermal stability and corrosion of metals with respect to thermal cycling. *Renewable Energy*, *28*(6), 939−948.

[41] Eddhahak-Ouni, A., et al. (2014). Experimental and multi-scale analysis of the thermal properties of Portland cement concretes embedded with microencapsulated phase change materials (PCMs). *Applied Thermal Engineering*, *64*(1−2), 32−39.

[42] Zhang, D., et al. (2004). Development of thermal energy storage concrete. *Cement and Concrete Research*, *34*(6), 927−934.

[43] Cui, H., Memon, S. A., & Liu, R. (2015). Development, mechanical properties and numerical simulation of macro encapsulated thermal energy storage concrete. *Energy and Buildings*, *96*, 162−174.

[44] Liang, C., et al. (2009). Microencapsulation of butyl stearate as a phase change material by interfacial polycondensation in a polyurea system. *Energy Conversion and Management*, *50*(3), 723−729.

[45] Cui, H., et al. (2014). Thermophysical and mechanical properties of hardened cement paste with microencapsulated phase change materials for energy storage. *Materials*, *7*(12), 8070−8087.

[46] Montes, F., & Haselbach, L. (2006). Measuring hydraulic conductivity in pervious concrete. *Environmental Engineering Science*, *23*(6), 960−969.

[47] Liu, P., et al. (2020). Vertical water transport model in concrete based on the coupled effects of the capillarity, gravity and evaporation. *Construction and Building Materials*, *240*.

[48] Renken, K. J., & Rosenberg, T. (1995). Laboratory measurements of the transport of radon gas through concrete samples. *Health Physics*, *68*(6), 800−808.

[49] Bennett, T. (2012). *Transport by advection and diffusion*. Hoboken, New Jersey, USA: Wiley Global Education.

[50] Tsang, Y., & Narasimhan, T. (1992). Effects of periodic atmospheric pressure variation on radon entry into buildings. *Journal of Geophysical Research: Solid Earth*, *97*(B6), 9161−9170.

[51] Nielson, K. K., et al. (1997). Radon penetration of concrete slab cracks, joints, pipe penetrations, and sealants. *Health Physics*, *73*(4), 668−678.

[52] Fattah, A. A. E., et al. (2020). Field validation of concrete transport property measurement methods. *Materials*, *13*(5).

[53] Wu, L., et al. (2020). Modelling of two-dimensional chloride diffusion concentrations considering the heterogeneity of concrete materials. *Construction and Building Materials*, *243*.

[54] Kočí, J., et al. (2019). Experimental determination of heat and moisture transport properties of AAC in the range of subzero to room temperatures. *International Journal of Thermophysics*, *40*(1).

[55] Nguyen, T. C., & Bui, A. K. (2019). Evaluation of the impact of parameter inputs of concrete mix on the distribution of temperature in the mass concrete structure. *IVK-Structural Integrity and Life*, *19*(1), 8−12.

[56] Aniskin, N. & Nguyen, T.-C. (2019). *Influence factors on the temperature field in a mass concrete. in E3S Web of Conferences*. EDP Sciences.

Concrete durability problems: physicochemical and transport mechanisms

3

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

3.1 Introduction

Concrete durability problems are the consequences of moisture penetration and the transport processes of harmful materials within concrete structures. The transport of water and other chemicals through the porous structure of concrete causes various attacks. These attacks are based on the physical and chemical reactions, which are driven by the unique characteristics of water. As introduced in Chapter 1, concrete durability is indicated by its service life under reactive surrounding conditions and it is also related to the sustainability of concrete structures subjected to water. Moisture within concrete is the carrier of many deleterious reactants and its phase change causes various thermo-mechanical effects on concrete. A long-time durability is usually the characteristic of a well-designed dense and waterproofed concrete [1], which is characterized with discontinuous pores networks [2].

In fact, durability threats start from the first moment of concrete casting, as a result of possible crack formation due to the rapid evaporation of mixing water and it continues through the full life of concrete. Durability is strongly related to concrete preparation, placing, and curdling and to the conditions of concrete from the surrounding environment. In Chapter 1, a general relationship of concrete chemistry with durability damaging problems is given.

Fig. 3.1 shows a schematic representation of the various transport processes involved in durability problems. These include heat and mass transfer processes and fluid flow in addition to the phase changes of water phases within the concrete structure. These transport processes and permeability are also associated with the reactivity of the compounds in cement paste and aggregates with soluble materials in water. The fundamentals of the transport processes involved in concrete attacks include fluid flow through porous medium, mechanisms of mass and heat transfer (e.g., diffusion, advection and conduction), which are detailed in Chapter 2. The governing transport characteristics lead to different rates of transport processes between the bulk of the paste and the interfacial transition zone (ITZ) due to structural differences as discussed in Chapter 2. In fact, water penetration does not occur by just the bulk flow mechanisms created by the pressure gradients as discussed in Chapter 2, but also by the capillary action that is described further in Chapter 5 after introducing the related

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00003-9

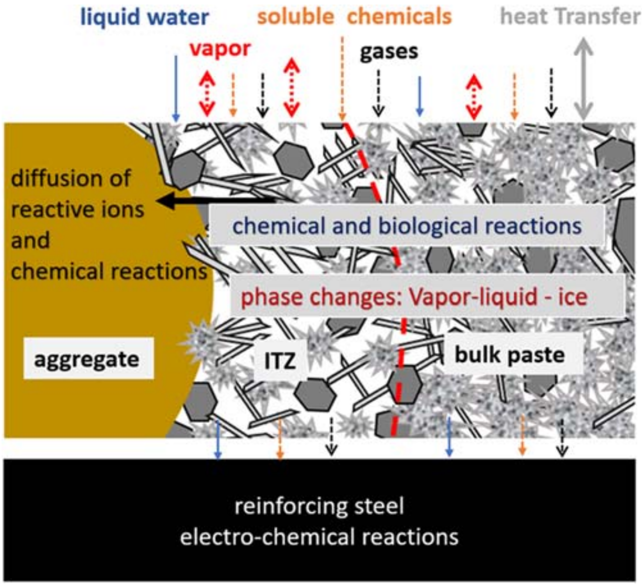


Figure 3.1 A schematic representation of various transport processes and reactions, which are involved in the concrete durability problems showing the interactions among the aggregates, the steel bars, and the paste (the bulk and ITZ).

fundamentals of surface chemistry. In this chapter, concrete durability problems and their impacts on concrete performance and properties are described. The mechanistic links between permeability and durability are analyzed, while discussing the main deterioration processes. Within this context, the required definitions are reviewed, the problems are summarized, and the solutions and the economic aspects are introduced. The chapter paves the road for the coming chapters on waterproofing and concrete durability solutions.

3.2 Concrete durability and structure sustainability

The sustainability of structures is threatened by the decrease in the quality of concrete during its service life as a result of its deterioration through various physical (mechanical and thermal), chemical, and biochemical mechanisms. As mentioned above, these attacks involve chemical reactions and physical interactions of concrete components and water in all phases (see Fig. 3.1). Concrete durability is simply the ability of concrete to resist any process of deterioration, including weathering, abrasion, chemical, and biological attacks [3]. It is determined by concrete stability against aggressive chemicals from the surroundings (e.g., deicing salts, seawater, acidic solutions, carbon dioxide) and from the exposure to the weather changes (e.g., freezing and thawing cycling), as well as the mechanical wear (e.g., abrasion) [4]. The durable concrete is designed, constructed, and maintained to perform satisfactorily under the expected service conditions for the desired targeted service life [3]. When concrete is durable, its structure, quality, and serviceability are supposed to be retained under the environmental exposure for a very long time [1].

uring the service life of concrete, the deteriorating causes affect each other. For example, the abrasion deterioration from mechanical impacts causes mass loss and a decrease in concrete integrity, which subsequently increases concrete porosity and permeability. Then, the promoted penetrations of more water and harmful chemicals initiate or accelerate further physicochemical and biological processes that cause further concrete degradation. The sizes and the connectivity of pores and cracks increase due to continuing thermal, mechanical, and chemical environmental impacts. These consequences allow more ingression paths for fluids and chemicals and promote leaching of mineral materials from the paste and aggregates. Consequently, the durability problems may be viewed as a kind of a combined chain reaction [2]. The actions of physical, chemical, and biological mechanisms attack the chemical and physical structure of the main constituents of the cement paste, aggregates, and reinforcing steel bars. Then, the chemical structure may be destabilized and the physical structure may be disintegrated. Concrete deterioration or degradation occurs in the form of loss of materials and decrease in integrity of concrete, as a result of these attacks. This is usually associated with decreasing the compressive strength, and with problems of cracking. The net result of these problems is a structure sustainability problem. Fig. 3.2 shows a picture of a concrete durability problem combining the corrosion of steel bars and spalling of the concrete [4]. Also shown are created cracks that increase the concrete problems. Usually, surface cracks with short depths [<5 mm (0.2 in.)] do not cause major

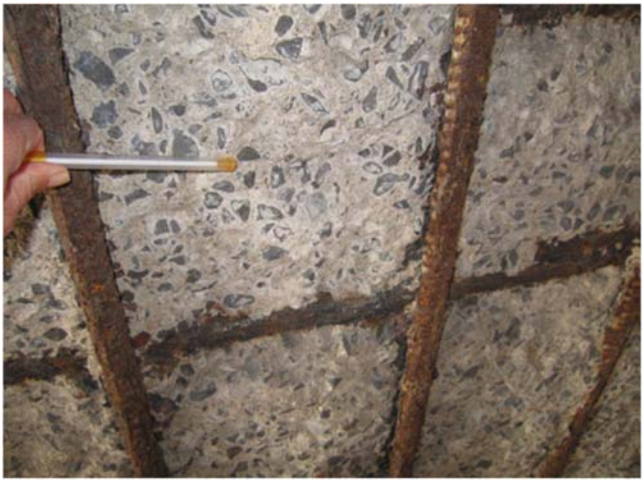


Figure 3.2 A picture of concrete damage as typical concrete durability problems from corrosion of steel bars and spalling of the concrete [4].

problems. However, the existence of larger cracks increases the rate of transport processes (e.g., the penetrations of water, carbon dioxide, and soluble ions from deicing chemicals) and hence causes larger damages.

The most popular concrete durability problems are caused by freezing and thawing cycles, mechanical loading, and chemical attacks such as those from the penetration of chloride ions, alkali aggregate reaction (AAR), and acid attack including carbonation and sulfate attack [4]. Biological activities are also the main causes of other durability problems that are less covered in concrete books. Other engineering causes include defaults of structural design, defects of construction, and exposure to fire damage [3], which are beyond the scope of this book.

It is worth mentioning that in practical cases, the distinction between physical, chemical, and biochemical processes and mechanisms of concrete degradation is not an easy task. This is usually done based on an arbitrary choice as several actions and causes are involved in a considered problem. It is also hard to differentiate between chemical and physical processes. In fact, it is practically rare that a concrete deterioration occurs due to a single cause. Usually, the physical and chemical processes are tangled and occur simultaneously and attacks work synergistically [4]. Some actions may be in competition among each other, for example, acidic soluble materials decrease pH while alkaline materials increase it. As mentioned above, these actions may take the form of a chain reaction [2], so that the separation of the cause from the effect may be difficult [5]. Consequently, it is not easy to classify concrete deterioration processes into separate and well-defined categories [1]. Overlooking these intertwined interactions and combined attacks may result in misleading judgments regarding concrete durability problems. This intertwined situation applies also to the transport processes that are involved in the mechanisms of these durability problems. It is well-known that combined transport processes may occur in a single natural process, such as concrete drying, in which a combined heat and mass transfer process occurs simultaneously.

In addition, it is difficult to design and establish experimental set-ups for evaluating concrete performance under such attacks, which can simulate and combine all surrounding conditions, for testing their long-term effects. Consequently, most of the required knowledge about these physical – chemical degradation processes are attained from field and construction history logs [1]. There are also standardized tests that are based on accelerating the attack conditions by creating an aggressive environment (see Chapter 7). A detailed categorization of mechanisms involved in the main durability problems is given in Section 3.4, after discussing the role of water in the following section.

3.3 Water as the medium for concrete durability problems

As said above, water permeability and concrete durability are strongly dependent on water penetration and phase changes. In fact, water is the cause, the medium, and the vehicle of most concrete durability problems, which are introduced in the previous section. Water penetrates the concrete structure and carries the aggressive chemicals. The rate of concrete deterioration is controlled by the types and the concentrations of dissolved materials, and the pH of the solution that is formed upon water penetration within the concrete pores (pore solution). Concrete is an alkaline material; therefore its stability is determined by the level of alkalinity in the water phase; the concrete structure is attacked when water becomes acidic. Water phase changes into solid or vapor create internal stresses that result in concrete deterioration. Overall, water is the agent for the various types of physical and chemical processes that result in concrete degradation. The water interaction mechanisms that participate in the concrete durability problems include flow, capillary absorption, diffusion, solvation, reaction, expansion, erosion, evaporation, crystallization, solidification etc. These behaviors are related to the following list of water properties:

- Water has a low viscosity and a small molecular size, which facilitates its penetrability and allows it to occupy small pores. Penetrating water provides the medium for the transport of the aggressive ions within concrete by percolation and osmotic pressure (differences in ionic concentrations) [6].
- Water has a polar molecular structure, which provides it with the ability to form hydrogen bonds, as schematically shown in Fig. 3.3. The hydrogen atoms in the water molecules can attract a negatively charged oxygen of a neighboring water molecule forming a hydrogen bonding. Hydrogen bonds are established due to the differences in the charge centers between hydrogen and oxygen atoms among two water molecules, or between a water molecule and a solid surface. This mechanism affects water arrangement in ice formation that is the cause of freezing and thawing durability problems. In addition, it affects water adhesion and adsorption onto solid surfaces (in gel pores).
- Water establishes capillary forces when it is contained in the pores of the paste. This behavior allows it to play an important role in the degree of saturation of these pores [6]. Then, it affects the level of crack development in concrete from drying effects.
- Water has a surface tension, which is a major parameter that creates the hydrophobicity (water repelling) and the hydrophilicity characteristics of various surfaces and materials involved in concrete (see Chapter 5). These surface behaviors are very important in concrete durability problems and solutions.
- Water has the ability of surface interactions with cementitious materials through adsorption/desorption of water vapor (see Chapter 5). These physical processes cause deformations, create mechanical stresses from the molecular forces on pores, and participate in shrinkage mechanisms.
- Water has the ability of physical interaction with hygroscopic crystalline materials (see Chapter 5), which then grow with vapor adsorption. This hygroscopic behavior may create an expansive effect in concrete pores. It may also be used as a pore blocking mechanism in concrete durability solutions (see Chapters 10 and 11).
- Water has a moderate freezing temperature that is encountered in typical winter conditions in most applications. This causes its solidification into ice within concrete pores that creates damaging internal stresses.
- Water has a unique thermodynamic property of expansion upon freezing with a density reduction, which causes internal stresses in winter, and results in concrete damages.
- Water has a moderate boiling temperature and a high volatility. This makes its phase change into vapor from the heat of cement hydration reactions possible under typical concrete casting conditions. This behavior has various impacts on temperature variations, and thermal and mechanical processes in concrete.

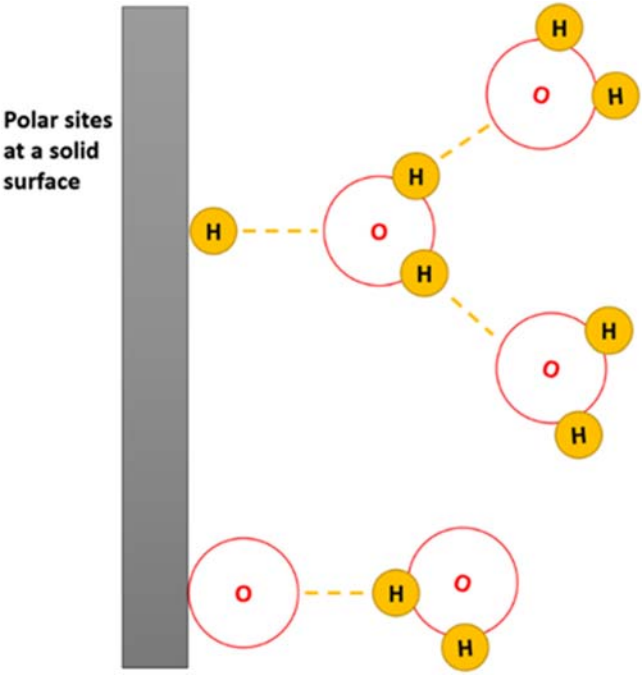


Figure 3.3 A schematic representation of polarity of water molecules and the formation of hydrogen bonds among water molecules and between water molecules and polar sites at a solid surface.

- Water phase change is associated with a large latent heat of vaporization. Consequently, it can absorb a large amount of sensible heat from concrete upon its phase change and then can release it back at a later stage or dissipate it gradually through a heat transfer process.
- Water has a high solvation capacity for various substances. This results in having several types of ions and dissolved gases within water, which then generate and accelerate various chemical reactions in concrete. This can also enhance the leaching out of ions from the concrete internal surfaces by the osmotic pressure. These properties transform the water phase into an aggressive solution, which then becomes an instrumental force for chemical deterioration of concrete.
- Water containing dissolved ions has an electrical conductibility, which participates in various destructive activities in concrete such as those related to acid attack and corrosion of reinforcing steel bars.
- Water has solubility limits for salts and other compounds. When these limits are exceeded, precipitations of solid materials within the pores of concrete can have an expansive behavior and thus create internal stresses (in addition to pore blocking effects for waterproofing, see Chapter 7).
- Water is reactive with various mineral compounds. This reactivity makes water an agent for durability problems such as its reaction with calcium oxide forming soluble calcium hydroxide. Its reactions with cement compounds make water an essential player in the concrete stability.
- Water thermal properties (conductibility and specific heat) manage the heat dissipation process during cement hydration and control concrete behavior during repeated cycles of

freezing and thawing. These thermal behaviors govern the level of crack development in concrete from thermal stresses.
- Water is a nutrition component and a medium for the growth of microorganisms and their biological activities. These biological characteristics make water an essential player in the formation of cracks and the release of other acidic solutions, which result in the biodegradation of concrete (and corrosion of steel bars).
- Water has transport characteristics that control various transport processes involved in concrete attacks (see Fig. 3.1).

In fact, the role of water in governing the durability of concrete structures does not restrict to the durability problems that start when concrete becomes in service, but it starts from its crucial role in proportioning and curing concrete. Water plays crucial roles during the preparation and casting of concrete. For example, for fresh concrete, water controls concrete rheology, bleeding, segregation (see Chapter 1). It impacts the distribution of cement particles in the mix, as well as the solubility of the various compounds of the cement. During concrete curing, water is a reactant in the hydration reactions, which govern the concrete strength and durability. Consequently, concrete durability is mainly a water-related issue and the technology of concrete waterproofing may be the key strategy for concrete durability. That is why the subsequent chapters on waterproofing technologies include sections on the impacts of each technology on these durability problems.

3.4 Fundamental mechanisms of concrete durability

Each of the aforementioned physicochemical and biochemical attacks that cause the concrete durability problems may involve one or several materials in the deterioration actions and results in one or several effects. These types of mechanisms and actions are categorized as listed in Table 3.1, and as described in the following:

1) Physical mechanisms of concrete deterioration

These mechanisms include the following two groups of actions [1]:

1. Mechanical actions of surface deterioration including abrasion, erosion, and cavitation. These actions cause losses in the concrete integrity and mass from wear effects.
2. Thermodynamic actions of deterioration. These actions cause the development of cracks within the body of concrete structure. They include the following:
   - **a.** Volume expansion from decreasing water density upon its exposure to freezing conditions at cold weather.
   - **b.** Crystallization pressure of salts upon their precipitation in pores.
   - **c.** Thermal stresses from temperature and humidity gradients.
   - **d.** Exposure to high temperatures under fire conditions.

2) Chemical mechanisms of concrete deterioration

These mechanisms include the following actions [1]:

1. The dissolution or hydrolysis of the mineral compounds of cement paste into water that causes losses in concrete mass and integrity from
2. the reactions of cation-exchange between hostile chemical and the mineral compounds of cement paste (e.g., exchange of magnesium and calcium ions) that causes losses in concrete integrity and strength from

Table 3.1 Mechanisms of concrete deterioration and types of actions and materials involved.

Main attack mechanism	Deterioration type	Deterioration actions	Participating materials	Structural changes
Physical	Mechanical actions	Wear	Moving mechanical parts that create erosion effects from surface loading.	Loss of material. Decreasing integrity. Increasing porosity and permeability. decreasing strength
		Abrasion	Flowing particle suspension that creates erosion effects.	
		Cavitation	Bubbles of water vapor evaporated from water due to a sudden pressure reduction, which creates internal stresses.	
	Thermodynamic actions	Exposure to freezing conditions.	Ice formed due to lowering surrounding temperature, which creates internal stress from the volume expansion due to decrease in water density.	Development of cracks. Decreasing integrity. Increasing porosity and permeability. Decreasing strength.
		Cycles of freezing and thawing.	Salts, water, and ice, which create internal stress from the cyclic volume change and crystallization pressure of precipitated salts in pores.	
		Temperature and humidity gradients.	Water and vapor, which create internal stress and shrinkage effects.	
		Exposure to high temperatures under fire.	Hydrated calcium silicate compounds that are disintegrated due to thermal destabilization.	
Chemical	Physicochemical interactions	Dissolution or hydrolysis of the paste constituents.	Water, cement hydration compounds, and the resulting dissolved ions.	Loss of binding material. Decreasing integrity. Increasing porosity and permeability.

				Decreasing strength.
	Chemical reactions	Cation-exchange reactions between ions and the compounds of cement paste.	Solutions of water and dissolved materials, and cement hydration compounds.	Loss of cementing material. Decreasing integrity. Increasing porosity and permeability. Crack formation.
		Reactions leading to formation of expansive products (e.g., ASR and corrosion of steel).	Solutions of water and dissolved materials, alkalinity, mineral compounds from aggregates, cement paste, and steel bars.	Crack formation. Weakening the aggregates. Decreasing strength. Increasing porosity and permeability.
		Reactions leading to formation of nonexpansive products (e.g., carbonation).	Solutions of water and dissolved materials, carbon dioxide, mineral compounds from aggregates.	Decreasing alkalinity. Destabilizing cementitious materials Increasing corrosion of steel bars. Crack formation. Spalling.
Biological	Biochemical reactions	Interactions of the growth of organisms.	Microorganisms, and nutrients including moisture, carbon dioxide, oxygen, some mineral compounds, and sunlight.	Increasing porosity and permeability. Crack formation. Decreasing alkalinity. Destabilizing cementitious materials. Increasing corrosion of steel bars.

3. crystallization pressure due to the formation of expansive products from the reactions of concrete constituents with aggressive chemicals, which are responsible for deterioration of a large number of concrete structures. These include the following types:
    - **a.** Sulfate attack.
    - **b.** AAR.
    - **c.** Corrosion of reinforcing steel.
4. Other changes in concrete structures from reactions with concrete constituents that do not form expansive salts. These include
    - **a.** carbonation reaction;
    - **b.** reactions of nonharmful acids with calcium hydroxide that do not form expansive salts, such as reactions with acetic acid.

3) Biological mechanisms of concrete deterioration

These mechanisms include the biochemical reactions of microorganisms in concrete, which cause concrete biodegradation from the interactions of organisms, moisture, and other materials.

As indicated earlier, these various types of mechanisms act simultaneously through a chain reaction and it is hard to differentiate between the cause and the consequence. For example, the solubilization of carbon dioxide into water forms an acidic solution that increases the concrete porosity and thus allows more water or solution penetration, which then increases the deterioration rate. It also changes the pH, which then affects the stability of the steel bars against corrosion. Similarly, cracks induced by freezing and thawing cycles create channels for the penetration of solutions of deicing salts [4], and thus cause further durability problems. Also, the chemical reactions that degrade concrete lead to other aggressive physical impacts such as increasing the porosity and thus increasing the permeability. The following sections detail each of the main durability problems.

3.5 Physical mechanisms of concrete deterioration

3.5.1 Mechanical actions of surface deterioration

Exposed concrete surfaces are usually subjected to mechanical actions from natural causes such as raindrops and storms and from human activities such as traffic and moving machines, which all cause surface degradation. The types of concrete degradation from mechanical impacts include (1) abrasion, which is a dry eating away of a concrete surface due to wear as encountered in concrete pavements and industrial floors [1], (2) erosion, which is a wet eating away of concrete by the hydraulic abrasive action of water containing suspended solid particles or rolling effects of particles as encountered in hydraulic structures, and (3) cavitation, which is the loss of concrete mass due to the formation and the subsequent collapse of vapor bubbles as encountered in hydraulic structures with rapidly flowing water. The abrasion of concrete is described in ACI 201.2R [7] and the erosion, cavitation, and other forms of wet mechanical actions in hydraulic structures are discussed in ACI 210R [8]. Erosion of concrete in hydraulic structures is defined in in ACI 210R [8] as “the progressive disintegration of a concrete by cavitation, abrasion, or chemical action.” Abrasion deterioration of concrete is encountered in industrial floors and warehouses from steel traffic or from operating equipment (e.g., heavy moving machines and fork lifts), and on concrete road from attrition, grinding, and beating from heavy trucks and automobiles [7]. Erosion deterioration is encountered in hydraulic structures such as dams, tunnels, and bridge piers, from the attrition and scraping action of particles of sand or stone in flowing water [7]. Cavitation action on concrete is encountered in hydraulic structures, which are subjected to high flow velocities and negative pressures. These mechanical actions have major impacts on concrete durability as they increase its porosity, which then increases the rate and severity of other physical and chemical attacks.

In certain applications, more than one mechanical impact may be involved. For example, [9] highlighted the deterioration of concrete under tie rail seats including the mechanisms of erosion abrasion, crushing, cavitation, and hydraulic pressure, in addition to other physical mechanisms such the cycles of freezing and thawing. These mechanical actions are affected by traffic load, the presence of abrasive particles, and curvature. Zeman et al. [9] indicated that abrasion was due to surface wear from the combined effects of the impact between the rail and the tie, rubbing of the tie pad and grinding effect of abrasive particles, while crushing was from the concentrated stresses, which were higher than the compressive strength of concrete and fatigue damage from the cyclic loading. Fig. 3.4 shows an image of mechanical degradation from an erosion test [10].

Cavitation erosion is referred to as cold boiling as it involves water phase change from liquid to vapor due to a sharp decrease in the pressure. When water velocity increases suddenly, the conservation of energy (or simply Bernoulli equation) imposes a sudden decrease in water pressure [11]. When the pressure of a flow of

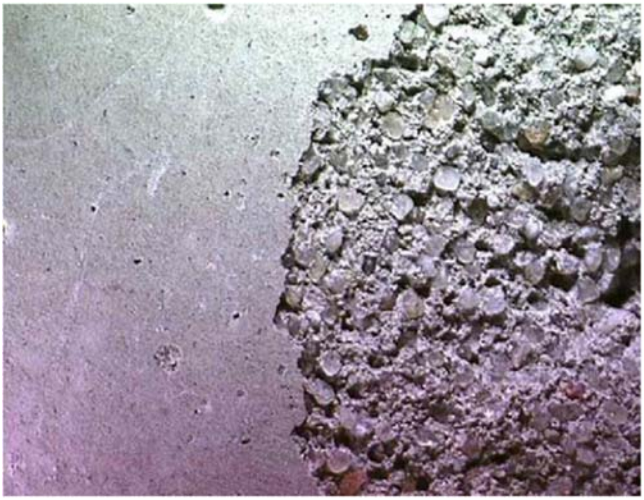


Figure 3.4 Damaged surface of concrete specimen (class C25) from erosion test, showing aggregate liberation due to cement layer removal concrete (image width: 17 mm; exposure time = 10 s) [10].

water reaches a value below that of the water vapor pressure at an ambient temperature, water vaporization occurs. Such a phase change leads to the formation of unstable vapor bubbles. Then, the bubbles break against a concrete surface where an extremely high pressure is exerted and thus an erosion impact is created [9]. This situation may be encountered in flow obstructions in dams, spillways, or water jet demolition of concrete surfaces. Cavitation erosion disintegrates the cement paste as it is weak compared to the aggregate. Then, the aggregates become exposed at the surface.

The abrasion resistance of concrete is defined as the "ability of a surface to resist being worn away by rubbing and friction" [7]. Based on tests and field experience, the abrasion resistance is proportional to the compressive strength of concrete [7]. The strength of concrete surface can be enhanced using proper mix design (e.g., using low w/c ratio < 0.45) and material selection (e.g., using hard and tough aggregates) and other treatments of fresh concrete (e.g., dry shakes and toppings of fresh concrete, finishing, and curing) [7]. Hence, the mitigation of concrete degradation from mechanical impacts can be achieved by improving the concrete proportioning and materials selection. When the abrasion is the main deterioration mechanism, the abrasion resistance can be increased through applying a protective coating or the use of reactive surface hardeners (see Chapter 7).

3.5.2 Concrete deterioration due to freezing and thawing cycles

Concrete deterioration by frost action of freezing and thawing cycles is one of the major durability problems, which consumes a large fraction of expenditures on concrete repair and replacement [1]. In cold climates, when the temperature of a wet concrete drops to 0°C or less, water freezes within its pores, then, when its temperature rises again above 0°C, water melts again. Fresh concrete can resist damage from a single freeze [7]. However, the sequential events, referred to as freezing and thawing cycles, create density changes. The volume expansion associated with the solidification of water upon freezing (9%) leads to high internal stresses. The volume increase of ice formation within concrete pores and voids occurs at a rate that is faster than that of the volume change of the paste [4]. Thus the differential volume change causes a pressure on the wall of pores leading to thermal stresses, which, upon exceeding the strength of concrete, rupture the surrounding microstructure and then create cracks. In these events, cement paste and aggregates respond differently to freezing conditions, as they have different porosities and permeabilities [6]. This may result in variations in stresses. Consequently, the deterioration action of the cycles of freezing and thawing is eventually of a mechanical type caused by the thermal effects. When ice is melted upon thawing, its volume shrinks faster than the holding pore space in the cement paste, then it allows more space to be filled by additional amounts of water from the condensation from humid air in these spaces. These effects cause a loss in mass, and a reduction in the mechanical characteristics.

This type of concrete deterioration is a typical moisture-related problem. It becomes more noticeable when the pores have a degree of saturation above 90% [3].

The degree of saturation is proportional to the relative humidity (RH) of surrounding air. A relatively dry concrete structure ($<75\%$ RH in pores) is normally safe from damage due to cycles freezing and thawing [7]. The crack formation due to freezing and thawing cycles is controlled by the degree of saturation of cement paste [12]. Water sources include the internal moisture in the saturated capillary pores in addition to penetrating water from the surface. Concrete deterioration by freezing and thawing cycles is dependent on the characteristics of capillary pores. It increases with increasing the pore size and connectivity. It is worth mentioning here that only bulk water can freeze at 0°C. However, as described in Chapter 1, water exists in concrete as free and bound water. Freezing happens for free water in the capillary pores only. However, bound water in gel pores does not freeze, unless its temperature drops to -78°C, due to its physical interactions with the cementitious surface [1].

In addition to the internal deterioration, the loss of strength and the reduction in structural integrity of the concrete, the deterioration from freezing and thawing cycles eventually results in scaling and spalling [4]. Spalling is a surface failure by just the break off part of the cement paste exposing aggregates. Scaling is similar to spalling, except that it is associated with freezing and thawing plus the dissolution of deicing chemicals in water, resulting in large concrete flakes. Surface scaling is the loss of paste and mortar from the surface of the concrete, which is accelerated by the use of deicing salts [7]. Surface scaling is categorized in ACI 201.2R [7] as "the most common form of damage from freezing and thawing in hardened concrete." The concrete attack by freezing and thawing cycles from the combined influences of water and deicing salts is larger than that from the freezing of water only.

Reducing the weather effects on concrete pavements is usually based on using deicing salts, such as sodium chlorides to lower the freezing temperature of water and prevent surface accumulation of ice. This practice causes additional expansive effects resulting from the penetration of the dissolved salts with water into concrete. Scaling resistance is determined by measuring the mass loss, the length change, and/or change in the relative dynamic modulus of a concrete specimen subjected to cycles of freezing and thawing in the presence of deicing chemicals (e.g., 4% by weight $CaCl_2$). The presence of salts creates additional mechanical impacts on the concrete pores due to the development of osmotic pressure from the variations in salt concentrations and the buildup of the associated hydrostatic pressure [1]. Salt crystallization occurs when the salt concentration in a solution exceeds its solubility limit in water (or the saturation concentration), which is dependent on temperature. In this case, an additional cracking associated with the crystallization of the expansive salts in the pores is caused [1]. Due to variations in porosities and permeabilities between the cement paste and the aggregates, a difference in the pH of the pore solution is created. Consequently, the paste and the aggregates respond differently to freezing and thawing cycles with deicing salts [6]. Although this deterioration mechanism involves the interaction of chemical species and ions, it is categorized as physical action. Other chemical impacts of deicing salts are explained in Section 3.6.

Concrete resistance against deterioration from cycles of freezing and thawing can be enhanced by the addition of air-entrainment agents to the concrete mixture, improving the quality of concrete, for example, reducing its permeability through minimizing its porosity and refining its pore structure. Reducing permeability eliminates the source of the problem by reducing the amount of freezable water in concrete, rather than accommodating its effect by creating voids. This can be achieved by designing concrete mixes with a low w/cm ($w/c < 0.50$ for mild exposure and $w/c < 0.45$ for severe exposure). It can be achieved also by adding supplementary cementing materials (SCMs) and other waterproofing admixtures and enhancers (see Chapters 9 and 11) and by some surface treatments (see Chapter 10). The standard mitigation of concrete damage from freezing and thawing cycles has been based mainly on entraining air through intentionally created voids in concrete paste (see Chapter 2). During ice expansion upon transient water freezing, the remaining liquid water is subjected to a hydraulic pressure from the reduction of available space. This pressure forces water to escape to any available surrounding spaces, which become more available by the entrained air voids. The level of such a hydraulic pressure depends on the distance between pressurized water and the boundary of escape space. Thus air voids are characterized by a limiting distance between voids, which is termed as spacing factor. According to ACI concrete terminology [13], spacing factor (Powers' spacing factor) is "an index related to the maximum distance of any point in a cement paste or in the cement paste fraction of mortar or concrete from the periphery of an air void." Increasing such a distance increases the level of cracking from cycles of freezing and thawing. The accepted value of spacing factor for attaining good resistance to freezing and thawing is approximately 0.20 mm (0.008 in.) [7]. The recommended air contents for concrete resistant to cycles of freezing and thawing depend on the level of exposure and the nominal maximum aggregate size, and it is commonly within a range of 3.5%–7.5% [7].

3.5.3 Shrinkage deterioration

Concrete cracks can be induced in the cement paste due to volume reduction, or shrinkage, which may occur in early and late stages of concrete. In general, the volume of cement paste changes during concrete curing and after, due to various thermodynamic and chemical actions, which are associated with changes in moisture content of concrete. The moisture content changes through self-induced actions from the consumption of water in cement hydration and through the thermodynamic interactions with the surrounding, which are associated with variations in temperature and humidity [6]. The self-induced moisture reduction creates tensile stresses that pull the walls of pores, causing contraction in the cement paste. The thermodynamic actions are associated with water evaporation and cause the shrinkage of the solid skeleton itself. It occurs through a combined heat and mass transfer process and it is dependent on temperature, humidity, and wind velocity. The mass transfer process is controlled by the advection (see Chapter 2), which is driven by the difference in humidity between the surrounding air and the air at interface region at the cementitious surface. The heat transfer rate occurs by radiation and convection that is proportional to temperature difference between concrete surface and the surrounding air.

The shrinkage is associated with internal stresses that cause crack development and result in a loss of integrity and strength, and an increase in the rate of penetration of water and aggressive materials. These effects accelerate other concrete deterioration mechanisms, and cause more durability problems. The types of shrinkage include plastic shrinkage, thermal shrinkage, drying shrinkage, chemical shrinkage, and autogenous shrinkage. They also include carbonation shrinkage that is associated with carbonation reaction due to the presence of carbon dioxide as detailed in Section 3.6.1. Regardless of shrinkage measurement (changes in volume or length), the obtained shrinkage is commonly a combination of various forms of shrinkages [14].

Plastic shrinkage causes surface cracking of newly laid concrete due to the rapid loss of water that occurs during hot weather concrete casting. It appears within a few hours of concrete placement, when the evaporation rate is higher than a certain limit (e.g., evaporation rate $>1.0\ \mathrm{kg/m^2/h}$ ($0.2\ \mathrm{lb/ft^2/h}$) [15]). When the evaporation rate is moderate, plastic shrinkage is hindered as the loss of water can be compensated for by the bleeding of mixing water to the surface. When the loss of surface moisture occurs at a rate higher than the rate of bleed water or capillary action, tensile stresses are induced within the surface layers, and are restrained by the nonshrinking inner concrete. Cracking occurs when these stresses exceed the tensile strength of fresh concrete that is commonly low in the plastic state [7]. The cracks induced by plastic shrinkage are discontinuous and superficial with a width up to 3 mm wide and a depth in the range of 20–50 mm. They are commonly short (e.g., >50 mm), while in some circumstances they may extend through the full depth of a concrete slab. Preventing plastic shrinkage can be accomplished by efficient approaches of water retention in fresh concrete. This can be accomplished externally through covering the concrete surface as early as possible (e.g., using sunshades to reduce the concrete surface temperature) and protecting it from the effects of drying winds (e.g., using windbreak to reduce wind velocity). The risk of cracking is also reduced by moistening the aggregate before mixing and by the use of fiber reinforcement, which enhances the concrete capacity for tensile strain of concrete in its plastic state. In some cases, cracks can be removed by vibrating the concrete or by power floating and troweling of flat surfaces. For fresh concrete, the drying rate can be decreased by reducing the gradient of humidity between the concrete surface and the bulk of air through continuous humidification (e.g., fogging to prevent plastic shrinkage of fresh concrete [6]).

Thermal shrinkage results from reduction of volume caused by creating an extreme temperature gradient between the outer and inner sections of concrete or within the concrete structures at the early stages of cement hydration due to the variations in the exothermic heat release. This occurs because the temperature of the inner concrete region (which gains heat from the exothermic cement hydration reactions) rises above that of the surroundings. Then, cracks are initiated when the thermal stresses exceed the tensile strength of the concrete.

Drying shrinkage occurs when water evaporates from the hardened concrete subjected to conditions of wind flow creating gradients of temperature and humidity. Drying shrinkage results from loss of internal moisture associated with the loss of adsorbed water from the hydrated cement paste (from gel pores) as a result of water evaporation to the surrounding environment when its humidity is lower than that within the paste poses [13]. Then, upon moisture loss from the fine pores of the concrete surface, the surface tension of the remaining water tends to pull the pores inward, leading to a reduction of volume with time [3]. The resulting volume changes exert a mechanical action and causes slow wearing of the surface [3]. The cracks are generated when the induced internal stresses become larger than the tensile strength of concrete. As indicated above, this mechanism involves a combined heat and mass transfer process (convection and advection) driven by the wind motion and the gradients in temperature and humidity between the concrete surface and the surrounding air. The nonuniform drying of cured hardened concrete through the escape of moisture from exposed concrete leads to internal stresses and cracking. Changes in the levels of the surface moisture are encountered from periodic changes in the humidity and the temperature of the surrounding air. This leads to cycles of expansion and contraction and causes cracking. Drying shrinkage can be minimized through controlling the evaporation rate at the concrete surface, for example, by sealing the surface of cured concrete, or by waterproofing treatments. It can also be reduced through the addition of shrinkage-reducing admixture to the concrete mixture (see Chapter 7).

Chemical shrinkage is the chemical contraction of the absolute volume of the cement paste from the hydration reactions [6], which is developed in all types of concrete, regardless of its w/c ratio. The original volume of cement paste is occupied by the cement particles and the mixing water. Water is then partially consumed by the hydration reactions and by the evaporation process while the hydration products occupy a smaller volume than the original volume. According to ASTM C125−15b [16], chemical shrinkage is the "reduction in volume of cementitious paste that occurs during hydration because the reaction products occupy less volume occupied originally by the water and unreacted cementitious materials." In fact, the volume occupied by each of the hydration products is larger than that of each of the starting cement compounds because of the decrease in their specific gravities: the specific gravities of the four main cement components ranges between 3 and 3.7, while those of the hydration products range between 1.8 and 2.5 [17]. However, after hydration, the net cementitious matrix composed of the hydration products (e.g., $C-S-H$ gel, CH crystals, ettringite) occupies a lower volume compared to the volume of the combined reactants (water and cement particles) [14]. Hence, the chemical shrinkage increases with increasing the degree of hydration [18]. Also, increasing the temperature increases the rate of the chemical shrinkage due to its effect on accelerating the rate of the hydration reactions, as shown in Fig. 3.5 [17]. Chemical shrinkage was found to have slight variations with different w/c ratios, which were unsystematic [17]. Theoretically, the chemical shrinkage can be estimated from mass balance calculations, based on reactions stoichiometry of cement hydration (see Chapter 1), and

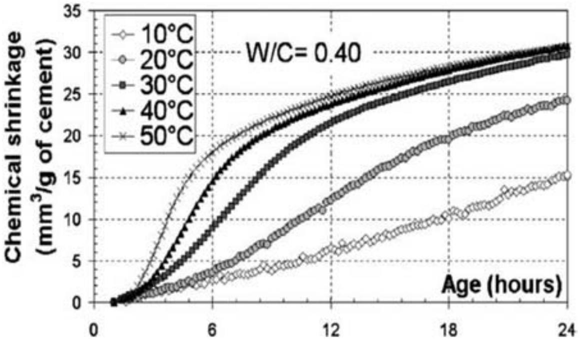


Figure 3.5 Evolution of chemical shrinkage of cement paste with a w/c ratio of 0.40 cured at various temperatures as a function of age [17].

from the knowledge of the specific gravities of hydration reactants and products, as reported by [18]. For example, the estimated chemical shrinkage associated with the hydration of dicalcium silicate (C_2S) is 10.8% [18]. Then, the total chemical shrinkage is determined based on the cement composition and the chemical shrinkage of each of the main cement constituents.

The autogenous shrinkage is a self-induced drying shrinkage caused by the hydration of cement itself, which becomes more severe at low w/c [14]. It is usually encountered in concrete made with low w/c ratios ($w/c < 0.4$) such as high-performance concrete. It results from the suction of water from fine gel pores and some capillary pores, for the hydration of the unreacted cement. It does not include any source of volume change from moisture exchange with the surroundings or from temperature variation (as in the case of drying shrinkage). As described in Chapter 1, when concrete mixture is prepared with w/c ratio < 0.38, the internal moisture is insufficient for the full hydration of all cement particles. Thus such a condition causes autogenous shrinkage from the volumetric contraction associated with the uniform reduction of internal moisture with the progress of cement hydration itself [14]. Then, fine pores resulting from the chemical shrinkage drains water from capillary pores, causing a reduction in humidity and hence autogenous shrinkage is driven by the chemical shrinkage. This self-induced internal drying effect creates tensile stresses on the capillary pores and leads to autogenous shrinkage [6]. Fig. 3.6 shows curves of autogenous shrinkage as functions of curing age for two mixtures at various w/c ratios [19]. With the progress of cement hydration, water is drained more significantly from the formed finer pores, developing more tensile stresses and resulting in a significant contraction of the apparent volume. The rate of this process depends on the paste porosity (or w/c ratio). Recommended methods of minimizing autogenous shrinkage [19] include the addition of fly ash, internal curing using lightweight aggregate and high water absorbent polymers, and adding low amounts of steel fibers.

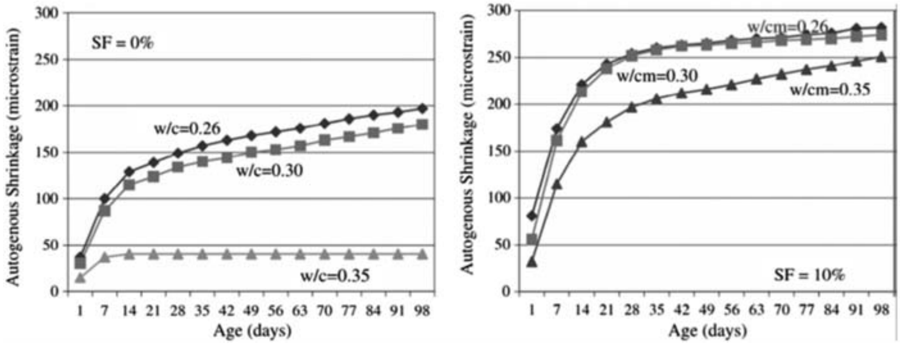


Figure 3.6 Effect of w/c ratio on autogenous shrinkage of high-performance concrete, using OPC (right) and using concrete with 10% silica fume (left) [19].

3.6 Chemical mechanisms of concrete deterioration

The chemical attacks of concrete are the results of various types of reactions of its constituents with aggressive materials coming from (1) the cement content such as alkalinity, (2) the hydration by-products (calcium hydroxide), or (3) the surrounding environment that penetrates with water and air. The chemical attacks occur when the aggressive chemicals exist in solution and when their concentrations are above certain limits. The gases have to be in contact with moisture in order to become aggressive. Solid or dry chemicals rarely attack concrete [7].

The products of reactions impact the pH of the pore solution, destabilize the cement paste, the aggregates, and the steel bars. The reaction products may involve the formation of expansive products within the paste, which can then lead to harmful effects such as cracking [1]. Sample effects of commonly used chemicals on concrete are summarized in Table 3.2. Other comprehensive tables are available in ACI 515.1R [20].

Factors influencing chemical attack on concrete include (1) porosity that increases water penetration, while void content increases air entrainment, (2) cracks from mechanical and thermal effects, and (3) water penetration and leaching effects from wetting and flow under a hydraulic pressure [20]. The mechanisms of the four main chemical attacks are described in the following subsections. These include chemical reactions of acid attack, sulfate attack, corrosion of steel in concrete, and AAR. Other harmful reactions also include the delayed hydration of free calcium and magnesium oxides (CaO and MgO) and reactions of soluble deicing salts.

3.6.1 *Acid attack*

Concrete is typically an alkaline material; thus acids have a general impact of altering the alkalinity conditions and destabilize concrete structure. The hydrates of

Table 3.2 Sample effects of commonly used chemicals on concrete [7].

Rate of attack at ambient temperature	Inorganic acids	Organic acids	Alkaline solutions	Salt solutions	Miscellaneous
Rapid	Hydrochloric Nitric Sulfuric	Acetic Formic Lactic	—	Aluminum chloride	—
Moderate	Phosphoric	Tannic	Sodium hydroxide[a] $> 20\%$	Ammonium nitrate Ammonium sulfate Sodium sulfate Magnesium sulfate Calcium sulfate	Bromine (gas) Sulfite liquor
Slow	Carbonic	—	Sodium hydroxide[a] $10\% - 20\%$ Sodium hypochlorite	Ammonium chloride Magnesium chloride Sodium cyanide	Chlorine (gas) Seawater Soft water
Negligible	—	Oxalic Tartaric	Sodium hydroxide[a] $< 10\%$ Sodium hypochlorite Ammonium hydroxide	Calcium chloride Sodium chloride Zinc nitrate Sodium dichromate	Ammonia (liquid)

[a] The effect of potassium hydroxide is similar to that of sodium hydroxide.

calcium silicate (C − S − H gel) and ettringite are relatively insoluble in water. However, calcium hydroxide, the hydration by-product, has a relatively high solubility in water (1.23 g/L), and thus it is readily solubilized forming the alkaline pore solution (usually with a pH in the range of 12−14 [3]). Normally, calcium silicate hydrates are in equilibrium with the pore solution as long as its pH is higher than 12.5. Such a high pH value of concrete is obtained and maintained from the dissolution of alkaline content of cement, coming mainly from sodium and potassium oxides (Na_2O and K_2O), and from the alkalinity of calcium hydroxide (CH). However, when concrete comes in contact with an acidic environment, the pH of the pore solution may go below the limiting pH value of 12.5 for concrete stability. The equilibrium state of C − S − H gel (the binding materials in concrete) will be affected when the acidic environment becomes aggressive on the stability of these hydration products. This nonequilibrium state leads to destabilization of the mineral compounds of cement hydration, and then reduces the paste integrity and the concrete strength. Additional effects of acid attack include corrosion of reinforcing steel, which is described in the following section. The severity of acid attack depends on the level of altered pH of the pore solution and the permeability of concrete. Acid attack of cement paste is more detrimental when the pH goes below 6 [1]. Table 3.2 lists the level of impacts of various inorganic and organic acids. Some inorganic acids such as oxalic and tartaric acids are known to have negligible rate of attack [20].

Carbonation is one of the popular acid attacks, which is simply an acid−base neutralization reaction between carbonic acid and calcium hydroxide [4]. In this case, the acid source for the pore solution may come from the solubilization of carbon dioxide (CO_2) coming from air leading to the formation of carbonic acid or from the acidity of industrial wastewater in contact with concrete. The dissolved CO_2 reacts with the dissolved calcium hydroxide from concrete (forming the pore solution) and results in the precipitation of white tops of calcium carbonate on the concrete surface, which is referred to as efflorescence [1]. Carbonation reaction proceeds with time from the outer surface of concrete toward the internal concrete structure through the diffusion mechanism of carbon dioxide. Eventually, carbonation decreases concrete porosity and makes the carbonated paste stronger [3]. Thus carbonation has a positive effect on concrete quality as it produces binding materials that fill the pores. In fact, intentional carbonation during concrete production may be promoted to enhance concrete strength and dimensional stability [7]. In addition, the carbonation mechanism has a positive effect on the environment through the mineral sequestration of carbon dioxide by storing it chemically in the form of solid carbonates [21]. However, it contributes to a major durability problem as it decreases the pH of the pore solution, which causes damaging sequences as described below. As mentioned in Section 3.5.3, carbonation is also accompanied by shrinkage [7]. Carbonation becomes more severe in hot and humid climates [3]. A fully carbonated concrete may be neutralized, reaching a pH value of 7 [3].

In the carbonation mechanism, carbonic acid (H_2CO_3) is formed as an intermediate compound from the solvation of CO_2 from air in water. The chemical attack of carbonic acid on cement paste belongs to cation-exchange reaction between carbonic acid and calcium hydroxide, known as carbonation reaction, as given by Eq. (3.1) [3]:

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \tag{3.1}$$

A similar chemical mechanism of acid attack by carbonation is obtained with magnesium hydroxide. A solution of magnesium hydroxide can be formed from the dissolution of magnesium oxide (MgO) coming from the original cement content (from the natural raw materials used in cement making as described in Chapter 1). Its content is typically in the range of 0.1%–4% of the cement weight. MgO is dehydrated in the alkaline environment of the solution in pore solution forming magnesium hydroxide ($Mg(OH)_2$), called brucite, according to Eq. (3.2). Then, magnesium hydroxide participates in three carbonation reactions given in Eqs. (3.3–3.5).

$$MgO + H_2O \rightarrow Mg(OH)_2 \tag{3.2}$$

$$Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3.3H_2O \tag{3.3}$$

$$5Mg(OH)_2 + 4CO_2 \rightarrow 4MgCO_3.Mg(OH)_2.4H_2O \tag{3.4}$$

$$5Mg(OH)_2 + 4CO_2 + H_2O \rightarrow 4MgCO_3.Mg(OH)_2.5H_2O \tag{3.5}$$

Carbonation is a chemical reaction that is governed by its reaction kinetics; however, the availability of the reactants is governed by the mass transfer process (see Chapter 2), which is dependent on the environmental conditions. These conditions include the concentration of carbon dioxide in air, the RH, and the temperature. Concrete structures in areas subjected to large emissions of carbon dioxide (industrial zone and highways) suffer considerably from the carbonation problem [3]. The air content of CO_2 is usually very small in the countryside (about 0.03% by volume), but can reach a higher range of 0.3% − 1.0% in the urban areas. Air permeation and gas diffusivity in concrete are directly dependent on the RH (see Chapter 2), thus the carbonation reaction decreases when the RH goes above a certain limit [3]. ACI 201.2R [7] indicates that when the RH is above 75%, saturation moisture in the pores reduces the diffusion of CO_2, while the largest rates of carbonation reactions are obtained when the RH is in the range of 50% − 75%. Increasing temperature enhances the reaction kinetics.

Similar harmful acid–base neutralization reactions of calcium content of paste occurs when concrete is exposed to acidic industrial wastewater, leading to the formation of various calcium salts [1]. Some types of organic acids such as acetic, lactic, and formic acids may exist in some industrial wastewater from food production. The reactions of these acids with calcium hydroxide produces calcium salts that are generally insoluble. Some of these salts are known to be nonexpansive in nature, and consequently, their reaction products are not deleterious. This is the case with calcium salts from reaction with industrial effluents containing oxalic, tartaric, tannic, hydrofluoric, or phosphoric acid [1] (see also Table 3.2). However, their impact may still be considerable from the perspective of reducing the alkalinity of the pore solution. Mineral waters may be concentrated with dissolved carbon dioxide, hydrogen sulfide, or both, and thus may cause harmful damage to concrete [7]. In the case of sulfuric acid attack, a further lethal deterioration is associated with the formation of calcium sulfate, which accelerates the sulfate attack mechanism [7]. In addition to the above-mentioned reactions with calcium hydroxide in cement paste, acids cause attacks to the aggregates of concrete when limestone and dolomitic aggregates are used [7].

3.6.2 Chloride attack and corrosion of embedded steel

Corrosion of reinforcing steel bars in concrete is an electrochemical process, which can occur in dry or wet conditions, depending on the attacking species in the vicinity of steel bars. Under wet conditions, electrochemical reactions occur between iron and dissolved ions in water, such as alkalis, chlorides, and oxygen, transforming iron into a rust with a detrimental expansive characteristic. Rust compounds occupy a larger volume than that of the reacted iron from the steel (e.g., volume expansion by a factor of 2−2.5) [3]. The volume increase depends on the state of iron oxidation in the corrosion products. Rust compounds create internal stresses on the surrounding concrete, and eventually result in crack formation when these stresses exceed the strength of concrete. The in-situ precipitation of corrosion products causes the concrete surrounding the steel bars to spall off (spalling problem [4]), making the corrosion problem of a larger impact on durability of concrete structure overall. Spalling of the concrete surrounding the emended steel bars become visible owing to the development of huge corrosion products, allowing the steel bars to be exposed to the atmosphere. Fig. 3.7 shows a typical damage of concrete from corrosion associated with carbonation of concrete [22].

The corrosion is commonly promoted by (1) the acidity of the surrounding conditions (e.g., due to carbonation reactions as described in the section above) or (2) the penetration of chloride ions. The basic corrosion reaction is initiated between iron, oxygen, and water, which produces ferrous hydroxide [$Fe(OH)_2$] [23] according to Eq. (3.6). The formed ferrous hydroxide is unstable; it is then further oxidized by reacting with oxygen and water producing ferric hydroxide [$2Fe(OH)_3$], according to Eq. (3.7).

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2 \tag{3.6}$$

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \tag{3.7}$$

The formed ferric hydroxide establishes a porous layer on the corroded steel bars. Then, it is slowly hydrated into red brown rust (hydrated ferric oxide,

Figure 3.7 Cracking and spalling owing to corrosion in a marine environment [22].

$Fe_2O_3 - H_2O$), which is impermeable for the diffusion of corrosive materials [23]. Consequently, after initial corrosion effects, the steel bars are covered by a thin impermeable layer, which prevents the diffusion of attacking chemical species toward the steel surface, protecting it from further corrosion. The steel covered with the oxide film is then considered to have a passive behavior against corrosion.

This protective oxide film has a very low solubility in the alkaline pore solution. This impermeable film is strongly bonded to the steel surface and remains stable under high alkaline conditions (i.e., $pH > 12.5$), which normally exists in pore solution. In fact, this protective film can remain durable with a self-repairing or healing property as long as the surrounding pH is higher than 11.5 [1]. This passive protection functions well as long as the concrete is not subjected to acid attack (e.g., carbonation) as described in the section above.

When the concrete is subjected to acid attack, the aforementioned acid–base neutralization reactions (e.g., carbonation) decrease the pH of the pore solution, which then destabilizes the film. Practically, when the pH drops below 10.5, the passive protective layer loses its integrity (depassivation), and thus the corrosion can be initiated again when the steel becomes exposed to moisture and oxygen. Consequently, further corrosion reaction occurs resulting in more rusting. As said above, such a corrosion problem is a subsequent event of the carbonation reaction. These corrosion effects are also induced by additional but less common effects of other gases such as sulfur dioxide (SO_2) [3].

Similarly, when the concrete is subjected to chloride attack, the protective film, formed at the surface of steel bars from the initial corrosion, is destroyed even at high pH values (i.e., $pH > 11.5$) [1]. This leads to what is referred to as chloride-induced corrosion of steel bars, or frequently referred to as the problem of chloride ion penetration or chloride attack [3]. The rate of destruction of the oxide protective film depends on the molar ratio of chloride to hydroxide ions (Cl^-/OH^-) [1]. When such a ratio is larger than 0.6, the steel bars become unprotected against corrosion, and the iron-oxide film becomes permeable for the diffusion of attacking corrosive ions. Consequently, chloride ions depassivate the steel bars and cause further corrosion as with the cause of carbonation. The corrosion reaction resulting from chloride ions penetration leads to the formation of ferric chloride ($FeCl_3$), which is a water-soluble compound. The formed ferric chloride diffuses to the concrete surface where it precipitates as a brownish bleeding stain [4]. The resulting rust exerts a volume expansion and results in internal stresses. The consequences of corrosion include cracking, spalling, delamination, and bleeding [4]. In addition, increasing concrete content of chloride ions increases the capacity of the pores to hold water.

Chloride attack also includes chloride binding to the cementitious surfaces, which causes another durability problem associated with the penetration of chloride ions. It occurs because chloride ions can be captured and adsorbed on the hydration products such as C—S—H gel and calcium mono-sulfoaluminate. It has destabilization effects on the hydration products and it involves the formation of complex salts such as Friedel's salt or Kuzel's salt and the physical adsorption of chloride ions on $C-S-H$ gel [24].

Chloride attack may occur as a consequence of using deicing salts. Dissolved chlorides can then penetrate into the concrete structure with water and then cause concrete deterioration. In fact, the types of deicing salts include chlorine salts and nonchlorinated organic salts [25]. The chlorine deicing salts include sodium, calcium, and magnesium chlorides. The nonchlorinated organic deicing salts include potassium acetate (CH_3COOK) [26], sodium acetate (CH_3COONa), calcium magnesium acetate ($C_8H_{12}CaMgO_8$), and potassium formate ($KHCO_2$). These nonchlorinated organic deicing salts, in addition to urea, and ethylene glycol, cover about 25% of the used deicers [23]. Experimental findings indicate that chlorides are more corrosive than acetates [23]. Measurement of corrosion rates for various deicers in concentration range of $0.25-1.0\,\mathrm{M}$ leads to the classification of their aggressiveness on bare steel according to the following order: sodium chloride > magnesium chloride > calcium chloride > potassium acetate [23]. Another main source of chloride ions comes from exposure of concrete to sea water, in marine structures [27]. In fact, exposure to seawater is associated with other lethal deterioration of concrete such as sulfate attack, as described in the subsequent section. These combined harmful effects may cause rapid severe concrete defects in tropical climates within a few years. Additional sources of chloride ions can come from concrete additives and admixtures, or from aggregates that naturally contain chloride salts (from natural sources of aggregates exposed to seawater or groundwater containing chlorides) [7].

Chloride attack is a combination of chemical reaction, mass transfer process, and water permeation. For dense concrete with low porosity and low diffusivity, the diffusion mechanism may control the process. The diffusion coefficient of chloride ion is influenced by the degree of saturation [3], as described in Chapter 2. Thus it can be controlled by improving the quality of concrete through reducing its porosity, permeability, and other transport properties (e.g., its diffusivity for chloride ions). This can be achieved by using a proper waterproofing technology (see Chapters 8 – 11).

3.6.3 Sulfate attack

Sulfate attack causes deterioration of concrete through destabilization of the cement paste and through creating expansive effects leading to cracking. The aggressive compounds include sodium, potassium, calcium, and magnesium sulfates. The chemical reactions occur between the sulfate ions and the constituents of the cement paste. The source of sulfates may be from exposure of concrete to seawater or wastewater or from natural sources, such as those dissolved in groundwater or found in soil adjacent to concrete structures [7]. Also, some sulfates come from the cement itself as it contains gypsum, which is added for controlling the setting time (see Chapter 1). Sulfates may also come from the admixtures.

The sulfate attack happens when the sulfate ions combine with hydrated calcium aluminate in the concrete paste, destroying it and forming ettringite (calcium sulfo-aluminate hydrate). As described in Chapter 1, during cement hydration process, crystals of mono-sulfate aluminate hydrate (C_4ASH_{18}) are formed from the reaction of the unstable ettringite ($C_3A \cdot 3CS \cdot H_{32}$) with available tricalcium aluminate (C_3A) in the cement, after the depletion of gypsum, from the cement [see Eq. (1.6)]. The mono-sulfate aluminate hydrate is stable in a solution containing no sulfates. The chemical mechanism of sulfate attack is based mainly on the reaction of sulfate ions (S) with the mono-sulfate aluminate, calcium hydroxide, and water, forming additional ettringite, according to Eqs. (3.8) and (3.9) [1].

$$C_3A \cdot CS \cdot H_{18} + 2CH + 2S + 12H \rightarrow C_3A \cdot 3CS \cdot H_{32} \tag{3.8}$$

$$C_3A \cdot CS \cdot H_{18} + 2CH + 3S + 11H \rightarrow C_3A \cdot 3CS \cdot H_{32} \tag{3.9}$$

The product of reaction (ettringite) is expansive and thus results in internal stresses and then the formation of irregular cracks. The size of ettringite is larger than the size of the mono-sulfate aluminate hydrates by a factor of 2.5; thus it causes a volume increase leading to expansion effects [7]. This means that the sulfate attack is a chemical action yielding to a mechanical action. These damages increase the concrete permeability and cause durability problems. It is also associated with a decrease in the compressive strength and a loss of concrete integrity. In fact, concrete cracking provides new channels for further penetration of aggressive chemicals. Fig. 3.8 shows a picture of deteriorated concrete due to sulfate attack [28].

Figure 3.8 Deteriorated concrete because of sulfate attack [28].

Other cation-exchange reactions occur between the sulfate ions and calcium hydroxide and produce gypsum, according to Eq. (3.10), which also creates expansive effects. The formation of gypsum can lead to softening and loss of concrete strength [7].

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH \tag{3.10}$$

In addition, concrete subjected to sulfate attack may suffer from other softening effects through destabilizing of the paste matrix, loss of integrity, and an increase in the overall porosity. This happens when magnesium sulfate reacts with $C-S-H$ gel and water, destabilizing the binding material ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) and producing gypsum that causes expansive effects according to Eq. (3.11). Magnesium sulfate also reacts with calcium hydroxide and water, producing additional expansive gypsum according to Eq. (3.12). These two reactions [Eqs. (3.11) and (3.12)] produce insoluble magnesium hydroxide [$Mg(OH)_2$] as a by-product, making the magnesium sulfate attack more severe on concrete than the sodium sulfate attack. The insolubility of $Mg(OH)_2$ prevents it from controlling the stability of $C-S-H$ against the attack, while the by-product (NaOH) from the reaction with sodium sulfate is soluble and assists in the stability of $C-S-H$ [1]. The following section provides more detail on concrete degradations from the presence of magnesium compounds.

$$3MgSO_4 + 3CaO \cdot 2SiO_2 \cdot 3H_2O + 8H_20 \rightarrow 3(CaSO_4 \cdot 2H_2O) + 3Mg(OH)_2 + 2SiO_2 \cdot H_2O \tag{3.11}$$

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 \tag{3.12}$$

Minimizing sulfate attack is usually based on maximizing the quality of concrete through adding SCMs or using low w/c ratio to reduce the permeability, or through the use of sulfate resistance cement (e.g., Type V with $C_3A < 5\%$, or Type II with $C_3A < 8\%$, according to ASTM C150 [29]).

3.6.4 Reactions with magnesium compounds

Magnesium compounds supply magnesium ions to the pore solution, which then cause a detrimental action on cement paste. Magnesium chemical attack occurs by the destabilization of the binding material of the cement paste ($C-S-H$ gel). Magnesium ions attack the hydrates of calcium silicate, causing a decrease in concrete strength and integrity. They replace calcium ions in $C-S-H$ gel, producing magnesium silicate hydrates, causing a loss in the cementitious characteristics [1]. The mechanisms of concrete damage from magnesium ions may involve hydraulic, osmosis, and crystallization pressures [30]. The harmful magnesium compounds include solutions of magnesium chloride, sulfate, or bicarbonate, which may come in contact with concrete from seawater or certain industrial wastewater. Among these compounds, magnesium sulfate ($MgSO_4$) is the most aggressive compound as it includes the detrimental actions of magnesium and sulfates as described in Section 3.6.3. Its damaging reactions are described above in Eqs. (3.11) and (3.12). Magnesium chloride ($MgCl_2$) is one of the most aggressive chloride-based deicing salts. It causes concrete damage through the formation of magnesium oxychloride, which has an expansive behavior and leads to crack development in the cement paste [31]. A reaction between $MgCl_2$ and $Ca(OH)_2$ occurs according to Eq. (3.13). It is worth mentioning here that calcium chloride causes a similar aggressive effect, through a similar reaction with calcium hydroxide forming calcium oxychloride, according to Eq. (3.14).

$$MgCl_2 + 3Mg(OH)_2 + 12H_2O \rightarrow 3Mg(OH)_2.MgCl_2.12H_2O \tag{3.13}$$

$$CaCl_2 + 3Ca(OH)_2 + 12H_2O \rightarrow 3Ca(OH)_2.CaCl_2.12H_2O \tag{3.14}$$

Minimizing concrete attack from reactions with magnesium compounds is partly related to minimizing sulfate attack (e.g., magnesium sulfate), through adding SCMs (e.g., fly ash [32]) or using low w/c ratio to reduce the permeability.

3.6.5 Alkali aggregate reactions

AAR are chemical reactions in either mortar or concrete, which occur between the reactive mineral compounds that exist naturally in the chemical structure of certain aggregates and the alkali hydroxides in the pore solution. The hydroxides come mainly from the alkaline content of the Portland cement and from the dissolved calcium hydroxide, which is the undesired by-product of the cement hydration. When the portlandite or $Ca(OH)_2$ is dissolved in the pore solution, it supplies the hydroxyl ions (OH^-). In addition, the alkaline content in Portland cement includes soluble and sodium oxide (Na_2O) and potassium oxide (K_2O) that are soluble in water and provide OH^- ions. Additional sources of alkalis may come from the alkaline content of aggregates themselves. There are also other possible sources of alkalis from surroundings, such as those that come from deicing salts, seawater, or industrial wastewater [4]. Fig. 3.9 shows a picture of a typical concrete damage due to alkali–aggregate reaction [4]. According to the type of reactive compounds within the aggregates structure, AAR are classified into two types: alkali – silica reaction (ASR) and alkali–carbonate reaction (ACR) [4]. The ACR occurs with aggregates containing $CaMg(CO_3)_2$, such as dolomitic rocks, in which $CaMg(CO_3)_2$ undergoes ACR and causes concrete deterioration within a time scale of 2–3 years. On the other hand, ASR is a slow reaction between the aggregates containing

Figure 3.9 Concrete damage due alkali–aggregate reactions [4].

reactive silica (SiO_2), forming an expansive gel that causes cracking within a time scale of 10–20 years. The rest of this section details the ASR as it creates the major durability problem of concrete in many applications such as concrete pavements [33].

The ASR attack is caused through chemical reactions by the expansive gel that is formed as a product of ASR reaction, which can be represented simply as stated in Eq. (3.15) [3].

$$\text{alkali} + \text{reactive silica} + \text{water} \rightarrow \text{ASR expansive gel} \tag{3.15}$$

In fact, the ASR reaction is governed by the type of silica that exists within the aggregate structure. The types of silica are governed by its structure within the aggregates. These include amorphous and crystalline silica and then classified into reactive and nonreactive silica. Based on the type of silica content, the aggregates are classified as reactive or nonreactive aggregates. Crystalline structures are usually more stable and less reactive as the molecules are arranged in well-defined structures with sufficient bonding. When the silica content of aggregates exists in the form of quartz crystalline structure, it is chemically inert, and thus the aggregates are classified as nonreactive. However, when the silica content is poorly crystalline or amorphous, it can be dissolved in water forming a reactive amorphous hydrous silica. The reactive aggregates include those that contain large portions of amorphous silica or microcrystalline silica, *meta*stable crystals, volcanic glasses, and some crystalline silica with lattice defects [33,34].

Overall, lethal ASR requires the following prerequisites [4]: (1) the presence of sufficient moisture in concrete (80%–90% RH), as water is essential as a diffusion medium for the dissolved species (see Section 3.3), and it is absorbed by the formed alkali–silica gel to create a deleterious expansion, (2) the presence of reactive aggregates, and (3) sufficient alkaline conditions (from the sources mentioned above), in order to facilitate the dissolution of the reactive silica (SiO_2) from aggregates. The mechanism of ASR is based primarily on the formation of alkaline pore solution from alkaline content of cement paste [33]. As indicated in Section 3.6.1, the pH of the pore solution is usually high (e.g., above 12.5). In fact, it is required to be high enough to prevent the corrosion of reinforcing steel bars. Then, these alkaline ions come in contact with the solubilized silica (e.g., amorphous silica) in the aggregates and dissolve it, though a process that is referred to as depolymerizing. The mechanism involves the following steps [33]:

1. The hydroxyl ions (OH^-) and the alkali metal ions (M^+) react with the reactive sites of SiO_2 at the silica surface producing silicic acid ($H{-}O{-}Si\equiv$), according to the reaction given in Eq. (3.16).
2. The produced silicic acid reacts further with the hydroxyl ions (OH^-) and with the metal alkali forming alkali silicate hydrate ($Si{-}O{-}R$) (gel) and water, according to the reaction shown in Eq. (3.17).
3. The produced alkali silicate gel has a strong affinity for water and forms an expansive gel with a swelling characteristic. Water is then physically bound within gel structure, according to Eq. (3.18).

4. The produced hydrated alkali-silicate gel [from Eq. (3.18)] migrates through the capillary network and cracks in concrete [3]. When it sneaks from aggregate structure toward the adjacent cement paste, it encounters the calcium ions (Ca^{2+}) and reacts with it forming alkali-calcium-silicate gel within the paste pores.
5. The alkali-calcium-silicate gel, within the paste pores, swells water from the surrounding pores and then expands. Its expansion creates internal stresses that exceed the tensile strength of concrete and thus causes cracking [33]. The formed cracks cause major losses in the paste integrity and strength.
6. The resulting cracks cause further damages [35] as they allow more water to penetrate into the cracked concrete structure, thus affecting its integrity, and motivating several processes of deterioration [34]. The resulting surface macrocracks form at right angles to the surface with a depth in the range of 25–50 mm [3].

$$\equiv \mathrm{Si-O-Si} \equiv \ + \mathrm{OH^-} + \mathrm{R^+} \rightarrow \equiv \mathrm{Si-O-R} + \mathrm{H-O-Si} \equiv \tag{3.16}$$

$$\equiv \mathrm{Si-O-H} + \mathrm{OH^-} + \mathrm{R^+} \rightarrow \equiv \mathrm{Si-O-R} + \mathrm{H_2O} \tag{3.17}$$

$$\equiv \mathrm{Si-O-R} + \mathrm{nH_2O} \rightarrow \equiv \mathrm{Si-O^-} - (\mathrm{H_2O})_n + \mathrm{R^+} \tag{3.18}$$

In fact, there is a scientific discussion in the literature on the swelling properties of the alkali silicate compounds (with sodium and/or calcium cations). There are inconsistent views about the influencing mechanisms of the composition of ASR gel on its swelling behavior. Sodium silicate gel is known to occur in a liquid state, whereas sodium calcium silicate gel occurs in a solid state. Liquid sodium silicate gels can penetrate easily to the pores, while solid gels expand [33].

The rate of ASR increases with increasing concrete porosity, permeability, and diffusivity for reacting species. Also, the size of aggregates and their surface area are other controlling factors as the reaction rate is governed by the contact area; large reactive aggregates (with small surface area) require years to result in detrimental ASR in concrete. The other contents of aggregates also impact the ASR rate, for example, when the aggregates contain very finely ground pozzolanic particles, the ASR may be reduced through the participation of these particles in a pozzolanic reaction with calcium hydroxide (see Chapter 1). Thus they reduce the alkalinity of the pore solution.

Solutions of durability problems of ASR include preventive measures of avoiding the use of reactive aggregate and limiting the alkali content of the cement as a source of reactant. They also include the selection of proper mix designs (see Chapter 4) such as using SCMs and using admixtures (e.g., lithium-based compounds) [36] (see Chapter 7), or using special concrete waterproofing systems for reducing concrete permeability [37] as detailed in Chapters 10 and 11. Mitigating the ASR using SCMs is the standard way and several national specifications and guidelines recommended the use of pozzolans with potentially reactive aggregates [7]. However, ACI 201.2R-08 [7] states that there is conflicting evidence regarding the efficacy of these materials in this role, and this is reflected in the lack of consensus advice. The available literature documents that the addition of SCMs reduces the permeability of concrete (see Chapter 4), and assists in reducing the pH of the pore solution by the mechanism of alkali binding. Consequently, the addition of SCMs reduces the dissolution rate of soluble components in the aggregates and hence reduces the resulting swelling pressure of the ASR gel. For example, the addition of 10% silica fume as a replacement of cement resulted in a 50% reduction in ASR expansion after 28 days of testing [33]. When reactive Spratt fine aggregates were used, a large cement replacement by ground granulated blast furnace slag ($>$ 50%) was required for decreasing the ASR expansion of concrete prisms to reach a value below the limit of 0.04% after the 2 years of testing. The use of fly ash for mitigating ASR has been discussed in detail in a review paper by Saha et al. [33]. The effectiveness of fly ash for ASR mitigation depends on its composition: fly ash with a low calcium content (e.g., Class F) is more effective than fly ash with a high calcium (class C). Fly ash F consumes a larger fraction of the soluble portlandite (calcium hydroxide) from pore solution and thus leads to a larger reduction in alkalinity, as it has the pozzolanic properties only. On the other hand, fly ash C has the cementing (hydraulic) and the pozzolanic properties and hence it contributes to the formation and solubilization of additional calcium hydroxide in the pore solution. Both of them reduce the paste porosity, which assists in reducing ASR.

3.7 Biochemical mechanisms of concrete deterioration

Biodeterioration of concrete occurs due to the biological activities of microorganisms during their growth. The required nutrients for their growth are obtained from various sources. These include sunlight, moisture, surrounding air, substrate on which the biofilm is formed, and from the biofilm environment itself [38]. The problem is governed by the growth rate that is dependent on moisture penetration into the concrete structure and the availability of the other nutrients for growth [39]. The biochemical reactions lead to visible stains with a bad appearance, but more seriously to a major concrete durability problem. Biodeterioration creates serious challenges to the infrastructures, and impacts integrity, durability, and functionality of concrete [40]. They can lead to the development of biofilms on concrete surfaces as one of the consequences of bio attacks of concrete as shown in Fig. 3.10. Surface roughness makes it easier for microorganisms to colonize [38]. These activities cause an accelerated structural deterioration. The bio-receptivity of concrete is enhanced with its porosity and it is dependent on the w/c ratio; biodeterioration increases with increasing w/c ratio, due to increasing moisture content and nutrient retention [38].

Biodeterioration of concrete is encountered in hot and humid climates for major concrete applications like bridges, concrete pavements, and buildings. There are various types of organisms that can attack concrete. These include mildew, mold, bacteria, fungus, yeasts, or any combinations of these types. The types of organisms that exist in buildings include *Aspergillus* species (e.g., *fumigatus*), *Penicillium*

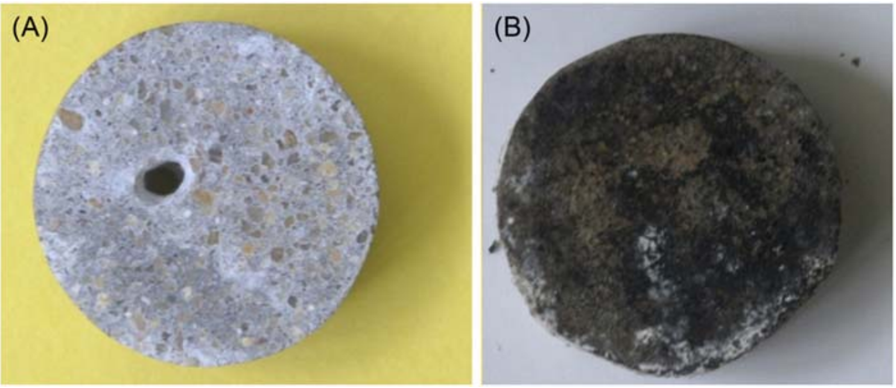


Figure 3.10 Normal concrete specimen (A) unexposed to humidity chamber and (B) exposed for a year in the humidity chamber showing dense growth of fungus, Fusarium sp. as black biofilm [41].

species (e.g., *brevicompactum*), *Cladosporium* species (e.g., *herbarum*, *sphaerospermum*), *Stachybotrys* species (e.g., *atra*), *Mucor* species, *Acremonium*, *Aureobasidium pullulans*, and *Alternaria alternata* [39].

Algae include a group of photosynthetic organisms that grow by the natural photosynthetic activity, which involves the conversion of carbon dioxide from atmosphere to organic carbon utilizing the light energy. Algae obtain part of the required chemicals for their metabolic processes from the cement paste, such as calcium and silica. Thus their growth creates small cavities and initiates sites for cracks development. This is referred to as "Microbiologically Influenced Deterioration" (MID) [40]. Damages from these microbiological activities are not restricted to cement paste; they also impact the reinforcing steel bars. Thus in addition to biodeterioration or MID, described above, these activities lead to biocorrosion of steel, or "Microbiologically Influenced Corrosion" (MIC). MIC is demonstrated nicely in a mechanistic review of algae by Javaherdashti et al. [40]. MIC is an electrochemical process, through which the organisms (corrosion-enhancing bacteria) affect the harshness and progress of corrosion by increasing the acidity that is required for corrosion, as described in Section 3.6.2. For example, the acid-producing sulfate-reducing bacteria produce hydrogen sulfide, which is then oxidized by aerobic bacteria in the biofilm to sulfuric acid. The acidity then depassivates the steel bars (in the same manner as in case of acid attack in the accelerated corrosion) causing further corrosion.

In fact, the mechanism of bio-attack of concrete involves the following three basic stages [38]: (1) colonization of organism that initiate the initial deterioration of concrete surface and increases its porosity; (2) penetration of organisms into the concrete structure while proceeding in bio-attack impacting its integrity; and (3) formation and devolvement of cracks within the concrete. Javaherdashti et al. [40] provided a more detailed bio attack mechanisms of concrete and steel bars, as summarized by the following five possible stages, which may occur individually, or simultaneously: (1) Algae attraction (absorption) of required chemicals from the cement paste, including moisture, which initiates cavities and voids, and eventually results in crack development. (2) Formation of biofilm, which attracts more participating organisms, forming clusters of attacking organisms, such as fungi and bacteria, which provides the MID process with an additional momentum. (3) Electrochemical reactions that lead to the corrosion of steel bars, through a created variation in oxygen partial pressures from algae biological activity (as the natural photosynthetic activity involves oxygen, carbon dioxide, water, and light energy). (4) Acid attack of concrete and reinforcing steel resulting from the biochemical production of acids by algae. (5) Alkaline embrittlement or destabilization of the paste, due to fluctuations in alkaline conditions associated with algae activities.

The rate of biodeterioration is dependent on both the characteristics of the available substrate for mold growth and the environmental conditions. The availability of moisture is the crucial factor that controls the mold growth. In fact, mold growth occurs only when moisture content is high enough, or when the RH is above a certain value. The required RH for mold growth depends on the surrounding temperature, time, and surface conditions [39]. For mold development, the minimum RH is within the range of 80%–95% [39]. Lence et al. [38] found that biofilms developed when RH was in the range of 60%–98% and the temperature was in the range of 21°C–35°C (70°F–95°F). These conditions are encountered in the hot and humid climates.

Such a required combination of moisture and temperature is usually expressed as a plot of isopleth representing a characteristic curve for a particular mold growth, as shown in Fig. 3.11 [39]. The isopleth curve represents a boundary between favorable and unfavorable biodegradation conditions. Modeling the growth of organisms leads to various relationships for various organisms, substrates, and construction materials [39]. All these models lead to the same general trend as shown in Fig. 3.11. In all obtained isopleth relationships, there is a critical RH (or minimum

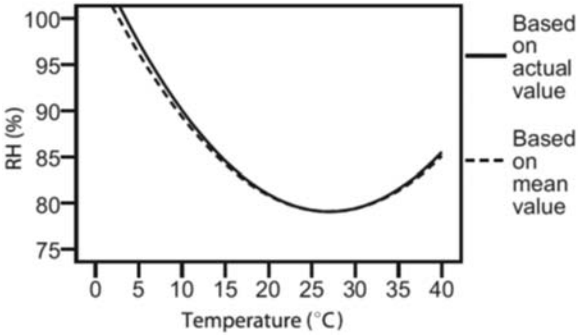


Figure 3.11 Mould growth limits of relative humidity (RH) as a function of temperature curves (favorable conditions are above the curve), based on actual values for chipboard and based on the mean values of parameters from other tested building materials (including Cement-based board) [43].

value), below which there is no growth and thus no biological activity or bio-attack on concrete [39]. Consequently, concrete dryness can hinder biodeterioration effectively.

Usually, the weather conditions (e.g., humidity) fluctuate on a daily or hourly basis, and thus bio-activities do not take place in conditions of fixed combination of RH and temperature. Thus a new parameter of time of wetness (TOW) is defined, in order to take into account the cyclic changes of RH. The TOW is used as an overall parameter of moisture availability for the growth of organisms, defined as the ratio of RH during the humid period (with $RH \geq 80\%$) and that during the dry period, under fluctuating conditions.

The impact of bio-attack on surfaces can be investigated experimentally by subjecting the materials to selected microorganisms, standardized with certain codes. In a typical bio-attack test, the following organisms may be used: Aspergillus of the types niger (ATCC 9642), flavus (ATCC 9643), and versicolor (ATCC 11730), using Penicillium of the funiculosum (ATCC 11797) and *Chaetomium globosum* strain (ATCC 6205) [42]. Then, the tested surfaces are inspected visually for the level of mold growth, and then assigned a mold index to indicate the severity of mold growth on building materials [39]. The mold index is specified by the standard MIL-STD-810G Method 508.6 Fungal Resistance Test. For example, 0 rating is assigned for the case with no observable growth and 1 rating for the case with trace scattered microbial growth. The index reaches up to 6 rating for the case with massive microbial growth, with 100% surface coverage that can be observed visually.

In the field survey of Lence et al. [38], the practices used in the United States to prevent and clean biofilms were categorized into cleaning and preventive methods. Cleaning methods include pressure washing, using biocides, while preventive methods include the addition of self-cleaning photocatalytic materials, such as titanium dioxide and zeolite. Nano coatings with TiO_2 is reported to be the most effective method for preventing microbial growth on concrete surfaces, due to the hydrophilic and photocatalytic characteristics of TiO_2. Recently, waterproofing technology has been shown to mitigate the bio-attack [42] (see Chapter 10).

3.8 Economic aspects of durability solutions

The costs of concrete structures include the initial costs of construction and the subsequent costs of maintenance and repair activities. Structural sustainability and concrete durability are associated with major impacts on the economic and socioeconomic consequences. Structure sustainability is reflected in various technical and economic parameters including concrete durability, service life, performance, economics, safety, and environmental impacts. The concept of conservation of natural resources is a key strategy in ecology and sustainability. The sustainability principle demands meeting the needs of the current generation without threatening the needs of the next generations. Replacements of structures due to failure from durability problems consumes more natural resources and creates additional pollution problems. In fact, in constructing environmentally sustainable concrete structures subjected to water, durability issues become more important than strength considerations [3].

From an economic perspective, durability problems demand high budgets for repair and replacement costs of structures, in order to prevent concrete failures upon service. These costs compose about 40% of the construction budgets [1]. These economic aspects highlight the importance of responding to the durability problems and the need for considering the life-cycle cost in project budgeting. In addition, the maintenance and repair activities might not be feasible in certain applications (e.g., large infrastructures that are built underground or underwater) [3]. Increasing concrete service life reduces the installments of the initial costs of construction, when distributed over the years. In addition, the improved concrete durability reduces its maintenance and repair costs. Also, in some concrete applications, there are additional economic advantages of durable and better-quality concrete from the savings coming from low frequencies of shut down of the construction sites. For example, in concrete pavement, enhancing road performance with a high road quality and eliminating concrete problems reduces the pavement repair related congestion. In addition, the roads become better for driving, so that the car mechanical problems and costs will be reduced.

In most concrete durability problems described in the sections above, water permeability is the main cause. Concrete impermeability, or water-tightness, is the main factor that governs its durability. Durability solutions can be planned and implemented, in advance, during concrete mix design and batching, or after concrete casting or full curing. The main approach of durability solutions is based either on minimizing the damaging effects by limiting the paths or channels for the damaging materials, or on accommodating the effect, for example, though creating space within concrete for "absorbing" the effect. The second approach is found in entraining concrete with air voids dispersed throughout the cement paste for accommodating the expansion of water upon freezing [44]. Other solutions are responsive to the problems as they appear during maintenance and repair activities.

Table 3.3 summarizes the typical mitigation methods for the durability problems discussed in this chapter. These durability solutions can be categorized generally into the following: (1) Optimizing mix design (see Chapter 4), including lowering w/c ratio, selecting suitable cements types, selecting suitable aggregates, adding SCMs, admixtures and other concrete enhancers (see Chapters 8, 9, and 11). (2) Surface treatment and densifying (e.g., waterproofing topical treatments) (see Chapters 7 − 10). (3) Applying protective-barrier systems and waterproof membranes and technologies (see Chapter 12). (4) Any combination of these methods. These solutions assist in lowering water permeability and in reducing the diffusivities of the aggressive chemicals through concrete. In most of these problems, waterproofing technologies can provide an effective solution. They include membrane and coating systems, which protects the surface of concrete from water penetration (see Chapter 12), and integral waterproofing systems that undergo certain physical and chemical reactions. The performance of the second type is based on reducing the porosity of concrete and thus reducing its permeability and/or making it hydrophobic and thus reducing its water absorption capacity (see Chapters 7 and 8). The addition of SCMs to concrete mixtures has established long records of solutions for many concrete applications. SCMs are part of the concrete mix designs for solving water-related problems (see Chapter 4). Their use reduces concrete porosity through chemical and physical mechanisms as introduced in Chapter 1. Thus they reduce water permeability and other transport properties. This chapter paves the road for the coming chapters on waterproofing technologies.

Table 3.3 Typical mitigation methods for the durability problems discussed in this chapter.

Concrete durability problem	Typical mitigation methods
Abrasion and erosion	Optimizing mix design. Selecting strong aggregates. Lowering w/c ratio (<0.45). Densifying by applying a surface hardening treatment.
Freezing and thawing cycles	Lowering w/c ratio. Adding air entraining admixtures. Using SCMs and other admixtures. Some topical waterproofing surface treatments. Adding concrete enhancers.
Plastic shrinkage	Covering the surface of the concrete using sunshades. Protecting it using windbreak. Moistening the aggregate before mixing. Using fiber reinforcement.
Drying shrinkage	Controlling evaporation rate by sealing the surface of concrete, or by waterproofing treatments. Using shrinkage-reducing admixtures.
Autogenous shrinkage	Using low temperature and spherical shape cement. Using certain SCMs (e.g., fly ash). Internal curing using lightweight aggregate and high-water absorbent polymers. Adding low amount of steel fibers. Using shrinkage-reducing admixtures.
Acidic attack—carbonation	Lowering w/c ratio. Applying protective-barrier system.
Corrosion of embedded steel—acidic or chloride ion penetration	Reducing electrical resistivity. Lowering w/c ratio. Using SCMs. Adding corrosion-inhibiting admixtures. Applying waterproof membranes. Adding concrete waterproof enhancers. Some topical waterproofing surface treatments.

(*Continued*)

Table 3.3 (Continued)

Concrete durability problem	Typical mitigation methods
Sulfate attack	Optimizing mix design. Using sulfate resistance cement (ASTM C150) (e.g., Type V with C3A <5%, or II with C3A <8%) Lowering w/c ratio. Using SCMs. Adding concrete enhancers.
Alkali-silica reaction	Optimizing mix design. Selecting low-alkali cement. Selecting nonreactive aggregates. Lowering w/c ratio. Using SCMs. Adding special chemical admixtures (e.g., lithium compounds). Adding concrete waterproof enhancers. Some topical waterproofing surface treatments or any combination of these methods.
Magnesium ion attacks	Lowering w/c ratio. Using SCMs (e.g., fly ash).
Bio-deterioration of concrete	Preventive methods through the addition of self-cleaning photocatalytic materials (e.g., TiO_2). Cleaning biofilms (e.g., pressure washing or using biocides). Applying nano coatings with TiO_2. Adding concrete waterproof enhancers. Some topical waterproofing surface treatments.

References

[1] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials.* New York, USA: McGraw-Hill Education.

[2] Wang, K., et al. (1997). Permeability study of cracked concrete. *Cement and Concrete Research*, *27*(3), 381.

[3] Jianxia, S. (2012). 6.14 - Durability design of concrete hydropower structures. In A. Sayigh (Ed.), *Comprehensive renewable energy* (pp. 377−403). Oxford: Elsevier.

[4] Fernandes, I., & Broekmans, M. A. (2013). Alkali−silica reactions: An overview. *Part I. Metallography, Microstructure, and Analysis*, *2*(4), 257−267.

[5] Cusson, D., & Isgor, B. (2004). Durability of concrete structures: Prevention, evaluation, inspection, repair and prediction. *Canadian Civil Engineer*, *21*, 4−5.

[6] Aïtcin, P. C. (2016). 5 - Water and its role on concrete performance. In P.-C. Aïtcin, & R. J. Flatt (Eds.), *Science and technology of concrete admixtures* (pp. 75−86). Woodhead Publishing.

[7] ACI. (2008). *Committee 201, ACI 201.2 R-08 Guide to Durable Concrete in 2008*, Farmington Hills, MI, United States: American Concrete Institute.

[8] ACI. (1987). *Committee 210, ACI 210R-93 Erosion of concrete in hydraulic structures, in ACI Materials Journal*. Farmington Hills, MI, United States: American Concrete Institute.

[9] Zeman, J. C., et al. (2010). Investigation of potential concrete tie rail seat deterioration mechanisms: Cavitation erosion and hydraulic pressure cracking. In *Proceedings of the transportation research board 89th annual meeting*.

[10] Momber, A. W. (2004). Aggregate liberation from concrete by flow cavitation. *International Journal of Mineral Processing*, *74*(1), 177−187.

[11] Bird, R. B. (2002). Transport phenomena. *Applied Mechanics Reviews*, *55*(1), R1−R4.

[12] Ye, G. (2003). *Experimental study and numerical simulation of the development of the microstructure and permeability of cementitious materials. Master of Engineering thesis*. Delft, The Netherlands: University of Technology, TU, Delft.

[13] ACI, (2018). *CT-18 Concrete Terminology 2018*, Farmington Hills, MI, United States: American Concrete Institute.

[14] Wu, L., et al. (2017). Autogenous shrinkage of high performance concrete: A review. *Construction and Building Materials*, *149*, 62−75.

[15] ACI. (2010). *Committee 305, ACI 305R-10 Guide to Hot Weather Concreting*. Farmington Hills, MI, United States: American Concrete Institute.

[16] ASTM. (2003). *C125 − 15b Standard terminology relating to concrete and concrete aggregates*. Annual Book of ASTM Standards: West Conshohocken, PA, United States.

[17] Mounanga, P., et al. (2004). *Predicting $Ca(OH)_2$ content and chemical shrinkage of hydrating cement pastes using analytical approach. Cement and Concrete Research*, *34*(2), 255−265.

[18] Tazawa, E.-i, Miyazawa, S., & Kasai, T. (1995). Chemical shrinkage and autogenous shrinkage of hydrating cement paste. *Cement and Concrete Research*, *25*(2), 288−292.

[19] Zhang, M. H., Tam, C. T., & Leow, M. P. (2003). Effect of water-to-cementitious materials ratio and silica fume on the autogenous shrinkage of concrete. *Cement and Concrete Research*, *33*(10), 1687−1694.

[20] ACI. (1986). *Committee 515, ACI 515. 1R-79 A Guide to the Use of Waterproofing, Dampproofing. Protective, and Decorative Barrier Systems for Concrete*. Farmington Hills, MI, United States: American Concrete Institute.

[21] Unluer, C., & Al-Tabbaa, A. (2014). Enhancing the carbonation of MgO cement porous blocks through improved curing conditions. *Cement and Concrete Research*, *59*, 55−65.

[22] Breysse, D. (2010). 3 - Deterioration processes in reinforced concrete: an overview. In C. Maierhofer, H.-W. Reinhardt, & G. Dobmann (Eds.), *Non-destructive evaluation of reinforced concrete structures* (pp. 28−56). Woodhead Publishing.

[23] Kolay, P. K., Tajhya, D., & Mondal, K. (2019). Corrosion of steel in MSE walls due to deicers and backfill aggregates. *Geotechnical and Geological Engineering*, 1−15.

[24] Fattah, A. A. E., et al. (2020). Field validation of concrete transport property measurement methods. *Materials*, *13*(5).

[25] Ke, G., Zhang, J., & Tian, B. (2019). Evaluation and selection of de-icing salt based on multi-factor. *Materials*, *12*(6), 912.

[26] Yuan, J., et al. (2019). Freezing-thawing resistance evaluations of concrete pavements with deicing salts based on various surfaces and air void parameters. *Construction and Building Materials*, *204*, 317−326.

[27] Mehta, P. K. (1991). *Concrete in the marine environment*. New York: Elsevier Applied Science.

[28] Mingyu, H., Fumei, L., & Mingshu, T. (2006). The thaumasite form of sulfate attack in concrete of Yongan Dam. *Cement and Concrete Research*, *36*(10), 2006−2008.

[29] ASTM. (2017). *C150/C150M-17, Standard Specification for Portland Cement*. Annual Book of ASTM Standards: West Conshohocken, PA, United States.

[30] Ghazy, A., Bassuoni, M. T., & Islam, A. (2018). Response of concrete with blended binders and nanosilica to freezing−thawing cycles and different concentrations of deicing salts. *Journal of Materials in Civil Engineering*, *30*(9), 04018214.

[31] Ksara, M., et al. (2019). Microbial damage mitigation strategy in cementitious materials exposed to calcium chloride. *Construction and Building Materials*, *195*, 1−9.

[32] Qiao, C., et al. (2018). *Damage in cement pastes exposed to $MgCl_2$ solutions*. *Materials and Structures*, *51*(3), 74.

[33] Saha, A. K., et al. (2018). The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials*, *171*, 743−758.

[34] Carlos, C., Jr, et al. (2004). *Accelerated laboratory testing for alkali-silica reaction using ASTM 1293 and comparison with ASTM 1260*. California Department of Transportation.

[35] Agarwal, R., et al. (2017). Alkali silica reaction (ASR) mitigation in concrete by using lithium nitrate. *International Journal of Engineering and Applied Sciences*, *4*(3).

[36] Thomas, M. D., Fournier, B., & Folliard, K. J. (2008). *Report on determining the reactivity of concrete aggregates and selecting appropriate measures for preventing deleterious expansion in new concrete construction*. United States: Federal Highway Administration.

[37] Al-Rashed, R., & Al-Jabari, M. (2021). Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete. *Case Studies in Construction Materials*, *15*, e00635.

[38] Lence, A., et al. (2014). Best practices for maintenance of concrete bridge elements against mold and mildew growth. In *Construction research congress 2014: Construction in a global network—Proceedings of the 2014 construction research congress*.

[39] Viitanen, H., et al. (2010). Moisture and bio-deterioration risk of building materials and structures. *Journal of Building Physics*, *33*(3), 201−224.

[40] Javaherdashti, R., et al. (2009). On the impact of algae on accelerating the biodeterioration/biocorrosion of reinforced concrete: A mechanistic review. *European Journal of Scientific Research*, *36*(3), 394−406.

[41] George, R., Ramya, S., Ramachandran, D., & Mudali, U. K. (2013). Studies on Biodegradation of normal concrete surfaces by fungus Fusarium sp. *Cement and Concrete Research*, *47*, 8−13.

[42] Al-Rashed, R., & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*, *13*, e00408.

[43] Johansson, P., Svensson, T., & Ekstrand-Tobin, A. (2013). Validation of critical moisture conditions for mould growth on building materials. *Building and Environment*, *62*, 201−209.

[44] Wong, H., et al. (2011). Effect of entrained air voids on the microstructure and mass transport properties of concrete. *Cement and Concrete Research*, *41*(10), 1067−1077.

Materials selection and proportioning for watertight and durable concrete

4

Maher Al-Jabari[1], *Radi Al-Rashed*[2], *Michael E. Ayers*[3] *and*
Doug Clement[4]
[1]Chem-Crete Europe, Holic, Slovakia, [2]International Chem-Crete Corporation, Richardson, TX, United States, [3]Global Pavement Consultants, Inc., Fithian, IL, United States, [4]Construction Materials Testing, Des Moines, IA, United States

4.1 Introduction

Impermeability of concrete is the core factor in governing durability [1]. It is well-established that a dense and watertight concrete is characterized with a long-time durability. Durability is characterized with low porosity [2]. Designing concrete with low porosity and permeability and hence long time durability demands the proper selection of concrete materials and the optimum mix proportions, as well as good casting and curing practice [2]. In fact, material selection and proportioning affects not only the mechanical strength of concrete but also the rates of water and gas permeabilities and the other transport processes that control concrete durability [3].

Reducing paste porosity, through optimizing mix design, increases both strength and durability [3]. Concrete porosity is governed by the water to cement (w/c) ratio or more generally by the water to cementitious materials (w/cm) ratio, and the selection and proportions of typical concrete ingredients and other concrete making additions. In general, durable and watertight concrete is characterized by a low w/cm ratio [3], the use of chemical admixtures [3], and by the inclusion of supplementary cementitious materials (SCMs) [4]. The use of air entrainment admixture is essential for minimizing concrete deterioration resulting from freezing and thawing. According to the American Concrete Institute (ACI) 212 report on chemical admixtures for concrete [5], low-permeability concrete and optimized performance of admixtures is achieved by governing the quality of the concrete mixture. This includes controlling the quality of raw materials and its proportioning and the additions of SCMs and other chemical admixtures.

The concrete mix designer manipulates the cement/paste/aggregate ratio, the w/cm ratio, the proportioning of fine and coarse aggregates, and the types and dosages of admixtures and SCMs [1,2]. The designer usually balances between the required characteristics that are listed in a certain project specification, which are usually set by the concrete application and the economic factors [6]. The designer selects the suitable concrete components from the available materials and makes an

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00004-0

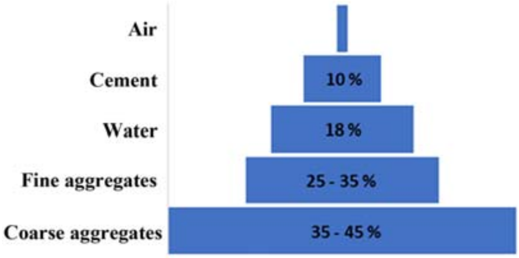


Figure 4.1 The general approximate proportions and ingredients for a typical concrete mixture.

optimum economic combination in order to obtain a concrete possessing a set of performance characteristics [1].

Materials selection is an art [2]. It includes the selection of the types of cement, aggregates, and admixtures. The concrete producer has many choices that control the cost and characteristics of fresh concrete (e.g., workability) and hardened concrete (e.g., strength and durability). The effects of these materials on concrete structure and durability performance has been discussed in Chapters 1 and 3. Proportioning of concrete is the process of determining the required quantities of cement, sand, coarse aggregate, SCMs, admixtures, and water for producing concrete with desired strength and quality. A typical concrete mixture contains the main ingredients at the approximate proportions that are schematically represented in Fig. 4.1. The exact proportions depend on the types of concrete and structure and the selection of concrete design approach.

Establishing a general background about the engineering approach for material selection and concrete proportioning is essential for understanding and applying various waterproofing technologies. Researchers and engineers working in the field of waterproofing require knowledge about the classes and grades of concrete that are then waterproofed by various technologies. In fact, the concrete mix design process specifies the inputs to the waterproofing process when waterproofing materials are applied at the surface of concrete. In addition, integral waterproofing materials are proportioned as parts of the concrete mixtures when they are added directly to the concrete mixture. For the purpose of guiding researchers and engineers in the field of waterproofing, the general types of concrete and the basics of the mix design approaches are presented in the following sections as a background for the other chapters of this book.

4.2 Materials selection and proportioning

In general, a watertight concrete is designed with a w/cm ratio less than 0.45 and with a minimum cement content of 300 kg/m^3. These basic requirements usually achieve sufficient strength and structural integrity as well as a reasonable low porosity for a durable concrete durability. However, more parameters and specifications are needed to be set for any concrete mixture and other materials are added for enhancing the concrete durability. The input data to concrete mix proportioning

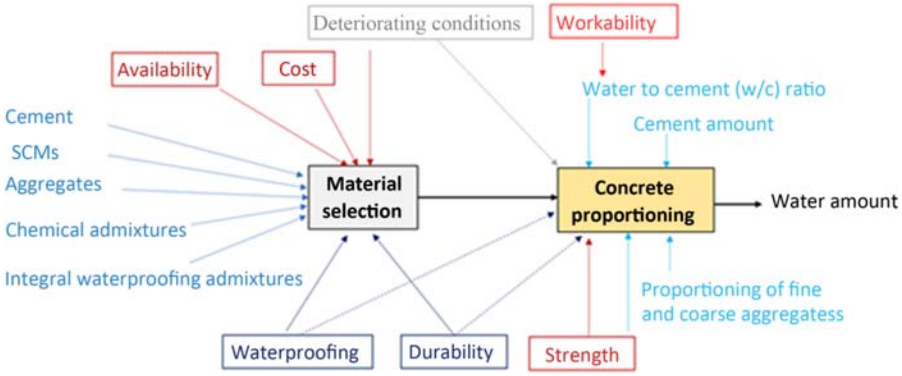


Figure 4.2 The process of material selection and concrete proportioning.

include type of cement, maximum w/cm ratio, minimum cement content, type of aggregates and their maximum nominal size, exposure to environmental conditions, admixture type, method of transporting and placing, and lastly, workability (see Fig. 4.2). The selection of mix characteristics (including cement, w/cm ratio, and aggregates) is determined based on the exposure conditions such as conditions of chemical or atmospheric attacks, the physical properties of the concrete (such as strength and durability) and the intended concrete application and structure.

According to ACI Concrete Terminology [7], a concrete mixture is “the assembled, blended, commingled ingredients of mortar, concrete, or the like; or the proportions for their assembly.” The process of preparing concrete mixtures is dependent on the type of concrete and its application as described in the following sections. The mix designing and material proportioning process aims at obtaining an engineered recipe of cement, water, aggregates, and admixtures for producing concrete according to application requirements and project specifications [1]. The process may target to develop a new mix to optimize proportions based on relationships between cost, performance, and dosage, or to obtain starting proportions for a trial mix based on project requirements and material selection. In addition, it may target to modify or tune a concrete mixture after obtaining testing data to maintain the required performance.

The technical terminology in this field involves mix or mixture proportioning and proportioning of concrete mixtures, which are used interchangeably with the term mix design, although they refer to different processes [4]. In specific technical terms, mix designing is the process of determining the required characteristics of a concrete mix for a given application and placement method, while mix proportioning is the process of specifying the types and quantities of the ingredients in the concrete mixture. The material proportioning process comes after setting the mix design parameters. According to ACI Concrete Terminology [7], mixture proportions are “the proportions of ingredients that make the most economical use of available materials to produce mortar or concrete of the required properties.” Often, a concrete mix is determined for a project and used for multiple purposes. On vertical construction a wall mix may be used on columns or on paving, a mainline mix may be used on small hand work areas by simply increasing workability using water or admixtures.

The estimates of material proportioning are usually based on setting some input parameters and then making material selections and mass balance calculations, using information tables, charts, and empirical relations (see Fig. 4.2). The technical principles governing the mix proportioning process are set by standards and guidelines of the best practices. The determination of the proportions of cement, water, and aggregates to attain the required concrete characteristics can be achieved either by designing the concrete mix or by adopting nominal or designated mixes recommended by certain standards and guidelines. Concrete mix designing and proportioning processes are standardized by international standards such as the British Standards (BS) and the ACI. For example, the standard practice of ACI (ACI211.1-91 [6]) describes the methods for selecting and calculating proportions for concrete made with or without SCMs and chemical admixtures. It guides the designer in obtaining a first approximation of proportions, then, allows for checking the estimated proportions and their adjustment through laboratory or field trial batches [6].

Approaches for setting mix designs and obtaining proportions are fundamentally empirical. The proportions for certain applications may be determined either by the process of designing the concrete mix, yielding a "design mix concrete," or through adopting a nominal concrete mix, referred to as "nominal mix concrete," or the use of prescribed concrete mixes. Thus the concrete specifier is offered more than one approach. The designer can choose a well-established designated concrete proportioning approach, which is suitable for a wide range of common applications or a designed concrete approach, which is suitable for all applications and enables the designer to meet some requirements that are not covered by designated concrete. Designers and specifiers may prefer design mix concrete over nominal mixes, particularly for use for large scale construction projects. The nominal mix concrete is commonly used for small scale applications and small buildings where concrete consumption is low. For example, the designed concrete approach is used for applications requiring a low heat of hydration or when the concrete is exposed to chlorides from seawater. In the United States, there are standardized prescribed concrete mixes that can be used for on-site batching or can be obtained from a ready-mix source, and are suitable for various concrete applications such as housing, pavement, mass concrete etc. A prescribed concrete mix specifies a recipe to produce a concrete of given characteristics. The characteristics of the prescribed concrete mixtures can be optimized by adding some enhancers [8].

The following section summarizes the basic steps in material selection and proportions. The process is related to concrete applications that are described in the Section 4.4.

4.3 Methods of concrete proportioning and mix design

Designing a concrete that meets all requirements of workability, strength, waterproofing, and durability is a task that involves specifying opposing parameters. For example, increasing w/cm ratio increases the workability of fresh concrete while it increases the permeability and decreases the strength of hardened concrete. In such a case, the aim of obtaining a watertight and durable concrete opposes the application requirement of workability. The concrete mix designer cannot adjust one component independent of other ingredients; for example, increasing the volume of the aggregates must be compensated by decreasing the volume of the paste. Thus the challenge of a concrete mix designer is to place all the required materials and their amounts within a fixed volume of concrete (e.g., one cubic yard or one cubic meter) taking into account all the opposing effects. Consequently, the concrete proportioning process is the art of balancing various conflicting parameters. These parameters usually include the characteristics of fresh and cured concrete as well as the economic factors. The concrete designer usually makes compensations in some characteristics for the benefit of others.

The process of mix proportioning includes a multivariable system, with opposing effects of parameters (see Fig. 4.2). There are various procedures for computing concrete mix proportions. There are ready software's for designing concrete mixes following ACI 211.1 [9], which provide the designer an opportunity to select a method of mix design and then enter the background data to obtain the proper mix design. In general, the cementitious system is chosen based on a balance between specification limits, performance quality, durability requirements, cost, and materials availability. The job specifications include slump, w/cm ratio, 28-days compressive strength, minimum air content, maximum size of aggregate. The selection of concrete proportions requires background-testing data or previous experience with the materials to be used in the concrete mixture. These include the characteristics of fine and coarse aggregates and cement (see ACI 211 [6]).

When certain characteristics (e.g., slump and maximum size of aggregate) are not set by the job specifications, the designer chooses their values from certain recommended ranges in the known standards. The designer chooses the w/cm ratio based on the required characteristics, then adds chemical admixtures to achieve the required workability and other set characteristics. The designer chooses the air content based on the level of exposure to aggressive environments and durability requirements (e.g., freezing and thawing conditions).

The material proportioning process starts by specifying these input specifications and selections to estimate the amount of water, then, the predetermined w/cm ratio (e.g., for strength and durability requirements) is used to calculate the required amount of cement. Then, the amount of coarse aggregates is determined based on aggregate characteristics, and the amount of fine aggregates is obtained by closing the mass balance to the full amount of fresh concrete (known from previous experience or from standard estimates). The other detailed steps include the adjustment for water content in aggregates and admixture solutions (when they are considerable), and the practical check of the proportions for meeting critical requirements. These estimations are based on volume basis or weight basis. The absolute volume method provides more accurate results than the weight method [1]. In both cases, a procedure of nine steps is followed to calculate the batch weights (e.g., in pounds per cubic yard or in kg per cubic meter). According to ACI 211 [6], the following logical sequence is used:

1) *Choice of slump*. This is possibly prescribed by the job specifications or it is selected from a recommended table (ACI211.1-91 [6]) for various applications. Slumps can also be altered using plasticizers or water reducers.
2) *Choice of maximum size of aggregate*. This is made based on economic considerations. Increasing the size of a well-graded aggregate decreases the void space between them, and hence reduces mortar requirement for a unit volume of concrete. Thus the maximum available size is preferred, as long as it is consistent with the structure dimensions (e.g., it must not exceed one-fifth of the narrowest dimension between the sides of the forms, one-third the depth of slabs, or three-fourths of the minimum clear spacing between reinforcing bars). For example, mass concrete for megastructures can accommodate up to 6 in. or 150 mm.
3) *Estimation of mixing water and specifying air content* to produce a required or selected slump. The quantity of mixing water is dependent on aggregates grading, maximum particle size and shape, and as well as on the amount of entrained air. Free water also affects cement hydration. For trial batches, an estimate of the mixing water for a given slump can be obtained from ACI 211 [6] recommendations. The use of chemical admixtures must be taken into account, due to their impact on slump (see Chapter 1). Estimates of mixing water are within the ranges of 190–410 lb/yard^3 for nonair-entrained concrete, and 180–365 lb/yard^3 for air-entrained concrete. The recommended total air content depends on the severity of exposure to durability problems and on the maximum size of aggregates. It ranges from 1% for mild exposure with coarse aggregates (6 in.) to 7.5% for severe exposure with small aggregates (3/8 in. maximum size).
4) *Selection of w/c (or w/cm) ratio or water/cementitious materials ratio (when using SCMs).* This selection is made by considering both strength and durability requirements. It is based on the available information on the relationship between strength and w/cm ratio for the selected materials. For concrete subjected to an aggressive environment, a low w/cm is selected regardless of strength requirements. For example, a w/cm of 0.40 is a recommended value for 5000 psi of air entrained concrete (see Section 4.4.1. In mix designs with SCMs, the percentage addition of SCMs, as a replacement of cement, is based on weight or volume bases. Mass balance equations are available for conversions between the two values.
5) *Calculation of the amount of cement*. This is performed by dividing the estimated amount of mixing water (Step 3) on the selected w/cm ratio (Step 4).
6) *Estimation of the amount of coarse aggregate*. This is performed based on the recommended tables of ACI 211 [6], as a function of nominal maximum size of aggregates and the fineness modulus of the fine aggregates.
7) *Estimation of the amount of fine aggregate*. This is obtained from the difference between the weight of fresh concrete (known from previous experience or from the listed first estimates in ACI 211 [6]) and the weights of all previous materials.
8) *Adjustments for aggregate moisture*. This step is made for determining the actual weight of aggregates and for adjusting the actual mixing water to be added by taking into consideration the free moisture contributed by the aggregates.
9) *Trial batch adjustments*. Trial batch mixtures are prepared in a laboratory, or as full-size field batches according to procedures and background testing described in Appendix 3 of ACI 211.1-91 [6]. Small trials are prepared for checking the calculated mixture proportions and for observing the finishing properties and workability, and confirming that no segregation occurs. The checks include the unit weight and yield of the mixture (according to ASTM C 138) and its air content (according to ASTM C 138, C 173, or C 231).

When a superplasticizer (e.g., naphthalene) is used, it is added at a dosage in the range of 5–15 L/m^3 (1–3 gal/yd^3). The SCMs are used as a partial cement replacement at a percentage in the range of 15%−25% for fly ash and 7%−10% for silica fume, or in addition to cement content. Proportioning methods for evaluating concrete mixtures containing these SCMs are based on preparing trial mixtures with a range of proportions of the ingredients [6].

The practice in the construction industry is being shifted from prescriptive toward performance-based specifications. New approaches to concrete mixture proportioning are proposed based on performance [4,10]. The performance-based mixture proportioning method proposed by Wang et al. [4] is based on analyzing the relationships between the selected mixture characteristics and their corresponding effects on concrete performance. The indicators of concrete performance include the typical main characteristics of workability, compressive strength, and durability. The method divides the process into determining three parameters, which are the combined aggregate system, paste quality, and quantity. The effects of these parameters on concrete performance has been investigated experimentally [10]. Then, the relevancy of each of them to the performance characteristics is indicated by a number of check marks.

4.4 Concrete types, grades, and classes

For obtaining a full picture of concrete mix design and proportioning in waterproofing and durability applications, it is essential to summarize concrete types, grades, and classes that are dealt with by waterproofing researchers and engineers. These types and classes are also reflected in material proportioning and mix design.

Concrete may be categorized according to the requirements and the types of applications, the strength, the concrete ingredients and proportions, the methods of construction etc. Concrete types include precast concrete, ready mix concrete, rapid-strength concrete, high performance concrete, self-consolidated concrete, pervious concrete, shotcrete concrete, and prestressed concrete. High-performance concrete is designed for long-term mechanical properties, toughness, low permeability, dimensional stability, and long-life durability.

Concrete grade refers to mix proportions of cement, sand, and aggregate required for a specific compressive strength. The grades of concrete are specified by the 28-days compressive strength and the proportioning of materials, where letter M stands for mix and the number represents the overall compressive strength at 28 days in MPa. For example, a standard concrete of grade M25 has a compressive strength of 25 MPa and is proportioned at 1:1:2 for cement, sand, and aggregates, respectively. It is used in construction for multipurpose concrete mix. Table 4.1 lists selected concrete grades, for ordinary, standard, and high-strength concrete categories.

Concrete class (e.g., A, B, C, or D) refers to the characteristic compressive strength of concrete (in psi), regardless of the mix components and proportions. The British/European standards (BS EN 206 [11]) and BS 8500-2 [12] define classes of concrete according to compressive strength with labels of C10, C20, C25 etc. In these labels, C refers to the class of concrete strength and the number after

Table 4.1 Concrete proportions of selected concrete grades, for ordinary, standard and high-strength concrete.

Category	Grade	Compressive strength (MPa)	Sample application
Ordinary concrete	M15	15	For floor blinding and pavement kerbs.
	M20	20	For domestic floors and foundations with light weight structure, workshop bases, garages, driveways.
Standard concrete	M30	30	For pathways and roadways with heavy road traffic—durable with weather resistant.
	M40	40	For creating foundations and beams for structural support and roads and in septic tanks—durable and resist chemical corrosion.
High strength concrete	M60	60	For high-rise buildings in columns, shear walls, high span beams, for bridges in pylons, piers, and for hydrostructures and wearing surfaces.

Table 4.2 Sample concrete classes according to British/European Standard (BS 8500−2 [12]).

Concrete class	Compressive strength (MPa)	
	Cylinder samples	Cube samples
C20/25	20	25
C30/37	30	37
C40/50	40	50
C50/60	50	60

C denotes the characteristic compressive strength at 28 days in MPa (or N/mm^2), as tested using cylindrical specimens with 15 cm diameter and 30 cm height. There is another labeling form that includes both the characteristic compressive strength at 28 days using cubic specimens as well as that of cylindrical specimens, such as C20/25, C25/30 etc. Table 4.2 lists some concrete classes and their compressive strengths.

There are various types of concrete structures components, which are encountered in the concrete industry and require certain grades or classes. The general descriptions of these structure types are presented in the following sections. The other two sections highlight background information on pavements and mass concrete, which are widely encountered in the waterproofing application.

4.4.1 General concrete types

The general cast-in-place constructions include foundations, walls, footings, caissons, beams, columns, pavements, slabs, and mass concrete. Depending on the water exposure and environmental conditions, each structural component may demand different levels of waterproofing and durability requirements. The suitable type, grade, or class of concrete for each application is set by a group of characteristics of fresh and hardened concrete. According to ACI211.1-91 [6], the general targeted characteristics for a particular application include placeability, density, strength, heat generation, and durability [6]. Concrete may be categorized based on any of these characteristics. From the perspective of placeability, ACI211.1-91 [6] recommends a range of slump for each type of concrete structure, as listed in Table 4.3.

Based on the 28-days compressive strength, concrete is categorized into low-strength, moderate-strength, and high-strength concretes, as listed in Table 4.4 [1]. The British/European standard (BS 8500-2) defines ordinary, standard, and high-strength concretes, for similar ranges of compressive strength. The BS EN 206-1 specifies high-strength concrete with a compressive strength class higher than C50/60. Low-strength concrete is used for nonstructural work such as patio slabs and pathways, for floor blinding and pavement kerbs, and for domestic floors and foundations with light weight structure such as workshop bases, garages, driveways.

Table 4.3 Types of structural components and the recommended range of slump according to ACI211.1-91 standard practice [6].

Types of structural components	Range of slump (in.)
Reinforced foundation walls and footings	1–3
Plain footings, caissons, and substructure walls	1–3
Beams and reinforced walls	1–4
Building columns	1–4
Pavements and slabs	1–3
Mass concrete	1–2

Table 4.4 Concrete categories based on compressive strength [9].

Category	Compressive strength	General applications	w/cm
Low-strength concrete	<20 MPa (3000 psi)	Nonstructural purposes such as backfill or road bases.	High
Moderate-strength concrete	20 – 40 MPa (3000–6000 psi)	Typical normal concrete applications.	Medium
High-strength concrete	> 40 MPa (6000 psi)	In the high-rise structures and bridges.	Low

Moderate-strength concrete (20 − 40 MPa or 3000−6000 psi) is commonly used in most of the structural applications. Moderate-strength concrete is used in foundations and beams for structural support, for external walls and slabs, for structural piling in commercial structures, and for pathways and roadways with heavy road traffic. According to ACI Concrete Terminology [7], high-strength concrete is specified with a compressive strength of 6000 psi (41 MPa) or greater. On the other hand, high-strength concrete is used for heavily reinforced structures subjected to dynamic loading such as high-level bridges, for high-rise buildings in columns, shear walls, high span beams, and for hydrostructures and wearing surfaces. It is made using a low w/cm ratio. Commercially, high-strength concrete of up to 130 MPa (20,000 psi) has been produced [1].

According to weight, concrete is categorized according to its density into three categories. These include light-weight, medium-weight, and heavy-weight concretes, as listed in Table 4.5. Ordinary concrete, which is the most commonly used concrete in structural applications, is of normal weight (medium weight) concrete. According to ACI Concrete Terminology [7], normal weight concrete has a density of approximately 150 lb/ft^3 (2400 kg/m^3) and made with normal density aggregates, while high-density concrete is usually obtained using high density aggregates and has a substantially higher density than that normal density aggregates. It is used for radiation shielding. On the other hand, lightweight concrete has an oven dry density of less than 50 lb/ft^3 (800 kg/m^3). Table 4.5 lists some applications for each of these categories.

On the basis of the level of heat liberation and dissipation, concrete structures can be categorized into typical thin structures (e.g., pavements) using normal concrete and megastructures (e.g., dams) using mass concrete, which demands efficient dissipation of the generated heat to minimize cracking [13]. These two types of pavements and mass concrete are described in the following two sections.

Categorizing concrete is also based on the surrounding environment, which impacts its durability. From waterproofing and durability perspectives, this

Table 4.5 Concrete categories based on density.

Category	Density	Types of aggregates	Applications
Light-weight concrete	<1800 kg/m^3 (3000 lb/yd^3)	Lightweight aggregates such as volcanic pumice, clay, slate, shale etc.	Insulating water pipes, walls, flooring, roofing etc.
Medium-weight concrete	2400 kg/m^3 (4000 lb/yd^3)	Natural sand and gravels or crushed-rock aggregates.	General concrete applications.
Heavy-weight concrete	>3200 kg/m^3 (5300 lb/yd^3)	High-density aggregates.	For radiation shielding.

categories include concrete for marine environments [2] and concrete for hydropower structures (hydraulic structure) [13]. For example, concrete for hydropower structures are designed for a long-life requirement of 80–100 years [13].

4.4.2 Pavement concrete

Concrete pavements are subjected to various water-related problems that usually require specific consideration of waterproofing issues. Concrete pavements are considered advantageous over asphalt for their life cycle cost, wear-resistance, durability, sustainability, and maintenance management. Properly designed and constructed concrete pavements offer a long life and low maintenance. Concrete pavements must be cured for a sufficient period of time to achieve a certain minimum compressive strength (e.g., 10 MPa) before it is placed in service under traffic. Concrete pavements are used in all types of pavement applications such as roadways, highways, bridge decks, parking facilities, industrial facilities, and airports.

A concrete pavement is a structure consisting of a concrete layer made from typical concrete materials, oftentimes, with the addition of secondary cementitious materials to enhance concrete properties. Concrete pavements are subjected to flexural stresses and load carrying conditions; hence its thickness is mainly determined by the flexural strength. Concrete pavement with a high modulus of elasticity and rigidity has a reasonable degree of flexural strength. Concrete grades of 35 MPa with characteristic 28-days compressive strength and 4.5 MPa flexural strength are typically used in pavement applications. The Departments of Transportation (DOT) in the United States may specify a minimum cement content for paving mixtures in a range of 500–650 lb/yr3. In fact, these specifications vary among states and some states do not specify a cement content. The concrete pavement may be supported by a subbase concrete layer on the subgrade. Most pavements are built on nonstabilized aggregate subbases. In order to handle heavy loads, concrete pavements may be reinforced with steel and/or plastic fibers.

The important concrete characteristics of pavements that require attention in concrete mix design and proportioning include: (1) the workability of the fresh mixture, which must be within a reasonable range, that is, not too wet nor too stiff, (2) the mechanical strength including compressive strength, flexural strength, and abrasion resistance, and (3) the durability including concrete resistance to thermal, chemical, and biological attacks (e.g., controlling damages from freezing and thawing, alkali – silica reactions (ASR), and mold growth). These required characteristics are reflected in the material selection (e.g., the use of SCMs and chemical admixtures) and in material proportioning as presented later in this chapter. In addition, waterproofing treatment and additions are crucial for controlling these impacts [8,14].

The chemical admixtures are part of the main materials in the concrete mixture used to obtain the desirable characteristics and to increase production efficiency. These include water-reducing and air-entraining admixtures, in addition to some integral waterproofing materials (see Chapter 7). SCMs are usually added to most mixes of pavement concrete for waterproofing and durability purposes as well as for economic factors. In plain concrete pavements, aggregate interlocking is considered as an important parameter in the control of cracks develop. The used aggregates include rock, natural stone, man-made materials, and recycled concrete materials. Aggregates selection has a noticeable effect on pavement strength; for example, crushed rock aggregates result in concrete with higher flexural strength than gravel. The reactivity of aggregate in the alkaline pore solution within is crucial in the control of damages from ASR (see Chapter 3).

Pervious concrete pavements are made with minimal amounts of fine aggregates in order to have a high porosity that allows water to percolate through pavement into the ground or subbase later [15–17]. They may be incorporated with recycled aggregates and fly ash or silica fume [16]. They are used in parking areas and occasionally on local roads [18]. They are utilized to address environmental issues and for managing stormwater. They allow recharging groundwater by allowing storm water to seep into the ground or substrata and thus reducing the runoff of storm water. It also enhances heat exchange between the atmosphere and the underlying soil and can decrease summer ambient air temperature by 2°F–4°F.

Depending on the joint system and the method of controlling crack development, concrete pavement structures are divided into continuously reinforced concrete pavement and jointed concrete pavements (using reinforced or plain concrete). Each type meets specific project requirements. The jointed concrete pavements are no longer designed or constructed in the United States. The control of crack development is made by creating enough joints, so that cracks are contained at joints and not elsewhere in the slabs. The jointed plain concrete pavements do not contain any steel reinforcement, but may include dowel bars to transfer the weight of vehicles across the slabs. Their mechanical function depends on the flexural strength and the tensile strength of the concrete, which are crucial for preventing cracking and supporting imposed loads. The jointed reinforced concrete pavements are constructed with steel mesh reinforcement. They are used when large concentrated loads and anticipated differential settlement are expected, such as in the construction of airfield runways and highway projects. They are thinner than jointed plain concrete pavements and have a larger joint spacing. This resulted in many of these pavements failing prematurely.

Concrete overlays are used for pavement rehabilitation and to extend its life for the benefits of cost reduction, improved durability, and reduced maintenance. There are many types of concrete overlays. These include bonded concrete overlays, which are thin concrete layers, placed on an underlying asphalt or concrete structurally sound pavement for preservation and improvement of surface characteristics. The unbonded concrete overlays, which are thick concrete layers, are placed on a stable base to serve as a new pavement section, to rehabilitate existing pavements. Other types of concrete pavements include precast pavements, which are used for constructing or repairing a pavement surface where casting and curing of panels are done in advance, to shorten the traffic closure period (e.g., overnight or weekend). They are highly durable finished pavements with a high load-carrying capacity.

4.4.3 Mass concrete

Mass concrete is subjected to thermal effects during cement hydration, which creates durability issues. Also, it is used in dams where waterproofing and durability are key parameters in material selection and concrete mix designing. The hydration of cement raises the concrete temperature by 10°F–15°F per 100 lb of Portland cement/yd^3 within a time period of $18-72$ hours [6]. In megastructures, the mass concrete generates a problematic temperature development, as a huge bulk of fresh concrete is cured in a thick concrete section at once [19]. Most of the heat generation in concrete occurs in the first 3 days after placement. For thin structures (e.g., pavements), the generated heat is usually dissipated quickly as it is released from the reactions. However, for thick concrete structures, the rate of heat dissipation is very slow as the heat transfer rate to the surrounding is slower than the rate at which heat is generated within concrete. Mass concrete is susceptible to thermal cracking and the associated durability problems resulting from thermal stress created by the temperature gradient within the concrete structure. Cracking due to thermal behavior of mass concrete causes a loss of structural integrity. Consequently, thermal energy is accumulated within the mass of concrete and causes a high temperature rise. Thus mass concrete requires the management of these thermal effects to prevent damage, minimize delays, and meet project specifications and concrete durability. Typical applications of mass concrete include dam, bridge piers, thick walls, mat foundations, pile caps, and tunnel linings.

When heat is accumulated within mass concrete, it causes higher temperature rise and temperature gradients within structure. These thermal effects generate tensile and compressive stresses that may exceed the strengths of concrete and thus cause cracking [20]. Consequently, mass concrete requires the management of these temperature rise and gradients in order to prevent damage, minimize delays, meet project specifications, and secure concrete durability. ACI CT-18 Concrete Terminology [7] defines mass concrete as “any volume of structural concrete in which a combination of dimensions of the member being cast, the boundary conditions, the characteristics of the concrete mixture, and the ambient conditions can lead to undesirable thermal stresses, cracking, deleterious chemical reactions, or reduction in the long-term strength as a result of elevated concrete temperature due to heat from hydration.” Different minimum lengths are set arbitrarily by different agencies to specify mass concrete. The minimum length varies from 0.5 m to 2.4 m. In fact, the definition of mass concrete may be based on the combined parameters of minimum length (e.g., 2 m) and minimum cementitious content (e.g., 392 kg/m^3) [21]. ACI 211.1-4 [6] specifies mass concrete with cement contents above 600 lb/yd^3. The increase in cement content causes an increase in temperature by 4.6°C for each 100 kg [22].

The thermal properties of mass concrete are described in ACI 207.2R [23]. These include adiabatic temperature rise, heat capacity, coefficient of thermal expansion, thermal conductivity, and diffusivity [23]. The water-related properties include permeability and durability. The mechanical characteristics of mass concrete include compressive and tensile strengths, modulus of elasticity, Poisson’s ratio, creep, and volume change during curing and drying. There are correlations that relate the compressive strength (f_c) with tensile strength (f_t) (e.g., $f_c = 7.5\ f_t^{0.5}$) [24]. The design criteria of mass concrete structures are generally based on concrete durability, thermal action, and economy, while strength is often being of a secondary concern. Structures using mass concrete withstand the mechanical loads mainly by their mass and shape factors, and only secondarily by their strength. Megastructures are not usually subjected to mechanical loads until the concrete is many months or years old. In fact, they are typically designed on the basis of the late compressive strength (e.g., 90 days to 1 year). Consequently, durability and thermal properties are more important than strength of mass concrete. Design engineers often use a safety factor of 10%–25% with regards to concrete strength.

Mass concrete is characterized by the thermal behavior, which is related to its integrity. This includes the maximum temperature and the maximum temperature difference within the structure of the massive concrete structure. A maximum temperature is set to prevent durability problems such as cracking from delayed ettringite formation, and reduction in strength associated with the increase in the size of pores. It is also required to limit the maximum concrete temperature for reducing cooling times and associated delays. The long-term durability is affected if the maximum temperature after placement exceeds the range of 155°F − 165°F (68°C − 74°C) [25]. Temperatures over 190°F (88°C) can reduce compressive strengths of mass concrete [25]. A standard maximum allowable concrete temperature is set at 135°F (57°C) [25]. The difference between the temperature at the section of the concrete with the highest temperature and temperature at the surface may result in thermal cracking. A standard temperature difference is set at 19.4°C, to prevent thermal cracking from surface tensile stress associated with internal restriction [19].

It is essential to control the thermal behavior of mass concrete by using a suitable mix design, or installing a cooling technique or an insulation system. Thermal cracking in mass concrete was first observed in dams. Thus most engineering practices of mass concrete were developed for dam applications. The effective temperature control approaches include the following: (1) proper selection and specification of the type and amount of cementitious materials in the mix design, (2) precooling of concrete constituents such as precooling of fine and coarse aggregates by evaporation through vacuum and liquid nitrogen or the addition of ice instead of mixing water [21], (3) postcooling of the mass concrete by methods of embedded cooling coils (with cold water circulation) [26] and the evaporative cooling of surfaces through water curing, and (4) construction management. The approach of construction management includes effective handling of fresh concrete, scheduling, and procedures of construction, according to seasonal changes and placing the cooled concrete mixture quickly using appropriate mixing and pouring equipment with minimum heat gain from the surroundings in order to prevent excessive temperature gradients. In addition, low heat generating concrete mixtures are used for mass concrete, through the selection of cement type, the use of pozzolans, and the use of air-entraining and chemical admixtures.

Material selection and concrete proportioning has major impacts on the performance of mass concrete (see Fig. 4.3). Mixture proportioning for mass concrete is discussed in ACI 211.1 [9]. Material selection and proportioning of mass concrete is usually based on controlling the rate of heat generation and the temperature rise, while maintaining the required strength and durability, which are governed by the w/cm ratio. In general, ASTM Type II cement is used in mass concrete, as its moderate heat of hydration assists in controlling the temperature rise, and it has other general favorable properties for most types of construction. Pozzolanic materials are also used for reduction of heat of hydration, as the heat contribution of a pozzolan, at early age, may be in the range of 15%–50% of that of an equivalent weight of cement. Thus the released heat from a combined mixture of Type II Portland cement and pozzolan is relatively comparable with that released from Type IV cement. Recent studies on the use of pozzolans (slag and fly ash) in mass concrete indicated that the pozzolans-to-binder ratio led to a reduction in the maximum temperature by 1.94°C for each 10% replacement of cement by pozzolans [22]. It is believed that above a certain temperature limit, the reactivity of fly ash is considerably increased, and thus fly ash loses its efficiency in decreasing the heat release of mass concrete when such a temperature limit is exceeded [20]. Increasing fly ash content decreases the temperature rise for concrete mixtures with cementitious contents less than 250 kg/m^3. However, for concrete with higher binder content, the temperature peak may exceed 60°C and thus there is no effect of fly ash content on controlling the temperature rise [20]. The use of phase changing material (e.g., barium oxide) in mass concrete mixtures reduces the rate of cement hydration and reduces the temperature peak [27]. On the other hand, it has been reported that the addition of 3.5% barium oxide has insignificant effects on the heat of hydration [28].

Large aggregates are preferred for mass concrete (up to 6 in. or 150 mm). They provide less surface area and hence less cement paste for coating them. This is then associated with a reduction in cement and water for the same w/cm ratio. Chemical

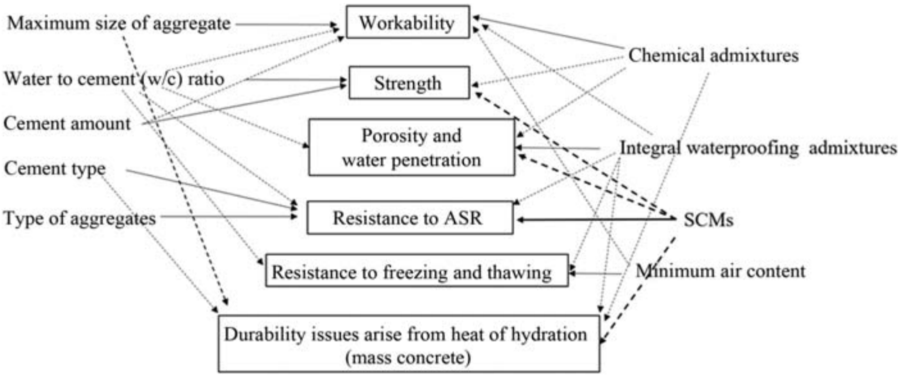


Figure 4.3 Interactions between the mix design parameters and some concrete characteristics.

admixtures, including water reducing and air entraining admixtures, are essential in mass concrete mixtures. The air entrainment admixtures are used to increase workability and reduce segregation and bleeding, and for obtaining improved durability. Water-reducing admixtures are used for reduction in the cement content by reducing water content while maintaining a constant w/cm ratio. They also assist in improving concrete response to structure vibrations, particularly in large aggregate mixtures.

There are theoretical studies on modeling the thermal behavior of mass concrete using the transport equations described in Chapter 2. The model equations are solved by finite element methods using software such as Midas civil [29] and the ABAQUS platform [30]. Governing parameters include the coefficient of adiabatic temperature rise, which is given by the ratio of the temperature rise (°C) and the binder content of concrete (kg/m^3), and is given in °Cm^3/kg [20]. A thermal efficiency index is proposed as a governing parameter that is defined as the ratio of the temperature rise to the adiabatic compressive strength of concrete (°C/MPa) [20].

4.5 Concrete mixture proportions

As mentioned earlier, concrete proportions are selected to obtain the required characteristics of fresh and cured concrete, demanded for a particular project application. The controlled characteristics of fresh concrete include placeability (satisfactory finishing properties) [6], workability (capacity of concrete mixture to be poured and consolidated appropriately and to be finished without excessive segregation), and consistency (measured in terms of slump). The controlled characteristics of hardened concrete include density, strength, and durability [6]. The compressive strength at 28 days age is presumed to be an index of overall concrete quality and other characteristics such as durability [2]. Fig. 4.3 shows the main interactions between the mix design parameters and the main concrete characteristics. It highlights the interactions of material selection and proportioning on porosity and water penetration and on three of the main durability issues of ASR, freezing, thawing, and thermal issues arising from the heat of hydration in mass concrete.

With emphasis on workability and strength, as practiced in routine mix design operations, a typical mix design usually focuses on specifying w/cm ratio and cement content. However, waterproofing and durability characteristics are demanded to be considered in the mix designing and material proportioning process for concrete applications exposed to aggressive environments [1], such as freezing and thawing conditions, and chemical and biological attacks (see Chapter 3). Procedures for concrete mix designs based on strength are more advanced, for which a plenty of codes and theories are available [13]. According to ACI 211 [9], the recommended w/cm ratios for typical low-strength and moderate-strength concretes are listed in Table 4.6.

The strength and durability requirements of a low w/cm ratio are commonly obtained by decreasing the water demand for a chosen cement content. This is done through the selection of the aggregates grading and the addition of water reducing admixtures [1]. For hydropower structures, the w/cm ratio is commonly in the range

Table 4.6 Recommended w/cm for concrete according to ACI 211 [9].

Compressive strength at 28-days (psi)	w/cm ratio by weight	
	Nonair entrained concrete	Air entrained concrete
6000	0.41	–
5000	0.48	0.40
4000	0.57	0.48
3000	0.68	0.59
2000	0.82	0.74

of 0.4–0.55. In such applications, the effect of cement content is less significant than that of the w/cm ratio. For concrete durability, the cement content is normally between 220 and 375 kg/m^3 [13]. According to ACI 211 [9], the recommended w/cm for structures under continuous or frequent wet conditions exposed to cycles of freezing and thawing is a maximum of 0.45 for thin concrete sections and 0.5 for other structures. On the other hand, for structures exposed to sea water or sulfates, the recommended w/cm is 0.40 for thin concrete sections and 0.45 for other structures. Due to their chemical effects on stabilizing cement particles in suspension, the use of air entrainment admixture results in reducing the required volume of mixing water. This effect must be considered in proportioning; air entrained concrete demands less amount of water than nonair entrained concrete of the same target slump (a decrease of up to 10%) [6].

The workability is also controlled by cement and SCMs, aggregate characteristics (grading, particle shape, and the proportions of fine and coarse aggregates), and the use of chemical admixture. Consistency is governed by the w/cm ratio and the use of admixtures. The required water content for a specific slump depends on aggregates shape and texture. The required water content can be decreased with increasing the size of coarse aggregates and by the use of chemical admixtures [1]. The cohesiveness and finishability of concrete can be enhanced by increasing the ratio of fine to coarse aggregates.

A typical batch of concrete may have proportions of 1:2:3:0.5 (by weight) of cement, dry sand, dry crushed stone, and water, respectively. For most popular nominal concrete mixtures, the proportions are expressed in the ratios of 1:*n*:2*n* (by volume) of cement, sand, and coarse aggregate, respectively (e.g., see IS 456:2000). For normal concrete applications, the general proportions (by volume) are 1:1.5:3 and 1:2:4. For very high-strength concrete, the proportions are 1:1:2 and 1:1.2:2.4. High-strength concrete can be obtained by reducing the w/cm ratio to a value less than 0.35. In such an application, the content of the weak by-product of cement hydration (calcium hydroxide) can be reduced by the use of silica fume as a partial cement replacement.

4.5.1 Sample prescribed proportions of concrete mixtures

There are various types of prescribed mix designs that are adopted by the DOT in the United States. As an illustrative sample approach, materials proportions (unit volumes) for structural concrete and pavement concrete suggested by the Iowa Department of Transportation (Iowa DOT) [31] are described in this section. Table 4.7 lists the selected representative classes of concrete mixes used by Iowa DOT. These mixes are based on Type I or Type II Portland cements (with a specific gravity of 3.15). The applications of these mix designs are listed in Table 4.7: C-mixes are used for normal paving mix, structures, and some bridge applications, including mass concrete, B-mixes contain the least amount of cement and has the least strength, which are used for sidewalks and trails, and high performance concrete (HPC) mixes are used in structures requiring high compressive strength and low permeability [31].

Iowa DOT provides a mix code for each mix design, for example, Iowa DOT C-4 WR C20. In such a code, the first letter (C) refers to the class of designated concrete (as listed in Table 4.7, the number (4) specifies ratio of fine to coarse aggregates according to an adopted list (e.g., 50%:50% for number 4). Then, the letters WR refers to the use of a water reducer. Any additional letters and numbers are designated for the type and the percentage of SCMs, for example, C20 is for 20% replacement of cement by fly ash C, F is used to refer to fly ash F, S for ground granulated blast furnace slag (GGBFS). The letters IS are used when GGBFS is included in a blended cement. The code C4 WR C20-S20 refers to a mix design of class C containing equal proportions of fine and coarse aggregates with water reducing admixture and both fly ash C and GGBFS added at 20% replacement of cement for each of them. In certain mix designations, the letter V or L is

Table 4.7 Classes of concrete mixes used by Iowa DOT.

Concrete mix class	Characteristic parameters	Applications
A	Low cement content and low w/cm ratio.	Used for paving with low traffic roadways or detour pavement.
B	Least amount of cement and the least strength of any paving mix.	Used for sidewalks and trails.
C	Normal paving mix.	Used in common paving applications and for structures, such as bridge piers, abutments, and decks.
M	High early strength.	Used for many applications.
O	Low slump concrete with a required water-reducing agent with a maximum w/cm ratio of 0.42 (basic of 0.40).	Used primarily in bridge deck overlays.
HPC	High performance concrete using blended cements, slag, and fly ash, with a basic w/cm ratio of 0.4 and a maximum of 0.42 (for decks) and basic w/cm ratio of 0.42 and a maximum 0.45 (for substructures).	Used in bridge substructures and decks with high compressive strength and low permeability.

added after the first hyphen to indicate that either Class V or Class L aggregates are used. Then, the total quantity of water, including water in the aggregate, shall not exceed a set maximum w/cm. Table 4.8 lists selected material proportions set by Iowa DOT. Some of these concrete mixes were used in investigating the performance of integral waterproofing materials for protecting concrete. For example, [8] used Iowa DOT C4WR, Iowa DOT C4WR C20, and HPC-D concrete mixes by a multicrystallization enhancer (MCE) at dosages of 1% − 4% MCE (by cement weight).

Fig. 4.4 compares curves of the development of compressive strength for two Iowa DOT concrete mixtures (Iowa DOT C4WR and for HPC-D) with a w/cm ratio of 0.42 (data obtained from results reported in reference [8]). Both of these concrete mixes are recommended for pavements and bridges applications (see Tables 4.7 and 4.8).

4.6 Material mix designing of concrete exposure to environmental actions

Concrete exposure to environmental actions requires special attention in mix designs (see Fig. 4.2). For this purpose, environmental damaging actions are classified into various types and levels. Then, these classifications are used in mix designs accordingly. This is reflected in the maximum w/cm ratio, minimum cement content, minimum strength classes, chemical admixtures etc. (see Fig. 4.3). ACI211.1-91 [9] classifies the severity of environmental exposure into three levels of mild, moderate, and high, which are then reflected in the selection of the levels of air content for each aggregate size. The class of mild exposure includes concrete for indoor or outdoor service conditions, which will not be exposed to freezing or to deicing agents. In this class, low air contents may be used for purposes other than durability (e.g., for workability or cohesion purposes). The concrete class for moderate exposure is used for exterior walls, columns, girders, or slabs, which are not subjected to contact with damp soil and not subjected to continuous exposure to moisture for long times and not exposed to deicing agents or other harmful chemicals. On the other hand, concrete class for severe exposure is used for pavements, bridge decks, sidewalks and canal linings, or water tanks or sumps, which are under continuous exposure to moisture for long times and may be exposed to deicing or other harmful chemicals.

For aggressive environments, ACI211.1-91 [9] recommends the use of functional ingredients such as low alkali cement, pozzolans, slug, silica fume, or nonreactive aggregates, which do not undergo harmful expansion from the alkali-aggregate reaction. In addition, air entrainment admixtures are recommended to be added to concrete mixtures in concrete exposed to climates with cycles of freezing and thawing. For special exposure conditions, ACI211.1-91 [9] sets maximum w/cm ratios. For example, to design a watertight concrete to be exposed to fresh water a maximum w/cm ratio of 0.5 is recommended, while when it is exposed to seawater or to freezing and thawing cycles, a maximum w/cm ratio of 0.45 is recommended. A lower maximum w/cm of 0.4 is recommended for protection of reinforced concrete from corrosion.

Table 4.8 Selected material proportions for Iowa DOT concrete mixes indicating basic absolute volumes of materials per unit volume of concrete.

Mix type	Basic w/cm	Max w/cm	Sample mix no.	Cement	Water	Air content	Fine aggregates	Coarse aggregates
A	0.474	0.532	A-2	0.101	0.150	0.060	0.276	0.413
B	0.536	0.600	B-2	0.088	0.148	0.060	0.282	0.422
C	0.430	0.488	C-3	0.114	0.154	0.060	0.302	0.370
			C-4	0.118	0.159	0.060	0.331	0.332
C-WR	0.430	0.489	C-3WR	0.108	0.146	0.060	0.309	0.377
			C-4WR	0.112	0.151	0.060	0.338	0.339
D	0.423	0.450	D-57	0.134	0.178	0.060	0.314	0.314
			D-57−6	0.134	0.178	0.060	0.377	0.251
M	0.328	0.400	M-4	0.156	0.161	0.060	0.311	0.312
O	0.327	–	O-4WR	0.156	0.160	0.060	0.312	0.312
HPC-O	0.390	0.420	HPC-S	0.118	0.156	0.060	0.333	0.333
HPC-D	0.400	0.420	HPC-D	0.118	0.148	0.060	Optimized	Optimized

Source: Data from Iowa-DOT, Portland Cement (PC) Concrete Proportions. 2014, Iowa Department of Transportation: Iowa, USA.

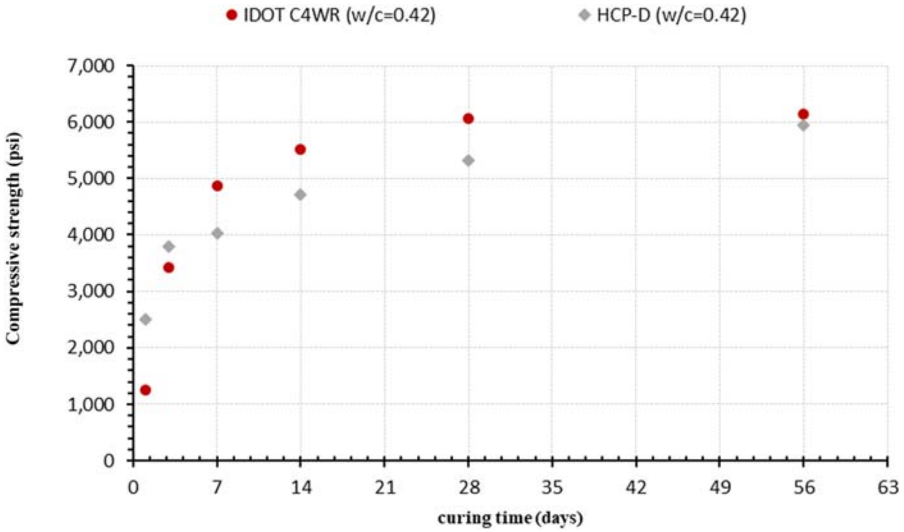


Figure 4.4 Compressive strength concrete mixtures for Iowa DOT C4WR and for HPC-D with a w/cm ratio of 0.42
Source: Data obtained from results reported in Al-Rashed, R. and M. Al-Jabari, Construction and Building Materials, 2020.

From the perspective of durability, the BS 8500 [12] focuses on the level of concrete exposure to aggressive environments and specifies maximum w/cm ratio, minimum cement content, and minimum strength classes for various classes of exposure. It specifies various levels of risks with a code for each, such as XC1 − XC4 for carbonation-induced corrosion, XS1 − XS3 for chloride-induced corrosion by sea water, XD1 − XD3 for chloride-induced corrosion by chloride from other sources than from sea water, XF1 − XF4 for freezing and thawing attack, and XA1 − XA3 for aggressive chemical environments.

4.6.1 Impact of concrete design on concrete permeability and durability

As demonstrated in Chapter 2, the concrete porosity is dependent on w/cm ratio, cement characteristics, aggregates types and reactivity, the type and the dosage of the admixtures, and SCMs. Material selection and proportioning have major impacts on concrete permeability as illustrated in Fig. 4.3. These impacts then affect the durability of concrete as water permeability is the vehicle for durability problems as described in Chapter 3.

It has been demonstrated in Chapter 2, that both concrete porosity and permeability increase with increasing w/cm ratio. Concrete mix designs using ordinary Portland cement are more porous and contain larger pores than modified concrete with mineral admixtures. The addition of SCMs to concrete mixtures has established long records of effective solutions for many applications and become parts of the concrete mix designs for solving water-related problems. Their use reduces concrete porosity through chemical and physical mechanisms (see Chapter 7). Consequently, their inclusion on concrete mixtures lowers the water permeability and other transport properties. The use of pozzolanic materials such as fly ash and silica fume decreases the total porosities and refines the pore structure by decreasing the volume of large pores [32]. The pozzolanic reaction (see Chapter 1) results in more $C-S-H$ gel formation and consumes calcium hydroxide and thus contributes significantly in refining the pore structure of cement paste. The refinement of the paste pores is governed by the characteristics of the incorporated pozzolanic materials (type, proportion, and fineness) [32]. The use of pozzolanic materials decreases the average pore radius substantially while it increases the amount of pores that are smaller than 15 nm [32]. This results in subdividing the coarse pores into fine ones. The achieved level of pore refinement is dependent on the type and characteristics of these mineral admixtures [32]. Chapter 7, describes the effects of various types of additions on water penetration through concrete. Recent advances in industrial applications are based on the use of waterproofing enhances for reducing water penetration and enhancing durability [8]. These aspects are detailed in Chapter 12.

As described in Section 4.4.3, the addition of fly ash to concrete mixtures is one of the solutions for reducing durability problems associated with the thermal effects from the excessive liberation of heat in mass concrete applications. Fig. 4.5 shows curves of heat liberation from cement hydration for two cementitious mixes (including plain cement as used in Iowa DOT C4 and cement with 20% fly ash as used in Iowa DOT C4-C20 (see Table 4.8) with a w/cm ratio of 0.4 (results from unpublished work). Adding SCMs shifts the heat liberation curve rightward and thus manages the initial temperature rise, which is demanded by requirements of mass concrete (see Section 4.4.3).

The types of aggregates and w/cm ratio are two important input parameters to the process of concrete mix designing that are related to the durability problems

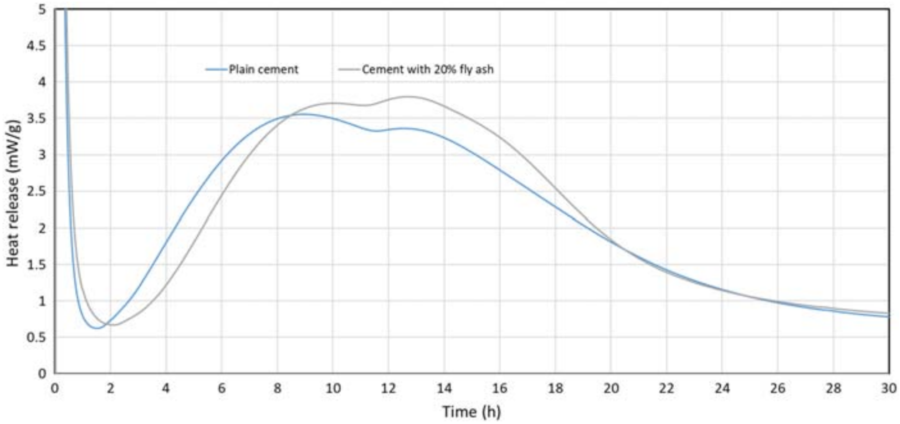


Figure 4.5 Curves of heat release from cement hydration for two types of cementitious mixtures with a w/cm ratio of 0.4 (unpublished work).

associated with ASR. The effects of these two parameters on damage from ASR are shown in Fig. 4.6 for two types of aggregates using Iowa DOT C4WR mix design (results of unpublished work). Fig. 4.6 shows the measured percentage length change due to ASR as a function of time from casting, for reactive aggregates (Platte River) and nonreactive aggregates (Ames Mine), at various w/cm ratios, measured according to the standard procedures of ASTM C1260 [33]. These curves show that increasing w/cm ratio increases the damage from ASR (increases percentage length change). This is due to the increase in the porosity and the permeability

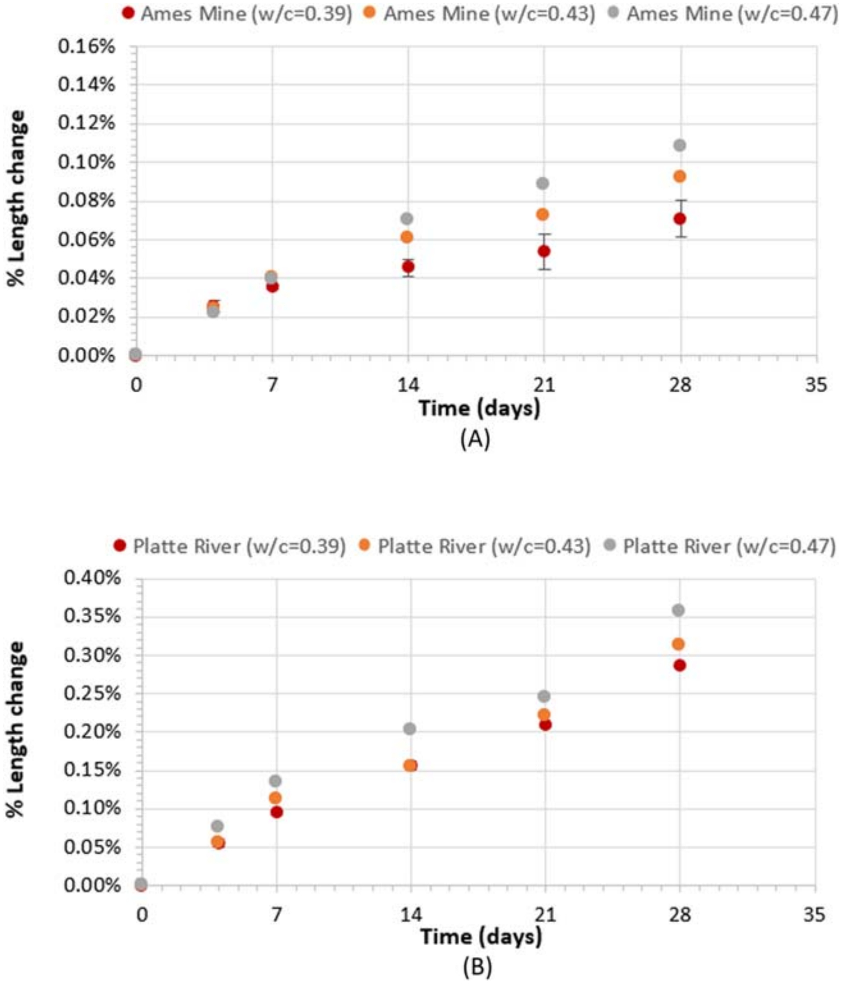


Figure 4.6 Curves of percentage length change (from ASR) with time using mortar samples with Iowa DOT C4WR mix proportions, using (A) Ames Mine aggregates (B) Platte River aggregates, for three investigated w/cm ratios of 0.37, 0.43, and 0.47, from results of unpublished work for tests performed according to ASTM C1260 (unpublished work).

of concrete by increasing the w/cm ratio. ASTM C1260 sets an allowable limit of 0.1% for percentage length change at 16 days after casting as an indication of innocuous behavior [33,34]. Fig. 4.6 shows that the Ames Mine aggregates yielded a percentage length within the limit of 0.1% as set by ASTM for all investigated w/cm ratio and even for a longer test period as recommended by some researchers [35]. On the other hand, the Platte River aggregates yielded a percentage length that is higher than the allowable limit of 0.1% for all investigated w/cm ratio and consequently the selection of this type of aggregates for a concrete mix may be associated with ASR-durability problems. As the 16-days percentage change for Platte River aggregates does not exceed 0.2%, there is a need for a further testing of these aggregates using concrete prism test ASTM C1293 [36] for 1 year in order to reach a solid conclusion on their ASR performance.

References

[1] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. New York, USA: McGraw-Hill Education.

[2] Mehta, P. K. (1991). *Concrete in the marine environment*. Boca Raton, FL, USA: CRC Press.

[3] Hover, K. C. (1998). Concrete mixture proportioning with water-reducing admixtures to enhance durability: A quantitative model. *Cement and Concrete Composites*, *20*(2), 113–119.

[4] Wang, X., Taylor, P., Yurdakul, E., & Wang, X. (2018). An innovative approach to concrete mixture proportioning. *ACI Materials Journal*, *115*(5), 749–759.

[5] ACI. (1999). *Committee 212, ACI 212.3R-91 Chemical admixtures for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[6] Standard, A. (1996). Standard practice for selecting proportions for normal, heavyweight, and mass concrete. *ACI Manual of Concrete Practice*, 1–38.

[7] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[8] Al-Rashed, R., & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*, *13*, e00408.

[9] ACI. (1996). *Committee 211, ACI 211.1R-91 Standard practice for selecting proportions for normal, heavyweight, and mass concrete* (pp. 1–38). Farmington Hills, MI, USA: American Concrete Institute.

[10] Yurdakul, E. (2013). *Proportioning for performance-based concrete pavement mixtures*. Ph.D. Thesis, Iowa State University.

[11] BS. (2013). *BS EN 206:2013 Concrete—Specification, performance, production and conformity*. London, UK: BSI Standards Limited.

[12] BS. (2012). *BS 8500 Concrete–Complementary British Standard to BS EN 206-1-Part 2: Specification for constituent materials and concrete*. London, UK: BSI Standards Limited.

[13] Jianxia, S. (2012). 6.14 - Durability design of concrete hydropower structures, In A. Sayigh (Ed.), Comprehensive renewable energy, Elsevier: Oxford. pp. 377–403.

[14] Al-Rashed, R., & Al-Jabari, M. (2021). Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete. *Case Studies in Construction Materials*, *15*, e00635.

[15] Montes, F., & Haselbach, L. (2006). Measuring hydraulic conductivity in pervious concrete. *Environmental Engineering Science*, *23*(6), 960−969.

[16] Adil, G., Kevern, J. T., & Mann, D. (2020). Influence of silica fume on mechanical and durability of pervious concrete. *Construction and Building Materials*, *247*, 118453.

[17] Tse, S.A., Tse, C.J., & Pierard, C.A. (1971). *Method of rendering water-pervious building materials hydrophobic*. Google Patents.

[18] Kosmatka, S.H., Kerkhoff, B., & Panarese, W.C. (2002). *Design and control of concrete mixtures*. Vol. 5420: Portland Cement Association Skokie, IL.

[19] Han, S. (2020). Assessment of curing schemes for effectively controlling thermal behavior of mass concrete foundation at early ages. *Construction and Building Materials*, *230*, 117004.

[20] de Matos, P. R., Junckes, R., Graeff, F. R., & Prudêncio Jr, L. R. (2020). Effectiveness of fly ash in reducing the hydration heat release of mass concrete. *Journal of Building Engineering*, *28*, 101063.

[21] ACI. (2006). *Committee 207, ACI 207.1R-05 Guide to mass concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[22] Chen, Y.-Y. (2019). Effects observed in temperature rise evaluation tests for mass concrete. 技術學刊, *34*(2), 81−94.

[23] ACI. (2002). *Committee 207, ACI 207.2R-95 Effect of restraint, volume change, and reinforcement on cracking of mass concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[24] Tasri, A., & Susilawati, A. (2019). Effect of cooling water temperature and space between cooling pipes of post-cooling system on temperature and thermal stress in mass concrete. *Journal of Building Engineering*, *24*, 100731.

[25] Gajda, J., & Vangeem, M. (2002). Controlling temperatures in mass concrete. *Concrete International*, *24*(1), 58−62.

[26] Hong, Y., Lin, J., & Chen, W. (2019). Simulation of thermal field in mass concrete structures with cooling pipes by the localized radial basis function collocation method. *International Journal of Heat and Mass Transfer*, *129*, 449−459.

[27] Hamid, H. and M.G. Chorzepa. (2019). Novel structural materials for use in mass concrete structures. In Structures *congress* 2019: Blast, *impact loading*, and *research* and *education*. American Society of Civil Engineers Reston, VA.

[28] Hamid, H., & Chorzepa, M. G. (2020). Quantifying maximum temperature in 17 mass concrete cube specimens made with mixtures including metakaolin and/or slag. *Construction and Building Materials*, *252*, 118950.

[29] Aniskin, N. & Nguyen, T.-C. (2019). *Influence factors on the temperature field in a mass concrete*. in E3S Web of Conferences. EDP Sciences.

[30] Xu, J., Shen, Z., Yang, S., Xie, X., & Yang, Z. (2019). Finite element simulation of prevention thermal cracking in mass concrete. *International Journal of Computing Science and Mathematics*, *10*(4), 327−339.

[31] Iowa-DOT, Portland Cement (PC) Concrete Proportions. (2014), Iowa Department of Transportation: Iowa, USA.

[32] Meddah, M. S., & Tagnit-Hamou, A. (2009). Pore structure of concrete with mineral admixtures and its effect on self-desiccation shrinkage. *ACI Materials Journal*, *106*(3), 241.

[33] ASTM. (2014). *C1260-14: Standard test method for potential alkali reactivity of aggregates (mortar-bar method)*, in Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[34] ASTM. (2013). *C1567-13: Determining the potential alkali − silica reactivity of combinations of cementitious materials and aggregate (accelerated mortar-bar method)*. In Annual book of ASTM standards. West Conshohocken, PA, USA: ASTM International.

[35] Saha, A. K., Md Nabi Newaz Khan, M. N. N., Prabir Kumar Sarker, P. K., Shaikh, F. A., & Pramanik, A. (2018). The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials*, *171*, 743−758.

[36] ASTM. (2020). *C1293-20a, Standard test method for determination of length change of concrete due to alkali − silica reaction*, in Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

Physical and chemical interactions of water with surfaces and particles

5

Maher Al-Jabari[1] *and Maen Husein*[2]
[1]Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine,
[2]Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, AB, Canada

5.1 Introduction

Concrete durability problems and solutions are strongly related to water − surface interactions. Both the thermodynamic and kinetic behaviors of these interactions are key parameters that govern the mechanisms of wetting of concrete surfaces, water penetration within pores, and drying. Also, the expansion of some cementitious materials and concrete ingredients with water may result from the chemisorption of water molecules. For example, reports showed that expansive hygroscopic salts may create internal stresses and result in concrete cracking. On the other hand, the formation of hygroscopic crystals within concrete pores is one of the most recent techniques for integral waterproofing [1,2]. In fact, water does not interact just as a pure compound with stable cementitious solid surfaces, but also interacts as a solution of various materials and ions, with surfaces that undergo various adsorption/desorption processes. Thus understanding the physical chemistry of water within the context of concrete is essential for attaining better understanding of concrete durability and waterproofing.

Most types of hydrophobic, hydrophilic, and hygroscopic materials can be potential waterproofing materials. Some of them have been the subject of various research papers. Others are being used among industrial formulations for waterproofing materials (see Chapters 7−9). There are generic industrial materials such as salines used in hydropic waterproofing and silicate compounds used in hydrophilic waterproofing materials and concrete hardening. As some of these materials are trade grade with proprietary formulations, the chemistry of these materials is discussed, in this chapter, from the perspective of available literature in different fields. For example, a thorough investigation of hydrophobicity is found in clothing and furniture sectors [3,4]. Similarly, hygroscopic crystals are used in pharmaceutical applications, and many characterizations have been made from the perspective of that application. There are other generic industrial materials such as saline used in hydropic waterproofing and silicate compounds used in hydrophilic waterproofing materials and concrete hardening. Hydrophobic materials are also used in other

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00005-2

industrial applications such as furniture and clothing. Water swelling behavior has been the topic of various publications for various industrial products (e.g., diapers), medical products (e.g., nanogels for protein delivery), and soil application (e.g., gel application for water hold-up and for managing water irrigation) [5]. Thus a large number of the swelling/deswelling studies are available in literature from these industrial and environmental perspectives.

Adsorption of molecules onto surfaces is a well-known phenomenon in chemical engineering and has been investigated for various industrial and environmental applications. Water adsorption onto cementitious surfaces is governed by the same principles that are well-covered in these other applications.

Taking all these points into consideration, this chapter covers the physicochemical interaction of water with cementitious material from all these backgrounds depending on the available literature. The last section in this chapter links these interactions within the context of this book, while subsequent chapters utilize this background chapter in presenting various waterproofing technologies. Bridging between various fields of science and engineering can assist in better understanding the mechanisms and may lead to developing new technologies. For example, the recycling of gel materials from diapers and mixing it with soil has been shown to achieve a better water management. This application has recently attracted a great attention [5]. A similar application may lead to novel water management approaches in concrete, such as managing water in the fresh mix for its slow release and better cement hydration kinetics and the use of polymeric water-absorbing materials in crack healing concrete [6].

5.2 Introduction to water chemistry

Section 3.3 has summarized the various physicochemical aspects of water interaction with concrete. It has been shown that water is the cause, the medium, and the vehicle for most of the durability problems, as it is the carrier of the aggressive ions. Water is also the medium for many physical and chemical processes that result in concrete degradation. Water undergoes frequent phase changes within concrete pores and thus creates internal stresses that result in concrete deterioration. Part of these phase changes may be considered as the mechanism of solution in waterproofing technologies (see Chapters 9 and 10). Water interaction mechanisms within concrete structures include fluid flow, imbibition, diffusion, solvation, reaction, crystallization, expansion, evaporation, and melting. A list of water properties that governs the physicochemical interactions of water is given in Chapter 3. These properties include polarity, viscosity, density reduction upon freezing, and other thermodynamic properties, as well as its chemical reactivity with mineral compounds and its biological characteristics (e.g., microorganism growth onto concrete).

The physicochemical properties of a water molecule arise from its chemical structure. The difference in electronegativity between hydrogen and oxygen gives rise to a permanent dipole, wherein partial negative charge appears closer to the oxygen atom leaving behind a partial positive charge close to the hydrogen atoms. This permanent dipole is measured by dipole moment, which is obtained by multiplying the partial charge and the distance between the charges. For water, the dipole moment is 6.17×10^{-30} C m (or 1.85 D), but differs depending on the phase owing to hydrogen bonding. The strength of hydrogen bonding is different among the different water phases. Polarity of water endows important properties onto this solvent, including the ability to dissolve different ionic compounds, polar solvents, and interact with charged surfaces. Hydration and wettability, as well as hydrophilicity and hygroscopicity of cementitious and waterproofing materials are direct outcomes of water polarity, especially considering the role of polarity in hydrogen bonding. Hydrogen bonding also plays a crucial role in water adsorption and adhesion onto the surfaces of fine pores of the cement paste and in installing water-repellents onto concrete surfaces.

Similar to all atoms and molecules, water molecules are polarizable. The polarizability of a molecule captures how easily can the electron cloud shift position under the influence of an electric field. Polarizability of a species is calculated as the ratio between the strength of its induced dipole moment to the electric field strength triggering it. This component of polarizability is termed as the electronic polarizability. Polar compounds tend to also orient themselves, on average, in the presence of an electric field. This orientation gives rise to orientational (or dipolar) polarizability, which is in the same order of magnitude as the electronic polarizability.

Both, permanent dipole and polarizability enable water molecules to interact among themselves and other species via dipole-dipole (Keesom), dipole-induced dipole (Debye), and induced dipole-induced dipole (London) forces. Other nonvan der Waals interactions are also possible, for example, ion-dipole and hydrogen-bonding. Strong ion – dipole interaction dictates the orientation of water molecules surrounding an ion. These water molecules are called the water of hydration (or "bound" water) and their number is referred to as the hydration number. Hydration is the mechanism of cement binding (see Chapter 1) and that of many crystallization waterproofing materials (see Chapters 9–11).

5.3 Water adsorption into cementitious surfaces

Adsorption is a surface phenomenon whereby soluble ions or molecules are transformed from liquid phases and reasonably stabilize onto solid surfaces or within the internal surfaces of porous materials. This physicochemical process is an outcome of the interaction of the adsorbed materials (adsorbates) with the surface of the adsorbing materials (adsorbents). The thermodynamic (equilibrium) and kinetic aspects of the adsorption process are governed by the types of intermolecular and surface forces as well as the hydrodynamics of the bulk and interfacial liquid. In addition to adsorption from liquids, molecular adsorption can occur from gases onto solid surfaces. In general, adsorption is a reversible process, and thus adsorbed molecules and ions may desorb back into the original fluid (liquid or gas) at a different rate than that of adsorption. Thus the net rate of adsorption is the difference between the rates of adsorption and desorption. In certain applications, where the net transport process is from the solid surface into the fluid, the process is termed as desorption. When the net rate of adsorption approaches zero, an equilibrium state is established, during which the concentration of the adsorbate on the surface remains constant.

These processes are encountered in concrete surface chemistry at various levels and stages. For example, adsorption is reported to be a fundamental process in the different stages of cement hydration and participates in governing the process kinetics [7]. In addition, desorption occurs as a step in the mechanism of the alkali − silica reactions (see Chapter 3). Adsorption is also part of the cement hydration process and water adhesion in gel pores in the cement paste; however, from waterproofing perspective, it is an important phenomenon in the installation of hydrophobic layers at concrete surfaces and in hygroscopic growth of some waterproofing materials (see Section 5.6).

In wet concrete structure, water can be present within concrete pores as adsorbed water and as free water. In has been demonstrated in Chapter 2 that moisture exists in the cement paste in various structures and attached through surface forces to pores and cementitious compounds. In addition to free bulk water, these structures include chemically bound water, which forms an integral part of the phase structure, that is, structural water, and cannot be detached or desorbed, and adsorbed water, which is attracted to cementitious surfaces by, for example, hydrogen bonding. The adsorbed water interacts with the calcium silicate hydrates (C − S − H) (see Chapter 1) and remains stable in the pores. Part of the adsorbed water molecules can be desorbed when their attraction forces are weak, which then interferes with durability problems such as concrete shrinkage (see Chapter 3). As discussed in Chapter 2, concrete pores are classified according to ASTM C125−15 [8] into impermeable pores, in which no free water is available, and permeable pores (capillary pores with a size ranging from 50 nm to 0.5 μm), which include free bulk water that can be transported by liquid penetration. Water is held in the medium capillaries of 10 − 50 nm sizes by capillary tension.

A similar concept is applied to water within the pores of aggregates, which is composed of adsorbed and bulk water. Thus when estimating the required amount of water for certain water to cement ratio, mix designers usually distinguish between free (bulk) water and adsorbed water. Thus the standard practice of the American Concrete Institute, ACI211.1−91 [9] demands the adjustments of aggregates and water contents in concrete mixtures, taking into consideration that the aggregate moisture is composed of free moisture and adsorbed water. Only free water is considered available to be contributed to the mix by the aggregates, while the adsorbed water is physicochemically attached to the cement hydrates and thus is not flowable. ACI211.1−91 [9] states that "The mixing water added to the batch must be reduced by an amount equal to the free moisture contributed by the aggregate, i.e. total moisture minus absorption." Precisely, it is "adsorption" that is meant in this statement. From the theoretical background of adsorption and desorption mechanisms, there are more complicated aspects that are ignored in such analysis, probably, for simplicity or practicality, as adsorbed water onto the internal surfaces of aggregates may desorb into liquid phase, and the transport of free water through the porous structure of aggregates depends strongly on the physicochemical conditions such as pH and salinity.

In addition to the adsorption of liquid water, concrete applications involve the adsorption of water vapor, as encountered in hygroscopic crystal growth (see Section 5.6).

Adsorption literature includes two types of behaviors: equilibrium and kinetics studies, at experimental and modeling levels. The following two subsections describe these two phenomena.

5.3.1 Water adsorption isotherms

Depending on the surface characteristics of the adsorbent and the physicochemical properties of the adsorbate, adsorption occurs by two main mechanisms: chemical interaction (chemisorption) and physical interaction (physisorption). These mechanisms control the level of adsorbent bonding to the surface and the maximum amount that can be adsorbed, as well as the thickness of the adsorption layer (e.g., single layer or multiple layers). Chemisorption results in more strong attachment to the surface in the form of chemical bonding, for example, covalent bonding. In concrete applications, the adsorption/desorption of ions from/onto cement particles is of chemisorption type, whereas the physical adsorption of water molecules (from liquid or vapor phases) is physisorption, as they are attached to the surface by hydrogen bonds or van der Waals forces, which are types of secondary bonding. The water in the fine gel pores was found to be strongly adsorbed and considered to be irreversibly adsorbed, that is, could not be removed through moderate drying at ambient temperatures [10].

The type of adsorption governs the surface capacity of the adsorbate as well as the adsorption and desorption rates. These are then reflected in what is called adsorption isotherm, which is the relationship between the concentration of adsorbate on the surface and that in the bulk fluid phase at equilibrium. In case of adsorption from a gaseous phase, the isotherm relates the concentration of adsorbate at the surface with its partial pressure in the gas phase. Thus in the adsorption of water vapor from air onto surfaces, the adsorption is governed by the relative humidity (RH) of the air within concrete pores.

There are various adsorption isotherms that specify the relationships between the equilibrium concentration of adsorbate on the surface (q_e) and that in the fluid phase (c_e); including linear, Langmuir, Freundlich, etc. Freundlich isotherm is given by the following equation:

$$q_e = K_F \, c_e{}^n \tag{5.1}$$

here K_F is the index of adsorption capacity and n is the adsorption intensity factor with a value that is dependent on the adsorption mechanism, when n is smaller than unity a favorable adsorption is obtained while when n is larger than unity an unfavorable adsorption is obtained. The linear adsorption isotherm is a special case of the Eq. (5.1) with $n = 1$, and may occur at the initial adsorption states and when the adsorbed amount is small. The Langmuir isotherm is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{K_L}\frac{1}{c_e} + \frac{1}{q_m} \tag{5.2}$$

where q_m is the maximum adsorption capacity of the surface and K_L is the Langmuir adsorption constant. Other types of adsorption isotherms are available in the literature [11].

There are various parameters that affect the equilibrium state of the adsorption. For the adsorption/desorption of ions and liquid-water from cement particles and other cementitious materials, these factors include concentrations of ions, pH, and temperature. For the adsorption/desorption of molecules of water vapor from cementitious materials and hygroscopic crystals (see Section 5.6), these factors include temperature and RH.

The water adsorption isotherms are typically prepared as plots of water content in the paste versus the RH in air. The equilibrium adsorption of water into crushed particles of cement paste has been investigated by [12]. Favorable adsorption isotherms have been reported for water vapor adsorption on cementitious surfaces [12]. The adsorption isotherms of cement paste are dependent on the water to cement ratio (w/c). The water adsorption isotherms were found to affect other transport properties of concrete such as gaseous diffusivity through cement paste [12]. Gas adsorption by concrete (e.g., nitrogen adsorption) is used to measure its porosity [13]. Freundlich adsorption isotherm was used to model the growth of hygroscopic crystals through water vapor adsorption [14] (see Section 5.4.2).

As the adsorption process is driven by the type and level of bonding between the adsorbate and the surface, the adsorption becomes weak with increased distance from the surface. This is especially applicable to physisorption and determines the number of adsorbed layers. For the adsorption of water molecules within the nanopores of concrete, the adsorption layer, 1.5 nm [15], can extend up to six molecular levels of water, and consequently these bonding forces decrease largely with increasing distance from the solid surface through these layers (see Chapter 2). The removal of adsorbed water from impermeable pores and the removal of water from other medium capillaries of $10-50$ nm sizes (in which it is held by capillary tension) create shrinkage problems. This can happen when the internal percent RH within the paste decreases to 30% or less [15].

5.3.2 Water adsorption kinetics

The adsorption process is primarily a transport process through which molecules or ions are transferred from a fluid to a solid surface. It may consist of multiple steps involving mass transfer and thermodynamic mechanisms. It starts by the transfer of the adsorbate from the fluid phase to the exterior surface of adsorbents (by convection and diffusion mechanisms), then intra-particle diffusion may transport the adsorbate within the porous structure of the adsorbent. Eventually, the thermodynamic adsorption step occurs within a thin interface at the adsorbent surface. The thermodynamic equilibrium is driven by the difference in adsorbate chemical potential across the interface. The rate limiting step of these mechanisms governs the net rate of the adsorption process. The difference in chemical potential of the adsorbate between the bulk fluid phase and the solid surface governs the overall driving force for the adsorption.

For example, the adsorption kinetics is controlled by the mass transfer in the fluid phase when the thermodynamic adsorption step is instantaneous (i.e., when the adsorbate reaches the surface it disappears from the fluid phase). When there is no internal diffusion and the adsorbent porosity is low, the external mass transfer rate equation can be used to model the adsorption kinetics for physical adsorption [16]. On the other hand, when there is no internal diffusion and the adsorbent porosity is low, and when the mass transfer step in the fluid phase is fast, the adsorption step at the interface dominates the adsorption kinetics [17]. This occurs through the continuous striking of the adsorbate molecules or ions with the free available sites at the adsorbent surface, which results in a fraction of them adhering to the surface (forward adsorption step). Simultaneously, a part of the previously adhered molecules or ions may continuously detach from the surface owing to the molecules' or ions' high energy level, resulting in a desorption step. The kinetics of such a reversible adsorption/desorption overall process is composed of these two elementary processes, given by Langmuir theory [18], described by the following equation:

$$\frac{dqi}{dt} = k_1 c_i \left(1 - \frac{q_i}{q_m}\right) - k_2 q_i \tag{5.3}$$

where c_i and q_i are the concentrations of adsorbate in the fluid phase and on the solid surface, respectively, t is the time, k_1 and k_2 are the adsorption and desorption rate constants, respectively, and q_m is the maximum adsorption capacity (for monolayer coverage) expressed as mass fraction. Both, k_1 and k_2 depend on the temperature and the molecular energy according to Arrhenius equation. The ratio between the adsorption and the desorption coefficients is the adsorption (Langmuir) equilibrium constant (K_L) appearing in Eq. (5.2).

In addition to these kinetic models, empirical models for adsorption kinetics are widely used in literature, for example, Elovich and Lagergren pseudo first-order and second-order equations. Critical reviews on adsorption kinetic models were published by Qiu [19], Kyzas and Kostoglou [20], and by Ho [21]. Tosun used *n*th-order model and a double exponential kinetic model [22]. Recently, Wang and Guo [23] reviewed 16 adsorption kinetic models and analyzed their physical meanings and applications.

There are limited studies on the kinetics of adsorption in concrete applications. For example, the dynamics of the pore structure of partially saturated contentious material (white cement mortars) under the influence of water adsorption and desorption was investigated experimentally by Zhou et al. [10]. They reported that water desorption leads to the collapse of $C-S-H$ interlayer pores in a partially reversible process. Even with readsorption (i.e., water resaturation), the irrecoverable contraction of $C-S-H$ gel is the main reason for the irreversible concrete shrinkage. On the other hand, water vapor adsorption was accompanied by continuous expansion of $C-S-H$ gel. The mass transfer controlled kinetics is used to predict the rate of adsorption of water vapor onto a hygroscopic material [24] (see Section 5.6).

5.4 Hydrophilicity

Hydrophilicity is correlated to the extent compounds, molecules and ions become water soluble and, hence, depart from one another in an aqueous phase. Hydrophilic molecules also tend to absorb water vapor and are termed hygroscopic. While both hydrophilicity and hygroscopicity relate to water sorption, from the perspective of cementitious materials, uptake of liquid water leads to swelling, whereas uptake of water vapor leads to crystal growth. A hydrophilic material can be ionic, nonionic, polar, and nonpolar, so long it possesses strong interaction with water molecules through for example van der Waals forces or hydrogen bonding. Higher populations of water molecules order themselves at hydrophilic surfaces into layers (positional ordering) with more restricted orientation (orientational ordering). Such ordering influences the oscillatory and steric forces as well as electrostatic and entropic charge transfer around the surface [25].

Hydrophilic surfaces tend to attract water vapor especially into their cracks leading to capillary condensation. The water interface with the air is concaved owing to the lower interfacial tension between the water and the hydrophilic solid relative to the surface tension between the solid and the air. According to Kelvin equation 5.4a,b [26], and depending on the pore/crack opening [related to R_d in Eq. (5.4a,b) below], the vapor pressure of the water in the crack, P^v, can be much lower than the saturation pressure at the atmospheric temperature. This pressure difference forces water vapor to condense.

$$\frac{P^v}{P^{sat}} = \exp\left[\frac{2MH\gamma_{wa}}{RT\rho_l}\right] \tag{5.4a}$$

and

$$H = \begin{cases} \dfrac{1}{R_d} & (\mathit{convex\ surface}) \\ \dfrac{-1}{R_d} & (\mathit{concaved\ surface}) \end{cases} \tag{5.4b}$$

where P^{sat} is the saturation pressure of water at T, ρ_l is water density, γ_{wa} is the surface tension of water, R is the universal gas law constant, H is the mean curvature (<0 for concaved surfaces), R_d is the radius of curvature, and T is the absolute temperature of the atmosphere. Recall that Eq. (5.4a,b) describes the pressure at the liquid − vapor interface of a pure substance, but when it comes to air, the RH becomes important.

Depending on the weather conditions, water condensing in the cracks may freeze leading to crack propagation and deterioration of the concrete. It is constructive to note that water residing on the surface of the crack freezes first, which entraps the rest of the water underneath. Once that water freezes, it expands into the direction of deepening the crack.

5.4.1 Water sorption, theoretical analysis

The flow of water into cementitious material can be described using Darcy's law [27]. The one-dimensional form of Darcy's law given in Chapter 2, is written here again:

$$q = \frac{kA_b}{\mu \Delta L} \Delta P \tag{5.5}$$

where q is the volumetric flow rate (m^3/s), k is the permeability coefficient of the porous medium (m^2), μ is the viscosity of the water (Pa.s), ΔL is the distance (m) across which the pressure drop, ΔP (Pa), is in effect, and A_b is the total surface area of the porous materials in contact with the fluid (including closed and open area of the surface pores). This law is considered valid for estimating the rate of water penetration into porous media whether it is driven by an external force coming from the hydrostatic pressure (permeation flow) or from capillary pressure depression (capillary suction). The analysis here is for the second type of water penetration. The driving force for capillary suction, ΔP, is the pressure difference between the water at the interface (P_a) and bulk water (P_w) at a distance ΔL upstream. The pressure of the water at the interface with the air in the pore is decreased by the capillary force as described by Laplace − Washburn equation

$$P_w - P_a = \frac{-2\gamma_{wa}}{r} cos\theta \tag{5.6}$$

where r is the radius of the capillary (m), γ_{wa} is the interfacial tensions at the water − air interface, θ is the contact angle between the liquid and the solid and the subscripts a, w and s denote air, water, and solid phases. Fig. 5.1 shows the variables relevant to Eq. (5.6) and the direction of the different forces. The forces are drawn keeping in mind that interfacial/surface tension acts to reduce the surface area of contact between phases. If one assumes the bulk water is at atmospheric pressure, that is, exposed to the atmosphere, then the driving force for the flow of water becomes

$$\Delta P = P_a - P_w \tag{5.7}$$

In addition to surface roughness, the contact angle, θ, results from force balance among the solid − water, solid − air, and water − air interfacial/surface tensions, as shown in Fig. 5.1. Assuming smooth surface, hydrophilicity increases γ_{sa}, while decreases γ_{sw} (and the contact angle $\theta \rightarrow 0$), which in turn increases the driving force for the water flow, as evident from Eq. (5.6). Assuming laminar flow of

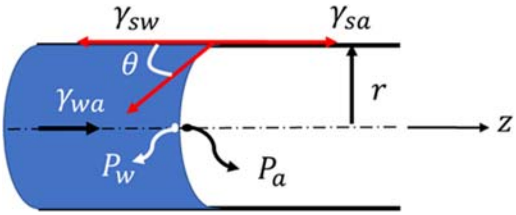


Figure 5.1 Water flow in a pore.

Newtonian fluid in the capillary shown in Fig. 5.1, Hagen − Poiseuille equation leads to

$$q = \frac{\pi r^4}{8\mu L}\Delta P \tag{5.8}$$

Exposure to bulk water for a period of time, t, drives water into cement pores. From the above equations, the velocity of water penetration into a single pore can be calculated as follows:

$$V = \frac{dL}{dt} = \frac{q}{A} = \frac{\pi r^4}{8\pi r^2 \mu L}\Delta P = \frac{r\gamma_{wa}}{4\mu L}cos\theta \tag{5.9}$$

Eq. (5.9) is valid for describing water swelling within a porous particle (or a hydrophilic crystal or a gel) and for estimating water absorption in a cementitious structure. The penetration distance into the pore is obtained by integrating Eq. (5.9) as follows:

$$L(t) = \left(\frac{r\gamma_{wa}}{2\mu}cos\theta\right)^{1/2} t^{1/2} \tag{5.10}$$

It is noted from Eq. (5.10) that the length of penetration is dependent on surface hydrophilicity, as suggested by the contact angle, θ. Multiplying Eq. (5.10) by water density, ρ_w (kg/m^3), helps determining the time-dependent water sorption per unit area of a cementitious material, $i(t)$, as follows. Using the definition of porosity

$$\varepsilon = \frac{V_p}{V_b} = \frac{A_p}{A_b} \tag{5.11}$$

where V_p and A_p are the total volume and the total cross-sectional area of pores, respectively, and V_b is the bulk volume of the porous material. Assuming uniform pores of radius r, A_p can be expressed as follows:

$$A_p = j_t \pi r^2 \tag{5.12}$$

where j_t is the total number of pores on the surface of the porous material. Per unit surface area of the bulk porous material, Eq. (5.11) becomes

$$\varepsilon = j\pi r^2 \tag{5.13}$$

where j is the number of pores per unit surface area of the bulk absorbent. Then, the water absorption per unit surface area of a porous material, $i(t)$, is given by Eq. (5.14):

$$i(t) = j\rho_w L(t) = j\rho_w \left(\frac{r\gamma_{wa}}{2\mu} cos\theta\right)^{\frac{1}{2}} t^{\frac{1}{2}} = S\, t^{\frac{1}{2}} \tag{5.14}$$

where S is termed the capillary sorption coefficient a.k.a. sorptivity (kg/m^{2}s$^{0.5}$). Sorptivity is an important parameter to report for cementitious materials. Sorptivity is proportional to hydrophilicity, porosity (captured by the number of pores per unit surface area, j, and the average radius of the pore), and the surface tension of water. It is noted, nevertheless, that as r increases, the driving force for capillary flow diminishes, as evident from Eq. (5.6). In fact, pore refinement usually decreases the pore size (r) but increases the number of pores (j). Thus the net effect of pore refinement comes from the combined effects of the two parameters (r and j). Consequently, when analyzing the effect of pore blocking as a waterproofing technology on water absorption, one must consider these two parameters, and not only the reduction in the pore size. The number of pores and pore size are dependent variables on the efficiency of pore blocking waterproofing.

5.4.2 Swelling

In addition to Eq. (5.14), other empirical models (first and second order) are also used to describe the swelling kinetic of hydrogels, which are encountered in the field of superabsorbent polymeric materials [28]. The pseudo first-order model for swelling kinetics is given by Eq. (5.15) [28]

$$\frac{dW_s}{dt} = k_s(W_e - W_s) \tag{5.15}$$

where k_s is the swelling rate coefficient (s^{-1}), W_e is the equilibrium swelling capacity (g/g), and W_s is the mass ratio of the water in the gel at a given time (g/g). The kinetic swelling process continues until reaching an equilibrium capacity (W_e). W_s can be obtained by multiplying $i(t)$ from Eq. (5.14) by the specific surface area of the swelling material. The initial specific surface area is used for simplicity. The mechanism of attaining equilibrium swelling capacity is well-described in the literature of polymeric gels [5]. Hypothetically, the gel structure is elongated upon swelling and elastic stresses are developed in the gel material during its expansion. These elastic stresses are opposed by the swelling or depression (capillary) pressure.

The gel attains an equilibrium swelling capacity when these two opposing stresses are balanced, that is, when the expansion stresses equals the capillary pressure.

The kinetic and equilibrium behavior of hydrogels or hydrophilic materials is governed by the hydrogel chemical and physical properties such as composition, surface characteristics (e.g., surface groups), pore size, and density. The swelling behavior is dependent on various physical and chemical conditions under which the materials are subjected to water. These include temperature, pressure, pH, and salt concentration. For polymeric gels, [28] reported that the equilibrium swelling capacities and the rate of swelling increase with decreasing the particle size of the gels, which is expected as a result of the increase in the surface area accessible to water penetration, that is, j in Eq. (5.14). Theoretically, decreasing the pore size, r, increases the depression pressure and hence increases the equilibrium swelling capacity [29]. The equilibrium swelling capacity decreases with increasing ionic strength. Increasing the ionic strength may lower the depression pressure and hence decrease the swelling rate of the gel. The effect of temperature and pH are well-reported for polymeric hydrogels but are not deeply discussed for cases of cementitious matrixes or hydrophilic crystals encountered in concrete waterproofing (see Chapter 9).

5.5 Hydrophobicity

The term hydrophobe comes from a Greek word (hýdrophóbos) combining hydro, which means water, and phobic means fear or repel [30]. Hydrophobicity essentially arises from the disruption of the intermolecular structure of water molecules within a continuous water phase. In the liquid phase, water molecules interact by van der Waals forces as well as hydrogen bonding. These interactions, especially hydrogen bonding, bring Gibbs free energy of the water phase to low values. Solute molecules disrupt the structure of the water continuum. Depending on the nature of the solute molecules, for example, polar, nonpolar, one or more of the van der Waals forces as well as the nonvan der Waals forces, may compensate for the rise in the Gibbs free energy of the disrupted water phase. Moreover, depending on the size of the solute molecule, water molecules may still interact through hydrogen bonding while accommodating the solute molecule. For relatively large, nonpolar molecules little compensation of the Gibbs free energy of the system through London interactions takes place, and a state of higher Gibbs free energy is reached for the mixture. This in turn promotes phase separation and gives rise to hydrophobic interaction, wherein water “fearing” species associate together to minimize their interaction with water. Hydrophobic interactions exceed the van der Waals interactions between hydrophobic species in vacuum and bring them closer together. There are no real hydrophobic bonds, but rather the higher hydrophobic interaction and the longer range of its effect is purely entropic resulting from the rearrangement of water molecules surrounding the solute molecules [25].

The “fear” of water effect prevents water spreading over a hydrophobic surface, that is, wetting the surface. Wettability is governed by the intermolecular interactions between water molecules and the surface and is expressed in terms of the contact angle between the solid and the fluids [31]. When the surface is not hydrophobic (i.e., hydrophilic surface), the attractive interactions between the water and the surface allow water molecules to spread over the surface leading to wetting. In such a case, and for a smooth surface, the contact angle between a static water droplet and the surface is less than 90 degrees, as shown in Fig. 5.2A. On the other hand, the hydrophobic surface repels the water molecules and prevents them from spreading over the surface, hence decreasing water capacity for wetting the surface. This is hypothesized to occur as a result of the increase in the interfacial tension, although some argue otherwise [30]. In such a case, the contact angle between a static water droplet and the surface becomes larger than 90 degrees Fig. 5.2B. Increasing the water repellency of a surface increases the static contact angle (θ). Superhydrophobic surfaces are obtained when the contact angle becomes >150 degrees, as shown in Fig. 5.2C. This is encountered in nature for the interaction of water with the lotus plant, hence superhydrophobicity is sometimes referred to as the lotus effect. Fig. 5.3 shows that treating a wood surface with potassium methyl siliconate as a hydrophobe changes wood from a hydrophilic surface with a contact angle of 57 degrees to a superhydrophobic surface with a contact angle of 153 degrees [32].

In fact, the criterion of 90 degrees static contact angle for switching between hydrophobic and hydrophilic surfaces is debatable. The molecular origin and the driving force behind such a classification as well as the definition of superhydrophobicity may not be very solid. Nevertheless, this classification is useful for the purpose of understanding water capillary action in cementitious materials. Alternatively, the contact angle can be measured based on a dynamic condition to help investigate the surface characteristics of wetting and adhesion. These include advancing, receding, and sliding angles as described elsewhere [30]. The adhesion force between a water droplet and the surface can be obtained from measuring the

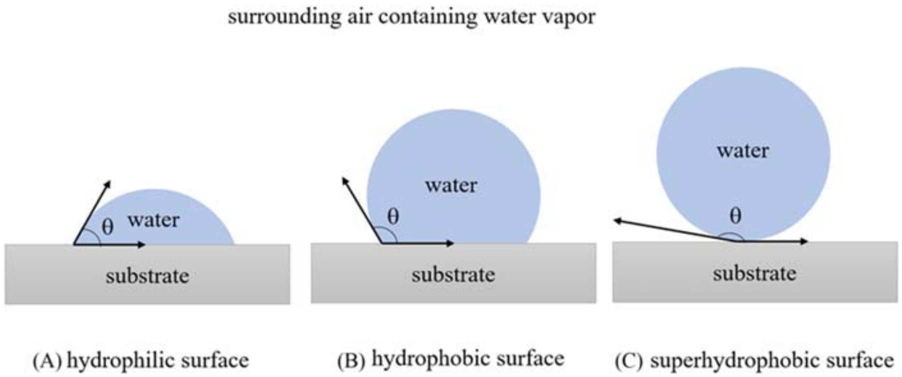


Figure 5.2 Interaction of a water droplet with various surfaces showing three contact angles for (A) a hydrophilic surface; (B) hydrophobic surface; and (C) superhydrophobic surface.

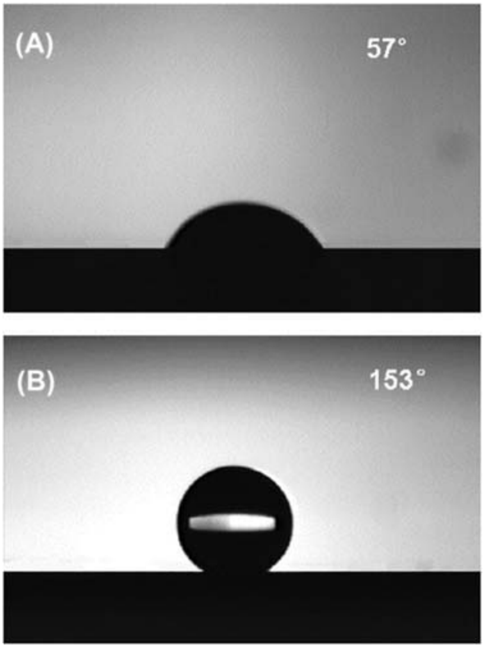
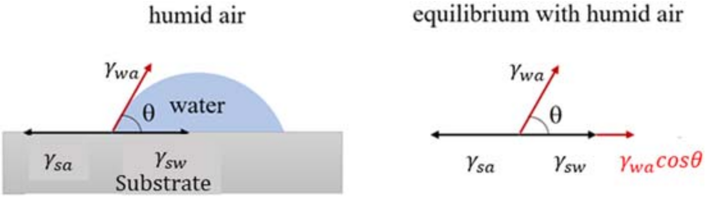


Figure 5.3 Images of water droplets captured by the goniometer on (A) nontreated wood and (B) potassium methyl siliconate-treated wood [4].

pull-off force for separating a water droplet from the surface after they have been in contact [30].

Wetting is a thermodynamic phenomenon. The extent of wetting is governed by the difference in free energy between a wet and an unwet surface [33]. As such, the distinction between hydrophobicity and hydrophilicity is based on the interfacial free energy of the surface in presence and absence of water. In presence of water, interactions with the surface may include van der Waals forces and hydrogen bonding, which compensate for Gibbs free energy for bringing a water molecule from bulk water to the surface. For cementitious materials, in absence of water the Gibbs free energy of the surface is calculated assuming exposure to air. The change in Gibbs free energy at the interface (ΔG_i) is determined, with state 2 being a water-covered surface, and then the surface is classified as hydrophilic when $\Delta G_i < 0$ and hydrophobic when $\Delta G_i > 0$. Quantitatively, the absolute value of ΔG_i indicates the degree of hydrophilicity or hydrophobicity. Based on the concept of liquid cohesion, wettability is obtained from the balance among the equilibrium interactions of three phases: solid, water, and air Fig. 5.4A), as introduced by Young [34]. The force balance per unit length of the interface Fig. 5.4B is given by the following equation

$$\gamma_{sa} = \gamma_{sw} + \gamma_{wa}\cos\theta \tag{5.16}$$



(A) (B)

Figure 5.4 Equilibrium interaction of (A) a water droplet with a surface and a humid air showing (B) the balance of forces at equilibrium.

where γ_{sa}, γ_{sw}, and γ_{wa} are the surface/interfacial tensions at the interfaces of the solid − air, solid − water, and water − air, respectively Fig. 5.4B. Eq. (5.16) is used for obtaining the wettability of the ideal case of flat and smooth solid surface. Fig. 5.4 is depicted for a hydrophilic surface, where the interfacial tension between the solid and the liquid, γ_{sw}, is lower than that between the solid and the gas, γ_{sa}. Hence, the surface tension, γ_{wa}, assumes the given static contact angle, θ, in order to balance the resultant force in the horizontal direction. For a hydrophobic surface, on the other hand, the contact angle would be >90 degrees, and the surface tension would be pointing in the opposite direction in order to balance the high value of γ_{sw}. It should be noted that the sign of the cosθ term in Eq. (5.16) determines the magnitude of the force resultant force, that is, γ_{sa}, and does not affect its direction.

5.5.1 Parameters affecting hydrophobicity

The effects of surface roughness on wettability were described by the two famous models of Wenzel [33] and Cassie and Baxter [35]. The two models are based on two different wetting behaviors of the hydrophobic surfaces. A complete wetting of the contact surface is considered in the Wenzel analysis (full wetting state). The Cassie analysis, on the other hand, pertains to a “nonwet” state, in which the water drop rests on the protrusions of the surface enclosing air pockets in between them. Cassie quantified the effect of fractional surface area exposed to air in rough surfaces by modifying the cosθ term in Eq. (5.16) by Eq. (5.17). Eq. (5.17) is known as the Cassie equation [36] or sometimes referred to as the Cassie and Baxter equation [29].

$$\cos\theta = \mathfrak{f}_s \cos\theta_1 + (1 - \mathfrak{f}_s)\cos\theta_2 \tag{5.17}$$

where $\mathfrak{f}_s$ is the fractional surface area of solid touching the water drop or the fractional contact of the solid/liquid (i.e., $\mathfrak{f}_s < 1$ for actual surface), θ_1 is the contact angle of a smooth surface of the solid sample, θ_2 is the contact angle of the water−air interface. The value of θ_2 is known theoretically to be180 degrees according to Young’s equation Eq. 5.16. Then, Eq. (5.17) simplifies to the form given by Eq. (5.18).

$$\cos\theta = \mathfrak{f}_s \cos\theta_1 + \mathfrak{f}_s - 1 \tag{5.18}$$

Then, knowing the contact angle for an ideal smooth surface and the fractional surface area that is exposed to air, the effect of surface roughness can be accounted for by Eq. (5.17). Increasing surface roughness increases the entrapped air between the water drop and the surface and thus decreases the value of $\mathfrak{f}_s$. Then according to Eq. (5.18), increasing the roughness of a hydrophobic surface increases the contact angle and makes the surface even more hydrophobic and less wettable.

In a different approach, the Wenzel model [33] considered the liquid to completely fill the voids in the rough surface and a different relationship between the contact angle and surface roughness was proposed. Wenzel [33] defined the roughness factor (f_r) as the ratio of actual solid/liquid interface or contact area over the superficial interface contact area or geometric surface (i.e., $f_r > 1$ for actual surfaces). Then, he related the actual contact angle to the ideal contact angle (for a smooth surface) by the following equation:

$$\cos\theta = f_r \cos\theta_1 \tag{5.19}$$

According to the Wenzel model Eq. 5.19, for a hydrophilic surface with $\theta < 90$ degrees, increasing the surface roughness increases f_r and thus decreases the actual contact angle, which in turn increases the level of hydrophilicity and enhances the wettability. On the other hand, for a hydrophobic surface with $\theta > 90$ degrees, increasing the surface roughness increases the actual contact angle and thus increases the level of hydrophobicity and enhances the nonwettability. These models were used by Di Mundo et al. [29] for various cases of textured surfaces and capillary action.

In concrete applications, the contact angle and thus the level of hydrophobicity may change with time due to changes in surface characteristics by chemical, physical, and/or mechanical interactions with the surrounding (see Chapter 3 for surface damages due to durability problems). It has been demonstrated that subjecting a hydrophobic cementitious surface to abrasion action decreases the contact angle [37]. If the cementitious surface is treated with a hydrophobic material, the abrasion action can degrade the treatment layer. Fig. 5.5 compares the interaction of a water drop of a hydrophobic cementitious surface Fig. 5.5A obtained by a surface

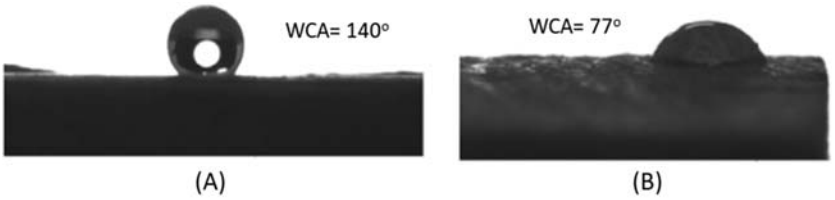


Figure 5.5 Interaction of a water droplet with a cementitious surface (A) treated with iso-octyltriethoxysilane and (B) the same surface after polishing [37].

treatment using iso-octyltriethoxysilane and that of the same surface after being polished Fig. 5.5B [37]. The polishing action removed part of the hydrophobic treatment and thus the contact angle decreased considerably. However, the contact angle of the beaten surface did not reach the contact angle of the original cementitious surface before treatment with iso-octyltriethoxysilane (which was reported to be 14 degrees), as the treatment penetrated within the surface to depths in the range of 1–3 mm, and thus a part of the treatment sustained after polishing [31]. The Cassie state of nonwetting with enclosed air pockets is considered to be unstable and may be transformed into the full-wetting state of the Wenzel case under pressure or other mechanical impacts such as vibrations [29]. Increasing the surface porosity may shift the wetting behavior toward Cassie state of "nonwetting." Consequently, reducing the porosity of concrete by filling the pores at the surface with pore blocking materials (see Chapter 7) smoothens the surface and thus makes it less hydrophilic or more hydrophobic.

5.5.2 Types and chemical structures of hydrophobic compounds

Hydrophobic compounds or hydrophobes, which are used in treating cementitious surfaces to obtain a nonwetting property, usually contain an organic part that prompts the state of high surface energy, and hence creates the property of nonwettability [29]. Typical hydrophobic materials include normal oils, fats, and greasy substances. These include vegetable and petroleum oils such as mineral oil and paraffin waxes. In many industrial applications, metalloorganic or organometallic compounds are used in hydrophobic treatments. They are composed of a metal or metalloid atom(s) bonded directly to carbon chain(s). Hydrophobic compounds include derivatives of oleic, caprylic, capric, and fatty acids such as stearates. Stearate compounds used in concrete applications [38] include the organic anionic group $(C_{18}H_{35}O_2)^-$ combined with an alkali ion such as calcium, sodium, or lithium, which are soluble in water.

In silicon compounds, the silicone atoms are covalently bonded to an organic group (i.e., $Si-CH_n$). The organic alkyl group is characterized by a fatty nature and thus it makes the surface water-repellent as it is extended outward from the surface. Organosilicon compounds include silanes, siloxane, and siliconates. Organosilicon hydrophobes used in concrete applications include silane methyl [39], trimethoxysilane [40], g-(methylpropyleneoxy) propyl trimethoxysilane [41], octyl triethoxysilane [42], iso-octyltriethoxysilane [37]. Di Mundo et al. [29] provided a full review of industrial organosilicon compounds used in concrete waterproofing and compared them to other types of materials. A more detailed discussion of the industrial applications of these materials in concrete waterproofing is given in Chapter 8. Fig. 5.6 shows the structures of three examples of hydrophobes that are encountered in the field of concrete waterproofing. These include sodium stearate, iso-octyltriethoxysilane, and potassium methyl siliconate. Each of them has at least one organic group that induces hydrophobicity.

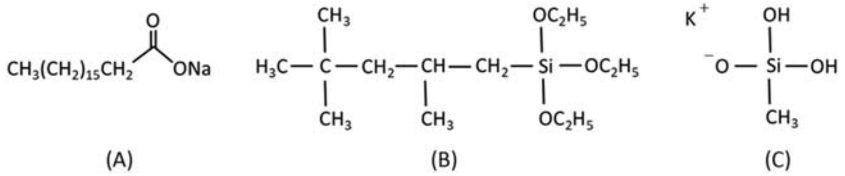


Figure 5.6 Selected hydrophobes: (A) sodium stearate, (B) iso-octyltriethoxysilane, and (C) potassium methyl siliconate.

5.5.3 Reactions of hydrophobic materials with surfaces

The setting mechanisms of hydrophobes onto cementitious surfaces include physicochemical and chemical mechanisms, which depend on the type and chemical structure of the hydrophobic molecules and the surface. A general background on the interactions between the surfaces and the hydrophobes is given here. A more detailed description is given in Chapter 8.

Physicochemical mechanisms are encountered with emulsions and suspensions of organic materials. The hydrophobic organic molecules (such as oils) can be adsorbed or adhere to the surface by deposition or they may coalesce into amalgamations of polymer materials within the pores of the cement paste. Then, they form water-repellent films or globules [38].

Chemical setting mechanisms are encountered with solutions of hydrophobic compounds. They are set at the surface through a chemical reaction between the hydrophobic compound/group and one of the cementitious constituents such as calcium ions from the byproducts of cement hydration [e.g., $Ca(OH)_2$] or with a hydroxyl group at the surface of the cement hydration products. In some cases, such a reaction requires the presence of carbon dioxide from surrounding air. This process is generally a chemical adsorption (chemisorption) process, which involves the creation of a chemical bond between the hydrophobe and the surface. The setting of organosilicon compounds and fatty acids belong in general to the category of chemical reaction. For example, sodium stearate is soluble in water and thus it forms an aqueous solution, in which stearate group are reactive. The setting of stearate hydrophobic compounds occurs through a reaction between the fatty acid and the calcium ions [38–43] leading to the deposition of hydrophobic layer of calcium stearate [38].

For the organosilicon compounds, the OH group (from the hydrophobe) combines with the OH group from the cementitious substrate forming a chemical bond between the hydrophobe and the surface. This reaction creates a hydrophobic film at the surface of the substrate, as the organic groups, which dislike water (CH_2 and CH_3), face outside the surface and effectively reduce the surface energy of the cementitious material. The reaction mechanism includes hydrolysis, formation of hydrogen bonds with the surface, and then condensation and polycondensation for converting the hydrogen bonds into covalent oxygen bonds while releasing water molecules. For aqueous solution of alkali methyl siliconate, the presence of carbon dioxide is essential for the hydrolysis as the first step in this mechanism. These mechanisms are detailed in Chapter 8.

The contact angle is a function of the level of surface treatment. For example, Liu et al. [4] found that the contact angle increased with increasing the concentration of potassium methyl siliconate hydrophobe up to a certain limit. The durability of the organosilicon hydrophobic layer was found to be pH dependent [32].

5.6 Hygroscopicity

The term hygroscopicity relates to the rate and equilibrium water vapor uptake by a solid under the environment temperature and relative humidity [44]. Interaction of the adsorbed water within the solid reduces the chemical potential of the adsorbed water creating a higher driving force for vapor diffusion toward the surface. Typical hygroscopic crystalline materials include sodium acetate, disodium malonate, disodium succinate, sodium pyruvate, disodium maleate, sodium formate, and humic acid sodium salt [45]. The organic acids can associate with cations such as sodium and potassium in the particle phase.

Water uptake of hygroscopic crystals is a complicated process. Below is a quick overview of the different mechanisms involved [44]. Water vapor may adsorb onto the solid surface and, depending on the type of adsorption, saturation may be achieved. Depending on the solid, some water molecules may penetrate into the bulk solid contributing to absorbed water. The total water vapor taken up by the solid is termed sorbed water. Alternatively, capillary condensation, as discussed earlier, may increase the amount of the sorbed water in the pores. If at the curved interface between the water and the surrounding air the mole fraction of water is lower than the RH, more water vapor molecules migrate to the interface contributing to more condensation. For highly water-soluble compounds, a continuous supply of water vapor from the surrounding air may lead to dissolution of the solid. This phenomenon is known as deliquescence. During deliquescence, the migration of the vapor molecules ceases once the chemical potential of the water in the aqueous solution equals that in the bulk air. Hydrophilic compounds may incorporate the water into their crystal structure contributing to hydrate formation. Water in the hydrate screens electrostatic repulsion among ions in the solid and/or forms hydrogen bonds with the functional groups of the solid (or other water molecules). Lastly, amorphous materials may take up lots of water vapor into their bulk structure, that is, absorption, forming a solid solution. The interaction of water vapor with cement, mortar, and concrete may follow any of the above mechanisms. Examples of hygroscopic crystals include [45]: sodium acetate, disodium malonate, disodium succinate, sodium pyruvate, disodium maleate, and humic acid sodium salt. The organic acids can associate with cations such as sodium and potassium in the particle phase. Some studies reported that water adsorption was mainly contributed to by OH groups of the organic compounds. Good correlations were indeed found between hygroscopicity and the number of OH groups in these compounds [44].

As a typical surface adsorption process Section 5.3, hygroscopic growth has kinetic and equilibrium behaviors. Assuming mass transfer limited adsorption, a general expression for the rate of water vapor adsorption into a hygroscopic material can be written in terms of chemical potential, μ_i, of the water as follows:

$$\frac{dm_w}{dt} = \frac{k_c}{MW}\left(\mu_v - \mu_{w,h}\right) \tag{5.20}$$

where dm_w/dt is the rate of water accumulation into the hygroscopic material (kg/s^{-1}), k_c is the rate constant (kmol^{-s}/m^2), MW is the molar mass for water (18 kg/kmol), and μ_v and $\mu_{w,h}$ are the chemical potentials of the water in the atmosphere and in the hygroscopic material, respectively (J/kmol). Further steps in the rate analysis may attempt to relate μ_v to the RH of the water in air and $\mu_{w,h}$ to an expression of the water activity/concentration in the hygroscopic material, for example, surface excess (mol/m^2). For example, the water activity in hygroscopic materials has been modeled using Flory − Huggins theory [24]. Also, if the rate of water adsorption is limited by the water interaction with the hygroscopic material, then other rate expressions might be written.

The rate of growth of hygroscopic materials has been successfully described by Köhler theory [46]. The classical Köhler theory was developed to describe the role of organic aerosols in promoting the growth of rain droplets [47]. At equilibrium, the droplet mass, m_e, relates to the dry mass of the hygroscopic material, m_h, and the RH as follows [14]:

$$\frac{m_e}{m_h} = 1 + \kappa \frac{\frac{\rho_w}{\rho_h}}{\left(\frac{1}{RH} - 1\right)} \tag{5.21}$$

where κ is the hygroscopicity parameter, ρ_w and ρ_h are the densities of the water and the dry hygroscopic material, respectively, (kg/m^3). Alternatively, Freundlich adsorption isotherm (see Section 5.3.1) has been used to relate m_e/m_h at equilibrium to the RH [14] as follows:

$$\frac{m_e}{m_h} = 1 + K_F(RH)^n \tag{5.22}$$

The hygroscopicity parameter, κ, depends on the hydrophilicity and the physicochemical properties (e.g., porosity and pore geometry) of the hygroscopic material as well as the temperature [45]. The role of solute in decreasing $\mu_{w,h}$ can be described using solution thermodynamics, for example, Flory − Huggins theory [24], whereas the impeding role of the small droplet size is accounted for through Kelvin equation 5.4a,b. The Kelvin equation predicts a higher vapor pressure across a small droplet interface relative to a flat surface at a given temperature, hence a decreasing mass transfer rate in the vapor phase. Solutes with surface activity display the opposing effects of reducing the surface tension, hence the vapor pressure, while lowering $\mu_{w,h}$. The increased vapor pressure at the interface of a small droplet or the decreased

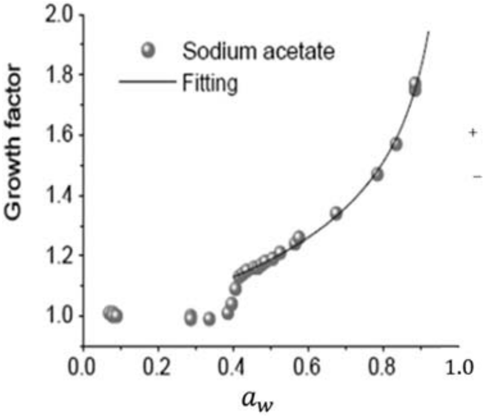


Figure 5.7 Hygroscopic growth factor of sodium acetate as a function of water activity, which is proportional to relative humidity in air [45].

interfacial tension associated with surface active solute can be more dominant under certain conditions [14].

Crystal growth of hygroscopic material is measured through the hygroscopic growth factor, GF(RH) [45].

$$GF(RH) = \frac{D(RH)}{D_h} \tag{5.23}$$

where $D(RH)$ is the particle mobility diameter at a given RH and D_h is the diameter of the dry particle. Fig. 5.7 shows the growth factor for sodium acetate, which increases exponentially with increasing RH. Sodium acetate has been tested for waterproofing applications, as indicated in Chapter 7. Similar curves of growth factor have been reported for other types of hygroscopic organic salts [45].

In concrete applications, some hygroscopic calcium organic insoluble salts are formed as a result of the acid attack of concrete resulting from the acid—base neutralization reactions of calcium content of the cement paste [48]. This occurs when concrete is subjected to organic acids such as acetic, formic, and lactic acids, which may exist in certain industrial wastewater from food production. The hygroscopic crystal growth might be associated with a damaging volume expansion of concrete. Some salts such as those of oxalic acid are reported to cause no harmful expansion when formed [48]. Hygroscopic materials are also used in pore blocking waterproofing technology (see Chapters 10 and 11).

5.7 Icephobicity and ice adhesion

The term icephobicity is used in recent concrete literature in association with hydrophobicity [29]. Similar to hydrophobicity, the word icephobicity is composed of ice and the Greek word phobocity to indicate "fear" or "repelling" to ice. In practical terms, icephobicity reflects the surface retardation to ice adhesion [15]. Ice build-up on surfaces leads to severe damage to the surface as well as the structure.

Passive ice protection systems are based on equipping the surface with hydrophobic attributes making it water repelling [15]. There are three lines of protection against ice-related problems on surfaces [29]: (1) increasing surface hydrophobicity, which prevents wetting and removes water drops from surfaces, (2) rapid removal of water from the surface to minimize the net rate of ice formation, and (3) ease of ice removal, even if forms, arising from the reduction in the strength of ice adhesion by the two previous methods. Icephobic surfaces usually portray water repelling/high water contact angle attributes [15], resist water freezing (from condensing or flowing water), and have low adhesion strength of ice. Superhydrophobic surfaces (contact angles >150 degrees) are considered highly icephobic [15], as they hinder freezing of water drops onto the surface [49]. Rather, water drops drain rapidly upon impacting these surfaces. If water drops settle onto the surface of a superhydrophobic material, the contact area would be too small resulting in low strength of adhesion. Capillary condensation within concrete is also an important parameter [29] making porosity a governing factor for ice adhesion. It is noted that hydrophobic surfaces make the water interface convex ($H > 0$ in Eq. 5.4a,b, hence reducing capillary condensation.

5.7.1 Quantification of icephobicity and ice adhesion

It is difficult to provide an explicit quantitative measure of icephobicity, and standard procedures for testing ice adhesion are not available [29]. Generally, a quantitative measure can be based on the analysis of energy/work or mechanical stresses at the interface between the formed ice and the surface. Stress analysis for quantifying the level of icephobicity is based on determining the adhesion strength, which is defined as the maximum force required to detach ice from a surface per unit area [50]. Nevertheless, the adhesion strength depends on the direction of the applied force with respect to the surface. The stresses involved include shear and tensile stresses or combination of stresses [26,40]. Shear stresses are believed to be more practical [29]. The "critical shear stress" is determined experimentally or estimated theoretically. Icephobic surfaces possess low shear strength (e.g., 150–500 kPa or as low as 15.6 kPa). The measured interfacial tensile strength for ice-concrete was found to be temperature dependent [50]. For $T < -7°C$, the interfacial tensile strength was $\sim 8.3\ kg/cm^2$, and at higher temperatures, it was $\sim 6.1\ kg/cm^2$. These measurements were also related to the strength of the ice itself. Generally, it is tedious to compare adhesion strength measurements, even under a controlled environment. Different variables influence the measurement, including thermal expansion of ice, loading arrangement, and interfacial stress distribution as well as the loading rate [51].

Theoretically, ice adhesion is characterized by estimating the energy/work of adhesion, which is defined as the work or the free energy required to detach the ice from a surface [15]. From a thermodynamic perspective ice formation and hydrophobic interactions with surfaces are driven by the minimization of the surface Gibbs free energy. Rearranging Eq. (5.16),

$$\gamma_{wa}\cos\theta = \gamma_{sa} - \gamma_{sw} \tag{5.24}$$

Following Dupre, a reversible work of adhesion could be defined according to

$$w_A = \gamma_{sa} + \gamma_{wa} - \gamma_{sw} \tag{5.25}$$

where w_A is the work of adhesion. As Eq. (5.24) suggests, the reversible work of adhesion, per unit area of the surface, is equivalent to detaching water molecules from a solid surface, while forming a solid surface and a water surface with the air. Assuming the same interfacial tension of water or ice on the solid surface [51], combining Eqs. (5.24) and (5.25), Young − Dupre equation can be written as

$$w_A = \gamma_{wa}(1 + \cos\theta) \tag{5.26}$$

According to Young − Dupre equation [15], the thermodynamic work of adhesion is approximated by the surface tension of the water and the contact angle of the liquid on the solid surface.

5.7.2 Mechanisms of ice adhesion

Ice formation is dependent on the temperatures of the surface and the surrounding air as well as the extent of capillary action and condensation due to air cooling. Experiments showed that increasing the hydrophobicity of a surface decreases the freezing temperature of water at that surface. Fig. 5.8 shows that for small water droplets ($\sim 10\ \mu$L), water freezes at lower temperatures when the degree of hydrophobicity/contact angle increases [49].

The mechanisms of ice adhesion involve physical and chemical interactions between the ice and the solid surface. The physicochemical bonds occur at the nanoscale, whereas the mechanical bonding occurs at a larger scale, in the order of micrometer. The physicochemical interactions between ice and the solid surface include hydrogen bonding and van der Waals forces [15]. These interactions are also responsible for water adsorption onto the surface and water contact angle with surfaces, as detailed in Sections 5.3 and 5.5 [50]. The mechanical bonding/forces (e.g., entanglement and interlocking of ice structure [50] arise from the roughness of the solid surface and its porosity. They are related to the penetration of water and porosity of concrete as well as to the mechanical properties of bulk ice [50]. Typically, the compressive strength of bulk ice is $\sim$ 36 kg/cm^2 and the tensile ring strength is $\sim$13 kg/cm^2 [50]. For rough, porous surfaces, the interface surface area between the ice and concrete is high and thus the mechanical forces (interlocking) are also higher. Hence, ice detachment may not be a purely adhesion failure [51]. In such a case, the fracture may occur within the ice structure itself. Meuler et al. [52] suggested

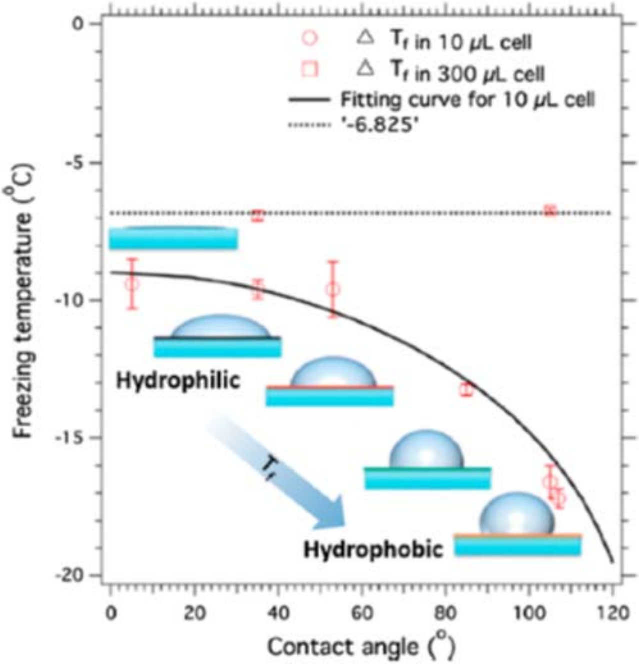


Figure 5.8 Freezing temperature of water droplets having different sizes as function of degree of hydrophobicity [49].

that icephobicity of smooth metal surfaces are better predicted by measuring the advancing/receding contact angle for water droplets on the substrate. They proposed a relationship between advancing/receding water contact angles and the strength of ice adhesion.

There are differences in adhesion strength of ice resulting from misting a surface with water drops and ponding or damping the surface in water. Also, adhesion strength of bulk-formed ice is different from that of ice formed by water drops impinging a surface [51].

Different approaches have been adopted to combat ice adhesion. The use of anti-icing coatings is based on reducing the permeability, adsorption capacity, and hydrophilicity of the solid surface. Examples of antiicing coatings include hydrophobic polymers, for example, Teflon [51]. Mechanical methods, on the other hand, have evolved from using mallets, axes, and bats to the use of motorized cutters [51]. Thermal methods are limited by the amount of latent heat needed to melt the ice and how carefully the melted ice is removed from the surface. The use of internal heating, for example, ultrasonic heating, has been developed [51]. Lastly, chemical and electrochemical methods have been limited by the effect of chemicals on the surface and chemicals distribution onto the surface [51]. Examples of such chemicals include ethylene glycol, urea, and salts. Electrolysis and corrosion might help in de-icing, but it has its toll on the material of construction [51].

5.8 Nanotechnology in concrete industry

Nanotechnology studies materials at the nanoscale level, that is, 1−100 nm, and explores their synthesis and application. The term nanoparticle (NPs) is not limited to materials having all their dimensions within the nanoscale (zero-dimensional: 0D), but also includes 1D materials with two of its dimensions falling within the nanoscale and 2D materials with only one of its dimensions falling within the nanoscale. Examples of 0D NPs are spherical NPs, 1D NPs are carbon nanotubes (CNTs), and 2D NPs are graphenes. NPs display attractive physical, mechanical, optical, and chemical properties that can be tuned through manipulating particle size. The size-dependence of the different NP properties enables engineering NPs with desired properties simply by controlling the particle size. Particle size control, on the other hand, has proven to be a challenging task and can be achieved through certain techniques [53,54].

In addition to having unique properties, inclusion of NPs into different materials has been shown to improve the material characteristics. For example, inclusion of NPs into drilling fluids has been shown to improve fluids filtration [55], lubrication [56], and wellbore strengthening [57] attributes. The addition of commercial NPs to a cement slurry is reported to enhance the mechanical properties of the hardened cement. A summary of these findings has been recently reported by Mehairi and Husein [58]. NP addition also enabled incorporating more by-products into a cement slurry, while maintaining the required cement properties. The implication from an environmental standpoint is twofold because less cement is required while enabling beneficial use of waste products. For example, addition of SiO_2 NPs reduced the porosity of high-volume fly ash concrete, hence increased its 3-day compressive strength by 80%. Inclusion of Al_2O_3 NPs increased the elasticity modulus of cement mortar, while did not affect its compressive strength. The early-age hydration and the compressive and flexural strengths of Portland cement were reported to increase upon addition of TiO_2 NPs. Cement containing TiO_2 NPs also possessed self-cleaning properties and higher abrasion resistance compared with cement containing SiO_2 NPs. Addition of ZrO_2 NPs decreased the permeability and porosity of cement by filling and bridging leading to enhanced microstructure and higher compressive strength. Inclusion of $CaCO_3$ NPs improved the hardened property, impact resistance, flexural strength of cement, and achieved lower water permeability and better sound absorption. The $CaCO_3$ NPs shortened the induction time for the hydration reaction of tricalcium silicates (C3S).

Addition of carbon nanofibers (CNFs) and CNTs to cement increased the modulus of elasticity and compressive and tensile strengths. Owing to the high interaction between CNTs and cement hydrates, the CNTs bridged across the cracks and the voids enabling smooth load transfer. Moreover, CNTs, CNFs, and Fe_2O_3 NPs contributed to smart, load-sensing concrete by reducing its electrical resistance.

Nano-clays present an advantage in terms of their natural occurrence, which saves the cost of NP synthesis. Nevertheless, separation of these clays still presents an important expense. Inclusion of nano-clay composites reduced cement permeability and shrinkage and increased its mechanical properties and resistance to chloride. Nano-clays enhance cement hydration through heterogeneous nucleation of the hydrated cement.

To address the cost of commercial NPs, which typically hinders field application of NPs, Mehairi and Husein presented methods for in situ, in house preparation of NPs within the cement slurry [59]. In situ prepared NPs have proven more effective than commercial NPs and at relatively low dose increased the compressive strength of hardened cement by 80%. Moreover, in situ prepared NPs enhanced the cyclic compressive stress (related to cement durability) while reducing cement permeability by 93% and its porosity by 55%.

Other applications of NP-containing cement focused on water proofing and low water adsorption, increasing Young's modulus, achieving flexible cement, antimicrobial activity as well as blast heat, corrosion and freeze/thaw resistant cement.

Within cement, NPs may have an inert role and only contribute to the different properties of the cement by filling the pores. These are termed inert additives/fillers. Alternatively, the NPs may interfere with the hydration reactions of the cementitious material and/or more actively interact at the surface. These NPs are termed functional filler. The extent of interaction is dictated by the NP surface properties. Additional discussion on the use of NP in waterproofing applications is given in the subsequent chapters.

References

[1] Al-Rashed, R., & Al-Jabari, M. (2020). Multi-crystallization enhancer for concrete waterproofing by pore blocking. *Construction and Building Materials*. Available from https://doi.org/10.1016/j.conbuildmat.2020.121668.

[2] Al-Rashed, R., & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*. Available from https://doi.org/10.1016/j.cscm.2020.e00408.

[3] Gretton, J. C., Brook, D. B., Dyson, H. M., & Harlock, S. C. (1998). Moisture vapor transport through waterproof breathable fabrics and clothing systems under a temperature gradient. *Textile Research Journal*. Available from https://doi.org/10.1177/004051759806801209.

[4] Liu, C., Wang, S., Shi, J., & Wang, C. (2011). Fabrication of superhydrophobic wood surfaces via a solution-immersion process. *Applied Surface Science*, *258*(2), 761–765. Available from https://doi.org/10.1016/j.apsusc.2011.080.077.

[5] Al-Jabari, M., Ghyadah, R. A., & Alokely, R. (2019). Recovery of hydrogel from baby diaper wastes and its application for enhancing soil irrigation management. *Journal of Environmental Management*. Available from https://doi.org/10.1016/j.jenvman.2019.03.087.

[6] Lee, H. X. D., Wong, H. S., & Buenfeld, N. R. (2016). Self-sealing of cracks in concrete using superabsorbent polymers. *Cement and Concrete Research*. Available from https://doi.org/10.1016/j.cemconres.2015.09.008.

[7] Artioli, G., & Bullard, J. W. (2013). Cement hydration: The role of adsorption and crystal growth. *Crystal Research and Technology*. *48*(10), Special Issue: International School "Adsorption, Absorption and Crystal Growth", October 2013, 903–918.

[8] ASTM. (2015). *Committee C09.91. ASTM C125-15a standard terminology relating to concrete and concrete aggregates*. Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[9] ACI. (2009). *Committee 211, 211.1-91. Standard practice for selecting proportions for normal heavyweight, and mass concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[10] Zhou, C., Ren, F., Zeng, Q., Xiao, L., & Wang, W. (2018). Pore-size resolved water vapor adsorption kinetics of white cement mortars as viewed from proton NMR relaxation. *Cement and Concrete Research*. Available from https://doi.org/10.1016/j.cemconres.2017.12.002.

[11] Geankoplis, C. J. (2014). *Transport processes and separation process principles*. New York City, New York, USA: Pearson.

[12] Houst, Y. F., & Wittmann, F. H. (1994). Influence of porosity and water content on the diffusivity of CO_2 and O_2 through hydrated cement paste. *Cement and Concrete Research*. Available from https://doi.org/10.1016/0008-8846(94)90040-X.

[13] Zhang, Q., Ye, G., & Koenders, E. (2013). Investigation of the structure of heated Portland cement paste by using various techniques. *Construction and Building Materials*. Available from https://doi.org/10.1016/j.conbuildmat.2012.09.071.

[14] Beeram, P. S. R. (2017). *Characterization of ice adhesion strength over different surfaces pertinent to aircraft anti-/de-icing*. MSc Thesis, Iowa State University.

[15] Beeram, P. S. R. (2017). *Characterization of ice adhesion strength over different surfaces pertinent to aircraft anti-/de-icing*. Iowa State University.

[16] Al-Jabari, M. (2017). Kinetic mass transfer adsorption model for treating dairy wastewater with stone cutting solid waste. *Environmental Technology & Innovation*. Available from https://doi.org/10.1016/j.eti.2016.11.004.

[17] Al-Jabari, M. (2016). Kinetic models for adsorption on mineral particles comparison between Langmuir kinetics and mass transfer. *Environmental Technology & Innovation*. Available from https://doi.org/10.1016/j.eti.2016.04.005.

[18] Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*. Available from https://doi.org/10.1021/ja02242a004.

[19] Qiu, H., Lv, L., Pan, B. C., Zhang, Q. J., Zhang, W. M., & Zhang, Q. X. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University: Science A*. Available from https://doi.org/10.1631/jzus.A0820524.

[20] Kyzas, G. Z., & Kostoglou, M. (2014). Green adsorbents for wastewaters: A critical review. *Materials*. Available from https://doi.org/10.3390/ma7010333.

[21] Ho, Y. S. (2006). Review of second-order models for adsorption systems. *Journal of Hazardous Materials*. Available from https://doi.org/10.1016/j.jhazmat.2005.12.043.

[22] Tosun, I. (2012). Ammonium removal from aqueous solutions by clinoptilolite: Determination of isotherm and thermodynamic parameters and comparison of kinetics by the double exponential model and conventional kinetic models. *International Journal of Environmental Research and Public Health*. Available from https://doi.org/10.3390/ijerph9030970.

[23] Wang, J., & Guo, X. (2020). Adsorption kinetic models: Physical meanings, applications, and solving methods. *Journal of Hazardous Materials*. Available from https://doi.org/10.1016/j.jhazmat.2020.122156.

[24] Liu, P., et al. (2018). Resolving the mechanisms of hygroscopic growth and cloud condensation nuclei activity for organic particulate matter. *Nature Communications*, *9*(1). Available from https://doi.org/10.1038/s41467-018-06622-2.

[25] sraelachvili, J. N. (2011). *Intermolecular and surface forces* (3rd ed.). Cambridge, MA, USA: Academic Press.

[26] Ghosh, P. (2009). *Colloid and interface science*. PHI Learning.

[27] Yang, L., Gao, D., Zhang, Y., Tang, J., & Li, Y. (2019). Relationship between sorptivity and capillary coefficient for water absorption of cement-based materials: Theory analysis and experiment. *Royal Society Open Science*, *6*(6). Available from https://doi.org/10.1098/rsos.190112.

[28] Shukla, N. B., & Madras, G. (2011). *Industrial & Engineering Chemistry Research*, *50* (19), 10918−10927. Available from https://doi.org/10.1021/ie200713y.

[29] Di Mundo, R., Labianca, C., Carbone, G., & Notarnicola, M. (2020). Recent advances in hydrophobic and icephobic surface treatments of concrete. *Coatings*, *10*(5). Available from https://doi.org/10.3390/COATINGS10050449.

[30] Law, K. Y. (2014). Definitions for hydrophilicity, hydrophobicity, and superhydrophobicity: Getting the basics right. *Journal of Physical Chemistry Letters*. Available from https://doi.org/10.1021/jz402762h.

[31] Mascini, A., Cnudde, V., & Bultreys, T. (2020). Event-based contact angle measurements inside porous media using time-resolved micro-computed tomography. *Journal of Colloid and Interface Science*, *572*, 354−363. Available from https://doi.org/10.1016/j.jcis.2020.030.099.

[32] Qu, M., Zhang, B., Song, S., Chen, L., Zhang, J., & Cao, X. (2007). Fabrication of superhydrophobic surfaces on engineering materials by a solution-immersion process. *Advanced Functional Materials*. Available from https://doi.org/10.1002/adfm.200600472.

[33] Wenzel, R. N. (1936). Resistance of solid surfaces to wetting by water. *Industrial & Engineering Chemistry Research*. Available from https://doi.org/10.1021/ie50320a024.

[34] Young, T. (1805). III. An essay on the cohesion of fluids. *Philosophical Transactions of the Royal Society London* (95), 65−87.

[35] Cassie, A. B. D., & Baxter, S. (1944). Wettability of porous surfaces. *Transactions of the Faraday Society*. Available from https://doi.org/10.1039/tf9444000546.

[36] van Oss, C. J. (2008). Chapter Eleven: The water − air interface. *Interface Science and Technology*, *16*(08), 149−160. Available from https://doi.org/10.1016/S1573-4285(08)00211-1, vol.

[37] Song, Z., Lu, Z., & Lai, Z. (2019). Influence of hydrophobic coating on freeze-thaw cycle resistance of cement mortar. *Advances in Materials Science and Engineering*, *2019*(1). Available from https://doi.org/10.1155/2019/8979864.

[38] ACI. (2018). CT-18 *Concrete Terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[39] Li, H., Xu, C., Dong, B., Chen, Q., Gu, L., & Yang, X. (2020). Enhanced performances of cement and powder silane based waterproof mortar modified by nucleation C-S − H seed. *Construction and Building Materials*. Available from https://doi.org/10.1016/j.conbuildmat.2020.118511.

[40] Liu, J., Pan, Z., Wang, X., & Xu, S. (2019). Properties and hardening mechanism of alkali activated slag based hydrophobic coating at ambient curing condition. *Materials Research Express*. Available from https://doi.org/10.1088/2053-1591/aaf950.

[41] Li, F., Liu, L., Liu, K., Zheng, A., & Liu, J. (2020). Investigation on waterproof mechanism and micro-structure of cement mortar incorporated with silicane. *Construction and Building Materials*. Available from https://doi.org/10.1016/j.conbuildmat.2019.117865.

[42] Zhang, W., et al. (2019). Study on unsaturated transport of cement-based silane sol coating materials. *Coatings*. Available from https://doi.org/10.3390/coatings9070427.

[43] A. 212. 3R-16 ACI. (2016). *Committee 212. Report on chemical admixtures for concrete*. Farmington Hills, MI: American Concrete Institute.

[44] Chen, D. (2009). Hygroscopicity of pharmaceutical crystals. PhD Thesis, University of Minnesota, http://purl.umn.edu/47878.

[45] Wu, Z. J., Nowak, A., Poulain, L., Herrmann, H., & Wiedensohler, A. (2011). Hygroscopic behavior of atmospherically relevant water-soluble carboxylic salts and their influence on the water uptake of ammonium sulfate. *Atmospheric Chemistry and Physics*, *11*(24), 12617−12626. Available from https://doi.org/10.5194/acp-11-12617-2011, vol.

[46] Ovadnevaite, J., et al. (2017). Surface tension prevails over solute effect in organic-influenced cloud droplet activation. *Nature*, *546*(7660), 637−641. Available from https://doi.org/10.1038/nature22806.

[47] Köhler, H. (1936). The nucleus in and the growth of hygroscopic droplets. *Transactions of the Faraday Society*. Available from https://doi.org/10.1039/TF9363201152.

[48] Mehta, P. K., & Monteiro, P. J. M. (2014). *Concrete: Microstructure, properties, and materials* (4th ed.). McGraw Hill.

[49] Zhang, Y., Anim-Danso, E., Bekele, S., & Dhinojwala, A. (2016). Effect of surface energy on freezing temperature of water. *ACS Applied Materials & Interfaces*. Available from https://doi.org/10.1021/acsami.6b02094.

[50] Ashworth, T., Tollefsen, B., & Weyland, J. (1979). Adhesion of ice to concrete surfaces—Preliminary results. *Transportation Research Board Special Report*.

[51] Makkonen, L. (2012). Ice adhesion—Theory, measurements and countermeasures. *Journal of Adhesion Science and Technology*, *26*(4−5), 413−445. Available from https://doi.org/10.1163/016942411X574583.

[52] Meuler, A. J., Smith, J. D., Varanasi, K. K., Mabry, J. M., McKinley, G. H., & Cohen, R. E. (2010). “Relationships between water wettability and ice adhesion. *ACS Applied Materials & Interfaces*. Available from https://doi.org/10.1021/am1006035.

[53] Husein, M. (2017). Preparation of nanoscale organosols and hydrosols via the phase transfer route. *Journal of Nanoparticle Research*. Available from https://doi.org/10.1007/s11051-017-4095-0.

[54] Husein, M. M., & Nassar, N. N. (2008). Nanoparticle preparation using the single microemulsions scheme. *Current Nanoscience*, *4*(4), 370−380, vol.

[55] Husein, M. M., Zakaria, M., & Hareland, G. (2012). *Novel nanoparticle-containing drilling fluids to mitigate fluid loss*. US Patent App. 14/377,438, 2016.

[56] Husein, M., Zakaria, G., & Hareland, M. (2017). *Use of nanoparticles as a lubricity additive in well fluids*. US Patent: 9,701,885B2.

[57] Husein, M. M., & Hareland, G. (2018). *Drilling fluids with nano and granular particles and their use for wellbore strengthening*. US Patent 9,920,233.

[58] Mehairi, A., & Husein, M. M. (2020). Enhancement of cement properties by means of in situ prepared nanoparticles. *Construction and Building Materials*, *261*, 120496.

[59] Husein, M., & Mehairi, A. (2020). *Cement compositions and methods of making the same*. PCT/CA2019/051014, WO/2020/019070.

Fundamentals and categorizations of waterproofing technologies

6

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

6.1 Introduction

Water may penetrate concrete structures under the driving force of pressure difference from the water head (permeation bulk flow) or under the driving force from surface tension or capillary absorption. Waterproofing (WP) technology is usually used for these various types of structures. The main aim of WP of concrete is usually to increase concrete resistance against the water penetration mechanisms, with or without a hydrostatic pressure. Concrete can be waterproofed by creating a barrier to prevent water from reaching the concrete surface. Alternatively, concrete is made a water-repellent through creating a physical resistance for wetting to prevent or minimize capillary suction, and/or it is made watertight by creating flow obstacles for decreasing concrete permeability for bulk flow of water under a hydrostatic pressure. The structural principles of porosity and permeability of concrete and the equations that relate the water penetration rate with the driving force for the transport (pressure drop) are introduced in Chapter 2. The wettability and related surface chemistry are introduced in Chapter 5.

As detailed in Chapter 3, concrete is subjected to various chemical, biological, and thermal attacks. Typical examples of water-associated concrete problems include: (1) concrete scaling and corrosion of embedded steel bar from the diffusion of chloride ion coming from deicing salts or other sources [1,2], (2) damages from acidic attack associated with carbonation reactions [3,4] and the associated corrosion [5], (3) deteriorations from the alkali aggregate reactions such as alkali − silica reactions (ASR) [6], (4) damages from the sulfate attack [7], (5) biological deterioration resulting from the biological activities such as mold growth [8,9], (6) plastic shrinkage and cracking resulting from the evaporation of water due the exothermic heat of hydration [10,11], (7) scaling and deterioration of concrete by thermal stresses resulting from water expansion-contraction during the freezing and thawing cycles [12]. These concrete problems loosen the concrete integrity and reduce the chemical stability of the binding material as well as the stability of aggregates. Consequently, these problems decrease concrete durability and structure sustainability. According to the European standard [BS EN 1504 [13]], the general principles of repair and protection of concrete include: (1) concrete protection against ingress, (2) moisture control within pores, (3) increasing concrete resistivity by minimizing moisture content, (4) improving the physical resistance of the surface, and

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00006-4

(5) increasing the concrete resistance to chemicals. These protection principles are all associated with WP systems. A long-time durability requires an efficient WP of concrete structure with discontinuous pores [14] and/or a protected surface from water reach [15]. For water retaining concrete structures, WP systems are used to prevent water absorption or penetration through the concrete structure. WP is an integral step in the process of preserving the building materials, and for improving the quality of interior spaces for human health.

WP of concrete can be a step in the process of concrete repair and protection or a basic process during construction. In fact, WP as a construction process is the responsibility of the entire construction team and suppliers rather than just an application of a system by a subcontractor [16]. As an integrated construction process, Kubal [16] introduced the "90%/1%" principle as the first WP principle. It indicates that 90% of water-related problems occur within external surface area that composes only about 1% of the body of the building or structure. This WP principle stresses on the need for proper handling of structure details in the below-grade structures within the overall construction process of the full project team.

In fact, concrete durability is also governed by the durability of the WP materials itself [17], and its proper installation. The WP materials may be attacked by the surrounding chemical, physical, and mechanical conditions and then they may be deteriorated. In such cases, the concrete structure becomes exposed back to water-related problems. The selection of WP materials is usually performance-based and it is set by the concrete designer and manufacturer specifications. There are general basic characteristics that are demanded for the selection of WP materials and for their effective applications. These include the chemical and physical characteristics of WP materials, and the chemical, physical, and mechanical conditions of the surroundings. The main issues for the durability of WP materials and hence the durability of the waterproofed concrete include the chemical stability of WP material, its bondability to the concrete surface, and its resistance to mechanical and thermal impacts from surroundings. The optimum selection and use of WP materials provide a strategic solution for water-related problems. This is also an economic parameter, as increasing the lifespan of concrete can be achieved by enhancing the durability [17] and reducing the maintenance cost of the structure.

This chapter builds on the aforementioned backgrounds for introducing the WP technologies. For the purpose of establishing a general background about the types of commercially available WP systems, this chapter introduces the basic WP concepts, definitions, approaches, mechanisms, categorizations, and requirements. Then, the internal WP systems are detailed in the subsequent chapters.

6.2 Waterproofing concepts and approaches

WP is a general terminology used in the construction industry as well as in other sectors such as clothing, furniture, paper packaging, electronic devices, etc. In the construction industry, WP is the process of hindering the flow or the absorption of water or aqueous solutions within the porous structure of cement paste in concrete or mortars. In general terms, WP is achieved by the application of a material onto or into a concrete structure for making it resistant for wetting, water absorption, and/or permeation flow, for the purpose of protection and/or retaining water within the structure. A watertight concrete, as specified by ACI Concrete Terminology [18], shall not allow the passage of water as it is made "impermeable to water except when under hydrostatic pressure sufficient to produce structural discontinuity by rupture." ACI Concrete Terminology [18] defines "waterproof" as "an idealized property of a material indicating imperviousness to water in either liquid or vapor state." The focus here is on minimizing the water penetration in liquid phase, the issue of vapor transmission is discussed in Section 6.6. In fact, it is not possible to obtain a completely impervious concrete structure. Thus the technical validity of WP term may be interrogated, as no material can be made completely impervious to water under infinite pressure over infinite time [18]. The WP term is widely used in the concrete industry using its relative meaning, that is, reducing water penetration.

WP of concrete can be based on installing a water barrier at the surface or treating the concrete with a material that has water-repellent characteristics, or filling or blocking the permeable space, which creates channels for water penetration including permeable pores and cracks. Based on such a wide spectrum of WP approaches, various definitions and classifications are used in the international standards and guides of WP. The guide issued by the American Concrete Institute (ACI) [ACI 515.1R [19]] focuses on the barrier systems as reflected by its title: "A Guide to the Use of Waterproofing, Dampproofing (DP), Protective, and Decorative Barrier Systems for Concrete." According to ACI 515.1R [19], WP techniques are categorized into capillary blocking, DP, and the use of membranes. On the other hand, the European standards [EN 1504−2 [13]] categorize surface treatments into coatings, hydrophobic impregnation (pore liners), and pore blockage (or pore sealing). The European classification is used by several authors [see, for e.g., [20]]. However, a more detailed and revised categorization is needed to provide a better differentiation between WP systems and to identify WP systems that are not listed, or not referred to sufficiently, in these standards, such as sealers and enhancers of chemical solutions that are added to mixing water during concrete mixing. For this purpose, the WP approaches are categorized, in this book, mainly into (1) creating an external water barrier at the structure surface that prevents or reduces the incoming water flux to the concrete, and (2) making the concrete structure, as a whole or as surface section, water-resistant to prevent or minimize water penetration. Fig. 6.1 shows schematic illustrations of these two main WP approaches: In Fig. 6.1A, WP of concrete is done externally by installing a continuous impermeable layer attached to the concrete surface without a noticeable penetration or significant effect on concrete pores. On the other hand, WP of concrete in Fig. 6.1B is done internally through redesigning of the pore structure in the paste, by pore blocking and refining the pore size, or by pore lining through changing the surface characteristics of the permeable pores (by making its internal surface water-repellent).

The first WP approach Fig. 6.1A includes various types of polymeric and nonpolymeric membranes and coatings while the second WP approach Fig. 6.1B involves internal modification of the concrete pores mainly through chemical (or physico-chemical) reactions. Each approach includes a group of applications. Fig. 6.2 provides the full hierarchal categorization of these WP approaches, which are further detailed in this chapter and in the subsequent chapters.

Traditionally, the prevention of water inward flow has been achieved through watertight barriers Fig. 6.1A that are installed at the dry surface of fully cured concrete. Barriers can be applied as liquid applied systems or preformed sheets. Internal WP is achieved by chemical additions and/or manipulation of the concrete mix design (see Chapter 4) or as a surface treatment using penetrating liquids that modify the pore structure. Integral WP admixtures and liquid penetrants make the concrete or a sectional part of it impermeable or water-repellent using reactive chemicals or densifying fillers. Internal WP is also referred to as integral WP because when the added chemicals react with cementitious materials, they become an integral part of the concrete structure (or more precisely, the chemicals become part of the structure of the cement paste). The functions of the integral WP materials are created either after their penetration into the concrete from a surface applied solution or dry shake powder or when they are premixed with the concrete ingredients during concrete production [21]. Some researchers and writers may restrict the use of internal/integral WP materials to those that are added to the concrete mixture including powder mixtures and solutions of active ingredients. However, the general classification of WP materials is better made simply to include surface applied systems (including membranes and coatings) and integral systems (including surface applied penetrants and concrete additions), which act from within the concrete structure and modify its pores [see, for e.g., Jalali and Afgan [21] and Biparva and

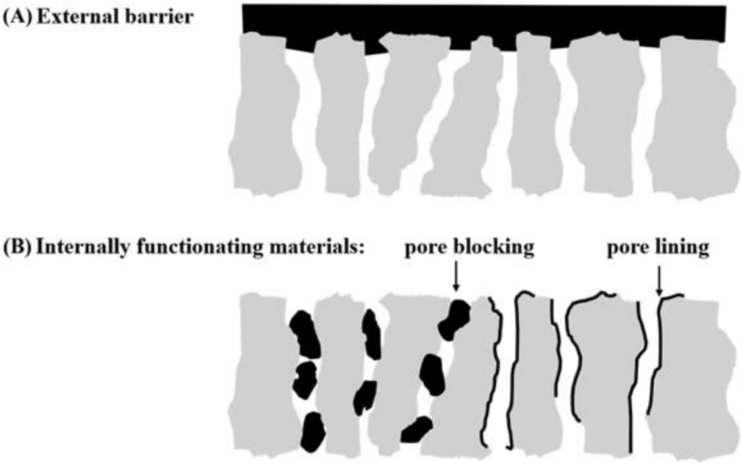


Figure 6.1 Illustrations of the two main waterproofing (WP) approaches indicating (A) the barrier systems and (B) the integral WP systems.

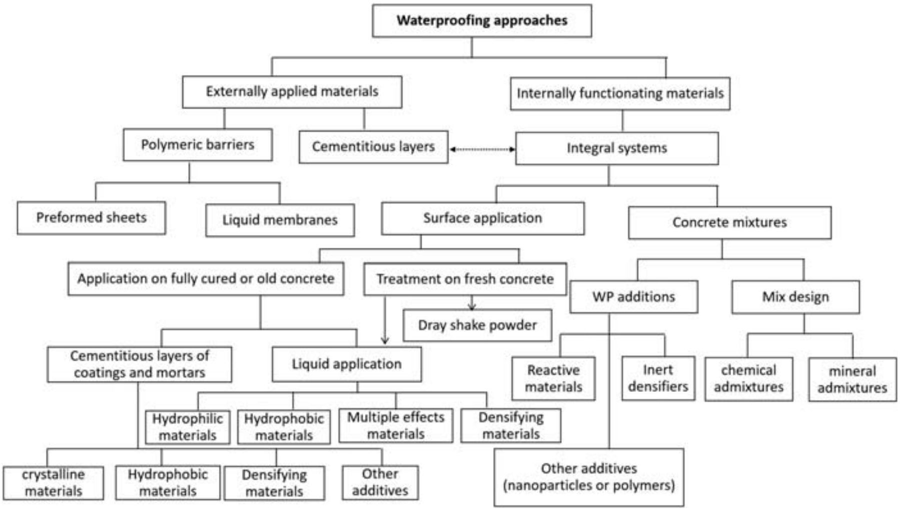


Figure 6.2 Full hierarchal categorization of waterproofing approaches.

Gupta [22]]. The detailed classifications listed in Fig. 6.2 create the ground for the general classification adopted in this book. These categories are believed to provide a better differentiation between the mechanisms of external barriers and internal pore modifiers and cover the full range of industrially available WP materials.

The used WP terminology may reflect some overlaps among various WP approaches. For example, it is hard sometimes to distinguish between coating systems and liquid membranes, or even to distinguish the coating terminology from the surface treatment penetrating materials. For example, in the two papers of Pan et al. [17,23], the surface applied WP systems were categorized into four types including coating, hydrophobic impregnation, pore blocking surface treatment, and multifunctional surface treatment. Such a categorization combines the coatings with liquid penetrating materials under "surface treatment." This is in line with the ACI Concrete Terminology [18] that defines coating as a "material applied to a surface of concrete by brushing, dipping, mopping, spraying, troweling, etc., to preserve, protect, decorate, seal, or smooth the substrate." ACI Concrete Terminology [18] also refers to chemical solutions applied to the surface of concrete under coating terminology, when it defines coatings as a "material used to protect a concrete surface from atmospheric contaminants and those that penetrate slightly and leave a visible clear or pigmented film on the surface." It links this definition to concrete sealers [18] and defines sealer as "a liquid that is applied to the surface of hardened concrete, is colorless, is absorbed by the concrete, leaves little or nothing visible on the surface, and either prevents or decreased the penetration of liquid or gaseous media" [18]. In the subsequent WP analysis in this book, membranes and coatings are grouped under external barriers, while reactive solutions applied to concrete surface are labeled under surface treatment. On the other hand, cement-based coatings and mortars are labeled under cementitious WP layers, which usually include pore penetrating integral WP materials among the cementitious materials used to create the external coating structure. Hence, from one perspective, they form continuous external layers, and from the other perspective, their ingredients penetrate into concrete pores and modify them. For this reason, the external WP layers may be considered to include polymeric barriers and cementitious materials as well as coatings that combine polymers with cementitious materials. There is an overlap within the integral WP materials between material additions to concrete mixtures for internal WP and similar additions to the external cementitious layers. The barriers are usually applied onto fully cured concrete, while liquid penetrating surface treatments can be applied to fully cured or freshly poured concrete.

6.3 Characterization approaches of waterproofing systems

In addition to the principal categorization of the WP approaches into external and internal systems, as described in Section 6.2, WP technologies can be categorized furthermore according to various characteristics and approaches. These various categorizations can be based on chemical compositions, basic WP structural functions, water hindering mechanisms, position of WP application with respect to concrete surface subjected to water, levels and severity of water exposure, permeability to vapor transmission, mechanisms of WP additions, application techniques etc. Table 6.1 lists the related sections or chapters, which discusses each categorization approach.

The generic chemical composition of WP includes polymeric membrane systems (sheet and liquid forms), chemical solutions of organic or inorganic compounds used for surface treatments or added to concrete mixtures, and mineral and organic powder admixtures. These types are detailed in Section 6.4. The application methods of WP materials depend on their physical and chemical characteristics and their general structural types (i.e., barriers or integral WP systems). These include a wide range of application/installation techniques that vary from adhering preformed WP sheets to the application of a liquid system onto hardened concrete, and the addition of WP materials into the concrete mixture at the time of batching. In precise technical terms, installation term is better restricted for placing preformed external barriers, while application may be used for the other WP systems. Fig. 6.3 shows pictures of sheet installation by adhesion and the application of liquid membranes by brushing. Fig. 6.4 shows a picture of the application of cementitious WP coatings, and Fig. 6.5 shows a picture of the application of a liquid penetrating solution by spraying.

WP of different structural components requires different characteristics, because of the differences in the ambient conditions. Concrete WP systems may be used for protecting a below-grade or an above-grade concrete structure. Differences include (1) the level of water exposure, for example, damping under a hydrostatic pressure versus periodic partial wetting without the buildup of a hydrostatic pressure, (2) the types of contaminations in water, (3) the temperature variations and possible phase change and wind effects, and (4) mechanical conditions (e.g., abrasion). These

Table 6.1 Approaches for waterproofing categorizations.

Categorization criteria	Sample types	Categorization perspective	Topic coverage
General	External versus internal waterproofing (WP) systems.	The depth of WP within the structure, and the time of its application (fresh concrete versus fully cured concrete).	Section 6.2
Structure and chemical composition	– External barriers and integral WP. – Polymeric, inorganic compounds, reactive etc.	The physical and the chemical structures of WP materials.	Section 6.4
Phases and application technique	Liquid membranes, semisolid sheets, slurries for cementitious coatings, solution sealers, powder admixtures, and solution enhancers.	The method that depends on the characteristics and the physical structures of WP materials at the time of applications.	Within the subsequent chapters according to their types.
Structure position with respect to the ground	Above-grade and below grade concrete structures.	Effects of the level of water exposure and the types of contaminations.	Introduced in this section.
Position with respect to the wetted concrete surface	Positive side versus negative side.	Possibility of concrete wetting and sandwiching effect of moisture and effects on the adhesion of WP materials.	Introduced in this section.
Water hindering mechanism	Pore lining for reducing capillary suction and pore blocking for reducing water flow.	Reducing capillary absorption versus reducing permeation flow.	Section 6.4
Level of exposure to water and the hydrostatic pressure	Waterproofing and dampproofing.	Continuous surface damping in water under a hydrostatic pressure versus a surface that is subjected to cycles of wetting and drying without a hydrostatic pressure.	Section 6.5

(*Continued*)

Table 6.1 (Continued)

Categorization criteria	Sample types	Categorization perspective	Topic coverage
Vapor permeability and breathability	Waterproofing and vaporproofing.	Differences in the permeabilities to liquid and vapor.	Section 6.6
Mechanism of water interaction	Water repelling or swelling and vapor adsorption.	The physicochemical interactions of WP materials with water including hydrophobic, hydrophilic, or hygroscopic.	Chapter 5 for the background, then detailed in the subsequent chapters.
Environmental concerns and toxicity	Solvent-based, water-based materials, powders.	The chemical type and the formulations of WP materials.	Section 6.9

conditions and the required characteristics are reflected on the suitable type of WP materials.

When WP materials are applied as a coating or a surface treatment, the position of its applications becomes crucial as it determines the level of accessibility of water to the concrete structure. This consideration is more critical for external barriers. From such a perspective, WP material can be applied to the negative or the positive side of water pressure on the concrete surface as shown in Fig. 6.6. Positive side WP is installed on the side that is wetted by water and faces the hydrostatic pressure. On the other hand, the negative side WP is applied on the opposite side of the wetted surface. In the common practices, most polymeric sheets and film forming materials are applied to the positive side. For new below-grade structures, the WP system is applied at the positive side before backfilling. Liquid penetrating integral WP materials are usually considered to be applicable to positive and negative side. On the other hand, the addition of integral WP solutions or powders treat the whole bulk of the concrete, not just one side and hence such a position consideration is not valid. This type may be considered as a third WP approach, which is not listed in ACI 515.1R [19].

The position of WP application has several impacts on concrete durability. For example, the negative side WP application allows moisture contact with concrete and hence promotes capillary absorption. This may cause a sandwiching effect of moisture due to moisture penetration from the unprotected surface subjected to water exposure. Such an effect may be considered as an advantage from the perspective of moistening the concrete structure [ACI 515.1R [19]], as it helps in minimizing drying and thus it assists in preventing shrinkage and the consequent cracking (see Chapter 3). However, from the perspective of freezing and thawing, this effect is detrimental as moistening the concrete increases concrete

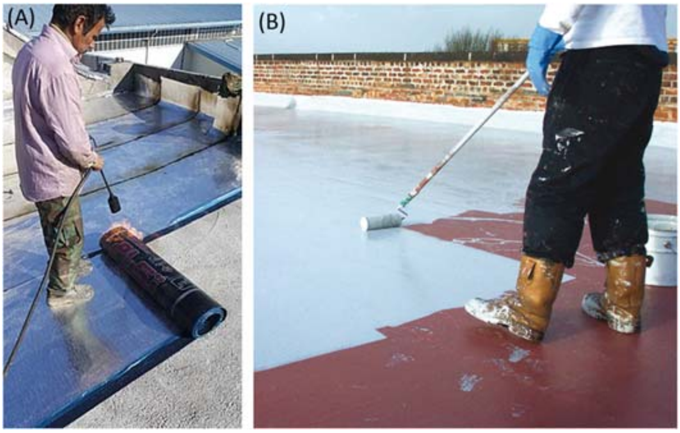


Figure 6.3 Application of (A) a sheet membrane by adhesion and (B) a liquid membrane.
Source: https://commons.wikimedia.org/wiki/File:%D9%86%D8%B5%D8%A8_%D8%A7%DB%8C%D8%B2%D9%88%DA%AF%D8%A7%D9%85.jpg https://commons.wikimedia.org/wiki/File:Liquid_roofing_process.jpg and https://commons.wikimedia.org/wiki/File:Liquid_roofing_process.jpg.

Figure 6.4 Application of cementitious coating by spraying.
Source: Courtesy of International Chem-Crete Inc.

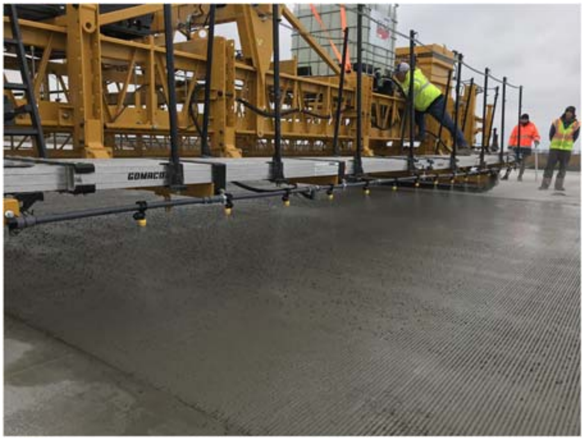


Figure 6.5 Application of waterproofing solution by spraying onto the surface of freshly poured concrete pavement.
Source: Courtesy of International Chem-Crete Inc.

deteriorations due to possible condensation and freezing within pores of cement paste (see Chapter 3). Also, the transfer of contaminants within the moisture transfer process leads to the penetration of aggressive chemicals into the concrete structure, which then causes other durability problems. For example, the penetration of dissolved materials (such as chloride ions) from the unprotected side may lead to the corrosion of reinforcement steel and lead to the associated expansive effects of corrosion products causing cracking (see Chapter 3). On the other hand, the application of internal WP within the bulk of concrete minimizes moisture penetration and causes no sandwiching, hence it decreases water-related problems. Other differences related to the position of WP application are associated with the accessibility of the WP side for repair and maintenance. This is obvious when backfilling is done for below-grade structures. Overall, positive side application and integral WP of concrete bulk are more efficient in protecting concrete from attacks by chemical, physical, and biological actions than negative side application of WP materials.

The other categorization approaches listed in Table 6.1 are discussed in the following sections. These include the general structures and chemical compositions of WP materials Section 6.4, distinguishing between WP and DP Section 6.5, distinguishing between WP and vaporproofing Section 6.6. Environmental concerns and toxicity of WP systems are discussed in Section 6.9. The subsequent chapters then detail the various WP systems.

6.4 Waterproofing compositions and structures

As described above, the wide range of WP materials include external barriers of membranes and coatings, penetrating liquids for surface treatment, and integral

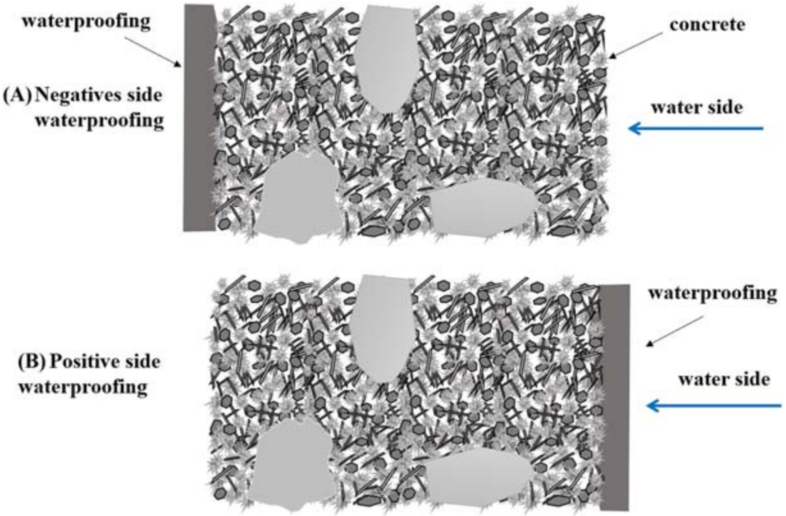


Figure 6.6 Application of waterproofing materials to the negative and to the positive side of water contact with the concrete surface, in (A) and (B), respectively.

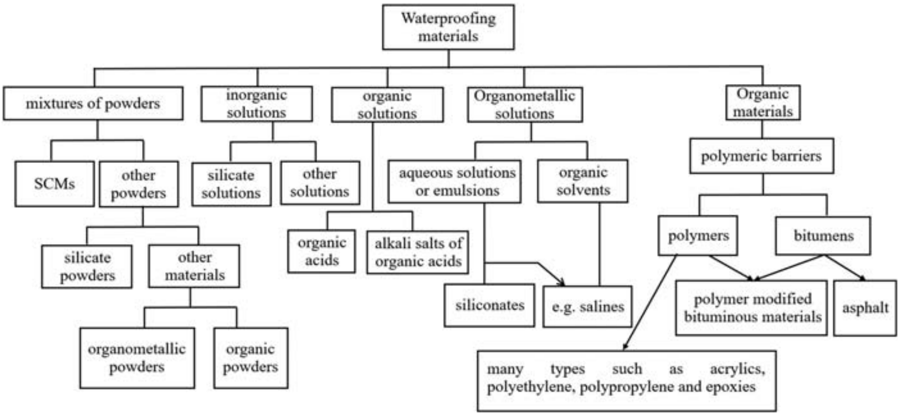


Figure 6.7 Chemical categorizations of the main constituents of waterproofing materials.

additions. Their physical structure at the time of application includes preformed semisolid sheets, polymeric liquids, dispersions and emulsions, chemical solutions, or dry blends of powders. The structure types and the compositions of WP materials depend on WP approaches as illustrated in Figs. 6.1 and 6.2. Some authors categorize the WP materials simply into organic and inorganic materials [17]. However, a more detailed chemical categorization is needed; the generic WP materials include organic-polymeric, organometallic, solutions of inorganic compounds, and mixtures of various types of powders and emulsions. The full hierarchy of the chemical categorizations of the main constituents of WP materials is shown in Fig. 6.7. These generic materials are formulated with other materials in order to make the WP system suitable for the required applications or installation methods. The main WP ingredients include reactive and nonreactive compounds, which exist as soluble materials, insoluble particles, or polymeric emulsified droplets or liquids. These types of chemicals are detailed in the subsequent chapters.

Other structural categorizations of WP materials are simply based on size of the functioning WP ingredients [see, e.g., [20]]. Muhammad et al. [20] focused on structural classifications more than chemical categorizations and hence they categorized WP materials into nanomaterials, micromaterials, and macromaterials. Other categorizations of WP materials combine physical structure, chemical composition, and WP approach in the same categorization system. For example, Diamanti et al. [24] categorized WP materials into film forming organic coatings, cementitious layers, pore-lining hydrophobic treatments, and pore filling treatments [24]. On the other hand, Nair and Gettu [25] categorized WP systems from the perspective of the basic structural function into the three main types of membranes, coatings, and modified cement mortars without assigning a category for surface treatment solutions or WP admixtures. They referred to some admixtures as additives to cementitious mortars. In the two papers of Pan et al. [17,23], WP materials applied onto concrete surfaces were categorized into coatings, hydrophobic impregnation, and pore blocking treatment agents. The applicable WP standards and industrial guides [see, for e.g., [13,26]] do not cover the full spectrum of the structures and the chemical compositions illustrated in Figs. 6.2 and 6.7. For example, the focus of ACI 515.1R [19] and ACI 515.2R [26] is mainly on polymeric materials, emulsions, and chemical solutions of organometallic compounds with only a brief description of the integral WP materials of crystalline type. On the other hand, ACI 212.3R-91 [27] covers WP additions under chemical admixtures and introduces the terminology of permeability reducing admixtures (PRA), as detailed in Chapter 7.

Table 6.2 lists the types and structures of all WP approaches (additions to concrete mixtures, solutions for surface treatments, cementitious layers, and polymeric barriers) in relation to their main WP mechanisms. The listed types of internal WP materials will be described furthermore in Chapter 7 and their main types will be detailed in the subsequent Chapters 8, 9, and 11. They are typically made in liquid or powder forms. WP powders are ready systems for mixing with concrete mixture. These include traditional mineral admixtures (Chapter 7). Other powder systems include organic and organosilicate compounds (Chapter 8) and other mineral particles (Chapter 9), which are used as admixtures, applied as a dry shake on fresh concrete or incorporated in the formulations of cementitious coating (Chapter 12). Liquid additions to concrete mixtures include traditional chemical admixtures (Chapter 7) and crystallization WP enhancers, which are added to the concrete mixtures at the time of batching (Chapter 11). The polymeric WP materials form external flexible impermeable barriers (Chapter 12).

The typical admixtures contribute with an integral WP role through reducing porosity. The mineral and chemical admixtures assist in pore refining through reducing the required mixing water and hence reduce water permeability. In both types of reactive integral WP admixtures, the active ingredients generally react with cementitious constituents, or in many cases with calcium hydroxide, which is the

Table 6.2 Materials and main mechanisms of waterproofing systems.

Main waterproofing (WP) category	Application method	Materials	Chemical family	Main waterproofing mechanism	Covered
Internal WP materials admixtures	Addition to concrete mixtures at the time of batching.	Mineral admixtures.	Cementitious powder.	Reducing porosity and permeability.	Chapters 1 and 7
		Chemical admixtures.	Chemical organic solutions.	Reducing porosity	Chapters 1 and 7
		Water repelling WP admixtures.	Organosilicon and other alkali organic powders.	Reducing concrete wetting.	Chapter 8
		Water swelling crystalline admixtures.	Cementitious powders.	Reducing porosity and permeability.	Chapter 9
		Multiple effect crystallization WP enhancers.	Proprietary reactive solution.	Reducing porosity and permeability and reducing concrete wetting.	Chapter 11
		Inert WP densifiers.	Cementitious powders.	Reducing porosity and permeability.	Chapter 9
		Other additions.	Polymeric powders.	Reducing porosity and permeability and reducing concrete wetting.	Chapter 7
Integral WP surface treatment	Topical surface treatment by spraying or brushing.	Water repelling materials.	Organosilicon and alkali organic solutions or emulsions.	Reducing concrete wetting.	Chapter 8

(*Continued*)

Table 6.2 (Continued)

Main waterproofing (WP) category	Application method	Materials	Chemical family	Main waterproofing mechanism	Covered
		Water swelling crystalline materials.	Silicate solutions.	Reducing porosity and permeability.	Chapter 9
		Multiple functional crystalline materials.	Proprietary reactive solutions of several materials.	Reducing porosity and permeability.	Chapter 10
		Densifying materials.	Solutions and emulsions of nonreactive compounds.	Reducing porosity and permeability (with possible reduction of wetting).	Chapter 9
Cementitious layers of coatings and mortars	Application of slurries as external layers by brushing, spraying, or troweling (or as a dry shake powder).	Water swelling crystalline ingredients.	Cementitious powders.	Reducing porosity and permeability.	Chapter 12
		Vapor adsorbing crystalline ingredients.	Cementitious powders.	Reducing porosity and permeability.	Chapter 12
		Water repelling ingredients.	Cementitious powders	Reducing concrete wetting.	Chapter 12
		Water repelling and filling inert particles.	Cementitious powders.	Reducing concrete wetting and reducing porosity and permeability	Chapter 12
		Polymer-modified cementitious barrier.	Polymeric powders incorporated in cementitious powders (or	Preventing water reach by formation of external flexible	Chapter 12

			emulsion for mixing with powders).	impermeable barrier.	
External flexible barriers of membranes and coatings	Spraying or brushing of the liquid membranes or adhesion of the sheet membranes.	Film forming liquid membranes.	Emulsions or reacting liquid polymers.	Preventing water reach by formation of external flexible impermeable barrier.	Chapter 12
		Preformed polymeric coatings.	Semisolid sheets.	Preventing water reach by the adhesion of flexible impermeable barrier.	Chapter 12

by-product of cement hydration. The products of reactions grow further within the concrete structure and create either (1) a pore-filling material leading to permeability reducing or (2) pore lining with a water-repellent deposited layer or precipitate, which reduces concrete wetting and reduces water absorption. Other integral WP materials act just as inert fillers that occupy a fraction of the pores and thus reduce its porosity. There are also polymeric additions to concrete mixtures for integral WP: ACI Concrete Terminology [18] specifies polymer-impregnated concrete as a hydrated hydraulic-cement concrete that has been impregnated with a monomer that is subsequently polymerized. These WP materials can be also incorporated in powder forms for cementitious coatings.

WP solutions for surface treatment include various types of active ingredients or precipitating inert fillers in water-based or solvent-based systems. After they are applied by spraying or brushing (see Fig. 6.5), the active ingredients react with cementitious constituents producing a thin layer of integral WP or forming insoluble precipitates or layers. They involve various types of interaction with water including water repelling and swelling and/or vapor adsorption. The precipitates (e.g., crystals) occupy a considerable fraction of the permeable pores and reduce water penetration. The formed water repelling layers minimizes capillary suction.

The cementitious layers of coatings and the modified cement mortars are usually made of dry mixtures of cement, fine sand, supplementary cementitious materials (SCMs), and possibly WP admixtures. The polymer-modified cementitious barriers are made from cementitious powders mixed with polymeric powders or with emulsion at the job site. The cementitious coatings may include crystalline ingredients, hydrophobic ingredients, hydrophilic inert particles, or polymeric additions blended with the mixture of cementitious powders. They are packaged in powder form ready material for mixing with water (or in some cases, mixing with a polymer emulsion) for application by troweling, brushing, or rolling (see Fig. 6.5). Then, as in the cases of liquid surface treatments, they perform by pore blocking, pore refinement, and/or pore lining mechanism depending on the types of the incorporated WP ingredients. In fact, they are essentially labeled under integral WP as the active ingredients penetrate, for example, by diffusion from the cementitious layers into the concrete structure, where they may react or deposit within the pores of concrete and become an integral part of the cementitious structure. The polymer-modified cementitious barriers prevent water reach by formation of external flexible impermeable barrier.

The polymeric barriers are mainly based on the formation of continuous external flexible impermeable membranes through chemical reactions and/or molecular crosslinking and entanglement. They generally prevent water from reaching the concrete surface. There is a wide range of polymeric materials that are used in the formulations of external WP barriers. The polymeric membranes and coatings come in precured sheet forms or in liquid-applied films, which are constructed in place and cured after installation on concrete [28] (see Fig. 6.3). The chemical formulation of barrier materials usually includes a film forming polymeric material or a combination of such materials in a carrier of organic solvent mixed with other additives such as fillers, and possibly with the addition of reinforcing fibers. Some formulations involve polymer emulsions in water. Typical polymeric barriers include asphalt, coal tar, acrylic, butadiene copolymer, chlorinated rubber, epoxy resin, oleoresinous, polyester resin, polyethylene copolymer, polyurethane etc [17,23]. These polymers have different chemical stabilities against environmental deterioration (e.g., resistance to degradation by UV radiation) and they have different mechanical properties (e.g., strength and elasticity). The types of liquid membranes include hot-applied and cold-applied membranes. From the perspective of the state of material before installation, liquid membrane systems include two types; single component membranes and multiple components liquid membranes. The single component membranes include bitumen WP materials of asphalt and coal tar [18]. They harden by curing through the evaporation of the volatile organic solvents, or through interaction with surroundings. The modified polymeric water-based emulsions cure by the evaporation of water. The multicomponents liquid membrane systems (e.g., polyurethane and epoxy) are polymers that cure through a catalytic reaction between a chemical catalyst from an additional component of the system. Sheet membranes are typically made of thermoplastics, vulcanized rubbers, or rubberized asphalts. Elastomers are macromolecular materials that are added in formulating high quality WP membranes due to their capability to undergo a reversible stretching upon loading. Sheet membranes are installed onto concrete surfaced by adhesion.

6.5 Dampproofing versus waterproofing

Preventing or minimizing moisture penetration in concrete usually demands the control of the ingress of moisture at various levels of hydrostatic pressures and various degrees of surface wetting and saturation, as illustrated in Figs. 6.8 and 6.9. The performance of WP material and its efficiency of hindering moisture penetration into concrete depend on the level of concrete exposure to water and the associated hydrostatic pressure. In general, the structure type, the depth in the underground, and the soil characteristics and contaminations are the governing factors for selecting the type of WP system. The water exposure level is determined by the period of concrete wetting, the level of concrete saturation, and the hydrostatic pressure exerted by water on the concrete surface. Typically, structures subjected to a hydrostatic pressure promotes higher penetration rates than structures subjected to partial cyclic concrete wetting, hence, they require more efficient and stable WP materials.

When the concrete structure is submerged in a body of water during its service life, a permanent hydrostatic pressure is exerted on its surface. In hydraulic [29] and marine structures [30], the hydrostatic pressure is dependent on the depth of water (see Fig. 6.8A and B). The pressure at any point can be obtained using Bernoulli equation [31]. Water penetration rate into concrete is strongly dependent on the pressure gradient. The governing relationship for permeation flow is given by the well-known equations for the flow through porous medium [31]. This is done using either the general Ergon equation [32] or using the specific cases of

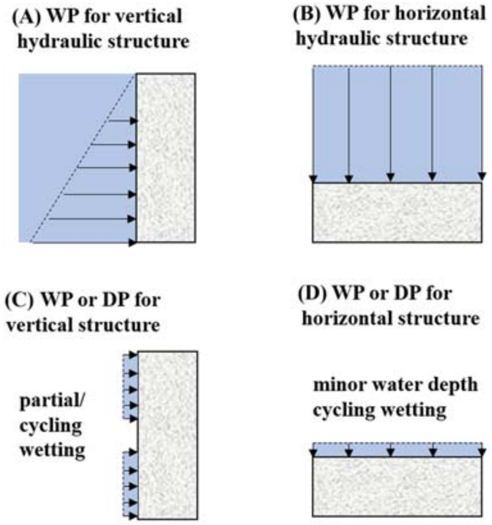


Figure 6.8 Waterproofing and dampproofing for typical concrete structures including hydraulic structures, (A) and (B), under hydrostatic pressure, and other normal structures, (C) and (D), without hydrostatic pressure.

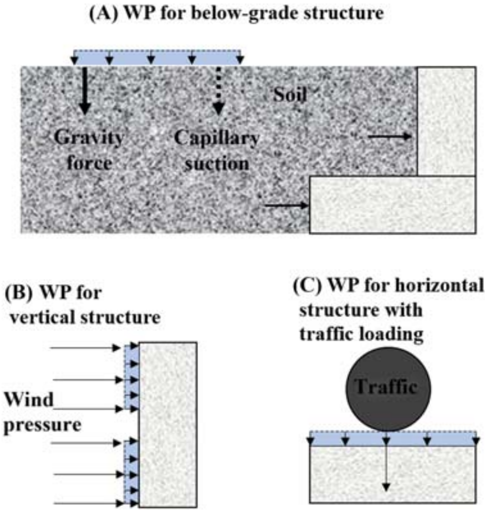


Figure 6.9 Waterproofing for typical concrete structures with hydrostatic pressure created by (A) water penetration within soil, (B) wind effect, and (C) from traffic loading.

Blake – Kozeny equation or Darcy's law for laminar flow in concrete, as described in Chapter 2. For below-grade structures, the concrete is usually subjected to a continuous water exposure due to water infiltration through soil (see Fig. 6.9A). In such a case, a hydrostatic pressure builds up on the concrete surface by gravitational flow and the capillary action of water in soil, which promotes moisture flow through soil voids. These effects drive water to migrate within porous structures at a flow (sorption) rate that depends on the porosity (e.g., distribution and size of pores of the soil), as described in Chapter 5. In addition, the water contents of mineral salts enhance water transport through the capillary pores due to the osmotic pressure. In some designs of below-grade structures, a drainage system may be used to reroute water around the structures, and thus preventing the buildup of a hydrostatic pressure.

In other structures, concrete may be exposed to just short periods of partial wetting, the water depths are typically within a few millimeters or centimeters (see Fig. 6.8C and D). In such cases no significant hydrostatic pressure is developed. Hence, water will not penetrate into concrete structure by permeation flow according to the above-mentioned laws. However, concrete is a hydrophilic material by nature and thus its surfaces possess strong interactions with water molecules through van der Waals forces and hydrogen bonding. These attractive forces create a water flow of capillary suction within concrete, as described in Chapter 5. The time-dependent water sorption rate per unit area of a cementitious material is strongly dependent on the pore structure. In general, the suction flow rate is governed by the porosity (pore size distribution and the average pore size), the surface roughness, and the water contact angle with the concrete surface. In these cases, water penetration length in concrete is dependent on the hydrophilicity, which is determined by the water contact angle as well as the time. Water penetration rate in this case is given by equations of sorptivity given by the capillary sorption coefficient or by other empirical swelling models (as described in Chapter 5). However, these structures with partial cyclic wetting may be exposed to hydrostatic pressure from wind effects and/or traffic loading (see Fig. 6.9B and C). Wind effects create additional driving forces for water penetration [16]. On concrete pavements, traffic loading may create a hydrostatic pressure at the point of traffic contact.

In order to distinguish WP according to the type of wetting conditions and the level of hydrostatic pressure, two different terminologies are used in industry. These are WP and DP. Hindering water penetration under a pressure with nearly continuous wetting is what distinguishes WP from DP materials. DP materials are used for minimizing water penetration in partially dry or unsaturated concrete [ACI 212.3R-91 [27]] (e.g., Figs. 6.8C and D). DP and WP terms are used in ASTM D449/D449M and highlighted in its title: “Standard specification for asphalt used in dampproofing and waterproofing” [33]. According to ACI 515.1R [19] WP is “the treatment of a surface or structure to resist the passage of water in the presence of hydrostatic pressure,” while DP is defined in the same manner but with changing the last sentence into “in the absence of hydrostatic pressure.” ACI 515.1R has been replaced by ACI 515.2R, in which protective treatment is used without reference to DP or WP terms. The DP is defined in the latest ACI Concrete Terminology [18] using a similar meaning to WP but with the inclusion of preventing vapor transport: DP is a “treatment of concrete or mortar to retard the passage or absorption of water or water vapor either by application of a suitable coating to exposed surfaces, or by use of a suitable admixture or treated cement, or by use of a preformed film such as polyethylene sheets placed on ground before placing a slab." Similarly, the WP handbook of Kubal [16] stressed the issue of preventing vapor transport with DP materials, by defining DP materials as those that resist the penetration of water vapor or minor amounts of moisture. In literature, WP terminology is widely used to describe the hindering or minimizing of water penetration in concrete, regardless of the presence or the absence of a hydrostatic pressure. In fact, it is meaningful to use these terms to distinguish between conditions of hydrostatic and nonhydrostatic pressure, as they reflect on the required mechanisms of internal WP materials, as they are discussed in the subsequent chapters. Another approach of categorizing WP systems based on the level of hydrostatic pressure is given in ACI 212.3R-16 [34]. ACI 212.3R-16 [34] distinguishes two types of PRA including PRA for hydrostatic conditions and PRA for nonhydrostatic conditions. These aspects are detailed further in Chapter 7.

In building applications, the depth of the foundations and the type of the utilization of the interior underground space govern the choice of WP and DP materials. WP materials are essential when the slabs and walls in below-ground structure are submerged in a water table continuously or periodically under a hydrostatic pressure. On the other hand, DP is used when the water table is lower than the concrete structure. DP materials should not be used if there is a chance that a hydrostatic pressure will be developed during the service life of concrete. These classifications are considered when describing the WP mechanism of integral WP materials in the subsequent chapters. For example, water-repellent WP materials usually cannot resist the penetration of water under a hydrostatic pressure. Consequently, the hydrophobic WP systems are usually suitable only for DP applications (as reflected in the title of Chapter 8). On the other hand, the use of pore blocking or filling WP materials increases the resistance to permeation flow through capillary pores and thus they are suitable for typical WP applications under a hydrostatic pressure.

6.6 Vaporproofing versus breathable waterproofing systems

Basically, vapor transport between concrete and the surroundings occurs by internal diffusion and possibly by convection (or more precisely advection) associated with wind effects (see Chapter 2), as illustrated in Fig. 6.10. The direction of vapor transfer between concrete and the surrounding air depends on the relative humidity and wind conditions of the surrounding air, in addition to the degree of concrete saturation. Then, internal transport of water vapor within concrete structure occurs from regions of high humidity and/or high pressure to regions of low humidity and/or low pressure. This occurs by the two transport mechanisms of molecular diffusion and advection (see Chapter 2), as illustrated in Fig. 6.10. Diffusional transport of moisture vapor is driven by the concentration difference within concrete. More specifically, the driving force in this case is the difference in humidity of air within concrete pores. The driving force for advection of vapor (moisture transport within

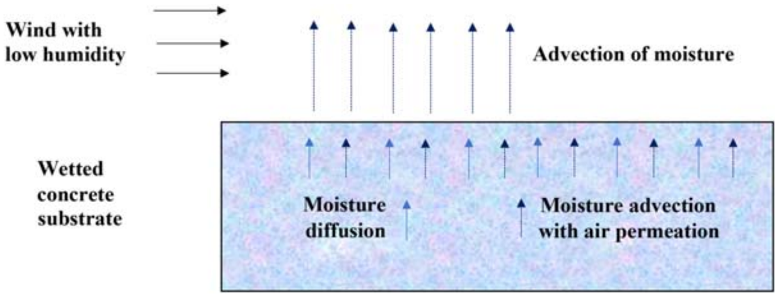


Figure 6.10 Moisture transport mechanisms between concrete substrate and the surroundings.

air permeation, as the carrier of the vapor) is the pressure gradient within concrete, which might be created because of pressure difference between internal and external areas in a structure, or within concrete. The vapor transport properties [35] are dependent on humidity and temperature gradient within the WP section or structure. It is also dependent on the types and magnitudes of the interactions between the vapor and the WP materials, such as possible adsorption/desorption process or hygroscopic interactions, as described in Chapter 5. Reducing concrete permeability for liquid water using WP systems may be associated with reducing the transport of water vapor and other gases. In principle, protecting concrete from moisture ingression considers the penetration of moisture in both phases of vapor and liquid. As detailed in Chapter 3, concrete durability problems are associated with various transport processes of gases (including water vapor) and water liquid. As mentioned in Section 6.2, ACI Concrete Terminology [18] defines the WP term by stressing on the concrete imperviousness to water in both phases.

Vapor transport into concrete may result in internal condensation (due to temperature variations). This leads to concrete wetting, which in turn interferes with various durability problems, and hence it is regarded as a negative impact. The permeability of a WP material to vapor transmission is correlated with concrete permeability for other problematic reactive gases. For example, the gas permeability of concrete for carbon dioxide causes carbonation durability problems as described in Chapter 3. Increasing air permeability increases the rate of carbonation, and thus increases the rate of corrosion of the reinforcing steel bars [17]. More extremely, gas transmission in concrete walls of buildings is related to health and environmental problems of the penetration of the hazardous Radon gas [36] from soil into the basements of residential buildings, which also occurs by diffusion and advection [37,38].

On the other hand, the promotion of vapor transmission is also essential for concrete durability. The ACI guide to selecting protective treatments for concrete [ACI 515.2R-13 [26]] suggests that ensuring a moist concrete through allowing moisture transmission into concrete may assist in preventing concrete shrinkage by drying. In addition, the outward vapor transmission from concrete is essential for controlling several water-related problems. This is referred to as “concrete breathing,” which is an advantageous characteristic of allowing outward vapor transmission from concrete. A sufficient vapor permeability is needed to ensure an acceptable level of breathability [17]. Such a breathability is required as humidity is an essential factor for mold growth within concrete, which creates a serious durability problem (see Chapter 3). Thus concrete dryness, by allowing the escape of water vapor through concrete capillary pores (concrete breathing), is demanded for preventing or minimizing biological attack associated with mold growth in concrete pores. Also, the condensation of entrapped water vapor within the pores increases the degree of pore saturation and then contributes negatively in the mechanisms of other durability problems such as concrete damage from cycles of freezing and thawing [17].

In addition, the breathability characteristic of WP barriers and concrete affects the level of adhesion of polymeric membranes and coatings with the concrete surface [17]. It is reported that the adhesion strength is decreased significantly when the rate of vapor emission through the WP material is larger than 283 μg/s [17]. Air permeability of many polymer coatings, such as epoxy and polyurethane, is almost zero. This is considered as one of the main disadvantages of polymer coatings [17] (see Section 6.9). Poor adhesion of WP barrier to the concrete surface may occur because of the vapor transmission from within concrete and then its accumulation under the WP material. When a WP membrane is applied on the negative side (see Fig. 6.6), the vapor transmission toward the waterproofed surface affects the bonding strength of the membrane to concrete. If the WP membrane does not allow the vapor transmission, water condensation at the interface between the concrete surface and WP membrane causes blistering. Surface accumulation of moisture below WP membrane after its curing may result in having a too damp surface and lead to peeling of the WP membrane. From this perspective, the European standard EN 1504−2 specifies breathability as an essential characteristic for preventing blistering of membranes and coatings from the buildup of pressure from vapor accumulation and condensation at the interface of concrete and the WP barrier [13]. Blistering of membranes and coatings is also related to the vapor transmission in concrete structure itself. In some concrete applications, a polymeric barrier may be applied on integrally waterproofed concrete, which reduces vapor emission considerably [39]. This would enhance adhesion and reduce membrane plastering problems.

For the above-mentioned reasons, the ability of WP systems to promote or reduce the penetration of water vapor is an essential criterion in evaluating and characterizing WP materials. Preventing vapor penetration through concrete is referred to as vaporproofing or vapor barrier. ACI Concrete Terminology [18] defines the vapor barrier (or moisture barrier) system as “a membrane located under a concrete floor slab that is placed on the ground to retard transmission of water vapor.” Typical DP barriers resist the vapor migration from soils into the interior of buildings.

The question of whether the WP materials shall be a vaporproofing and hence a gas barrier material or not is a dualistic issue. The effect of WP materials on vapor and air permeabilities must be carefully considered [17]. Considerations in this regard shall be given to the specific job application and requirements of WP durability and public health. Overall, the reduction in the permeability of WP materials to moisture vapor is an important criterion in selecting WP systems. In the review of Nair and Gettu [25], several WP systems were favorably described as “breathable” [13]. For integral WP systems such as hygroscopic crystallization (see Chapters 10 and 11), vapor transmission is associated with interaction mechanisms between WP crystals and humidity (i.e., reversible hygroscopic mechanism as described in Chapter 5). The hygroscopic crystals grow by the adsorption of water vapor on the crystals. Such crystal growth consumes water vapor [39], resulting in a lower moisture transmission through concrete, without the accumulation of vapor within the pores. Instead, the vapor is consumed in enhancing the pore blocking efficiency, which assists in reducing further moisture penetration [39].

6.7 Selection of waterproofing materials and application requirements

Similar to any selection process of an engineering material, cost, availability, service life, and track record of previous applications are the basic selection criteria for WP materials [28]. The proper selection and the appropriate application of WP enable project engineers to avoid most of the failures of WP systems. Kubal [16] stated that only 1% of WP failures in buildings are related to the failure of WP systems due to manufacturing problems. On the other hand, most of the failures are related to other reasons of material selection and application. Based on such observations, Kubal [16] defined the 99% principle by stressing that approximately 99% of WP leaks are attributable to causes other than material failures, but resulting from improper specifications, installation, insufficient surface preparation, and incompatibility of WP and other structural materials. Overall, the selection criteria of the WP materials for effective applications and service can be categorized into technical, economic, and environmental parameters.

The technical selection of WP materials includes the review process of their basic characteristics, ensuring compatibility with application and service conditions and satisfying the requirements of the concrete surface that receives the WP material. The basic required characteristics for efficient WP service functions include a range of chemical and physical characteristics and mechanical properties. These include, for example, WP stability against degradation by environmental actions in order to ensure the durability of the waterproofed concrete. The surface of the concrete structure must satisfy a range of requirements in order to have suitable physical and mechanical conditions before installing the WP materials.

The effective application of WP materials requires suitable characteristics of WP materials, surface preparation, proper ambient conditions, and material installation practice. These aspects are normally detailed and well-documented in the technical literature of the WP manufacturer (e.g., application guides and manuals). The application-related features of WP materials include surface preparation requirements, brushing and spraying characteristics, tolerance to substrate moisture, temperature dependence, and site access [40]. The efficiency of WP materials is governed by the application method (e.g., for internally mixed in or externally applied materials) and the dosage or the surface coverage of the WP treatment [17]. The efficiency of surface applied WP material (solutions, cementitious coatings, and polymeric membranes) is strongly governed by surface characteristics of the concrete substrate. These include concrete age, quality, and moisture content. Concrete preconditioning methods of old and fully cured concrete include typical cleaning methods by water and detergents as well as other mechanical (e.g., sand blasting) and chemical preconditioning (e.g., acid etching) [19]. Other application and curing-related characteristics of WP materials include penetration of WP ingredients, thickness of WP barrier, adhesion capability to wet concrete. The effective application of WP materials is also strongly affected by the ambient conditions (e.g., temperature and humility of the surrounding air and temperature of concrete surface). The temperatures impact the level of moisture content in concrete and pressure of entrapped air within concrete pores. For example, film forming WP membranes are recommended to be applied in midday time to ensure proper conditions [ACI 515.1R [19]]. Surface preparation is essential for ensuring sufficient bonding and structural integrity [13] in order to ensure the best performance of WP membranes [13], and other penetrating WP materials. These requirements demand that the concrete surface must be solid and sound without unrepaired defects or residuals of debonding noncompatible materials with WP materials. For the application of polymeric barriers, surface smoothness and dryness are required [28]. On the other hand, wet surfaces are demanded for the application of cementitious slurries to form coatings [17]. Some surface treatment solutions can be applied efficiently onto fresh concrete [41]. However, typical hydrophobic WP surface treatments are believed to be better applied on fully cured concrete, as less WP efficiency is obtained when it is applied on fresh concrete [17].

For externally applied WP materials, the penetration affects the efficiency of WP materials. Polymeric coatings usually have a limited penetration depth [e.g., 100–300 μm for acrylic and 200–400 μm for epoxies [17]] and their function is based on the external barrier they form. For liquid membranes, ensuring the formation of a continuous membrane under the conditions of structure application is more crucial than their penetrability. In fact, the WP functions of polymeric coatings are not based on changing the characteristics of the concrete pores and hence their limited penetration depths are usually accepted. However, the liquid penetrating internally functioning WP materials are required to have higher penetrability. Hence, they have much higher penetrability than liquid membranes. For example, typical reported penetration depths are about 12 mm for silanes and more than 19 mm for ethyl silicate [17]. The effectiveness of surface treatment is enhanced by its penetrability, which is increased with increasing the concrete porosity [17]. The surface applications (e.g., number of brushings or number of coats) affect the effectiveness of WP treatment [17]. In some applications, surface treatment by concrete immersion in solution is believed to yield a better performance than brushing and spraying [17]. Additional brushing of hydrophobic surface treatment does not lead to a proportional increase in the effectiveness [17].

Compatibility of WP materials (e.g., admixtures) with the cementitious materials without having significant negative impacts on the cement hydration process are very vital characteristics for adding integral WP materials (solutions and powders) to concrete mixtures at the time of batching. These requirements include compatibility with cementitious materials so that these additions will not cause destabilization of cement particles in fresh mixes or does not cause negative impacts on its workability or slump of fresh concrete. In addition, these additions shall not interfere natively with the reaction kinetics of cement hydration or with the rate and the level of heat liberation from these reactions. In fact, these additions must target WP and durability benefits without any other negative impacts on mechanical properties [39]. These aspects are further detailed in Chapter 11.

The cost-related parameters for coatings include cost of unit materials, surface coverage, number of required coats, film thickness, labor and maintenance costs [40]. The environmental parameters include, for example, the level of toxicity of the WP materials and the impacts of their production and applications on environment, water resources and public health. The external polymeric barriers are petroleum-based materials, which are usually harmful to the environment [22]. Their production and installation is associated with pollution problems such as emissions of CO_2 and volatile organic compounds (VOCs). VOCs are harmful to the environment and public health and involve fire and explosion risk during application (e.g., spraying). These problems are also associated with some integral hydrophobic WP materials since solvent-based solutions release (VOC). On the other hand, WP materials that are based on environment friendly formulations pose no or low level of toxicity and hence are environmentally favorable [39]. Nontoxicity characteristics are also essential during the application and flushing of any residuals of WP materials.

6.8 Performance characteristic of waterproofing materials

The WP materials may degrade by several physical and chemical interactions with the surroundings. The service lives of the waterproofed concrete and the WP treatment are shortened by the slushy attacks. The durability of a waterproofed concrete is strongly dependent on the durability of protection treatment itself. The main characteristics and performance parameters of WP systems include: (1) efficiency in reducing concrete wetting and/or water penetration, (2) efficacy in enhancing durability, and (3) impact on the mechanical properties and other concrete characteristics. The efficiency of WP materials in reducing water penetration is usually investigated and evaluated through structural tests and through measuring water absorption, and/or permeability in addition to measuring water contact angle with the surface. Additional groups of transport characteristics of concrete, which are related to durability, are normally investigated. These include gas permeability such as those for water vapor, air, and CO_2, and ionic diffusion such as chloride ion penetration. The required durability characteristics of the treated concrete include resistances to freezing and thawing cycles, scaling, chemical attack, acid attack, sulfate attack, ASR attack, biological attack, and carbonation, as well as corrosion resistance of embedded steel, shrinkage deterioration, and crack bridging ability. The required mechanical characteristics of treated concrete include compressive strength, tensile strength, flexural strength, surface hardness, and bond strength. These characteristics are usually investigated and compared for various WP systems [see, e.g., the review of Pan et al. [17]]. Many relevant ASTM standards for evaluating the WP membranes are listed by Russell [28]. A review of types of tests and methods usually used for evaluating characteristics with integral WP materials is presented in Chapter 7. The performance trends of various WP materials are given in the subsequent chapters for each type of WP materials.

The durability of WP/protection material itself is dependent on the level of the potential defects and possible disintegration caused by the surroundings. The chemical stability of WP material and its resistance to thermal and mechanical surroundings' impacts, and its integrity or bondability to the concrete service are the key characteristics for the durability of WP treatment and hence the durability of the waterproofed concrete. Durability of WP material is dependent on the temperature cycle, dry-wet cycle, and radiation [23]. According to Basheer et al. [40], the required characteristic for ensuring the coating durability must include adhesion, UV resistance, water resistance, chemical resistance, impact resistance, elasticity, film hardness, abrasion resistance, toxicity, dirt pick-up, and color retention. The main required characteristics of the WP materials are categorized and described in the following groups:

1. Chemical characteristics of WP materials.

   The chemical stability of WP material must ensure its resistance to degradation or disintegration by thermal and chemical actions of the surroundings. These include its resistivity to chemical and biological attacks and its resistance to UV from sunlight. For pavement applications, the WP has to be appropriately resistant to deicing salts [42]. Other related characteristics include color retention and preventing dirt pick-up [40]. The stability of WP materials becomes more crucial when the concrete and WP material will be exposed to physical, chemical, and/ or biological attacks. The chemical durability of the polymeric WP membranes depends on the type of polymer used in their formulations. For example, bitumen-based WP materials may have a limited service life under the exposure to sunlight, as they lose their ductility and become fragile due to long exposure to UV radiations. Reemulsification of bituminous WP membranes [25] is another issue of instability due to the interaction with water from the surroundings in continuously wet or water-damped applications. The chemical solutions and admixtures (liquids and powders) used for internal WP materials are not usually associated with stability issues as they become an integral part of the concrete. However, organic-based materials may face biodegradation and/or UV degradation problems.
2. Mechanical characteristics of WP materials.

   The required mechanical characteristics of WP materials demand that WP materials (or the waterproofed concrete) must be capable of absorbing the mechanical impacts without causing damage in its structure or integrity. The key mechanical characteristics of the installed WP material include bond strength, surface resistivity to mechanical actions (e.g., hardness and abrasion resistance), and elasticity. In some cases, sufficient flexural, tensile, and compressive strengths are essential for external barrier systems.

Adhesion bond strength is a key criterion for polymeric membranes. The barrier must be bonded to the concrete substrate strongly for ensuring its long-term performance. The adhesion of WP material to the concrete surface depends on material characteristics and setting mechanism (e.g., chemical or thermal), on the state of the barrier at the time of installation (e.g., a liquid or sheet), and on the type of adhesive material used for installing the sheets on concrete surface. Bond strength becomes more crucial when WP material is applied to the negative side, as water penetration from the positive side toward the WP interface with concrete and/or vapor transmission and condensation below the vapor-proofed membrane may create a hydrostatic pressure that pushes the WP barrier off the surface. ACI 515.1R [19] requires that the bond strength should be at least equal to tensile strength of concrete so that the barrier does not detach unless the mechanical action cannot be resisted by the concrete itself. Typically, the adhesion bond strength must not be less than 1.4 − 1.75 MPa [17]. Such a requirement is met by several typical coating systems. For example, the bond strength of cementitious coatings and mortars is within the range of 2.2−3.3 MPa and that of the epoxy systems is within the range of 2.9−4.0 MPa [17]. The bond strength is governed by the properties of the materials of the coatings and primer as well as the quality and preconditioning of concrete substrate and application [17]. The bond strength may be improved by ensuring surface requirements before WP installation as described in Section 6.7.

Abrasion resistance (or surface resistance to wear action) is a significant parameter when WP materials are applied on exposed surfaces subjected to eroding surroundings such as traffic, water flow, and/or moving machines (e.g., pavements, parking decks, bridge decks, water canals). When a WP membrane is applied at the positive side of an exposed concrete in the above-grade structures, the bond strength becomes more critical, in order to enable the WP material to resist the traffic-bearing application and to prevent blistering. In such cases, surface hardeners with WP function such as silicate solutions (see Chapter 9) may assist in responding to the wear effects.

Cracking resistance is one of the required mechanical characteristics [17]. The WP material must have the ability to absorb mechanical impacts from structural instability and movement in order to prevent or minimize cracking. For this purpose, the barrier WP materials must have a sufficient flexural strength to absorb concrete shrinkage effects. In addition, the WP barrier must have a suitable thermal expansion coefficient to absorb stretching from temperature variations within concrete. For elastic membranes, stretching and sufficient elastic reforming are essential to prevent concrete cracks that may form after WP application. Hence, many polymeric WP materials are formulated to include an elastic polymer and/or they are reinforced with fibrous materials. On the other hand, some WP materials are required to have the ability to bridge cracks that occur before WP application or that develop during service life through the criterion of self-healing. For this purpose, many industrial integral WP formulations are developed to ensure self-healing or self-sealing by having a reactive material that can bridge possible cracks utilizing the products of crystallization reactions (see Chapters 9−11). For cementitious protective coatings and mortars, a sufficient compressive strength is required for coating durability. Cementitious crystalline WP coatings have the self-healing characteristics (see Chapter 12).

3. Service and environmental characteristics of WP materials.

The characteristics of WP materials that are related to environment and public health include safety and nontoxicity, as mentioned in Section 6.7. For example, the WP materials must not possess any negative impact on the quality of portable water when it is used in water retaining structures [39]. The safety criterion is also critical for WP applications that will be under traffic such as concrete pavements and floorings. For this purpose, the

WP material must have a sufficient skid resistance and interface friction coefficient. In addition, the WP systems must require minimal repair and maintenance activities during the service life of concrete.

6.9 General comparison of waterproofing systems

Each WP approach of external layers and internally functioning materials has its own advantages that attracts designers and specifiers specially for certain project requirements. In fact, the two approaches have wide ranges of materials and characteristics that makes it hard to provide an extensive comparison among these systems considering the full spectrum of WP characteristics and ranges of materials and structures. Table 6.3 highlights selected general comparative aspects between the polymeric barriers and the internal functions of WP systems from structural perspectives and other installation, maintenance and economic parameters. The comparative highlights can be summarized in the following points:

1. Structure continuity and integrity.

   Membranes are made of heterogeneous material with respect to cementitious constituents. They consist of organic compounds that are not typically homogeneous with cementitious mineral oxides. On the other hand, internal WP materials penetrate inside the concrete and in most cases react to produce compatible materials that are integrated with cementitious constituents. Thus the internal WP materials provide better bonding characteristics than heterogeneous barriers of polymeric nature. The internal WP materials form stable solid compounds within the capillary pores, which create structural bonds with concrete internal surfaces and become an integral part of the cement paste. Some of the internal WP materials have the ability to interact with moisture and grow inside the pores prompting better concrete filling. Overall, integral WP have better compatibility and bondability to the concrete than the polymeric WP barriers and they do not encounter adhesion problems, which are usually encountered with polymeric membranes. Integral WP admixtures and enhancers make the concrete itself a full WP barrier.
2. Structural dynamic activity.

   It is known that the flexibility and elasticity of many membranes provide them with the ability to bridge or accommodate moving and developing cracks during the service life of concrete [28]. However, the membrane systems are susceptible to puncturing damages from the external mechanical impacts during service for exposed surfaces [43] or during backfill of below-grade structures [21]. The resulting holes and breaches threaten the integrity of the entire WP system [21]. On the other hand, the integral WP systems are not subjected to puncturing or tearing [21]. A localized failure of a membrane may lead to the failure of the entire membrane system [43]. However, a localized failure of integrally waterproofed concrete can be handled separately. In fact, the self-healing characteristics of many internal WP systems assist in maintaining concrete integrity. Many crystallization WP materials have better response to concrete cracking through crack healing reaction and crystal growth (as described in Chapters 9−11).
3. Stability.

   Most of the integral WP materials form stable solid compounds (similar to cementitious constituents) within the capillary pores that structurally become an integral part of the

Table 6.3 Overall comparison between waterproofing systems.

Materials	**Polymeric membranes and coatings**	**Cementitious coatings and mortars**	**Solution surface treatment**	**Internal waterproofing (WP) additions to concrete mixtures**
Structure continuity	Heterogeneous	Homogeneous	Compatible integral compounds	Compatible integral compounds
Bonding problems	Crucial	Important	Integrity is ensured	Integrity is ensured
Flexibility	Flexible	Rigid but can be flexible with polymer modification	Rigid	Rigid
Structural dynamic activity	Crack bridging through membrane elasticity	Crack self-healing through crystal growth	Crack self-healing through crystal growth	Crack self-healing through crystal growth
Possible rupturing and blistering	Possible	Possible rupturing	Less frequent surface damages	No
Overall stability	Low	High	Typically, high but low for organosilicon compounds	High
Durability	Low	Moderate	Moderate	High
Breathability	None or minimal	Reasonable	Reasonable	Reasonable
Required surface condition of concrete	Dry substrate and smooth surface	Saturated with water	No special requirements	Not applicable

(*Continued*)

Table 6.3 (Continued)

Materials	**Polymeric membranes and coatings**	**Cementitious coatings and mortars**	**Solution surface treatment**	**Internal waterproofing (WP) additions to concrete mixtures**
Required concrete age	Fully cured	Coatings and mortars for fully cured and dry shake powder for fresh concrete	Fresh or fully cured concrete	Added to concrete mixture
Application position	Positive side	Positive and negative sides	Positive and negative sides	The entre concrete structure
Installation complexity/ simplicity	Requires special equipment and well-trained applicators and expertise	Requires well-trained applicators	Requires trained applicators	No special requirement
Repair accessibility	Very difficult or impossible	Feasible with difficulty	Easy	Not particularly needed for WP material
Overall cost	Very expensive	Expensive	Reasonable	Nonexpensive
Safety	Involves handling hazardous materials	Safe with no toxicity	Safe with no toxicity for some types	Safe with no toxicity

concrete. On the other hand, the polymeric materials and surface barriers may be subjected to deterioration effects from the surrounding. Polymeric coatings usually degrade with aging [17]. Hence, integral WP materials are more durable and have a better chemical stability than the polymeric WP barriers, which are usually susceptible to damages. Membranes are known to deteriorate over time while integral WP materials are resistant to physical damage and chemical deterioration [21]. Typical crystalline WP materials are reported to be very resistant to chemical attack and are stable within a pH range of 2—12 for cyclic contact and 3 for continuous contact [21]. Some organic integral WP materials may be subjected to chemical or physical deterioration at the concrete surface and cannot resist UV radiations. Also, the stability of hydrophobic surface treatment (e.g., organosilicon compounds) is also affected by UV radiations (see Chapter 8).

4. Vapor permeability.

Many polymeric membrane WP systems are vaporproofing materials, while most of the integral WP systems are breathable and characterized with a reasonable permeability to vapor transmission. The promotion of concrete breathing by the integral WP systems creates better dryness conditions. The breathability of integral WP systems is considered as an advantage over polymeric membrane systems, as humidity has a crucial role in promoting the biological attack and other durability problems (as described in Section 6.6). Such an advantage of minimizing concrete moistening reduces possible damages from cycles of freezing and thawing. In addition, the internal WP admixtures create a bulk WP characteristic for the entire concrete structure; thus they do not suffer from the sandwiching effect of moisture, which is one of the drawbacks of applying WP membranes on the negative side (see Section 6.3).

5. Installation complexity/simplicity.

The surface condition and age of concrete is crucial for the successful installation and adhesion of the polymeric membranes [e.g., dry substrate and smooth surface [21]]. However, for integral WP materials, wet surfaces are either needed or acceptable for applications. Usually, the installation of membrane systems requires special equipment and well-trained applicators and expertise [21]. Gupta and Biparva [43] highlighted that workmanship is one of the drawbacks of polymeric membrane systems. Possible installation errors have been identified as disadvantages of the polymeric membranes [21]. Poor installations were identified in the survey of Russell [28], as reasons for not using membranes (asphalt overlays). For example, in Quebec, the use of liquid membranes was stopped due to installation issues related to the difficulty of ensuring the required thickness [28]. On the other hand, integral or crystalline WP systems are simple to apply with minimal application errors [21]. For integral WP admixtures the material is simply added as other concrete ingredients. The service life and performance of integral or crystalline WP systems are not dependent on the skillful installation workmanship [21]. They do not demand high surface requirements of dryness and smoothness.

It is also worth recalling that the polymeric membrane WP systems are applied on one side of concrete and can ensure concrete protection from the ingress of water and chemicals from that protected side [43]. The positive side application is usually a must for most of the polymeric membranes. On the other hand, such a condition of position (negative or positive) is not applicable for integral WP admixtures, as the entire concrete structure is waterproofed and the whole concrete is made as a WP barrier without any consideration to the water side. In addition, the crystalline WP surface treatments and cementitious coatings can be applied to positive and negative sides, as their active ingredients have the ability to penetrate deep below the surface layers [21].

6. Repair accessibility.

The inaccessibility of the top surface of the concrete deck with membrane systems to be inspected was identified as one of the reasons for not using membranes (asphalt overlays) [28]. Russell [28] indicated that adopting an integral WP approach (e.g., full-depth low permeability concrete) offers the advantage of maintaining the concrete deck exposed for accessible visual inspection of future deterioration. Failure of the membrane system may allow water to penetrate under the membrane through the easiest flow route and penetrate into the whole concrete structure. This problem makes identifying and repairing the membrane damage almost impossible [43]. Gupta and Biparva [43] highlighted that difficulty to repair membranes is one of the drawbacks of membrane systems. In addition, replacing the damaged WP system is usually a complicated, costly, and very time consuming process [43]. For the below-grade structures, replacing the damaged WP system requires the excavation processing and then backfilling after maintenance [21].

7. Safety and environment.

The external polymeric barriers and solvent-based integral WP materials pose harmful impacts on the environment and public health [22]. On the other hand, the crystalline WP materials are typically nontoxic mineral materials. They can be used for water retaining structures [e.g., potable water storage [21]]. In addition, the integral or crystalline WP materials assist in sustainability as the concrete is maintained to be recyclable at end of its life, unlike the polymeric coated concrete [22].

8. Cost.

The polymeric barriers are usually expensive, from the perspective of material cost per covered area and from the perspective of the installation process. Their service life may be limited by the wearing conditions [28]. Gupta and Biparva [43] highlighted that cost and construction time are among the drawbacks of membrane systems. In the survey of Russell [28], the short service life of asphalt overlays was one of the reasons for not using membranes (asphalt overlays). Gupta and Biparva [43] believed that the membrane WP systems are most superior in terms of effectiveness on day one, then their effectiveness decreases with time as the bond strength between the membrane and concrete decreases and the quality of the membrane itself declines. In addition, the external WP systems are applied onto cured concrete structures, which require additional construction management activities and costs [43]. On the other hand, the integral WP admixtures are usually added to concrete mixture without the need for further work, and some integral WP solutions can be applied to fresh concrete. The WP admixtures need almost no additional labor cost or scheduling application time during construction [21]. Also, as indicated in point 6 above, the membrane maintenance process is usually costly and may need weeks for replacing the external WP barrier [22]. On the other hand, integral WP materials are usually associated with less repair activities and hence require less overall cost [22].

Overall, a noticeable trend of decreasing the use of some membrane systems over concrete bridge decks was highlighted in the survey of Russell [28]. This reflection was identified from feedbacks of several Departments of Transportations (DOT) in the United States and Canada. For example, the DOT in New Mexico reported that membranes have not worked well. In Canada, New Brunswick reported that it discontinued the use of some self-adhering preformed sheets due to debonding failures and Quebec reported that it discontinued the use of some liquid membranes due to installation difficulties (ensuring the required thickness) [28]. The shift was toward adopting an integral WP approach [i.e., full-depth low permeability concrete [28]]. Hence, a future expansion of the use of internal WP approach is foreseen, with a continuing use of the barrier systems for certain types of project requirements such as preventing excessive concrete damage from deicing salts and the cycles of freezing and thawing.

References

[1] Glass, G., & Buenfeld, N. (2000). Chloride-induced corrosion of steel in concrete. *Progress in Structural Engineering and Materials*, *2*(4), 448–458.

[2] Pastore, T., et al. (2011). Evaluation of the corrosion inhibition of salts of organic acids in alkaline solutions and chloride contaminated concrete. *Materials and Corrosion*, *62*(2), 187–195.

[3] Guo, L., et al. (2013). Influence of deterioration on the carbonation resistance capability of concrete with coatings. *Journal of Xuzhou Institute of Technology (Natural Sciences Edition)*, *2*, 13.

[4] Tran, P. C., et al. (2018). Carbonation proofing mechanism of silicate-based surface impregnations. *Journal of Advanced Concrete Technology*, *16*(10), 512–521.

[5] Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C. (2002). *Design and control of concrete mixtures* (Vol. 5420). IL: Portland Cement Association Skokie.

[6] Hobbs, D. W. (2015). *Alkali − silica reaction in concrete*. London: Thomas Telford Publishing.

[7] Mingyu, H., Fumei, L., & Mingshu, T. (2006). The thaumasite form of sulfate attack in concrete of Yongan Dam. *Cement and Concrete Research*, *36*(10), 2006–2008.

[8] Lence, A., et al. (2014). Best practices for maintenance of concrete bridge elements against mold and mildew growth. In *Proceedings of the construction research congress*. Atlanta Georgia, USA.

[9] Viitanen, H., et al. (2010). Moisture and bio-deterioration risk of building materials and structures. *Journal of Building Physics*, *33*(3), 201–224.

[10] Wu, L., et al. (2017). Autogenous shrinkage of high performance concrete: A review. *Construction and Building Materials*, *149*, 62–75.

[11] Zhan, P.-m., & He, Z.-h. (2019). Application of shrinkage reducing admixture in concrete: A review. *Construction and Building Materials*, *201*, 676–690.

[12] Zou, C., et al. (2008). Degradation of mechanical properties of concrete caused by freeze-thaw action. *Journal of Building Structures*, *1*.

[13] BS. (1998). *BS 1504-2, Products and systems for the protection and repair of concrete structures—Definitions, requirements, quality control and evaluation of conformity*: British Standards Institution.

[14] Wang, K., et al. (1997). Permeability study of cracked concrete. *Cement and Concrete Research*, *27*(3), 381.

[15] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. New York, USA: McGraw-Hill Education.

[16] Kubal, M. T., (2008). *Construction waterproofing handbook*. New York, NY, USA: McGraw-Hill.

[17] Pan, X., et al. (2017). A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578–590.

[18] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[19] ACI. (1986). *Committee 515, ACI 515.1R-79 A guide to the use of waterproofing, dampproofing. Protective, and decorative barrier systems for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[20] Muhammad, N. Z., et al. (2015). Waterproof performance of concrete: A critical review on implemented approaches. *Construction and Building Materials*, *101*, 80–90.

[21] Jalali, U. H., & Afgan, S. (2018). *Analysis of integral crystalline waterproofing technology for concrete. International Research Journal of Engineering and Technology (IRJET)*, *5*(10).

[22] Biparva, A., & Gupta, R. (2010). Smart waterproofing system: A review. *Proceedings of the International Conference on Future Concrete*.

[23] Pan, X., et al. (2017). A review on surface treatment for concrete—Part 2: Performance. *Construction and Building Materials*, *133*, 81–90.

[24] Diamanti, M. V., et al. (2013). Effect of polymer modified cementitious coatings on water and chloride permeability in concrete. *Construction and Building Materials*, *49*, 720–728.

[25] Nair, P. S., & Gettu, R. (2016). Commercially available waterproofing agents in India: A review. *Indian Concrete Journal*, *90*, 36–53.

[26] ACI. (2013). *Committee 515, ACI 515.2R-13 Guide to selecting protective treatments for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[27] ACI. (1999). *Committee 212, ACI 212.3R-91 Chemical admixtures for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[28] Russell, H.G., (2012). *Waterproofing membranes for concrete bridge decks*. Vol. 425. Transportation Research Board.

[29] Jianxia, S. (2012). 6.14 - Durability design of concrete hydropower structures. In A. Sayigh (Ed.), *Comprehensive renewable energy* (pp. 377–403). Oxford: Elsevier.

[30] Mehta, P. K. (1991). *Concrete in the marine environment*. New York: Elsevier Applied Science.

[31] Geankoplis, C. J. (2003). *Transport processes and separation process principles: (Includes unit operations)*. Prentice Hall Professional Technical Reference.

[32] Montes, F., & Haselbach, L. (2006). Measuring hydraulic conductivity in pervious concrete. *Environmental Engineering Science*, *23*(6), 960–969.

[33] ASTM. (2014). *D449/D449M Standard specification for asphalt used in dampproofing and waterproofing*. West Conshohocken, PA, USA: Annual Book of ASTM Standards.

[34] ACI. (2016). *Committee 212, ACI 212. 3R-16 Report on chemical admixtures for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[35] Gretton, J. C., et al. (1998). Moisture vapor transport through waterproof breathable fabrics and clothing systems under a temperature gradient. *Textile Research Journal*, *68*(12), 936–941.

[36] Ackers, J. G., et al. (1985). Radioactivity and radon exhalation rates of building materials in The Netherlands. *Science of the Total Environment*, *45*, 151–156.

[37] Tsang, Y., & Narasimhan, T. (1992). Effects of periodic atmospheric pressure variation on radon entry into buildings. *Journal of Geophysical Research: Solid Earth*, *97*(B6), 9161–9170.

[38] Roelofs, L. M., & Scholten, L. C. (1994). The effect of aging, humidity, and fly-ash additive on the radon exhalation from concrete. *Health Physics*, *67*(3), 266–271.

[39] Al-Rashed, R., & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*, *13*, e00408.

[40] Basheer, P. A. M., et al. (1997). Surface treatments for concrete: Assessment methods and reported performance. *Construction and Building Materials*, *11*(7), 413–429.

[41] Al-Rashed, R., & Al-Jabari, M. (2021). Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete. *Case Studies in Construction Materials*, *15*, e00635.

[42] TII. (2019). *DN-STR-03009: Waterproofing and surfacing of concrete bridge decks*. Standards and Research Section, Transport Infrastructure Ireland.

[43] Gupta, R., & Biparva, A. (2017). Do crystalline water proofing admixtures affect restrained plastic shrinkage behavior of concrete? *Revista ALCONPAT*, *7*(1), 15–24.

Concepts and types of integral waterproofing materials

7

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

7.1 Introduction

Waterproofing (WP) materials are added to concrete in order to minimize the water penetration, thereby reducing water-related deteriorations which are caused by chemical, biological, physical, and thermal attacks. The water-associated durability problems are detailed in Chapter 3. Examples of concrete attacks include freezing and thawing cycles [1], chloride ion penetration [2,3], alkalisilica reactions (ASR) [4], sulfate attack [5], acid attack, carbonation reactions [6,7], corrosion of embedded steel bars [8], mold growth [9,10], and shrinkage [11,12]. These durability problems are driven and accelerated by water penetration through permeation flow under a hydrostatic pressure and/or capillary absorption under the driving force of the attractive forces between the liquid and capillary wall, without the need for hydrostatic pressure, as discussed in Chapters 2 and 5. In addition, water penetration is increased by gravitational effects, traffic loading, and wind currents that can create hydrostatic pressures [13], as described in Chapter 6. Preventing or minimizing water penetration in concrete is achieved mainly by (1) installing external water barriers at the concrete surface for preventing or reducing the incoming water flux or (2) transforming the concrete structure, or a surface section, into a waterproofed structure. The mechanism of WP barriers is based simply on creating an impermeable barrier for water transport, which prevents water penetration and protects concrete. On the other hand, integral WP materials protect concrete by increasing its resistance for wetting, water absorption, and/or permeation. This is done through redesigning the pore structure for decreasing the capillary action and/or decreasing concrete permeability. The integral WP systems are formulated in the forms of chemical solutions or powders, which are applied as surface treatment or added to concrete mixture for reducing concrete permeability or wetting characteristics. The internal WP functions are created mainly through chemical reactions between the active ingredients and concrete constituents, and in some cases through the use of densifying fillers. The internal WP materials include chemical solutions, suspensions, emulsions, and powders.

Typical concrete applications of integral WP materials include structures that are exposed to moisture, salt solutions, wicking, and damping in water under hydrostatic pressure. These include below-grade foundations, walls of basements, pavements, parking garages, bridges, marine structures, and hydro-structures such as

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00007-6

dams, tunnels, pipelines, water containment tanks, and aquatic facilities. Integral WP materials can be equally applied to below-grade and above-grade structures, as they are stable for enhancing concrete resistance against water wetting, and they do not dissolve or re-emulsify in water, a problem that is encountered in some membrane WP (bituminous) [14].

This chapter expands the fundamentals of integral WP approach, which are introduced in Chapter 6. It describes the integral WP systems and highlights the WP role of the typical concrete admixtures, which are used for optimizing the concrete mix design. These include the chemical admixtures and the supplementary cementitious materials (SCMs) or mineral admixtures. Then, a chapter is devoted for each type of the industrial integral and integral WP approaches.

7.2 Terminologies and categorizations of internal waterproofing approach

The internal WP approach is achieved by the internally functioning WP materials that act from within the pores of concrete itself. These treatments can be done for the entire structure of concrete or for a section at its surface as shown in Fig. 7.1. The surface layer of concrete is typically about 30 mm thick [15]. As is introduced in Chapter 6, instead of installing an external impermeable barrier at the surface of concrete, the internal WP of concrete is based on impregnating or incorporating ingredients that redesign the pore structure. The internal WP materials protect

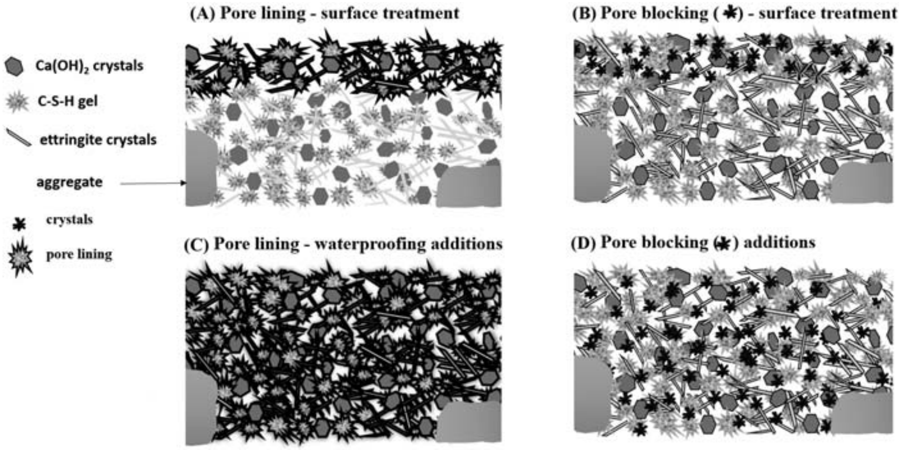


Figure 7.1 Schematic illustrations of the types of integral WP systems showing a section of cement paste (A) treated at the surface with a pore lining material, (B) treated at the surface with a pore blocking material, (C) treated with a pore lining material added as a part of the concrete mixture, and (D) treated with a pore blocking material added as a part of the concrete mixture (showing the cement paste only).

concrete by (1) lining the pores with a water-repellent layer, which when established on their surfaces decreases capillary action, and/or (2) blocking the pores by precipitating stable particles, which minimize concrete porosity and permeability and hence restricting water permeation flow. These functions are created either after the penetration of a surface applied material within concrete or throughout the concrete curing process when they are premixed with the concrete ingredients during its production [16]. This is the rationale behind the use of the term “internal” WP (i.e., internally functioning WP materials). This terminology provides the basic insight that distinguishes internal WP materials from external WP barriers of polymeric membranes and coatings.

These materials can be added to concrete after its casting or hardening through a surface treatment using a penetrating material, which sets within the internal pores of a concrete section Fig. 7.1A and B. Fig. 7.1A shows the pore lining with a water-repellent molecular layer formed at the surface of the constituents of the cement paste within a surface section of concrete (indicated as dark boundaries). Fig. 7.1B shows the pore blocking materials indicated as interlocked needles within a surface section of concrete. When the integral WP materials are added to the concrete mixtures at the time of batching, the resulting effects are distributed within the whole concrete structure and are set within the paste structure as shown in Fig. 7.1C and D, for pore lining and pore blocking mechanisms, respectively. These chemicals are also referred to as integral WP materials as in most cases, the active ingredients react with the cementitious materials and become an integral part of the matrix of the cement paste.

The standard categorizations of WP approaches do not adequately highlight the terminology of integral or internal WP although the concepts are referred to. Even when referring to the internally functioning WP materials, various terminologies are used in the previous literature. These include pore blocking, capillary blocking [17], pore filling, pore lining [18], permeability reducing admixtures (PRA) [19], WP admixtures, WP enhancers, crystallization WP, and water repellents. For example, ACI 515.1R [17] divides WP materials into capillary blocking, dampproofing, and the use of membranes. The European standard EN 1504-2 [20] divides surface treatments into pore blocking, hydrophobic impregnation (pore liners), and coatings. EN 1504-2 [20] refers to surface treatments of hydrophobic impregnation (pore liners) similar to Fig. 7.1A and pore blockage (pore sealing) similar to Fig. 7.1D. Such a categorization is also used by some authors [see, e.g., Muhammad et al. [21]]. In fact, some researchers may restrict the use of internal/integral WP materials to additions to the concrete mixture including powder mixtures and solutions of active ingredients. However, Fig. 7.1 shows that the integral WP systems are better categorized into the illustrated four types.

In fact, the terminology and the definition of integral WP materials witnessed a development over the last few decades as it became more popular in industry. In the past, the concrete guides and standards focused mainly on specifying and classifying membrane WP materials, while integral WP additions were less covered in the previous literature. For example, in 1986, ACI 515.1R [17] mentioned capillary blocking WP materials as ingredients in the cementitious membranes and coatings.

Then, ACI 515.2R-13 [22] defined the internal WP admixture as "a chemical which is added to the cement matrix that promotes the development of additional gel or other precipitate within concrete voids, after its diffusion to the pore water." ACI 515.2R-13 [22] lists crystalline coatings and admixtures as internal WP admixture; however, it considered crystalline modification of concrete as a second level of defense below a topical barrier system. In addition to WP additions, ACI 515.2R-13 [22] discusses the reactive chemical solutions used for surface treatment. The Concrete Terminology of ACI [23] includes definitions of these surface treatment solutions in relation to concrete applications. On the other hand, ACI 212.3R-10 report on chemical admixture [19] devotes a chapter onto PRA, which decrease concrete porosity and thus reduce water permeability, based on internal WP mechanism (as those illustrated in Fig. 7.1D. In fact, only the pore-blocking or filling materials Fig. 7.1B and D can noticeably reduce permeability [17]. Some polymeric materials may be deposited within the concrete pores causing pore filling and reducing the wettability due to their water repelling nature. The adopted general classification of WP materials in this book distinguishes integral systems (including surface applied penetrants and concrete additions) from the external barriers applied above the concrete surface (including membranes and coatings) (see the hierarchy in Fig. 6.2). This classification is used in other previous publications [16,24].

The scientific terminology of the WP functions of these materials is based on water interactions with the formed WP materials within concrete pores. These include hydrophobic, hydrophilic, and hygroscopic interactions, which are detailed in Chapter 5. The hydrophobic integral WP materials are simply pore liners forming a layer at the cementitious constituents while the hydrophilic and hygroscopic crystals are pore blockers occupying a fraction of the permeable pores. Most of the hydrophilic and hygroscopic materials are crystalline materials and hence crystallization WP terminology is frequently used to describe them. However, hydrophobic materials form a molecular layer that is not crystalline and hence the use of hydrophobic crystallization WP terminology, as observed in some WP literature, is not valid. The behaviors of these types of WP materials are further detailed in Section 7.4.

Integral WP technologies can be categorized and evaluated in different approaches. These include additional purpose, materials phases, structure, composition, reactivity, setting mechanism, physical behavior, interaction mechanism with water vapor, moisture hindering mechanism, the level of the hydrostatic pressure they can resist, application method, and surface characteristics (wetting conditions). These categorization approaches are listed in Table 7.1.

The integral WP approach includes manipulation of the concrete mix design through the use of typical admixtures and the use of WP materials for the sole purpose of WP. Table 7.2 lists the full range of integral WP materials and their main WP functions. The WP is the set target for the WP additions and treatment and thus it can be termed as direct integral WP materials. On the other hand, in the approach of concrete modifications through mix designs utilizing the traditional admixtures, the WP effect is a consequence and/or an associated effect of the traditional

Table 7.1 Categorization approaches of integral WP technologies.

Categorization approach	**Description**
Purpose	Direct WP purpose (e.g., from crystalline materials) or a WP consequence of other concrete modifications, for example, from chemical and mineral admixtures.
Phases of additions	Powders, liquids, water-based, or solvent based solutions (or suspensions and emulsions).
Method of incorporations of the active ingredients	Blends of powders added (admixtures, incorporation with cementitious coatings, or powders for dry shake application), or chemical solutions for surface treatments or additions to concrete mixture.
Chemical reactivity	Inert and reactive materials.
Chemical structural and composition	Mineral oxides, organosilicon compounds, organic salts, drying oils etc.
Setting mechanism	Reactions with calcium hydroxide and moisture or reactions with active sites on the paste constituents.
Interactions with water and vapor	Hydrophobic, hydrophilic, and hygroscopic materials.
Mechanism for reducing water penetration	Reducing capillary action (water absorption) or reducing permeation flow.
Mechanism for water resistance	Pore blocking versus water repellency.
Level of hydrostatic pressure	Resistant versus nonresistant for hydrostatic pressure.
Application conditions	Waterproofing or dampproofing.

admixtures and thus they can be termed as indirect integral WP materials. Indirect integral WP through mix designs is achieved when typical solutions of chemical admixtures or powders of SCMs are added to concrete mixture. In fact, although direct integral WP materials are usually added into concrete mixture for the sole purpose of minimizing concrete permeability or wettability, they may cause a range of secondary required impacts on the characteristics of fresh and hardened concrete, as those obtained by traditional admixtures. For example, some integral WP admixtures have additional functions of acting as low-range water reducers, air entertainers, and/or set-retarders. They may also enhance workability, consistency, and slump retention. Typical integral WP admixtures may also impact the compressive strength, and other mechanical properties of fully cured concrete. Hence, the direct integral WP additions may be labeled as indirect traditional admixtures. In fact, ACI 212.3R-91 [25] highlights this point by indicating that dampproofing admixtures may have a secondary function not reflected by the name such as promoting air entrainment and suggests that they may be labeled as air-entraining admixtures.

According to their chemical reactivity with concrete constituents, the ingredients of integral WP materials can be classified into reactive and nonreactive compounds. The nonreactive materials are mainly stable fillers that are added as powders to the concrete mix designs, or possibly formulated in liquid as polymeric materials that

Table 7.2 Materials and main WP function of integral WP systems.

Description	Application/ addition	Typical chemicals	Main mechanism
Mineral admixtures	Powder admixtures	Mineral compounds SCMs such as fly ash, silica fume, and slag.	Filling effects and pore refinement through hydraulic and pozzolanic reactions as introduced in Chapter 1.
Chemical admixtures	Solution admixtures	Organic compounds such as water-reducing admixtures and superplasticizers.	Reducing concrete porosity by enhancing the quality of fresh concrete and reducing the water demand as introduced in Chapter 1.
Water repelling WP admixtures	Powder admixtures or solution surface treatment	Organosilicon compounds such as saline and other organic compounds such as fatty acid derivatives.	Pore lining mechanisms based on forming hydrophobic layers.
Crystallization swelling WP admixtures	Powder admixtures or solution surface treatment	Mineral compounds such as silicate compounds.	Pore blocking based on forming hydrophilic crystals.
Multiple effect crystallization WP enhancers	Solution enhancer for concrete mixture or solution surface treatment	Aqueous solutions of a mixture of several proprietary reactive compounds.	Pore blocking and pore lining mechanisms based on forming hydrophilic and hygroscopic crystals combined with hydrophobic layers.
Inert WP densifiers	Powders or solution surface treatment	Mineral compounds in inert powder materials such as bentonite and talc powders or suspensions of nonreactive compounds such as lithium silicate.	Pore blocking hydrophilic particles and densifiers.

(*Continued*)

Table 7.2 (Continued)

Description	Application/ addition	Typical chemicals	Main mechanism
Other additions	Powders	A wide range of other materials such as nanoparticles of silica and impregnating polymers.	Pore blocking and/or pore lining mechanisms based on precipitating nanoparticles or on polymerizing an impregnated low viscosity monomer by means of microwaves or high temperature.

coalescence into particles within pores. Reactive WP materials are used in various industrial formulations. Sections 7.3–7.6 describe the types and mechanisms of direct integral WP materials, then each type is detailed in the subsequent chapters while Section 7.7 is devoted to the indirect integral WP materials.

7.3 Types of direct integral waterproofing technologies

Table 7.2 covers (1) chemical solutions, which are used as sealers or liquid admixtures (or enhancers) that are added to concrete mixtures and (2) powders, which are added as admixtures to concrete mixtures or applied as slurry coatings, mortars, or by dry shake at the concrete surface. Powders are typically incorporated in the industrial formulations in a dry blend of Portland cement, fine sand or silica particles, and active powder ingredients. The liquids include water-based and solvent based solutions, suspensions, and emulsions. The WP additions are usually considered in industrial systems as admixtures, and some types are referred to also as enhancers. The generic chemical families of integral WP materials are given in Chapter 6, among other types of WP systems (refer to Fig. 6.7). These include mineral oxides, organosilicon compounds, organic acids and salts, oils etc. The industrial integral WP materials can be formulated to include a single active ingredient or multiple active ingredients. The chemical formulations of most commercially available products are confidential or proprietary chemical solutions. However, the published literature covers various typical families of active ingredients such as those referred to in Table 7.2. These families of chemicals, which are used separately or in combination for obtaining wide ranges of performance [19], are summarized in the following types:

1. *Silicate*-based compounds such as sodium silicate, which react with calcium hydroxide to form pore blocking materials.

2. *Fatty acid* derivatives such as stearic, oleic, caprylic and capric, and their organic alkali salts, which react with calcium hydroxide to form water repelling materials and possibly partial pore filling (e.g., calcium stearate).
3. *Organosilicon* compounds such as silanes, siloxane, and siliconates, which react with active sites at the siliceous content of concrete to form water repelling layers at the pore surface.
4. *Natural oils* such as vegetable oils, tallows, soya-based materials, and greases, which coalescence within concrete pores and form a firm that covers the surfaces of pores providing them with a water-repellent characteristic.
5. *Petroleum derivatives* such as mineral oil, paraffin and bitumen emulsions, which deposit on the surfaces of pores providing them with a water-repellent characteristic.
6. *Polymers* such as latex, water-soluble or liquid polymer, which when coalescence deposit on the pore surface providing them with a water-repellent characteristic.
7. *Inert particulate matters* and fillers such as talc, bentonite, clay, hydrocarbon resins, and coal tar pitches, which partially fills the concrete pores and assist in pore blocking (with a nonwetting effect for some of them).

Powders are usually mineral oxides. Powder additions include industrially patented proprietary formulations. The reactive pore blocking powder materials are typically composed of reactive mineral compounds such as silicates and other mineral additives, which react with concrete constituents to form hydrophilic materials that fill the pores. These materials are detailed in Chapter 9. The chemical solutions of concrete sealers contain reactive chemicals that improve the integrity of concrete surface and decrease its porosity through a chemical reaction with concrete constituents. They are referred to using different terminologies, including concrete hardeners, densifiers, and sealers (see ACI concrete terminology [23]). The sole purpose of such a sealer is usually to reduce dusting and to harden the surface by chemical action, and hence increase concrete resistance to abrasion attacks. The types of concrete hardeners include silicate solutions, which are applied to concrete floors to reduce wear and dusting [23]. In addition, ACI 515.2R-13 [22] describes the use of solutions of magnesium, zinc, or calcium fluosilicate compounds for surface treatment of old concrete as hardeners. The ACI guide [22] does not discuss the integral WP function of these surface hardeners; nevertheless, the integral WP function effect of these solutions is discussed in literature as detailed in Chapter 9. Industrially available chemical solutions may include combinations of these chemicals. Industrial solutions for surface treatment include dual crystallization WP materials [26], which will be detailed in Chapter 10. Suspensions of densifiers include fine particle fillers such as bentonite and talc. Bentonite is “a clay composed principally of minerals characterized by high adsorption and large volume change with wetting or drying” (ACI concrete terminology [23]). Water repelling materials include solutions of fatty acid derivatives (stearic, oleic, caprylic capric), soaps and emulsions of oils (tallows, soya-based), and petroleum derivatives (mineral oil, paraffin, bitumen emulsions). They also include solutions and emulsions of organosilicon compounds. Some of the water repelling materials are solvent based. These materials are detailed in Chapter 8. Liquid additions (enhancers) include similar solutions used for surface treatments, which, when they are mixed with concrete mixture, lead to various impacts on the characteristics of fresh and hardened concrete, as detailed in Chapter 11.

7.4 Setting and formation of integral waterproofing materials

The application method of integral WP materials depends on the phase of the product in which they are incorporated. From the perspective of applications, the internal WP materials are divided simply into (1) chemical solutions (or emulsions), which are used as sealers or as liquid admixtures (or enhancers) that are added to concrete mixtures and (2) powders, which are added as admixtures to concrete mixtures at the time of batching or applied as slurry coatings, mortars, or by dry shake at the concrete surface. These integral WP systems are applied by (1) spraying, brushing, or rolling onto the surface when they formulated in systems of penetrating solutions (e.g., solutions of crystallization WP materials, surface hardeners, densifiers, and sealers), (2) troweling, brushing, or spraying onto prewetted substrate concrete when they formulated in systems of powders ready for mixing with water at the job site to be applied as cementitious coatings and mortars, (3) dry shake application on fresh concrete when they formulated in systems of dry powders, or (4) direct additions to concrete mixture in liquid or powder forms.

Liquids of water-based or solvent-based solutions are formulated to have low viscosities so that they can penetrate the concrete easily. They are used for topical surface treatment of fully cured or fresh concrete. For fully cured concrete, the solutions can be applied to the negative (dry) or the positive (wet) side of water pressure on the concrete surface (see, Chapter 6, Fig. 6.3). The powder coating systems are made ready for mixing with water to form a creamy consistency and applied onto concrete surface for creating a cementitious coating, which has the characteristics of integral WP. Cementitious coatings and mortars are applied onto fully cured concrete to the negative or the positive side. Fig. 7.2 shows the penetration mechanisms of surface applied integral WP materials. After their application at the surface at certain coverage, the soluble active ingredients in the aqueous chemical solutions or the cementitious powders penetrate the concrete structure by capillary absorption and/or diffusion. The soluble active ingredients reach a certain average penetration depth that depends on structural and transport properties. Then, the formation reactions occur where the WP materials (crystalline particles or molecular layers) start to appear within the WP penetration depth.

In general, the reactive integral WP materials react with the by-products of the cement hydration (mainly the calcium hydroxide), or other cementitious surfaces, possibly in the presence of other materials from the surroundings such as moisture and carbon dioxide. When integral WP materials are added to concrete mixtures, the setting reactions occur within the full concrete depth in association with the curing process and hence there is no relevance to the term WP penetration depth. For surface

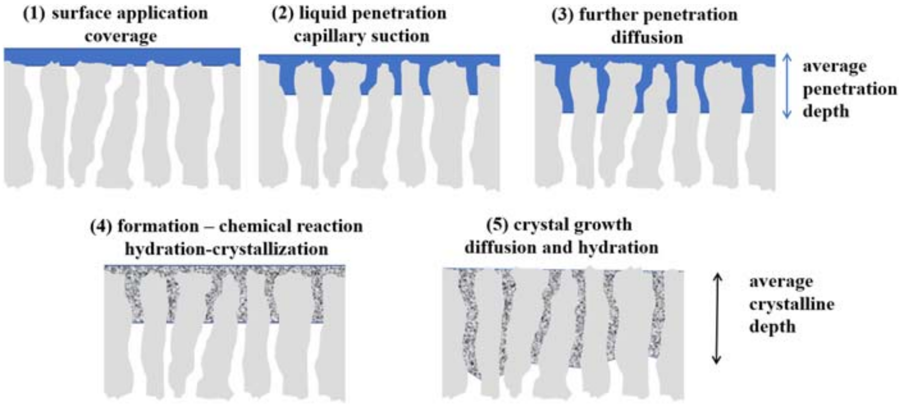


Figure 7.2 The mechanisms of penetration and formation of surface applied integral WP materials showing liquid penetration depth, diffusion depth, and crystalline depth.

applied integral WP materials, these reactions occur within the penetration (suction and/or diffusion) depth of the active ingredients (see Fig. 7.2). For crystalline WP materials, the WP penetration depth goes deeper within the concrete structure through the mechanism of crystal growth associated with the interactions of the formed crystals with moisture (as described in Section 7.5). Hence, for cases of aqueous chemical solutions, it is essential to distinguish between the liquid penetration depth and the crystalline depth, as illustrated in Fig. 7.2. The liquid penetration (suction and diffusion) depth is typically detected experimentally by adding a dye to the WP solution and splitting the concrete specimen to visualize and measure the depth.

The active ingredients in the pore lining WP materials react with active sites at the surface of the cementitious materials (e.g., CSH gel and ettringite) and form molecular layers that make the surface nonwettable. For hydrophobic surface treatment, the penetration depth can be also detected by observing the depth of water repelling characteristics (after splitting the treated concrete specimen). This is typically similar to solution penetration depth as hydrophobic layers do not grow deeper with moisture interaction. On the other hand, the crystalline depth cannot be simply detected using a dye because the crystals grow deeper as illustrated in Fig. 7.2. In this case, microstructural analysis is required. The ranges of penetration depths will be described in the relevant subsequent chapters.

The size ranges of integral WP crystals and layers are illustrated in Fig. 7.3. Particularly, the active ingredients in the pore blocking integral WP materials produce insoluble materials that fills the pores. The size range of the produced crystals starts from hundreds of nm and grow to micrometer scale. They can grow and expand with moisture swelling or vapor adsorption to much larger sizes. The hydrophobic layers are within the molecular size of the used hydrophobe. The thickness of the hydrophobic molecular layers (pore lining) is much smaller than the size range of the crystals (in nm). In order to demonstrate the formations and interactions of integral WP materials, it is important to visualize and compare the size

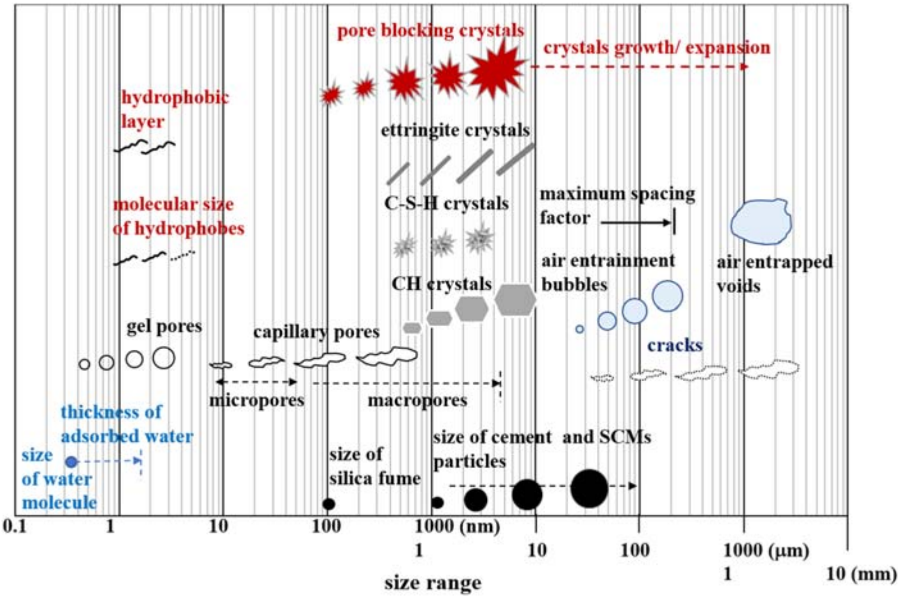


Figure 7.3 Illustrations of the typical ranges of sizes of integral WP crystals and layers compared to typical (approximate) dimensions of concrete constituents.

scales of the various constituents and acting species that have or may have a role in the process of water penetration and durability solution as shown in Fig. 7.3. Integral WP materials target reducing water penetration in concrete (permeation and capillary suction), which is associated only with free bulk water [27]. The molecular size of water is about 0.275 nm [28], which represents the lowest scale in Fig. 7.3. It is also essential to recall from Chapter 2 that nonfree water exists in concrete as chemically bonded water within the hydrates of cement [27] and as physically bonded or adsorbed water within the gel pores. The layer thickness of the adsorbed water can reach about 1.5 nm [29]. The chemically bonded water is part of the structure of cementitious constituents (e.g., CSH and ettringite) that are formed from the hydration reactions at the surfaces of cement particles (size range of micrometers). The cement hydration products have a size that ranges from hundreds of nanometers to a few micrometers. They form the cement matrix and create its porosity, which is characterized by the pore size distribution and connectivity [30,31]. Concrete permeability increases exponentially with increasing porosity of cement paste [32]. Concrete pores include permeable and impermeable pores (ASTM C125-15b [33]) (see Chapter 2). The size ranges of gel and capillary pores and air voids are shown in Fig. 7.3. The gel pores that have a size range of 0.5–2.5 nm are not open for permeation and do not create flow channels. Capillary pores, which are typically larger than 10 nm, form irregular flow networks. They include micropores, which have a size range of 10–50 nm, and macropores the size of which can reach up to 5 m in pastes with a large water/cement (w/c) ratio and at early ages of hydration [29]. The size of cracks is much larger (e.g., up to few mm), thus they create wide flow channels. Hence the integral WP materials are required to target treating and redesigning the structures of both capillary pores and cracks. On the other hand, air entrained bubbles (hundreds of micrometers) and air entrapped voids (millimeters) are not believed to take a role in water permeation although some researchers believe they may do contribute to concrete permeability [31]. In general, the integral WP materials may not (or are not required to) alter the air void system. The water suction of such large air voids is negligible (see Chapter 5 for the dependence of water suction rate on pore or void size). However, air voids may disrupt the packing of cement particles and increase the heterogeneity of the microstructure and porosity distribution [34] creating an interfacial transition zone with a higher porosity than that in the bulk paste [35] [approximately 2–3 times [36]]. Their contribution to permeability may appear when they are interconnected by the capillary pores [37,34]. Overall, when integral WP materials reduce the permeation flow and/or water suction through redesigning the capillary pores, they allow air voids to return to their original structure as spaced-way and isolated voids. The integral WP material may cause little impact on the spacing factor of air voids. From the illustrated size ranges of WP crystals and hydrophobic layers shown in Fig. 7.2, it is expected that the crystals can block a fraction of the permeable pores while the molecular layers cannot contribute noticeably in pore blocking but only in pore lining. As mentioned above, the WP crystals target only capillary pores and cracks. This is also valid for the hydrophobic WP materials; however, some of hydrophobic molecules have a relatively small molecular size and they may be thought to be able to diffuse into gel pores altering their characteristics. However, the size range of the active ingredients of the hydrophobic WP materials is close to the size range of gel pores and hence they cannot penetrate them easily (see Chapter 8) [38].

7.5 Interactions of integral waterproofing materials with water

The responsive behaviors of integral WP materials to water contact depends on their surface chemistry and on the porosity of concrete. Industrial integral WP systems are usually formulated to include hydrophobic, hydrophilic, or hygroscopic materials, or combinations of more than one type. The types of water interaction mechanisms (see theoretical descriptions in Chapter 5) are shown in Fig. 7.4. Table 7.3 lists the functions and the mechanisms of WP materials for industrially available integral WP systems.

The obtained hydrophobic WP materials hinder water penetration by capillary action (water absorption) through the formed hydrophobic layer at the cementitious constituents that prevents pore wetting. As indicated in Chapter 5, hydrophobicity is obtained when the static contact angle between the solid surface and the water drop is higher than 90 degrees and superhydrophobicity is obtained when the static contact angle is higher than 150 degrees. A water-repellent cement (or waterproofed

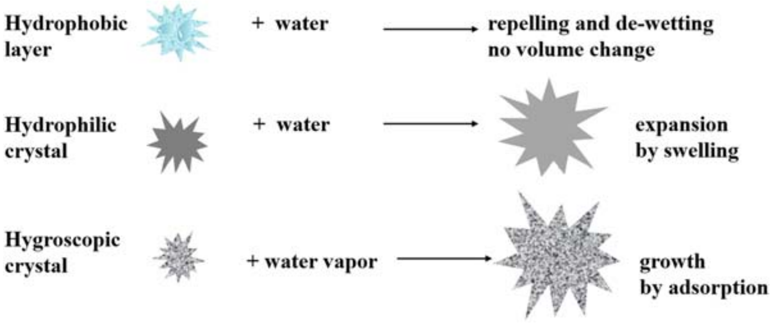


Figure 7.4 Types of water interaction mechanisms with hydrophobic, hydrophilic, and hygroscopic WP materials.

cement) is typically made by adding a small fraction of hydrophobic additives such as stearates to the cement clinker during final grinding in order to reduce the capillary water absorption [39]. In precise terms, water-repellency is a resistance property against surface wetting for either liquid or vapor state [23]. While the hydrophobicity is usually defined based on liquid nonwetting rather than vapor. According to ACI concrete terminology [23], a water repellent is resistant but not impervious to penetration by water.

The hydrophilic and hygroscopic WP materials hinder water permeation by creating obstacles for permeation flow. A watertight concrete is obtained when the internal structure of concrete is filled with particulate matters of hydrophilic and/or hygroscopic crystals. By such a physical occupation of the permeable pores, the total porosity of concrete is decreased. Decreasing porosity of cement paste decreases water permeability exponentially [32], as explained in Chapter 2. In fact, this is the concept behind the terminology of PRA [19] (see Section 7.6). Many of the pore blocking or filling WP materials behave as swelling gels that expand when immersed in water. Thus they occupy a larger portion of the pore volume and enhance the pore blocking mechanism. Other unique pore blocking WP materials have the ability to grow with moisture by their hygroscopicity and thus can fill a more fraction of the permeable pore fraction. Both swelling and hygroscopic size enlargement of the crystalline WP materials are reversible. In some industrial systems, combined behaviors are obtained by having hydrophilic and hygroscopic crystallizations as will be detailed in Chapters 10 and 11.

7.6 Levels of water resistance of integral waterproofing materials

The selection of integral WP materials for certain structural application must take into consideration the level of concrete engagement with water (e.g., damping or partial wetting) and the level of hydrostatic pressure applied on concrete surface as

Table 7.3 Types of water interaction mechanisms of integral WP materials.

Type of WP materials	Redesigning pore structure	Mechanism of hindering moisture penetration	Formation mechanism	Typical chemicals	Details
Hydrophobic materials	Pore lining	Formation of water-repellent layers or deposits, while the pores remain physically open for flow under a hydrostatic pressure.	• Adsorption of hydrophobic compounds through chemical reactions forming a chemically bonded layer. • Deposition of hydrophobic particles within pores. • Coalescence of polymer compounds forming water repelling films or globules with a capillary blocking effect.	Organosilicon compounds such as silanes, siloxane and siliconates, soaps, fatty acid derivatives, salts of fatty acids such as alkali stearates, vegetable and petroleum oils.	Chapter 8
Hydrophilic materials	Pore blocking	Formation of insoluble particles or crystals that densify the concrete, occupy permeable pores, and physically restrict the passage of water with particle expansion by swelling.	• Chemical reaction of active ingredients with water and calcium hydroxide forming crystalline gels. • Precipitation of inert particles.	Proprietary active chemicals (e.g., silicates).	Chapter 9

Hygroscopic crystalline materials	Pore blocking	Formation of insoluble particles or crystals that densify the concrete, occupy permeable pores, and physically restrict the passage of water with crystal growth from the adsorption of water vapor.	• Chemical reaction of active ingredients with water and calcium hydroxide forming crystalline organic precipitates.	Proprietary active chemicals (e.g., crystalline organic salts such as sodium acetate, which was tried at the lab scale).	Chapter 12
Multifunctional materials	Combined pore lining and pore blocking	Combined formations of water-repellent layer and deposition of hydrophilic and/or hygroscopic crystals that block a fraction of the permeable pores and expand by swelling and/or crystal growth by the adsorption of water vapor.	• A series of chemical reactions of active ingredients with water, calcium hydroxide, and active sites on cementitious surfaces, forming more than one type of crystals and adsorbing hydrophobic compounds.	A system of proprietary active chemicals, which may combine various materials listed above.	Chapters 10 and 11

well as any possible variations of these conditions during service. These issues are described in Chapter 6 (see, e.g., Figs. 6.8 and 6.9). Usually, these conditions affect the WP performance and the stability of WP materials. In fact, integral WP materials are generally stable when damped in water as most of them are based on precipitating insoluble crystalline particles (or they may have low solubility in water). In addition, rather than destabilizing the crystals, their moisture interactions enhance the WP efficiencies (e.g., by swelling of hydrophilic crystals and vapor adsorption of hygroscopic crystals).

Structural service conditions of nonhydrostatic pressure are defined as those exposed to little or no water under hydrostatic head pressure, primarily when the main mechanism of water movement is capillary absorption [19]. These are usually encountered in the above-grade structures in which concrete is exposed to partial wetting within short periods of time. Structural service conditions of hydrostatic pressure are encountered usually in water submerged structures such as marine structures [40] and hydraulic structures [41]. Also, they are encountered in below-grade structures. Even in the above-grade structures, conditions of hydrostatic pressure may be created occasionally by loading from traffic impacts on wetted concrete surfaces or from pressure by wind currents [13]. From this perspective, the resistance of a WP material for hydrostatic pressure governs its performance and efficiency for hindering moisture penetration into concrete structures. Fig. 7.5 illustrates the levels of water exposure and water penetration mechanisms through concrete.

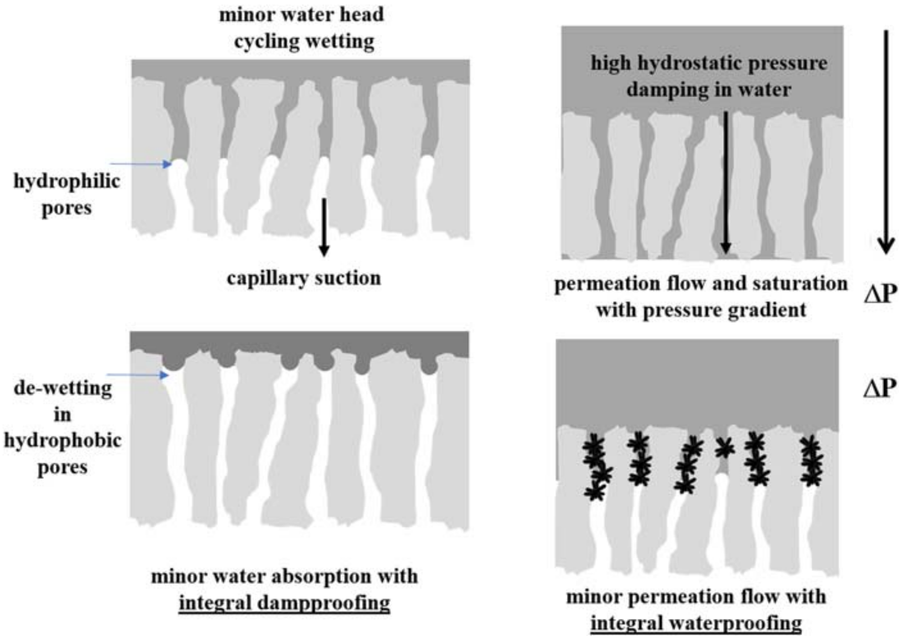


Figure 7.5 Illustrations of the levels of water exposure and water penetration mechanisms through concrete.

According to ACI concrete terminology [23], a watertight structure is "impermeable to water except when under hydrostatic pressure sufficient to produce structural discontinuity by rupture." From this perspective, integral WP materials are categorized into resistant for hydrostatic pressure and nonresistant to hydrostatic pressure. Based on ACI definition, PRA admixtures are subdivided according to ACI 212.3R-10 [19] into PRA for nonhydrostatic conditions (PRAN) and PRA for hydrostatic conditions (PRAH). The two types are compared in Table 7.4 based on ACI literature (ACI 212.3R-10 [19] and ACI 212.3R-91 [25]). As mentioned earlier, water repellency is a surface property of material that resists wetting but promotes the flow of water under a hydrostatic pressure [23]. For this reason, integral hydrophobic WP materials or pore liners are used for concrete structures that are not subjected to hydrostatic pressure while the pore blocking WP materials of hydrophilic and hygroscopic types are more demanded when the structure is subjected to hydrostatic pressure (see Fig. 7.5). As described in Chapter 6, the used terminologies in construction industry include waterproofing materials, which resists the passage of water in the presence of hydrostatic pressure (ACI 515.1R [17]), and dampproofing, which resists the passage of water in the absence of hydrostatic pressure [17]. Traditionally, PRANs are labeled as dampproofing materials [42]. Dampproofing materials assists in detaching water from the surface of the concrete, reducing the ability of rain to penetrate it or reducing the wicking properties of

Table 7.4 Classification of integral WP additions to concrete (permeability-reducing admixture).

Wetting conditions	**Classification of integral WP admixture**		**Mechanism and benefits [19]**
	According to ACI 212.3R-91 [25]	**According to ACI 212.3R-10 [19]**	
Partial wetting without a water head	Dampproofing admixtures	Permeability-reducing admixture: nonhydrostatic conditions (PRAN).	Forming a water-repellent surface, which reduces water absorption [19] and retards moisture penetration into unsaturated concrete.
Continuous wetting or damping under high water head	Permeability-reducers (waterproofing admixtures)	Permeability-reducing admixture: hydrostatic conditions (PRAH).	Reducing concrete porosity and densifying its structure, which reduces permeability, increases resistance to water penetration under a pressure.

concrete [25]. Dampproofing materials reduce the rate of moisture penetration into the pores of nonsaturated concrete. ACI 212.3R-91 [25] specifies "dampproofing" for prevention of water penetration of dry concrete or stoppage of water transmission through unsaturated concrete. ACI 212.3R-91 [25] highlights that the additions of hydrophobic dampproofing materials to concrete of low porosity cannot lead to an appreciable improvement in reducing moisture penetration. It also indicates that testing results indicated that these hydrophobic additions do not show effectiveness in reducing the moisture transmission through concrete slabs on ground (further details are given in Chapter 8). For the above-grade structures, when the water table is lower than the ground structure, concrete may be exposed to just short periods of partial wetting, without building a hydrostatic pressure and thus dampproofing can function well. Hydrophobic WP materials are considered by ACI 212.3R-16 [19] to be effective at reducing the capillary absorption but they should not be used if there is a possibility of a hydrostatic pressure devolvement during the service life of concrete.

Theoretically, it is estimated that the hydrophobically modified concrete with full pore lining can resist water up to 4 m of water head or even higher [43]. However, as usually the pores are not fully lined and due to the presence of large pores that create wide flow channels, a hydrophobically treated concrete can practically withstand only a few centimeters of water head [19]. On the other hand, integral crystalline WP materials can withstand very high hydrostatic pressures (e.g., up to 122 m of water head for a fully cured crystalline WP system [13]). In fact, the level of resisted pressure depends on the type and dosage of crystalline WP materials. PRANs cannot block the flow of water under a hydrostatic pressure condition encountered in the below-grade structures and water-retaining structures [19]. As previously mentioned, PRAN reduces only water absorption and thus they are suitable only for dampproofing applications. In precise scientific terms, PRAN cannot be considered as permeability-reducing materials, and thus the terminology of dampproofing admixtures used in ACI 212.3R-91 [25] provide better technical description for them than that in ACI 212.3R-10 [19]. Dampproofing admixtures do not reduce the permeability of saturated concrete [25], thus it is not suitable to classify them under PRA for nonhydrostatic pressure. The previous ACI terminologies of dampproofing admixtures and permeability reducers is used in concrete books, when discussing admixtures [8,39].

For below-grade structures sitting in the water table continuously or periodically, a hydrostatic pressure will be developed and the water permeation rate is high. Also, high pressures are encountered for concrete submerged in water as in the case of hydraulic structures [41] or marine structures [40]. PRAHs can sufficiently resist water penetration under hydrostatic pressure and withstand ponded water through their pore-blocking mechanism [19]. Thus they are suitable for watertight construction. In fact, hindering water permeation by pore blocking and reducing the porosity may be associated with an increase in water absorption in narrow capillaries. Some industrial literature of water repellents highlights the increase of water absorption when pore blocking crystallization WP materials are used due to the increase in the capillary action associated with pore refinement. This issue is discussed in

Chapter 5 when presenting the equation that models the rate of capillary suction. Thus in analyzing experimental results for testing the performance of WP materials, it is essential to distinguish between results of sorptivity and those of permeability. Crystallization WP materials decrease permeability while they may increase sorptivity. Some experimental results may show that capillary water absorption of integrally waterproofed concrete specimens (e.g., by crystallization) is higher than that of a control sample. In response to these behaviors, some industrial products use the dual actions of pore blocking and water repelling in the same formulations [26,44,45].

7.7 Indirect integral waterproofing approach through concrete mix design

Watertight concrete can be achieved by proper material selection and proportioning as described in Chapter 4. In general, indirect integral WP materials involve the selection and addition of typical admixtures used to improve workability, strength, and durability characteristics. Although the main goal of the use of traditional admixtures is controlling certain characteristic(s) of fresh and hardened concrete, the indirect integral WP materials target usually more than a single purpose. Purposes include concrete hardening and strengthening, reducing shrinkage, and resisting other harmful physical, chemical, and biological attacks. They yield WP enhancement by reducing the permeability of hardened concrete through (1) reducing the required water content in fresh concrete and (2) filling effects and pore refinement through reactions (hydraulic and/or pozzolanic reactions described in Chapter 1). The WP roles achieved by the chemical admixtures and the mineral admixtures (SCMs) (see Table 7.2) are described in Sections 7.7.1 and 7.7.2, respectively.

7.7.1 Integral waterproofing function by chemical admixtures

Most of the chemical admixtures usually reduce watercement (w/c) ratio, and hence reduce the water demand for a specific required workability and consistency of fresh concrete mixture. This reduces concrete porosity and hence hinders the permeability of hardened concrete as described in Chapter 2. From such a scientific perspective, most of the widely used traditional chemical admixtures can be categorized as integral WP materials (indirect). Within this context, ACI report on admixtures [19] indicates that the formulations of PRAs include high range water-reducing admixtures. In fact, most of the standard chemical admixtures are labeled as PRA in concrete reference books (see, e.g., [8,39]). Their role in reducing water penetration may be achieved from combined mechanisms of WP and improved porosity resulting from the reduced water content in fresh concrete [19]. However, as mentioned earlier, the sole use of the chemical admixtures targets characteristics other than WP, and thus they are usually characterized under the main function they are used for [e.g., water-reducing and shrinkage-reducing admixtures (SRA)]. The types of admixtures that are related to WP and concrete protections are covered in ACI 212.3R-10 [19]. These include admixtures for air-entraining, water-reducing, shrinkage-reducing, and lithium admixtures. The roles of these chemical admixtures in enhancing concrete WP are summarized by the following types:

1. *Integral WP through air-entraining and water-reducing admixtures*

   The admixtures for air entraining and water reducing have been introduced in Chapter 1. Water-reducing admixtures contain organic compounds of lignosulfonic acids and their salts, carboxylic acids, and carbohydrate-based compounds such as sugars. Their role in reducing the required amount of water for achieving certain workability and decreasing porosity contributes in a WP benefit for the concrete as they lead to less permeable concrete. More noticeably, some carboxylic acids and their salts may also be included in the formulations of direct integral WP materials. In a recent study, modified lignosulphonate, used as water-reducing admixture, was reported to reduce the permeability of hardened concrete and thus was considered as integral WP materials [45]. Similarly, air-entraining admixtures contain organic salts of sulfonated hydrocarbons and sulfonated lignin, and fatty acids and their salts. Some of these materials are also used in the formulations of hydrophobic direct WP materials. Some other admixtures contribute with a temporary WP effect; however, they may not affect the final permeability. For example, some accelerating admixtures such as calcium chloride increase the rate of cement hydration and hence shorten the time period required for attaining a certain level of impermeability [25]. However, the use of calcium chloride creates harmful effects associated with chloride ions (see Chapter 3). Some accelerating admixtures contain aluminates and silicates, which are used in the formulations of pore blocking WP and PRA.
2. *Integral WP through shrinkage-reducing admixtures*

   SRA are multipurpose durability enhancing materials used for ordinary Portland cement concrete and modified concrete with fly ash [12,46–51]. The types of SRA materials, available industrially or investigated at the lab scale, include various glycol compounds such as glycol ether, propylene glycol (PG), triethylene glycol, and dipropylene glycol tert-butyl ether [52]. A patented SRA material was based on polyoxyalkylene alkyl ether, labeled as “the world’s first shrinkage-reducing admixture” [50]. There are other SRA materials that combine more than one active ingredient such as polyoxyalkylene alkyl ether, glycol ether, and urea. These materials also have other durability benefits: SRA enhances concrete resistances against damages from freezing and thawing and against chloride ion penetration and increases electrical resistivity [12]. The review paper of Zhan and He [12] summarized the durability parameters for various SRA compounds. They reported that the reduction in shrinkage ranged from 15% to 70%, depending on the type and the dosage of SRA active ingredient [12]. The chemical families of SRA can assist in resisting biological attack; the antibacterial and antifungal properties of some SRA materials (e.g., PG, hexylene glycol, and 1,3-butylene glycol) have been reported in studies of other fields [48]. However, there is no existing study on their use with concrete for such a purpose. SRA improves the workability and retards cement hydration. They decrease the temperature peak resulting from the exothermic hydration reactions and delay the time at which it occurs. They reduce the crack formation and concrete porosity.

   They contribute with a WP function and hence can be considered as a category of indirect integral WP materials. In fact, reducing cracking from shrinkage leads to a noticeable reduction in concrete porosity and permeability. In addition, some SRA can lead to hydrophobic pore surface. The SRA review paper of Zhan and He [12] summarized the reported reductions in water absorption. However, other studies showed that SRA increased water permeability. Actually, it is worthwhile here to recall the different impacts of integral WP materials on water absorption (under no hydrostatic pressure) and permeability (under a hydrostatic pressure), as mentioned in Section 7.6. The dosage of SRA is typically in the range of 1%–3% of cement weight [12]. The application of SRA materials is not limited to their use as admixtures for concrete. They can also be incorporated in chemical solutions for topical surface treatment of fresh concrete [50]. The SRA solution is applied to the concrete surface after the initial set at a coverage rate in the range of 100–300 mL/m^2, either by brushing or spraying. Then, the solution penetrates the concrete structure and functions through chemical reactions as described in Section 7.4. The coverage rate and the WP performance are governed by porosity, density, and the w/c of the treated concrete and the drying conditions at the concrete surface.

The use of glycol ether as SRA was reported in several publications [46,49,51]. In addition, glycol ether has been included in the formulations of hydrophobic integral WP materials, as reported in a patent published in 2010 [53]. Kim et al. [47] investigated extensively the use of glycol ether as SRA for durability improvement of concrete with various dosages of glycol ether (in the range of 1%–3% by cement weight), for concrete mixes of ordinary Portland concrete (OPC) and modified concrete with fly ash. Their results indicated that at an optimal dosage of SRA at 3% of cement weight, the drying shrinkage was reduced by 40% and a positive effect on the relative dynamic modulus of elasticity was obtained. At the optimum dosage, glycol ether leads to an enhanced resistance to carbonation (by 30%) and enhanced resistance to cycles of freezing and thawing. The early age shrinkage and moisture loss of concrete with the use of glycol ether were investigated by Berke and Li [54]. They found that the addition of a glycol ether was the most effective means of obtaining a low moisture vapor emission rate and thus found it very effective in lowering drying and autogenous shrinkage.

3. Integral WP through lithium compounds

   Lithium compounds are added to concrete mixture for reducing the ASR. As described in Chapter 3, ASR are dependent on the alkalinity of the pore solution of the concrete, and on the dissolution of reactive silica in aggregates; thus lithium compounds mitigate the ASR through lithium bearing. The lithium-bearing admixtures include lithium nitrate, lithium nitrite, lithium carbonate, and lithium hydroxide [19]. They are believed to reduce the reactions between alkalis, which are normally present in the cement and reactive silica in the aggregates [55]. In fact, the mitigation mechanism is not thoroughly established [55]. The hypothesized mechanisms include (1) increasing the stability of the reactive silica in aggregate by decreasing its dissolution rate from the surface of aggregate through reducing the pH of the pore solution and (2) decreasing the formation of the expansive ASR gel from the repolymerization of reactive silica that causes cracking (see Chapter 3). This is achieved through the replacement of sodium and potassium ions in the produced silicates from ASR by lithium ions, which convert the silicates into nonswelling particles. In addition, the precipitation of stable and nonswelling lithium silicate at the paste/aggregate interface assists in aggregate stabilization. Actually, the effectiveness of lithium compounds is governed by the types of the conjugated anion in the used lithium compound; hydroxides and carbonates increase alkalinity as the hydroxide concentration in the pore solution is increased [19]. This enhances ASR. The use of lithium admixtures impact other concrete properties such as strength, and resistance to cycles of freezing and thawing [55].

The role of lithium compounds as indirect integral WP materials comes from the attained dimensional stability by reducing concrete expansion from ASR. This maintains concrete integrity with low permeability. In addition, the produced lithium silicate contributes to pore blocking (see Chapter 9). Also, lithium nitrate is an alkali metal nitrate, which is a hygroscopic material. It has the ability to adsorb water-forming hydrated salt crystals (lithium nitrate trihydrate), which may assist in pore blocking mechanisms. This hypothesis of pore blocking contribution is developed by the author but not handled in previous publications.

The application of lithium compounds is based on adding a powder material (e.g., lithium hydroxide and lithium carbonate) or an aqueous solution (e.g., lithium nitrate) as an admixture to the mix water prior to its addition to concrete mixture [19,56]. The dosage of lithium admixture is set by the required level of hindering the ASR expansion, which is governed by the alkali content (sodium equivalent) of the concrete and the type of reactive aggregates. This is dependent on the ionic ratio of lithium to sodium and potassium [$Li^+/(Na^++K)$]. In fact, insufficient addition of lithium admixture may actually increase the ASR expansion. The equivalent amount of lithium admixture is estimated from mass balance calculations knowing the stoichiometric ratios [19]. For example, the standard dosage of lithium carbonate is 0.88 by mass of sodium equivalent. A molar ratio within the range of 0.60 1.00 is believed to be sufficient to defeat the ASR expansion [57], and it is nominally standardized at 0.74 [19]. It is worth to highlight that lithium nitrate is toxic and thus its use is not favorable specially for water retaining structures.

7.7.2 Integral waterproofing function of supplementary cementitious materials

OPC are more porous and contain larger pores than modified concrete with mineral admixtures (see Chapters 1). The level of reduction in concrete porosity is governed by the type, reactivity, percentage cement replacement, and fineness of the incorporated SCMs [58]. The types of mineral admixtures include fly ash, slag, silica fume, and natural pozzolans. SCMs are categorized into reactive and nonreactive or poorly reactive minerals (see Chapter 1). The types of reactivities of the SCMs include (1) the hydraulic (or cementitious) activity, which is a self-initiated cementitious activity in the presence of water, and (2) the pozzolanic activity, which demands the presence of calcium hydroxide to be activated. The pozzolanic reaction of the SCMs produces additional amounts of CSH gel and consumes part of the hydration by-product (calcium hydroxide) and hence it contributes significantly to refining the pore structure of concrete. The nonreactive or poorly reactive SCMs act simply as fillers to the pores of the cement paste. The nonreactive SCMs contribute to the concrete integrity by densifying and pore blocking effects of insoluble components. Limestone powders (as nonreactive SCMs) are added to cement for filling purposes, and for modifying the grindability of the clinker or the rheology of the paste.

The SCMs are considered as integral WP materials as they participate in the hydration process and become an integral part of the paste filling of the pores and reducing the permeability. The use of SCMs usually decreases the total concrete porosity and refines the pore structure by reducing the volume of large permeable pores [58]. The filling and pore blocking of SCMs result in dividing the coarse pores into fine ones. It was reported that the incorporation of pozzolanic materials considerably reduces the average pore radius while it increases the fraction of pores smaller than 15 nm (micropores) [58]. The achieved level of pore refinement is dependent on the type and characteristics of the mineral admixtures [58]. The reduction in concrete porosity by some SCMs is also related to their role in enhancing the workability of fresh concrete and thus reducing the water demand for a specific required slump. The additions of SCMs lead to other positive impacts on concrete durability such as increasing concrete resistances against scaling, sulfate attack, chloride ions penetration, and ASR.

Table 7.5 lists the main characteristics and summarizes the effects of fly ash, silica fume, slag, and natural pozzolans on concrete permeability and on other mechanical and durability parameters [as partially summarized by Taylor [59] and as obtained from other sources]. In general, the use of SCMs enhances the strength of the fully cured concrete and increases concrete resistances against penetration of chloride ions [19,60], deicer-scaling, chemical and sulfate attacks, and ASR. They also reduce the corrosion of embedded steel bars and decrease the thermal conductivity [19,61]. Neutral effects have been reported for SCMs on concrete resistance for cycles of freezing and thawing [62].

Fly ash is widely used in the mix design for concrete pavements and mass concrete (see Chapter 4) as it has a noticeable impact on pores and porosity of modified concrete: adding fly ash (with high lime content) to concrete reduces the total porosity, increases its density, and refines its microstructure [63]. Fly ash containing concrete has lower permeability due to two main reasons: (1) reducing the pore size of the paste matrix by the products of the pozzolanic reaction and filling effect of the fine unreacted particles and (2) reducing the thickness of transition zone between surrounding aggregates and cement matrix [64]. The hydration of fly ash consumes the cement hydration by-product, $Ca(OH)_2$, and thus fills the preformed pores by its own hydration product, which leads to a more compact pore structure [65]. On the other hand, Papadakis [66] indicated that the porosity increased proportionally with the percentage replacement of cement by fly ash of low lime content. Fig. 7.6 shows the microstructure of 20% fly ashcement paste showing the densifying of the structure with curing age [63]. Fig. 7.7 shows that the porosity decreases with the addition of fly ash. Although it is widely acceptable that fly ash reduces concrete damages from the ASR [67], the literature includes other contradictory opinions on the role of fly ash for ASR mitigation [64]. Actually, its effectiveness for ASR mitigation depends on its chemical composition (e.g., Class F or C) [64]: low calcium fly ash (e.g., Class F) is more effective in mitigation of ASR than high calcium fly ash [64]. The use of fly ash as cement replacement reduces the pH of the pore solution by alkali binding and thus reduces the aggregate dissolution rate and decreases the swelling pressure of the ASR gel (see Chapter 3). Also, the reduction in permeability reduces water absorption and expansion of the ASR gel. The use of fly ash increases carbonation slightly [67] and improves the resistance of concrete to sulfate or seawater attack [68]. When Portland cement is partially replaced by

Table 7.5 Main characteristics and effects of SCMs on concrete permeability and on other mechanical and durability parameters [as reported by Taylor [59] and combined with information from other sources].

Type of SCMs replacing a fraction of cement	**Fly ash modified concrete**	**Slag modified concrete**	**Silica fume modified concrete**	**Natural pozzolans Calcined clays**
Main constituents (see Chapter 1)	Class C: close to cement composition with high SiO_2 and high CaO. Class F: high SiO_2 and low CaO. Both types contain Al_2O_3.	High SiO_2 and high CaO.	Amorphous silica (over 90% SiO_2).	High SiO_2 and high Al_2O_3.
Reactivity	Reactive silica with pozzolanic and cementitious (Class C) and only pozzolanic (Class F).	Cementitious and pozzolanic.	Only pozzolanic.	Only pozzolanic.
Size	Close to the size of cement ~ 20 m.	Larger than the average size of cement but l< 45 m.	Very fine ~ 0.1 m.	Fine ~1–2 m.
Permeability and water absorption	Reduces permeability (no effect on water absorption).	—	Reduces permeability significantly.	Reduces permeability.
Water demand for a given slump	Decreases.	Decreases.	Minor effects at low percentages—increases at high percentages.	Have little effect—decreases slightly.
Workability	Improves.	Improves.	Increases stickiness of a concrete.	Improves.
Bleeding and segregation	Decreases bleeding and segregation.	Increases rate and amount of bleeding, but no adverse effect on segregation.	Very effective in reducing both bleeding and segregation.	Has little effect on bleeding.
Heat of hydration	Decreases.	Decreases.	Increases.	Increases slightly.
Setting time	Retarding effect.	Retarding effect.	Accelerating effect.	Accelerating effect.

Strength	Contributes to the strength of fully cured concrete.	Contributes to the strength of fully cured concrete.	Contributes to strength development over the full period (3–28 days).	Contributes to the strength gain of concrete.
Air entrainment	Noticeable air entraining effect—less air entrapped air.	Similar to mixtures of only Portland cement.	Less air-entraining less entrapped air.	Similar to mixtures of only Portland cement.
Plastic shrinkage cracking	Little effect.	Little effect.	Increases.	Little effect—increases.
Deicer scaling resistance	Improves.	Improves.	Improves.	Improves.
Chemical resistance	Improves.	Improves.	Improves.	Improves.
Sulfate resistance	Improves.	Improves.	Minor effect.	Minor effect.
Penetration of chloride ions [ACI [19], Zhang and Zhang [60]]	Reduces.	Reduces.	Reduces.	Reduces.
Corrosion of embedded steel	Reduces.	Reduces.	Reduces.	Reduces.
Alkali-aggregate reactivity	Reduces significantly.	Reduces significantly.	Reduces significantly.	Reduces significantly.
Thermal conductivity [ACI [19], Demirboğa and Gül [61]]	Decreases.	Decreases.	Decreases.	Decreases.

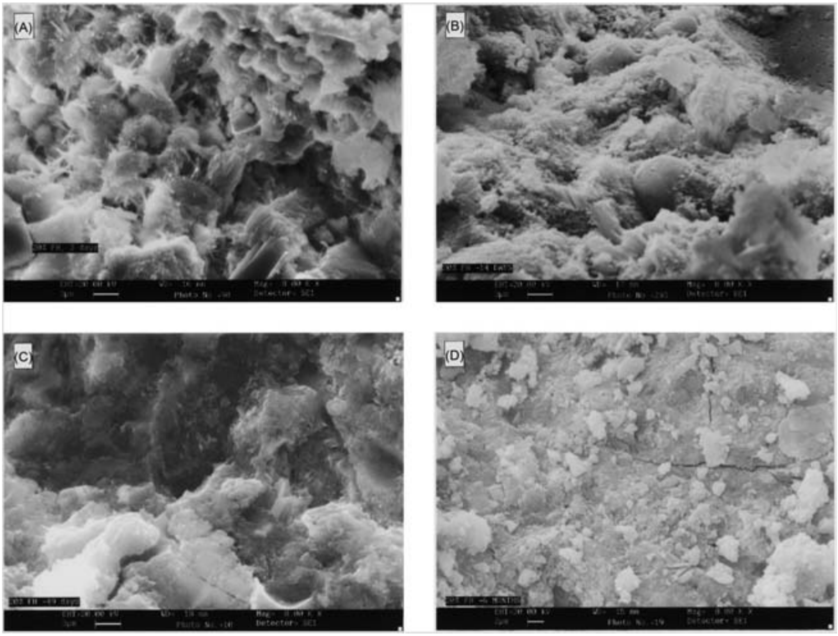


Figure 7.6 Scanning electron micrographs (8000X) of 20% fly ash cement paste after (A) 3 days of hydration. (B) 14 days of hydration. (C) 49 days of hydration. (D) 182 days of hydration [63].

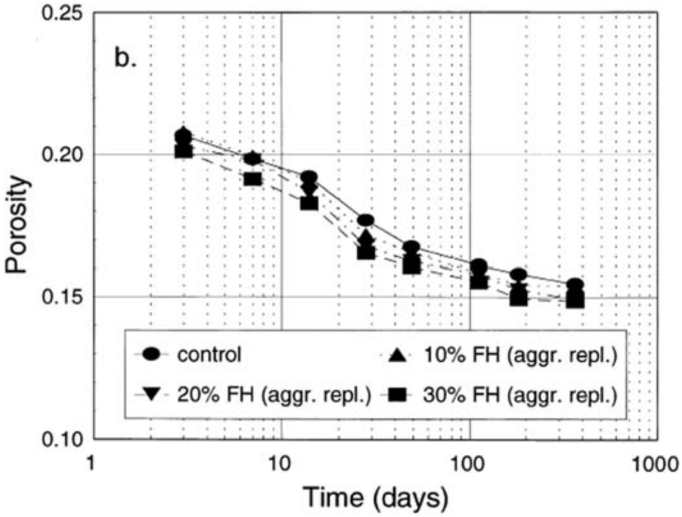


Figure 7.7 Mortar porosity showing different dosages of fly ash as a replacement of the aggregates (0%, 10%, 20%, and 30% addition to the cement weight) [63].

silica fume or slag, the structure of CSH crystals are changed from fibrillar to foil-like, which results in a less connected capillary pores [68]. Silica fume reduces the overall capillary porosity [69]. Silica fume also improves the resistance of concrete to sulfate or seawater attack [68]. Silica fume reduces concrete diffusivity and permeability through its densifying mechanism. It produces pozzolanic CS gel, which has a lower permeability than the typical CSH gel of normal concrete. The use of silica fume enhances concrete resistance for chloride ion penetration [68].

7.8 Performance characteristics and testing of integral waterproofing materials

The performance of integral WP systems is usually evaluated by observing reductions in water penetration and hence increases in concrete resistances against the ingress of harmful chemicals that cause the durability problems. The efficiency of WP is typically evaluated by measuring water absorption by capillary action and/or the permeability for water under a hydrostatic pressure. The survey of Muhammad et al. [21] indicated that water absorption test is the most common test in this research field. However, differences in behaviors and percentage improvements may be obtained when the WP materials are tested under different pressure levels due to differences in water penetration mechanism (see Section 7.6). The permeability tests are usually performed by subjecting the surface of the specimen to a high-water pressure [19]. In many cases, the flow rate is measured when a steady state permeation flow is achieved. In other cases, the penetration depth is measured after allowing the permeation flow under pressure for a certain time. On the other hand, water absorption tests are typically performed by immersion or surface capillary suction tests under a minor water head. Immersion tests are performed by measuring the mass of dry concrete specimen, then immersing the specimen in a water bath for a certain period of time at a certain temperature and then measuring its saturated mass after immersion. Then, the water absorption is obtained from the percentage difference in concrete mass after immersion expressed. Tests of water absorption by surface capillary suction are performed using the pipe method at the concrete horizontal or vertical surface [e.g., using Karsten tube [70] or autoclam sorptivity test [71,72]]. It measures the rate of water penetration under low pressure (a minor water head close to 10 cm). Then, the cumulative water absorption per unit area [e.g., in g/m^2 [71]] is determined.

Actually, integral WP materials are typically formulated to meet other basic characteristics of stability, strength, and integrity, as described in Chapter 6. They can also possess other advantages such as reducing cracking and offering self-sealing capability. Hence the performance and efficiency of WP systems are tested through a group of tests, which include direct and indirect WP testing methods [70]. Direct WP testing methods include testing water absorption, permeability, and structural-related tests, which detect reduction in porosity. Indirect WP testing methods include testing other transport properties and permeabilities, which are used to deduce moisture permeability information such as chloride ion penetration [19]. Other tests are performed to measure the percentage enhancements in mechanical and durability characteristics [15,21,73]. These types of characteristics and the testing methods are listed in Table 7.6. The listed performance characteristics are summarized in the following groups [71]:

1. Structural characteristics: They are performed for confirming the formation of WP crystals or layers within the cement paste matrix, and for determining the chemical and physical structures, pore size distribution, and air voids (e.g., SEM [74–77], BSEM [78], FTIR spectra [76], XRD [76], EDX [75], EDS [78], combined SEM/EDS [42]).
2. Transport characteristics: They include direct WP characteristics such as percentage water absorption, sorptivity, coefficient of water permeability, water penetration depth, and indirect transport characteristics such as vapor transmission and emission, gas permeabilities (air, carbon dioxide, and oxygen), ion diffusivity (e.g., diffusion of chloride ions), and level of the obtained hydrophobicity (by measuring the water contact angle).
3. Durability characteristics: They include resistance to damages from freezing and thawing cycles, salt scaling, penetration of chloride ions, corrosion of steel bars, chemical attack, acid attack, sulfate attack, carbonation, ASR, and biochemical attacks. Crack bridging or self-healing ability is also tested. Some durability characteristics are deducted from the measured transport characteristics (group 2) such as gas permeabilities and ionic diffusivity.
4. Mechanical characteristics: They include compressive, tensile, and flexural strengths as well as abrasion resistance, bonding, and adhesion strength.
5. Service and environmental characteristics: They include skid resistance and the level of toxicity of WP materials.
6. Application and curing-related characteristics: These tests include the measurements of penetration depth of WP ingredients, and effects of WP additions on concrete setting time and hydration kinetics.

For this purpose, the concept of durability index is frequently used in concrete research to characterize the intrinsic potential of a material to resist certain attack using selected transport parameters such as gaseous and ionic diffusion and water absorption [82,87]. The measured index can then allow the waterproofed concrete to be classified according to an overall matrix of index values. The durability index values cover various penetration mechanisms. These include, for example, sorptivity for water absorption under capillary action, oxygen permeability index for permeation flow under a pressure difference, and chloride conductivity for diffusion flux under a concentration difference [87]. In most WP studies, a selected group of characteristics is usually considered as a group of dependent variables [21]. Then, the investigated independent variables can be summarized as follows [21]:

- Types of WP, formulations, and the use of nanomaterials.
- Materials proportions and content, w/c ratio, WP dosage, and WP coverage rate.
- Surface preparation, level of roughness, degree of saturation, and porosity.
- Curing duration and conditions such as temperature and winds.
- Coating thickness or penetration depth of WP materials.
- Service conditions such as hydrostatic pressure, temperature, wetting conditions, and moisture variation.

Table 7.6 Main performance characteristics and tests for WP systems.

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
Structure	Chemical structure.	Detecting the formation of WP compounds and the adsorption of functional groups onto the cementitious surfaces.	Infrared (IR) spectroscopy, scanning electron microscopy (SEM), backscattered mode scanning electron microscopy (BSEM), FTIR spectra, X-ray diffraction (XRD), energy dispersive X-ray (EDX), energy dispersive X-ray spectroscopy (EDS) technique, and thermogravimetric analysis (TG and DTG).	• Confirming the presence of organic groups and chemical bonding to hydration products [79,80] (e.g., detecting an increase in carbon content and the formation of CH, C=O, and SiOSi bonds in treated concrete compared to nontreated [70]). • Confirming the presence and observing the types of hydrated products and gel in crystallization WP. • Confirming a percentage reduction in the content of calcium hydroxide (e.g., from TG and DTG analysis) as an indication of reaction conversion to crystals.
	Microstructure.	Obtaining images of the microstructure and determining the pore size distribution and the sizes of crystals.	Scanning electron microscopy (SEM) and X-ray diffraction (XRD).	• Visualization of the pore modification and confirming a percentage reduction in the average pore size (i.e., shifting the peak of pore size distribution toward the left).

(*Continued*)

Table 7.6 (Continued)

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
				• Observing the shape and the size of crystals.
	Integrity/ porosity.	Measuring density and voids content.	ASTM C642-13: Standard Test Method for Density, Absorption, and Voids in Hardened Concrete	Confirming a percentage increase in the specific gravity and a percentage decrease in the pores in hardened concrete with the WP material.
	Air content.	determining the air content and spacing factor of air voids (i.e. petrographic analysis)	• ASTM C642-13: Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. • ASTM C457-98: Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete. • ASTM C231/C231M—17a: Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method.	Confirming no major effects of WP additions on air content (there might be reduction in spacing factor).
Waterproofing efficiency	Water absorption by immersion.	Measuring the weight gain after immersing the concrete specimen in water for a given time.	• ASTM D6489-99 (2020): Standard Test Method for Determining the Water Absorption of Hardened Concrete Treated with a Water Repellent Coating.	The measured percentage absorption in hardened concrete with the waterproofing material must not exceed a certain limit (e.g., $<2.5\%$ by weight) or

			• ASTM D6532-00 (2014): Standard Test Method for Evaluation of the Effect of Clear Water Repellent Treatments on Water Absorption of Hydraulic Cement Mortar Specimens.	obtaining a significant reduction in water absorption in hardened concrete with the waterproofing material (e.g., >75%) [71].
	Capillary suction (water absorption from an exposed surface).	Measuring the rate of water penetration by capillary water absorption under low pressure (pipe method), typically with a water head of about 10–12 cm, then determining the cumulative water absorption per unit area.	• ASTM C1585-20: Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes [81]. • ASTM D 6489-99 (water absorption percentage). • BS 1881-122:2011+A1:2020: Testing concrete. Method for determination of water absorption. • BSI—BS 1881-208: Testing concrete—Part 208: Recommendations for the determination of the initial surface absorption of concrete. • BS EN 13057:2002: Products and systems for the protection and repair of concrete structures. Test methods. Determination of resistance of capillary absorption.	• Obtaining a significant percentage reduction in sorptivity in hardened concrete with the WP material compared to a control concrete [e.g., sorptivity $<10\,\mathrm{mm/(h)^{0.5}}$ [82]]. • Obtaining a significant percentage reduction in penetration depth and water absorption in hardened concrete with the waterproofing material compared to control concrete.

(*Continued*)

Table 7.6 (Continued)

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
	Water permeability—flow rate.	Measuring the steady state water flow rate under a hydrostatic water pressure (200 psi or 1.38 MPa) and using Darcy's law to estimate the permeability coefficient.	The US Army Corps of Engineers CRC C48-92 (1992): Standard Test Method for Water Permeability of Concrete.	• The waterproofing material must resist the hydrostatic pressure and the permeability coefficient in hardened concrete with the waterproofing material must not exceed a certain limit. • Obtaining a significant percentage reduction in permeability in hardened concrete with the waterproofing material compared with control concrete.
	Water permeability—depth.	Measuring the depth of water penetration in concrete under a hydrostatic water pressure [e.g., 72.5 psi (0.5 MPa) for 72 h (modified to 150 psi (1.0 MPa) for 96 h)], then splitting the specimen for measuring the depth (then the coefficient of permeability can be calculated).	• BS EN 12390-8:2019-TC: Tracked Changes. Testing hardened concrete. Depth of penetration of water under pressure. • DIN 1048 part 5 Water Permeability Test (at a pressure of 0.5 N/mm^2 for 3 days) [75]. • Using Germann Water Permeability Test.	• Obtaining a significant reduction in water penetration depth and permeability in hardened concrete with the waterproofing material compared to a control concrete (reported reductions in the depth of water penetration for pore blocking WP materials are in the range of 50%90%) [19] and for typical crystalline

				waterproofing materials the reported reductions in the Darcian permeability are 57%–75%. • The reduction according to DIN 1048 (Part 5) is 62% [24].
Other indirect waterproofing characteristics (transport and surface characteristics)	Water contact angle.	Measuring the contact angle of a water droplet with the concrete surface (static or receding contact angles).	Using goniometer device [74].	Obtaining an increase in the level of hydrophobicity for concrete with water-repelling WP materials and confirming that >90 degrees (better with >150 degrees).
	Water vapor transmission.	Water vapor permeability (breathability).	ASTM E96/E96M16: Standard Test Methods for Water Vapor Transmission of Materials.	Depending on the concept of vaporproofing or breathability, for example, for vaporproofing the transport of water vapor of surface-treated concrete should be 60% less than that of untreated concrete [15].
	Water vapor emission and absorption.	Measuring the rate of moisture emission from a concrete surface and measuring the amount of moisture absorbance by concrete subjected to water vapor introduced from boiling water in a flask.	• ASTM F1869-16a: Standard Test Method for Measuring Moisture Vapor Emission Rate of Concrete Subfloor Using Anhydrous Calcium Chloride. • ASTM F2659-10 (2015): Standard Guide for Preliminary Evaluation of Comparative Moisture	• Obtaining a low vapor emission from concrete treated with waterproofing materials (e.g., when it will receive an additional polymeric coatings). • The absorption of vapor by concrete with crystalline waterproofing material may conform the presence and the

(*Continued*)

Table 7.6 (Continued)

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
			Condition of Concrete, Gypsum Cement and Other Floor Slabs and Screeds Using a Non-Destructive Electronic Moisture Meter.	interaction of hygroscopic crystals.
	Interaction with water vapor.	Measuring the relative humidity inside the concrete pores using suitable sensors.	ASTM F2170-19a: Standard Test Method for Determining Relative Humidity in Concrete Floor Slabs Using in situ Probes.	Obtaining reductions in internal humidity at various depths of concrete specimen with waterproofing [which indicate the consumption of the vapor by interaction (adsorption) on the WP hygroscopic crystals].
	Gas permeability.	Measuring the gas permeation flow rate though a concrete specimen under a constant pressure gradient by measuring the pressure decay or the pressure rise in a vacuum cell placed on the surface of a concrete specimen.	• Torrent Air Permeability Test (SIA 262/1) [83]. • TR 31 Permeability testing of site concrete: review of methods and experience [84].	Obtaining a sufficient coefficient of gas permeability [e.g., Oxygen Permeability Index (OPI >10), defined as the negative log of the coefficient of permeability] [82].
	Gaseous diffusion.	Measuring the rate of diffusion of a specific gas [e.g., carbon dioxide [71]] under a gradient of concentration difference.	Typical gas diffusion test (in which a concrete specimen is placed between two chambers and is exposed to two different concentrations).	Obtaining a significant reduction in the diffusion coefficient of the tested gas in hardened concrete with the waterproofing material compared to a control concrete.

	Ionic diffusion (rapid chloride ion penetration).	Measuring the current passage with time through a concrete specimen maintained at a potential difference of 60 volts DC for 6 h and subjected to NaOH at one side and NaCl on the other side.	• ASTM C1202-19: Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration. • AASHTO T-277, Rapid Chloride Permeability Test.	• Obtaining a significant reduction in chloride ion penetration in hardened concrete with the waterproofing material compared to a control concrete [e.g., of 25%95% [71]]. • Obtaining a total charge passed <100 coulombs for negligible chloride ion penetration, in the range of 100–1000 for very low chloride ion penetration and in the range of 1000–2000 for low chloride ion penetration.
	Ionic diffusion (bulk diffusion).	Determination of chloride ion concentration after subjecting the concrete specimen to natural diffusion under a very high concentration gradient of sodium chloride solution.	• ASTM C1556-11a (2016): Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion ASTM C1218/C1218M20. Standard Test Method for Water-Soluble Chloride in Mortar and Concrete.	• Obtaining a low diffusion coefficient and a significant percentage reduction in the diffusion coefficient in hardened concrete with the waterproofing material compared to a control concrete. • Obtaining a low chloride content in hardened concrete with the WP material compared to a control concrete.

(*Continued*)

Table 7.6 (Continued)

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
Durability	Resistance to deterioration due to freezing and thawing cycles.	Measuring the mass loss, length change, and/or change in relative dynamic modulus of a concrete specimen subjected to a number cycles of freezing and thawing in water.	ASTM C666/C666M15: Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing.	Obtaining major reductions in the length change, the mass loss, and/or less loss of strengths (when measuring the flexural strength and compressive strength) for the treated specimen when compared to nontreated specimens.
	Scaling resistance.	Exposing a concrete specimen to freezing and thawing cycles in the presence of deicing chemicals (e.g., 4% by weight $CaCl_2$) then measuring the mass loss, length change, and/or change in relative dynamic modulus of a concrete specimen subjected to a number cycles of freezing and thawing in water.	• ASTM C672/C672M-12: Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals. • BS EN 13687-1:2002 Products and systems for the protection and repair of concrete structures. Test methods. Determination of thermal compatibility. Freeze-thaw cycling with deicing salt immersion.	Obtaining major reductions in the mass loss or less loss of strengths for the treated specimen when compared to nontreated specimens.
	Resistance to ASR.	Measuring length change (expansion) of a mortar specimen subjected to accelerated ASR conditions (concentrated sodium	• ASTM C1567-13: Standard Test Method for Determining the Potential AlkaliSilica Reactivity of Combinations of Cementitious Materials and	• Obtaining a percentage length change less than the allowable limit of length change (≤0.1% at 16 days according to ASTM C1567

		hydroxide solution with possible high temperature conditions).	Aggregate (Accelerated Mortar-Bar Method). • ASTM C1260-14: Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method). • ASTM C1293-20a: Standard Test Method for Determination of Length Change of Concrete Due to AlkaliSilica Reaction.	and $\leq 0.04\%$ at 1 year according to ASTM C1293). • Obtaining a significant reduction in ASR expansion in hardened concrete with the waterproofing material compared to a control concrete.
	Resistance to carbonation.	Measuring the depth of carbonation in a concrete specimen exposed to an accelerated carbonation process.	Accelerated carbonation method [85].	Obtaining a percentage reduction in penetration depth in hardened concrete with the WP material compared to a control concrete.
	Resistance to sulfate attack.	Measuring the length change of a mortar bar after immersing it in a standard sulfate solution.	ASTM C1012/C1012M18b: Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution.	• Obtaining a percentage reduction in the measured percentage length change in hardened concrete with the WP material compared to a control concrete [the degree of sulfate attack can be also evaluated by measuring the percentage reduction in compressive strength of concrete cubes with the WP material compared to a control concrete [86]].

(*Continued*)

Table 7.6 (Continued)

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
	Resistance to fungal attack.	Measuring the level of growth of fungus after subjecting the materials or inoculating it by the microorganisms (visual observation of the level of mold growth and assigning a mold index).	• ASTM D3273-16: Standard Test Method for Resistance to Growth of Mold on the Surface of Interior Coatings in an Environmental Chamber. • BS 3900-G6:1989: Methods of test for paints. Assessment of resistance to fungal growth. • MIL-STD-810G Method 508.6: Fungal Resistance Test.	Obtaining a low mold index for hardened concrete with the waterproofing material (the obtained mold index indicates the severity of mold growth on building materials: zero rating is assigned for the case with no observable growth and 1 for the case with trace scattered microbial growth).
Mechanical characteristics	Compressive strength.	Measuring the load for fracture of a concrete specimen in a typical compressive test.	• ASTM C39/C39M-20: Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens. • ASTM C109/C109M-20b: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars. • ASTM C1074-19e1: Standard Practice for Estimating Concrete Strength by the Maturity Method. • CEN EN 12190:1998 (MAIN) Products and systems for the protection and repair of concrete structuresTest	• Obtaining no percentage loss in the compressive strength when waterproofing materials are used (the measured compressive strength for concrete specimen with WP materials must not be less than that for control equivalent concrete). • Obtaining an increase in the strength is an additional advantage for integral WP systems.

			methodsDetermination of compressive strength of repair mortar.	
	Flexural strength.	Measuring the load for fracture of a concrete specimen in a typical flexural test.	• ASTM C78/C78M-18: Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading). • ASTM C348-20: Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars. • BS EN 196-1:2016: Methods of testing cement. Determination of strength.	• Obtaining no percentage loss in the flexural strength when waterproofing materials are used. • Obtaining an increase in the flexural strength is an additional advantage for integral waterproofing systems.
	Abrasion resistance.	Measuring the weight loss in a concrete specimen after subjecting its surface to a standard mechanical impact (e.g., rotating cutter or abraser).	• ASTM C779/C779M-00: Standard Test Method for Abrasion Resistance of Horizontal Concrete Surfaces. • ASTM C944-99: Standard Test Method for Abrasion Resistance of Concrete or Mortar Surfaces by the Rotating-Cutter Method. ASTM D4060-19: Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser EN ISO 5470-1.	• Obtaining no percentage loss in the abrasion resistance when waterproofing materials are used. • Obtaining an increase in the abrasion resistance is an additional advantage for integral WP systems (the test is needed for structures subjected to traffic, movement machines, or flowing fluids).

(*Continued*)

Table 7.6 (Continued)

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
	Bond strength. Adhesion strength. Pull-off strength.	Measuring the load for the failure of bonding of a polymeric coating to the surface of concrete specimen in a typical tensile test.	• ASTM C1583/C1583M-20: Standard Test Method for Tensile Strength of Concrete Surfaces and the Bond Strength or Tensile Strength of Concrete Repair and Overlay Materials by Direct Tension (Pull-off Method). • ASTM D7234-19: Standard Test Method for Pull-Off Adhesion Strength of Coatings on Concrete Using Portable Pull-Off Adhesion Testers adhesion strength. • ASTM D4541: Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers [26]. • ASTM C900: Standard Test Method for Pullout Strength of Hardened Concrete.	• Obtaining no percentage loss in the bond/adhesion strength when waterproofing materials are used. • Obtaining an increase in the bond/adhesion strength is an additional advantage for integral WP systems (the test is important for cementitious coatings and mortars and for concrete treated with integral waterproofing and will be then coated with polymeric coatings).

Service characteristics	The coefficient of friction. Skid resistance.	Measuring the coefficient of friction between a concrete surface and a standard material.	- ASTM F609: Static Slip Resistance of Footwear Sole, Heel, or Related Materials by Horizontal Pull Slipmeter (HPS). - ASTM E303-93(2018): Standard Test Method for Measuring Surface Frictional Properties Using the British Pendulum Tester. - EN 13036-4:2011: Road and airfield surface characteristics—Test methods—Part 4: Method for measurement of slip/skid resistance of a surface: The pendulum test.	- Obtaining no significant reduction in slipping resistance for treated concrete [74]. - Obtaining a possible surface smoothness may indicate a reduction in surface porosity due to pore filling.
	Toxicity.	Measuring the percentage survival of a standard microorganism subjected to the waterproofing chemicals and/or observing the effect of the waterproofing material on the color and turbidity of water when in contact with portable water.	- EPA-821-R-020012: Methods for measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition. - BS 6920-1:2014: Suitability of non-metallic materials and products for use in contact with water intended for human consumption with regard to their effect on the quality of the water.	Obtaining no growth of fungus (no observable toxicity must be detected) for waterproofing materials (the treated concrete specimen or the WP material must not show any visible growth of fungus) (e.g., zero rating according MIL-STD 810G).

(*Continued*)

Table 7.6 (Continued)

General	Characteristics	Test description	Typical methods—Standards	Typical performance—Criterion
Application and curing-related characteristics	Penetration depth of waterproofing material.	Measuring the penetration depth of the waterproofing solution within a concrete specimen [e.g., by visual observation of the thickness of the hydrophobic layer or the colored layer when a dye is incorporated in the WP solution [15]].	Typical methods for liquid penetration depth in concrete under simple wetting conditions.	Obtaining high penetration depth (the test is important for waterproofing solutions applied as surface treatment and for cementitious coatings with active penetrating ingredient).
	Water retention in fresh concrete.	Measuring the rate of escape of water from a cementitious mortar during the hydration process.	ASTM C156-20: Standard Test Method for Water Loss [from a Mortar Specimen] Through Liquid Membrane-Forming Curing Compounds for Concrete.	Obtaining a minimum escape rate of water during the curing period (with possible contribution of waterproofing materials in impeding the escape of water during curing).
	Slump of concrete.	Measuring the difference between the height of the slump mold and that of the highest point of fresh concrete in a typical slump test.	ASTM C143/C143M-20: Standard Test Method for Slump of Hydraulic-Cement Concrete.	Obtaining little differences in the reported slump for fresh concrete for the case with the addition of waterproofing materials compared to control concrete mixture (in many cases, adding WP materials may enhance the fluidity of freshly mixed concrete).

	Concrete setting.	Measuring the initial time of set of fresh concrete (e.g., using penetration resistance apparatus in which the initial time of set is determined when the mix reaches a penetration resistance of 500 psi).	ASTM C403/C403M-16: Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance.	Obtaining little differences in the setting time of concrete with the WP materials mixed in the concrete mixture and the control concrete mixture (in many cases, adding WP materials may cause a delay in the setting and hence an increase in the setting time).
	Hydration kinetics of concrete.	Measuring the temperature as a function of time for a cementitious mixture placed in an isothermal calorimetry during the early period of curing.	ASTM C1679-17: Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry.	Obtaining little differences in the hydration kinetics of concrete with the WP materials mixed in the concrete mixture and the control concrete mixture.

References

[1] Zou, C., et al. (2008). Degradation of mechanical properties of concrete caused by freeze-thaw action. *Journal of Building Structures*, *1*.

[2] Glass, G., & Buenfeld, N. (2000). Chloride-induced corrosion of steel in concrete. *Progress in Structural Engineering and Materials*, *2*(4), 448−458.

[3] Pastore, T., et al. (2011). Evaluation of the corrosion inhibition of salts of organic acids in alkaline solutions and chloride contaminated concrete. *Materials and Corrosion*, *62* (2), 187−195.

[4] Hobbs, D. W. (2015). *Alkalisilica reaction in concrete*. London: Thomas Telford Publishing.

[5] Mingyu, H., Fumei, L., & Mingshu, T. (2006). The thaumasite form of sulfate attack in concrete of Yongan Dam. *Cement and Concrete Research*, *36*(10), 2006−2008.

[6] Guo, L., et al. (2013). Influence of deterioration on the carbonation resistance capability of concrete with coatings. *Journal of Xuzhou Institute of Technology (Natural Sciences Edition)*, *2*, 13.

[7] Tran, P. C., et al. (2018). Carbonation proofing mechanism of silicate-based surface impregnations. *Journal of Advanced Concrete Technology*, *16*(10), 512−521.

[8] Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C. (2002). *Design and control of concrete mixtures* (Vol. 5420). IL: Portland Cement Association Skokie.

[9] Lence, A., et al. (2014). Best practices for maintenance of concrete bridge elements against mold and mildew growth. In *Proceedings of the construction research congress: Atlanta Georgia, USA*.

[10] Viitanen, H., et al. (2010). Moisture and bio-deterioration risk of building materials and structures. *Journal of Building Physics*, *33*(3), 201−224.

[11] Wu, L., et al. (2017). Autogenous shrinkage of high performance concrete: A review. *Construction and Building Materials*, *149*, 62−75.

[12] Zhan, P.-m, & He, Z.-h (2019). Application of shrinkage reducing admixture in concrete: A review. *Construction and Building Materials*, *201*, 676−690.

[13] Kubal, M. T. (2008). *Construction waterproofing handbook*. New York, USA: McGraw-Hill Education.

[14] Nair, P. S., & Gettu, R. (2016). Commercially available waterproofing agents in India: A review. *Indian Concrete Journal*, *90*, 36−53.

[15] Pan, X., et al. (2017). A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578−590.

[16] Jalali, U. H., & Afgan, S. (2018). Analysis of integral crystalline waterproofing technology for concrete. *International Research Journal of Engineering and Technology (IRJET)*, *5*(10).

[17] ACI. (1986). *Committee 515, ACI 515.1R-79. A guide to the use of waterproofing, dampproofing. Protective, and decorative barrier systems for concrete*. Farmington Hills, MI: American Concrete Institute.

[18] Mundo, R. D., et al. (2020). Recent advances in hydrophobic and icephobic surface treatments of concrete. *Coatings*, *10*(5), 449.

[19] ACI. (2016). *Committee 212, ACI 212. 3R-16. Report on chemical admixtures for concrete*. Farmington Hills, MI: American Concrete Institute.

[20] BS, BS 1504-2. (1998). *Products and systems for the protection and repair of concrete structures—Definitions, requirements, quality control and evaluation of conformity*. British Standards Institution.

[21] Muhammad, N. Z., et al. (2015). Waterproof performance of concrete: A critical review on implemented approaches. *Construction and Building Materials*, *101*, 80–90.

[22] ACI. (2013). *Committee 515, ACI 515.2R-13. Guide to selecting protective treatments for concrete*. Farmington Hills, MI: American Concrete Institute.

[23] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI: American Concrete Institute.

[24] Biparva, A., & Gupta, R. (2010). Smart Waterproofing System: A Review. *Proceedings of the International Conference on Future Concrete*.

[25] ACI. (1999). *Committee 212, ACI 212.3R-91. Chemical admixtures for concrete*. Farmington Hills, MI: American Concrete Institute.

[26] Al-Rashed, R., & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*, *13*, e00408.

[27] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills. MI, USA: American Concrete Institute.

[28] Bohus, S., & Drochytka, R. (2012). Cement based material with crystal-growth ability under long term aggressive medium impact. *Applied Mechanics and Materials*, Trans Tech Publ.

[29] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. New York, USA: McGraw-Hill Publishing.

[30] Chindaprasirt, P., et al. (2008). Cement paste characteristics and porous concrete properties. *Construction and Building materials*, *22*(5), 894–901.

[31] Van Breugel, K. (2004). Modelling of cement-based systems—The alchemy of cement chemistry. *Cement and Concrete Research*, *34*(9), 1661–1668.

[32] Ye, G. (2005). Percolation of capillary pores in hardening cement pastes. *Cement and Concrete Research*, *35*(1), 167–176.

[33] ASTM. (2003). *C12515b. Standard terminology relating to concrete and concrete aggregates*. Annual Book of ASTM Standards: West Conshohocken, PA.

[34] Wong, H., et al. (2011). Effect of entrained air voids on the microstructure and mass transport properties of concrete. *Cement and Concrete Research*, *41*(10), 1067–1077.

[35] Rashed, A. I., & Williamson, R. B. (1991). Microstructure of entrained air voids in concrete, Part I. *Journal of Materials Research*, *6*(9), 2004–2012.

[36] Ye, G. (2003). Experimental study and numerical simulation of the development of the microstructure and permeability of cementitious materials. Master of Engineering thesis, University of Technology, TU, Delft. Delft, The Netherlands.

[37] ACI. (2010). *Committee 212, ACI 212.3R, Report on Chemical Admixtures for Concrete*, Farmington Hills, MI: American Concrete Institute.

[38] Zhan, H., Wittmann, F., & Zhao, T. (2003). Chloride barrier for concrete in saline environment established by water repellent treatment. *International Journal for Restoration of Buildings and Monuments*, *9*(5), 535–550.

[39] Shetty, M. (2005). *Concrete technology theory and practice* (pp. 420–453). New Delhi, India: S.Chand and Company LTD.

[40] Mehta, P. K. (1991). *Concrete in the marine environment*. Boca Raton, FL, USA: CRC Press.

[41] Jianxia, S. (2012). 6.14—Durability design of concrete hydropower structures. In A. Sayigh (Ed.), *Comprehensive renewable energy* (pp. 377–403). Oxford: Elsevier.

[42] de Souza Oliveira, A., et al. (2020). Crystalline admixture effects on crystal formation phenomena during cement pastes' hydration. *Journal of Thermal Analysis and Calorimetry*, *139*(6), 3361–3375.

[43] Aldred, J. (1989). The short-term and long-term performance of concrete incorporating dampproofing admixtures. In: *Supplementary Papers of 3rd CANMET/ACI International Conference on Superplasticizers and Other Chemicals in Concrete*.

[44] Al-Rashed, R., & Al-Jabari, M. (2021). Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete. *Case Studies in Construction Materials*, *15*, e00635.

[45] Matar, P., & Barhoun, J. (2020). Effects of waterproofing admixture on the compressive strength and permeability of recycled aggregate concrete. *Journal of Building Engineering*, *32*, 101521.

[46] Berke, N., et al. (2003). Improving concrete performance with shrinkage-reducing admixtures. *Special Publication, 217*, 37–50.

[47] Kim, K.-K., Song, I.-M., & Jung, S.-J. (2007). A study on durability improvement of concrete using glycol ether chemical admixture. *Journal of the Korean Institute of Building Construction*, *7*, 117−124.

[48] Kinnunen, T., & Koskela, M. (1991). Antibacterial and antifungal properties of propylene glycol, hexylene glycol, and 1, 3-butylene glycol in vitro. *Acta Dermato-Venereologica*, *71*(2), 148.

[49] Mohammed, T. U., & Hamada, H. (2003). Durability of concrete made with different water-reducing chemical admixtures in tidal environment. *ACI Materials Journal*, *100* (3), 194−202.

[50] Nmai, C., et al. (1998). Shrinkage-reducing admixtures. *Concrete International*, *20*(4), 31−37.

[51] Sugiyama, M., et al. (1987). Durability of concrete containing a shrinkage-reducing admixture. *Special Publication, 100*, 1103–1120.

[52] Chindaprasirt, P., & Rattanasak, U. (2011). Shrinkage behavior of structural foam lightweight concrete containing glycol compounds and fly ash. *Materials & Design*, *32*(2), 723−727.

[53] Aldykiewicz Jr, A. J., et al. (2010). *Integrally waterproofed concrete*. Google Patents.

[54] Berke, N., & Li, L. (2004). Early age shrinkage and moisture loss of concrete. In: *International RILEM Symposium on Concrete Science and Engineering: A Tribute to Arnon Bentur*. RILEM Publications SARL Evanston, IL.

[55] Agarwal, R., et al. (2017). Alkali silica reaction (ASR) mitigation in concrete by using lithium nitrate. *International Journal of Engineering and Applied Sciences*, *4*(3).

[56] Thomas, M. D., Fournier, B., & Folliard, K. J. (2008). *Report on determining the reactivity of concrete aggregates and selecting appropriate measures for preventing deleterious expansion in new concrete construction*. United States: Federal Highway Administration.

[57] ACI. (2008). *Committee 201, ACI 201.2 R-08. Guide to durable concrete*. Farmington Hills, MI: American Concrete Institute.

[58] Meddah, M. S., & Tagnit-Hamou, A. (2009). Pore structure of concrete with mineral admixtures and its effect on self-desiccation shrinkage. *ACI Materials Journal*, *106*(3), 241.

[59] Taylor, P. (2014). *The Use of Ternary Mixtures in Concrete*. Ames, IA, USA: National Concrete Pavement Technology Center, Iowa State University Research Park.

[60] Zhang, Y., & Zhang, M. (2014). Transport properties in unsaturated cement-based materials—A review. *Construction and Building Materials*, *72*, 367−379.

[61] Demirboğa, R., & Gül, R. (2003). Thermal conductivity and compressive strength of expanded perlite aggregate concrete with mineral admixtures. *Energy and Buildings*, *35* (11), 1155−1159.

[62] Wang, X., et al. (2018). An innovative approach to concrete mixture proportioning. *ACI Materials Journal*, *115*(5), 749−759.

[63] Papadakis, V. G. (2000). Effect of fly ash on Portland cement systems: Part II. High-calcium fly ash. *Cement and Concrete Research*, *30*(10), 1647−1654.

[64] Saha, A. K., et al. (2018). The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials*, *171*, 743−758.

[65] Zeng, Q., et al. (2012). Determination of cement hydration and pozzolanic reaction extents for fly-ash cement pastes. *Construction and Building Materials*, *27*(1), 560−569.

[66] Papadakis, V. G. (1999). Effect of fly ash on Portland cement systems: Part I. Low-calcium fly ash. *Cement and Concrete Research*, *29*(11), 1727−1736.

[67] Sakai, E., et al. (2005). Hydration of fly ash cement. *Cement and Concrete Research*, *35*(6), 1135−1140.

[68] Bapat, J. D. (2012). *Mineral admixtures in cement and concrete*. Boca Raton, FL, USA: CRC Press.

[69] Song, H. W., et al. (2007). An estimation of the diffusivity of silica fume concrete. *Building and Environment*, *42*(3), 1358−1367.

[70] Weisheit, S., et al. (2016). Assessment of test methods for characterizing the hydrophobic nature of surface-treated high performance concrete. *Construction and Building Materials*, *110*, 145−153.

[71] Basheer, P. A. M., et al. (1997). Surface treatments for concrete: Assessment methods and reported performance. *Construction and Building Materials*, *11*(7), 413−429.

[72] Liu, J., et al. (2014). Study on water sorptivity of the surface layer of concrete. *Materials and Structures*, *47*(11), 1941−1951.

[73] Russell, H. G. (2012). *Waterproofing membranes for concrete bridge decks* (Vol. 425). Transportation Research Board.

[74] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2019). Moisture evaluation of concrete pavement treated with hydrophobic surface impregnants. *International Journal of Pavement Engineering*, 1−9.

[75] Azarsa, P., Gupta, R., & Biparva, A. (2018). Crystalline waterproofing admixtures effects on self-healing and permeability of concrete. In: *1st International Conference on New Horizons in Green Civil Engineering (NHICE-01)*: Victoria, BC, Canada.

[76] Rahman, M., & M. Al-Kheetan (2019). Integration of Anhydrous Sodium Acetate (ASAc) into Concrete Pavement for Protection Against Harmful Impact of De-icing Salt, JOM 71(12): 4899–4909.

[77] Thompson, J. L., et al. (1997). Characterization of silicate sealers on concrete. *Cement and Concrete Research*, *27*(10), 1561−1567.

[78] Azarsa, P., Gupta, R., & Biparva, A. (2020). Inventive microstructural and durability investigation of cementitious composites involving crystalline waterproofing admixtures and Portland limestone cement. *Materials*, *13*(6), 1425.

[79] Mora, E., et al. (2019). Control of water absorption in concrete materials by modification with hybrid hydrophobic silica particles. *Construction and Building Materials*, *221*, 210−218.

[80] Song, Z., Lu, Z., & Lai, Z. (2019). Influence of hydrophobic coating on freeze-thaw cycle resistance of cement mortar. *Advances in Materials Science and Engineering*, 2019.

[81] Chen, H., et al. (2020). The influence of surface treatment on the transport properties of hardened calcium sulfoaluminate cement-based materials. *Cement and Concrete Composites*, *114*, 103784.

[82] Alexander, M., Mackechnie, J., & Ballim, Y. (1999). Guide to the use of durability indexes for achieving durability in concrete structures. *Research Mmonograph*, *2*, 102.

[83] Kucharczyková, B., Misák, P., & Vymazal, T. (2010). Determination and evaluation of the air permeability coefficient using Torrent Permeability Tester. *Russian Journal of Nondestructive Testing*, *46*(3), 226−233.

[84] Salvoldi, B. G., Beushausen, H., & Alexander, M. G. (2015). Oxygen permeability of concrete and its relation to carbonation. *Construction and Building Materials*, *85*, 30–37.

[85] Atiş, C. D. (2003). Accelerated carbonation and testing of concrete made with fly ash. *Construction and Building Materials*, *17*(3), 147–152.

[86] Al-Akhras, N. M. (2006). Durability of metakaolin concrete to sulfate attack. *Cement and Concrete Research*, *36*(9), 1727–1734.

[87] Olorunsogo, F. T., & Padayachee, N. (2002). Performance of recycled aggregate concrete monitored by durability indexes. *Cement and Concrete Research*, *32*(2), 179–185.

Hydrophobic integral dampproofing materials

8

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

8.1 Introduction

Water penetration in concrete occurs through permeation under a hydrostatic pressure (Chapter 2) and/or through capillary action without a hydrostatic pressure (Chapter 5). The theoretical analysis of capillary absorption in cementitious material (Chapter 5) indicates that the cumulative water absorption per unit area (W_{cs}) is described by the square root of time relation as given in Eq. (8.1) [1,2].

$$W_{cs} = S\sqrt{t} \tag{8.1}$$

where S is the capillary absorption coefficient or simply the sorptivity (kg/m^2 s$^{1/2}$). The experimental water absorption curves are typically modeled well with Eq. (8.1) when W_{cs} is plotted versus the square root of time [3]. The capillary absorption coefficient is obtained from the slope of the plot.

The resulting water-associated problems reduce concrete quality and shorten its service life (Chapter 3). In response to water-related durability problems, concrete structure can be protected by reducing the ingress of water using waterproofing (WP) and dampproofing (DP) systems. WP and DP materials involve various types of interactions with water: The mechanisms of water interactions with cementitious surfaces are described in Chapter 5. Based on the types of hydro-mechanisms, the mechanisms of WP performance are divided into hygroscopic, hydrophilic, and hydrophobic systems (see Chapter 7). The hydrophobic DP materials are reactive compounds that lead to lining the capillary internal surfaces with a water-repellent layer, which reduces the capillary absorption of water. The other systems of hydrophilic and hygroscopic WP materials are detailed in the subsequent chapters. WP materials reduce concrete permeability and thus can be applied for water submerged concrete under a hydrostatic pressure, as encountered in below-grade and water-retaining concrete structures. Typically, hydrophobic DP materials are applied for above-grade concrete structures. DP materials are suitable for nondamped concrete, which might be under cyclic wetting-drying conditions in building. It can be applied for below-grade concrete structures subjected to humidity condensation at the concrete surface (see Chapter 6).

The hydrophobic DP materials react with the cementitious content in concrete and become integral constituents of its structure. Hence, they belong to integral

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00008-8

DP systems. As described in Chapter 7, the integral WP and DP materials include solutions used in penetrating surface treatments, powder or liquid systems used as additions to concrete mixture at the time of batching, and powders incorporated in the formulations of cementitious coatings and mortars that are applied as a slurry coat or dry shake. The cementitious coating systems are discussed in Chapter 12. DP and WP solutions are referred to in ACI Concrete Terminology as penetrating materials of low viscosity [4]. ACI 515.2R-13 [5] discusses various types of solutions. DP and WP additions to concrete mixture are described in ACI 212.3R-10 report [6] using the terminology of permeability reducing admixtures (PRAs). PRAs include systems for applications under conditions of hydrostatic pressure (PRAH) and others for applications under conditions of nonhydrostatic pressure (PRAN) [6]. Frequently, PRANs are known as DP admixtures and PRAHs are known as WP admixtures [7]. A discussion on the suitability of PRAH terminology is introduced in Chapter 7, while it is detailed further in this chapter. This chapter discusses the types, mechanisms, and performance parameters of DP solutions and additions. The physicochemical backgrounds and mechanisms of hydrophobic integral DP technology are detailed and linked to the hindering mechanism of water penetration by capillary action. The parametric trends of the impacts of hydrophobic integral DP materials on the durability enhancement are discussed. The chapter builds on the definitions and backgrounds given in Chapters 6 and 7.

8.2 Concepts of hydrophobic dampproofing materials

Hydrophobic integral DP materials are compounds that have the ability to be adsorbed or precipitated/deposited onto the cementitious surfaces and then line the pores. From this perspective, hydrophobic DP materials are referred to in EN 1504-2 [8] as pore liners. A typical hydrophobic compound that is adsorbed on the pore surfaces is composed of a hydrophobic organic group (alkyl) at one end and a reactive group at the other end. The reactive group promotes chemical bonding to the cementitious structure forming a molecular layer within concrete pores. The hydrophobic alkyl group is stable and remains extended outward from the surface creating the water-repellency characteristic [9]. Other hydrophobic compounds form precipitates with hydrophobic carbon-based groups. When the pores are lined with the hydrophobic layer, their capacity for capillary action (water absorption) is significantly reduced. This is achieved by increasing the water contact angle (WCA) between the water drop and the surface and by lowering the surface energy (see Chapter 5). Fig. 8.1 illustrates the types of interactions of water droplets with cementitious surfaces showing levels of hydrophobicity and hydrophilicity. Typical cementitious concrete surfaces are hydrophilic with static WCA (θ) <30 degrees and hence they suck water. When $\theta > 90$ degrees, the surface is considered hydrophobic and hence it repels water. Increasing θ increases the level of hydrophobicity and hence decreases the capillary action and increases the efficiency of DP performance [10]. When θ is between 120 and 150 degrees, the surface is commonly

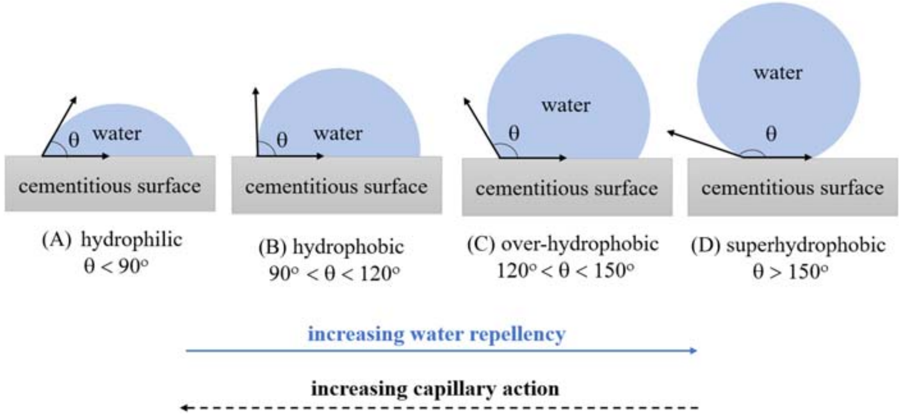


Figure 8.1 Illustrations of the types and levels of interactions of a water droplet with cementitious surfaces.

categorized as overhydrophobic [11,12]. Furthermore, when θ exceeds 150 degrees, the surface is commonly described as superhydrophobic, and associated with a high DP performance [10,12]. The level of the hydrophobicity is governed by the structural characteristics of alkyl groups according to the following two points [9]: (1) hydrophobes with large molecular weight (e.g., isobutyl and n-octyl) lead to surfaces with larger hydrophobicity than those of small molecular weight (e.g., methyl and ethyl), (2) the hydrophobicity is enhanced with structure complexity of the alkyl group, the level of hydrophobicity for branched structure > straight chained > cyclic structure.

A goniometer device is commonly used to measure the static WCA (θ) [13,14]. Measurement of the WCA of concrete is dependent on time. Fig. 8.2 shows the measurements of static WCA on a concrete surface as a function of time [14]. It is shown that θ decreases with time of measurement indicating instability of water droplet. Concrete porosity and fine capillary network structure generate a time-dependent sink action that promotes concrete wetting and swelling through capillary absorption. Hence, the water drop does not remain stable on the surface for a sufficiently long time. In fact, information regarding the stability of the water drop during measurements, commonly missing, should be reported with the measurement [11]. When $\theta < 90$ degrees, decreasing the value of θ indicates an increase in the level of hydrophilicity (i.e., increasing capillary action, see Fig. 8.1. Fig. 8.2 shows that the concrete external surface becomes more hydrophilic with wetting time.

The driving force for capillary suction in concrete is the pressure drop between bulk water (P_w) and the water at the interface (P_a) (at pores surfaces). As described in Chapter 5, such a pressure drop ($P_w P_a$) is given by the following equation (Laplace equation):

$$P_w - P_a = \frac{2\gamma_{wa}}{r} cos\theta \tag{8.2}$$

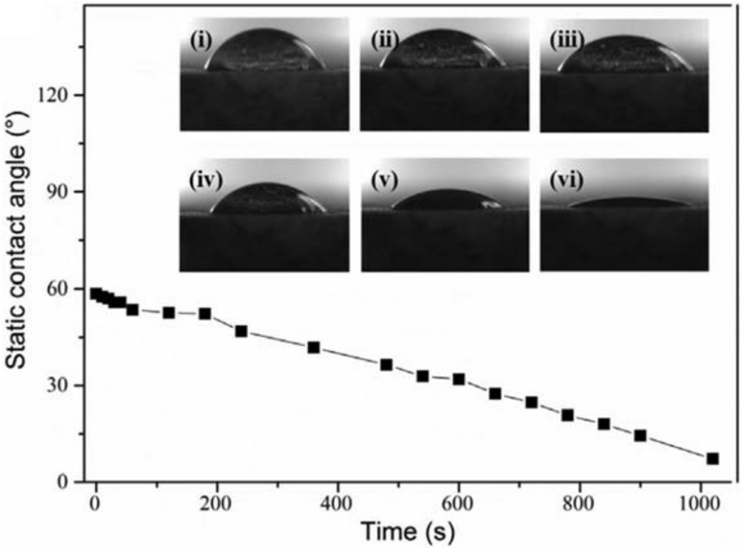


Figure 8.2 Static water contact angle () as a function of time of measurement from the time of placing the droplet on a concrete surface. Inset: Typical images of water droplets on concrete at (i) 10 s, (ii) 1 min, (iii) 2 min, (iv) 4 min, (v) 9 min, and (vi) 14 min ([14]).

where $_{wa}$ is the surface tension of water, r is the radius of the capillary pore, θ is the static WCA between the water and the solid. For a hydrophilic cementitious surface, $P_w > P_a$, due to the capillary force that reduces P_a below P_w. Thus the value of (P_wP_a) for an untreated concrete surface is positive and hence a water droplet will spontaneously penetrate the pores. On the other hand, the value of P_wP_a for a hydrophobic concrete surface is negative as $\cos\theta < 0$ (with $\theta > 90$ degrees) and hence the surface repels water away from the surface. Water-repellency is a property of a surface that resists wetting but promotes the flow of water when hydrostatic pressure is applied [4]. If the pressure of the bulk water (P_w) is increased by applying a hydrostatic pressure over the value of P_a, the resulting pressure difference (P_wP_a) becomes larger than that estimated from Eq. (8.2), and hence water can penetrate the pores [1]. Typically, the hydrophobically modified concrete can withstand a hydrostatic pressure of only a few centimeters [6], although theoretical estimations indicate that a hydrophobic concrete surface with full pore lining can resist a pressure of about 4 m or higher [15]. A typical pressure limit for inhibiting water penetration of hydrophobic materials (of silane and siloxane types) is 120 $\mathrm{kg_f/m^2}$ (12 cm water) [16]. This is because the pore lining is not completely achieved [6]. Hereafter, water repellents are not impervious to water penetration by permeation when the water head is high. This analysis calls for the review of the suitability of PRAN term for describing DP materials as referred to by ACI 212.3R-16 [6]; as PRANs do not reduce permeability but they reduce capillary action when the hydrostatic pressure is lower than the interface pressure (P_a). In fact, the labeling of such materials as simply DP materials, according to ACI 212.3R-91 [17] and some concrete books [18,19], is believed to provide a better technical term. In this chapter, integral DP terminology is used while PRAN is not considered valid. According to ACI 212.3R-91 [17], DP admixtures are not acceptable in controlling moisture migration through slabs-on-ground [17].

Fig. 8.3 shows WCA for several specimens of high performance concrete treated with silane/siloxane copolymer and the corresponding images of the water drop on untreated, treated, and weathered samples after being treated [20] (the impact of weathering is discussed in Section 8.6.1). For the control specimen, the average value of θ is about 30 degrees, which is a typical value for concrete. However, when the surface of the cementitious specimen is modified with the hydrophobic material, θ becomes >90 degrees, confirming the hydrophobicity of the treated surface. Such a thermodynamic surface change hinders water penetration into the concrete pores and minimizes wetting of the cementitious surface.

The WCA, and hence the level of hydrophobicity, is governed by the type, the dosage, and the efficiency of the DP system as well as the original cementitious surface. For example, [21] found that the WCA increased with increasing the concentration of the used potassium methyl siliconate in the surface treatment solution up to a certain limit. The surface hydrophobicity (or the WCA) is governed by structural surface characteristics such as surface roughness [22]. The protruding points of roughness drive the water drop to set on the protrusions rather than touching the full surface; then the entrapped air below the drop causes incomplete wetting of the surface and make rough surfaces more hydrophobic than polished or smooth surfaces [23]. This increase in hydrophobicity by increasing surface roughness is predicted by the Cassie model of a “nonwet” state (see Chapter 5). Also,

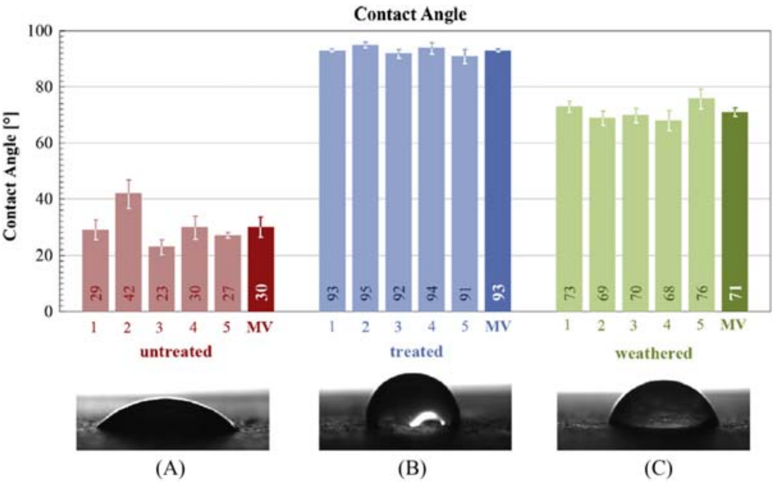


Figure 8.3 Static water contact angles () for several specimens of high performance concrete and the corresponding images of a water drop on surfaces including (A) untreated, (B) treated with silane/siloxane copolymer, and (C) weathered samples after being treated with silane/siloxane copolymer ([20]).

according to the Cassie model (see Chapter 5), increasing the porosity of concrete at the surface enhances the nonwetting conditions. According to Wenzel model [24], the rough surface is considered to be completely filled with water and a roughness factor (f) is defined as the ratio of actual contact area over the geometric surface, that is, $f > 1$ for real surfaces (see Chapter 5). Thus for a hydrophobic surface, increasing the surface roughness increases f and increases WCA and the level of hydrophobicity. Other factors that govern the WCA and the level of hydrophobicity related to the impacts from surrounding during the service life of concrete (i.e., stability of the hydrophobic treatment with time as detailed in Section 8.6.1).

In most cases, hydrophobic materials do not contribute in pore blocking or refining (obtained by crystallization WP materials), although some researchers reported some pore refinement effects of organoiron compounds [25]. Furthermore, hydrophobic DP systems cannot bridge existing cracks or cannot heal formed cracks (no self-healing) and they cannot protect concrete from further cracking. Thus they maintain the crack network physically open for water permeation under a hydrostatic pressure [5]. In fact, some studies have indicated an increase in the porosity of concrete when modified with the addition of hydrophobic DP materials. For example, [1] reported that the addition of stearic acid to cement paste reduced the compactness of the hardened paste and increased the porosity, the pore size, and the pore connectivity. Furthermore, the hydrophobic dampproofed concrete surfaces remain open for the flow of vapor and gases [6,9]. Vapor transmission through concrete is essential for its breathing. It has been reported that the hydrophobic DP pore liners hardly affect the diffusion of water vapor and other gases [26,27]. It has been shown that the permeability of water vapor through hydrophobic-treated concrete surfaces (e.g., silanes and siloxanes) is similar to that of untreated concrete [3] (see Section 8.8.4). The use of DP materials decreases the internal humidity in concrete [11], which in turn minimizes various moisture-related problems (see Chapter 3). This behavior opposites that of the vaporproofing or vapor barriers of polymeric systems (see Chapters 6 and 12). On the other hand, the breathability allows water vapor to penetrate small pores and then condensates by cooling (i.e., capillary condensation). The condensate is permeated further through unreached hydrophilic pores under the capillary action [2]. Hence, the inward vapor penetration can create durability problems. Consequently, concrete breathability can be considered a dualistic issue (as demonstrated in Chapter 7).

8.2.1 Antiicing and icephobicity of hydrophobic damproofing materials

The pore lining effect of hydrophobic DP materials has a significant effect on the mechanism of ice adhesion and on the ease of its detachment from concrete surface. This phenomenon has impacts on the serviceability and durability of concrete pavement applications in highways and airports. Within such a context, the term icephobicity is used to refer to nonice-adhesion with concrete surfaces, that is, ice repelling or surface retardation to ice adhesion [28]. The physicochemical aspects of ice adhesion and icephobicity are presented in Chapter 5: Ice adhesion is based on the types and levels of interactions between the ice and the cementitious surface. These include (1) physicochemical interactions [water adsorption onto the cementitious surface, hydrogen bonding, and van der Waals forces [28]] and (2) mechanical actions between the ice and the solid surface (e.g., entanglement and interlocking of ice structure), which are associated with surface roughness and porosity [29]. Quantification of ice adhesion (or icephobicity) is practically based on measuring the strength of ice adhesion [11,29], which is preferably done using shear stress testing [11]. Reported shear stress for icephobic cementitious surfaces is typically in the order of hundreds of kPa [11].

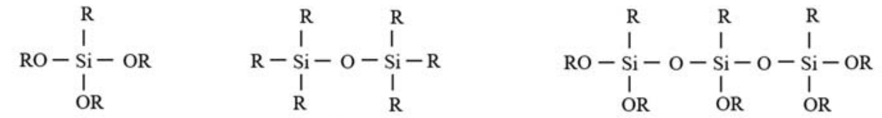
The antiicing effect of hydrophobic DP systems is an additional benefit of these materials [11]. Icephobicity of a concrete surface increases with increasing WCA [11,28]. Highly antiicing surfaces are obtained with superhydrophobic surfaces (i.e., contact angles >150 degrees) [30]. The mechanism of the DP materials in preventing ice adhesion is basically based on water repelling and reducing surface wetting. A superhydrophobic surface has an antiicing characteristic as it increases the time for freezing and has icephobicity as it reduces the ice adhesion strength [14]. These effects promote the rapid removal of water drops from surfaces and enhance the rain drain when it impacts the surfaces. These nonwetting conditions minimize the opportunity for ice nucleation and growth. From thermodynamic and heat transfer perspectives, the level of ice formation is governed by the temperatures of the concrete surface and the surrounding air and the rate of vapor condensation in capillary networks upon cooling. The decrease in water penetration also reduces interlocking effects and decreases the strength of ice adhesion. In more precise technical terms, minimizing nucleation of ice at the surface is better referred to as antiicing while reducing ice adhesion is better referred to as icephobicity [11]. It has been demonstrated that increasing the hydrophobicity of a concrete surface reduces the freezing temperature of water at that surface. A decreasing graphical relationship between freezing temperature and static WCA is given in Chapter 5 [30]. It has been reported that the icephobicity of treated concrete was significantly improved when superhydrophobic nanoparticles assisted in clogging the pores [14].

8.3 Types of hydrophobic damproofing materials

The types of hydrophobic DP materials include reactive and nonreactive carbon-based compounds of the following chemical families: (1) solutions and powders of organosilicon compounds (e.g., silanes, siloxane, and siliconates), (2) solutions and powders of soaps, salts, and derivatives of fatty acids, (3) natural and mineral oils and fats, (4) suspensions and emulsions of synthetic polymeric materials [e.g., fine rubber droplets suspended in an ammonia solution and emulsions of bitumen, acrylic, or latex [31]], and (5) nano and particulate systems.

Silicon-based materials are organosilicon compounds, which include silane, siloxane, and siliconates. In fact, the root name of silane refers to SiH_4 in analogy with methane naming (CH_4). Each hydrogen atom in SiH_4 can be replaced by a certain element or a group leading to a wide range of organosilicon compounds [32]. These replacements include alkyl groups (R) such as methyl (CH_3) or ethyl (CH_3CH_2) or alkoxy (alkyl and oxygen) groups (RO) such as methoxy (CH_3O) and ethoxy (CH_3CH_2O) [32]. For example, replacement of one hydrogen by a methyl group (CH_3) yields the methyl silane (CH_3SiH_3). The structures of the main organosilicon compounds are shown in Fig. 8.4. These structures commonly include a single or multiple silicon atom(s) connected to the two types of functional groups: (1) the hydrophobic organic group (the alkyl group) that creates the water-repellency of the treated surface, and (2) the reactive alkoxy group(s) carrying the hydroxyl groups that participate in bonding with the concrete substrates and in interbonding or crosslinking among the organosilicon compounds. The hydrophobic carbon-based group can be of hydrocarbon type (CH_x) or fluorocarbon type (CF_x) [11]. Alkoxy silane compounds, which include at least one RO group, are used in pore lining: the RO group is reactive with the OH-group on the cementitious surface [32]. For obtaining a hydrophobic behavior, at least one organic group directly attached to silicon through an SiC bond is required, as it remains unreactive and stable during the setting reactions of organosilicon compounds (see Section 8.5.1.1). For example, in methyl trimethoxy silane [$CH_3Si(OCH_3)_3$], the methoxy groups will react with water, while the methyl group will remain stable and attached to silicon, throughout setting reactions, yielding to hydrophobicity. By various combinations of reactive alkoxy and nonreactive alkyl groups, hundreds of compounds can be produced forming siloxane bonds [32]. The stability of these compounds and their resistance against degradation in alkaline conditions are governed by the length of the organic groups and their structural complexity (e.g., branching). These structural parameters also affect the capability for water repelling. A full review of industrial organosilicon compounds for concrete applications was published by [11].

The common types of saline compounds include alkyl trialkoxy silanes [5], which are among the smallest silicon-based compounds, and thus they have high penetrability in concrete [5]. Alkoxy silanes are sometimes called alkyl silicates [12]. Alkyl trialkoxy silanes are composed of an organic group of alkyl type (R)


alkyl alkoxy silane siloxane alkyl alkoxy siloxane (polysiloxane)

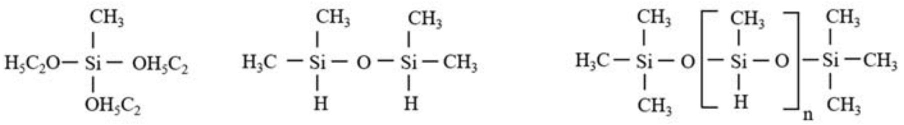

methyl tri ethoxy silane tetra methyl di siloxane poly methyl hydroxy siloxane (PMHS)

Figure 8.4 Sample structures of organosilicon compounds.

that has the character of water repellency, and three reactive alkoxy (RO) groups, which are involved in creating the chemical bonding with silicon atoms on the concrete substrate and interbonding among the hydrophobic molecules (see Section 8.5.1.1). The organic group can be short such as methyl or ethyl group or long such as octyl group (straight or branched). Examples of used saline compounds include octyl triethoxy silane [33], isooctyl triethoxy silane [10], trimethoxy silane [34], and -(methylpropyleneoxy) propyl trimethoxy silane [35]. Some alkyl silicate compounds (e.g., ethyl silicate or tetraethyl orthosilicate, TEOS) have been classified by some researchers as reactive hydrophilic crystallization agents (see Chapter 9) although they belong to alkoxy silane compounds which undergo hydrolysis reactions and produce a hydrophobic molecular layer with just a secondary pore filling effect [9,36,37]. TEOS has the ability to penetrate into the gel pores of C–S–H gel and create a hydrophobic molecular layer that reduces the sizes of the gel pores [38,39]. Such a secondary pore refining effect obtained by TEOS has a little effect on medium and large pores and thus it is less than that obtained from alkali silicate compounds [38]. For the same reasons, it has been shown that the level of enhancement in the abrasion resistance of surface-treated concrete with TEOS is less than that with sodium silicate (which densifies the surface, see Chapter 9) [16].

Siloxanes used for concrete are oligomeric alkyl alkoxy siloxanes, composed of short chains of silanes (oligomers) [37]. The common types of siloxane compounds include poly methyl siloxane, tetra methyl di siloxane. Similar to silanes, siloxane compounds include the two types of functional groups attached to a siliconoxygen chain: the alkyl groups in siloxanes are either all of similar type (e.g., methyl or ethyl groups), or mixed types. The stability of alkyl groups against degradation in alkaline conditions and the level of their hydrophobicity are governed by the structural parameters of these groups (molecular size and complicity) [5]. However, as the sizes of siloxane molecules are much larger than those of the silanes, they have a lower volatility and a lower penetrability than silanes. Their main advantages over silanes are their high reaction rates and their low volatilities [37]. The low volatility is an environmental advantage as it releases low volatile organic compounds (VOC) and causes low pollution problems during application. The low volatility is also an economic advantage as it causes minimum escape of active ingredients in hot and windy conditions. Consequently, siloxanes solutions are usually formulated with a lower solid content than those of silanes solutions. The low penetrability of siloxanes is considered as a disadvantage for typical concrete applications as the resulting efficiency and sustainability of the treatment are decreased by decreasing penetrability. It is worth mentioning that low penetrability is considered sometimes advantageous when siloxanes are used for highly porous concrete [5]. In fact, siloxanes are believed to function better when they are blended with a silane. Other types of silicon-based materials are film forming polysiloxane resins such as polydimethylsiloxanes, which are capable of crosslinking when subjecting to moisture yielding an elastomeric film.

The organosilicon compounds are used in liquid systems for surface treatment or in powder forms as admixtures. For surface treatments, liquid or semiliquid compounds are formulated as penetrating solutions, emulsions, gel, or cream systems [11]. Solutions of silanes and siloxanes are usually formulated in solvent-based systems. Cream type octyl triethoxy silane (e.g., 80%) is prepared by its mixing in water in the presence of emulsifiers [2]. Gel type silane is produced by adding mineral thickeners [2]. Particulate silane systems that are incorporated in cementitious mixtures include powders of octyl triethoxy silane [13] and methyl silane [10]. Alkali methyl siliconates are aqueous solutions of salts of methyl silanes, which are produced from the reaction of sodium (or potassium) hydroxide with methyl trichloro silane. Methyl siliconates are water-soluble salts of methyl silanes.

Organic solutions and powders of soaps, salts, and derivatives of fatty acids include stearic, oleic, caprylic, and capric acids. The use of stearic acid is considered as an ecological approach [11]. The common hydrophobic alkali stearate compounds include the salts of stearic acid, which are composed of the organic anionic group combined with an alkali positive ion such as calcium, sodium, or lithium [6]. In addition, these types include ammonium stearate and butyl stearates [6]. Calcium stearate [$Ca(C_{18}H_{35}O_2)_2$] is a precipitate that is commonly used in powder form as an admixture [4]. The sodium stearate ($NaC_{18}H_{35}O_2$) is a white powder, which is used as a common soap. Other alkali salts of stearate include lithium stearate ($LiC_{18}H_{35}O_2$) and potassium stearate ($KC_{18}H_{35}O_2$). Ammonium stearate ($C_{18}H_{39}NO_2$) is used as a cement additive [40]. Ammonium stearate mixed with cement and conditioned with an admixture was patented to obtain a water-repellent concrete [40]. Butyl stearate ($C_{17}H_{35}COOC_4H_9$) is a colorless and oily material [4]. Other types of fatty acids can be used as hydrophobic DP materials such as oleates water-repellent admixtures [31].

Systems of polymer-emulsion admixtures are used for DP concrete overlays for bridge and parking decks. Drying oils are used as DP materials for surface treatment of fully cured concrete. Oils are obtained from natural sources including vegetable oils and animal fats (e.g., tallows, soya-based materials, and greases). For example, raw, boiled, or polymerized linseed oil is formulated in various types of solvents. Petroleum sources include mineral oil, paraffin waxes, and bitumen emulsions. Organic solvents (e.g., mineral spirits and kerosene) are essential for improving penetration of the materials within concrete pores [5].

Nanocarbon-based materials have been used to obtain superhydrophobic surfaces [41]. Mineral nanomaterials used in hydrophobic systems include nanoparticles of SiO_2 and ZnO_2 incorporated in cementitious mixtures to improve water repellency [41]. Also, the hydrophobic action of silanes can be enhanced by adding nanosilicons or clay nanocomposites [41]. Nanoparticles of TiO_2 and SiO_2 incorporated with perfluoro decyl triethoxy silane and sprayed on fresh concrete were found to form highly efficient hydrophobic surface treatment with superhydrophobic characteristics (e.g., $\theta > 160$ degrees) [11]. A suspension of fluorosilane functionalized silica ($FSiO_2$) nanoparticles (particle size about 300 nm) was used for producing superhydrophobic material [14]. Other investigated particulate systems incorporated in concrete mortars included hydrophobic silica particles functionalized with an alkyl group such as n–dodecyl groups ($–C_{12}H_{25}$) [42].

8.4 Applications of hydrophobic dampproofing materials

The penetrating materials [solutions, emulsions, gel, or cream systems [11]] are applied as a surface treatment onto cured concrete. The successful surface application of solutions, emulsions, gels, and creams is dependent on the application methods and coverages, penetrability within the concrete structure, and setting reactions or precipitation. Liquid materials are typically applied by using low pressure spraying, brushing, or rolling [5]. The surface coverage of DP materials is usually in the range of 2.5–5 m^2/L (100–200 ft^2/gal) [5]. In certain cases, higher coverages in the range of 6.7–10 m^2/L are used for some silanes and siloxanes (with 31 wt.% solid content) [20]. For gel types, much lower surface coverages of about 1.5 m^2/L are used [5]. The obtained performance is usually enhanced with increasing the solid content of the silanes and siloxanes solutions; however, such an increase may darken the surface of concrete [5]. Parameters that are crucial for the application of surface treatment include surface preparation, contact time, pH, moisture content of substrate, and age of concrete at time of treatment [3]. A dry concrete surface is a favorable condition for the penetrating surface treatments in order to obtain a sufficient absorption into the capillary pores and to reach an adequate penetration depth [3]. A maximum efficacy of silane is obtainable when it is applied to fully dry concrete or to concrete with low moisture content (e.g., $<2\%$) [43]. In fact, siloxane cannot be applied on wet surfaces, while alkyl triethoxy silanes undergo hydrolysis during its setting mechanism and hence it can be applied on wet concrete surfaces [9]. Long-term performance is better achieved when it is applied on early age concrete [9]. The penetration of a DP material (determined by the achievable penetration depth) is governed by (1) its chemical and hydrodynamic characteristics, (2) coverage rate and wetting contact time, and (3) the properties of concrete substrate including w/c ratio, porosity, transport properties, and initial moisture content [44]. The characteristic parameters of DP materials include molecular structure [3] (molecular size and complexity, volatility and reactivity), viscosity, and composition [e.g., presence of enhancing agents such catalysts and the type of the carrier (solvent)] [9].

From the perspective of molecular structure, the penetrability of silanes or siloxanes is governed by the complexity of the alkoxy group (e.g., ethoxy or methoxy) [9]. Because of the small molecular structure, the penetration depth of isobutyl-triethoxysilane in concrete was reported to be larger than other silicon-organic compounds (e.g., siloxanes) [27]. The penetrability governs the penetration depth in concrete structure and the types of pores that can be reached within the concrete structure. When the molecular size of the hydrophobe is relatively large, their penetration into nanopores is limited. As detailed in Chapter 2, the gel pores (with a size range of 0.5–2.5 nm) are not open for permeation. Only capillary pores (micropores and macropores, which are typically larger than 10 nm) are open for permeation flow [45]. The size range of the active ingredients of the hydrophobic WP materials is close to the size range of gel pores (see Fig. 7.3, Chapter 7) and hence they cannot penetrate them straightforwardly [2]. The molecular size of silane structures is in the range of 1–1.5 nm, thus the silane molecules can penetrate into a fraction of the gel pores [38]. On the other hand, the molecular size of siloxane is in the range of 1.5–7.5 nm, which is larger than the sizes of most of the gel pores. Hence, siloxanes cannot penetrate the gel pores, and the internal surfaces of the fine gel pores remain hydrophilic [2].

However, the volatility of silanes (associated with their small size molecules, see Fig. 8.3 causes their rapid evaporation in hot or windy surrounding conditions. Hence, the wetting period and actual surface coverage are lower than the equivalent estimated values. It is well-reported that the penetration depth is dependent on contact time or the length of period of the wetting of DP solution on the concrete surface (the residence time of liquid on the surface) [3]. From such a perspective, siloxane and polysiloxane molecules are larger than silane molecules (see Fig. 8.3) and hence they are less volatile and less affected by the warm and windy air conditions; they can wet the surface for a longer period than silanes. Despite such a volatility effect of silanes, [3] emphasized that larger penetration depths were obtained for silane in comparison with other compounds. The resident time of a DP material on the surface is also dependent on its physical state (i.e., type of formulation as a solution or a gel). For example, both silane-based gels and creams can achieve deeper penetration than liquid silane [44], due to their lower volatility and higher residence time than those of liquid silane [9] and due to more solid content [44]. In addition, the penetration of alkyl triethoxy silane was found to be deeper than those of other silanes due to its lower reaction rate [9].

The penetration depth of silanes increases with increasing the w/c ratio [44]. The surface quality (e.g., porosity) and its moisture content (saturation degree) have considerable effects on the penetration [3]. Fig. 8.5 shows the absorption of silane as a function of time for three ordinary concrete specimens and one for a modified concrete specimen with fly ash. The total absorption of a DP material increases

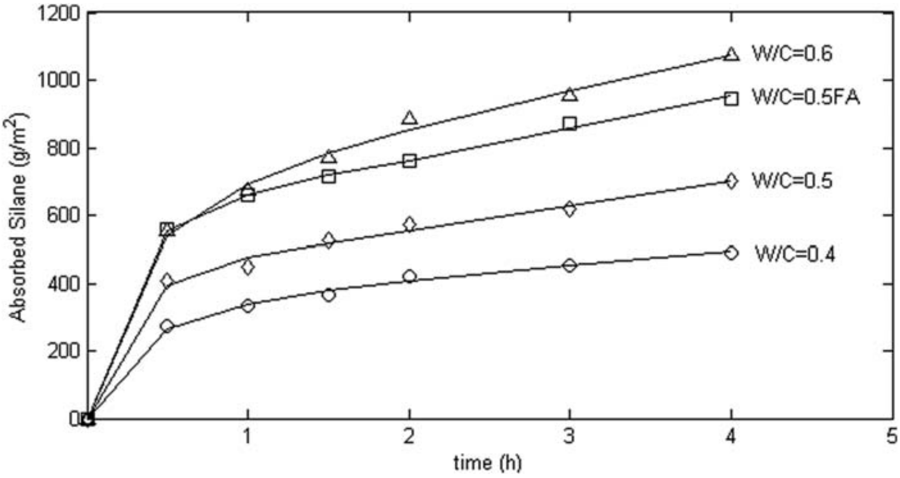


Figure 8.5 Absorption of silane into concrete as a function of time for ordinary concrete with w/c=0.4, 0.5, and 0.6 and for concrete modified with 20 wt.% fly as a cement replacement ash with w/c=0.5 ([2]).

with increasing concrete porosity, that is, with decreasing w/c. A similar trend was also reported for other hydrophobic DP systems [silane-based gel (80 wt.%), and silane-based cream (85 wt.%)] in which the active silane ingredients were isooctyl triethoxy silane and isobutyl triethoxy silane. The penetration mechanism of liquid hydrophobic DP materials is achieved by capillary absorption and diffusion, as discussed in Chapter 7. This transport mechanism is a time-dependent process; it increases with time during the first few hours from the time of application [2]. Such a liquid penetration process is typically governed by the capillary suction model (typical swelling kinetics) that relates the total absorption per unit area (S) with the square root of time (t), as per the analysis given in Chapter 5 [see Eq. (8.1)]. However, as the penetration process of the reactive DP materials is also accompanied with heterogeneous reactions with the cementitious surface, the time-dependent total or cumulative water absorption per unit area (W_{cs}) usually deviates from the W_{cs} value predicted by the liquid swelling kinetics of nonreactive liquids Eq. 8.1 [2]. The capillary absorption of silane deviates from the swelling equation given by Eq. (8.1) because of its reactions when penetrating the concrete. The coefficient of capillary suction of silane, expressed as function of time (S(t)), was found to decrease with time by an exponential function [2]. Usually, concrete with high w/c ratio (high porosity) is better for testing the effects of surface treatment materials on durability parameters such as chloride ion penetration, the corrosion of steel reinforcement [44], and cycles of freezing and thawing [26].

The reported penetration depths for silane (liquid, cream, and gel) were in the range of 4–15 mm, for w/c=0.5 [2], or within a wider range of 2–25 mm [44]. In the review of Basheer et al. [3], lower penetration depths (<1 mm) were reported for some silane and siloxane materials. Multiple applications of hydrophobic DP materials do not yield a substantial enhancement in the penetration depth [11]. In fact, after the first application, the resulting hydrophobicity will decrease the capillary suction of further DP solution.

Powder materials are incorporated additions (or admixtures) to the concrete mixture at the time of batching. In some applications, the powders are added to cementitious coatings (see Chapter 12). The successful application of DP admixtures is dependent on their dosage in the concrete mixture. The dosage of DP addition is usually specified as a fraction of cement or cementitious binder (including the supplementary cementitious materials). For example, calcium stearate was added to self-compacting concrete at dosages up to 2.9% of the cement weight [46]. An emulsion of stearic acid (30 wt.% solid content) was added to cement paste mixture at a dosage of 1% of the cement weight [1]. The successful application of DP admixtures is also dependent on their setting reactions and precipitation mechanisms as well as on their impacts on other characteristics of fresh and cured concrete. For example, DP admixtures typically have a retarding effect on the cement hydration reactions.

8.5 Mechanism of hydrophobic dampproofing systems

The hydrophobic DP materials are cured and function through physicochemical mechanisms. These include setting mechanism and water-hindering mechanism.

When these materials are applied as liquids on the surface, they first penetrate into the concrete structure, as discussed in the section above. Then, their setting mechanism starts when the solution occupies the pores. When the hydrophobic DP materials are added as admixtures, they start their setting process after the creation of concrete pores, when the cement hydration process proceeds to a certain level. The types of setting mechanisms depend on the type and the chemical structure of the hydrophobic molecules and the concrete surface. These include (1) chemical reactions of hydrophobic materials with cementitious surface encountered in the cases of organosilicon compounds and stearates, (2) particle deposition of materials in concrete pores encountered in the cases of waxes and bituminous emulsions, (3) coalesce of polymer materials within the concrete mass in the form of water-repellent films or globules lining the pores, and (4) settling of fine particles from a suspension after the evaporation of the carrier within the pores of concrete such as fine rubber particles suspended in an ammonia solution. The chemical setting mechanisms are encountered in the cases of soluble and reactive hydrophobic compounds such as organosilicon compounds and fatty acids and their salts. The types of reactions depend on the chemical structure of the active ingredients of the hydrophobic materials. For organosilicon compounds, the mechanism is generally a chemical adsorption (chemisorption) process and it involves the creation of a chemical bond between the hydrophobe and the surface [6]. For hydrophobic systems of fatty acids and their salts, reactions of acidbase precipitation and cation exchange are involved. These chemical mechanisms are further detailed in Sections 8.5.1 and 8.5.2. Physicochemical setting mechanisms are encountered in the cases of emulsions and suspensions of organic materials (see Section 8.5.3). The hydrophobic organic molecules (such as oils) can be adsorbed or adhered to the surface by physical deposition or they may coalesce into amalgamations of polymer materials within the pores of the paste. Then, they form water-repellent films or globules [6].

After setting, the DP mechanism for hindering water absorption is the same for the various types of hydrophobic DP systems. The hydrophobic groups of the hydrophobic molecules decrease the surface tension of the concrete surface, lowers its surface energy, and increases its WCA as described in Section 8.2. The formed hydrophobic layer along the pores of concrete repels water while the pores remain physically open. Water becomes unable to wet-out the surface. Such a pore lining effect hinders water penetration into capillary pores by capillary action. The physical and thermodynamic aspects of the hydrophobic mechanism are explained in Chapter 5. In fact, the formation of such a hydrophobic layer serves additionally in occupying the accessible sites on the cementitious surface, which otherwise will be available for attracting water molecules through hydrogen bonding and cause water swelling within pores [47]. Most of the hydrophobic systems are DP materials that cannot resist a hydrostatic pressure [5]; however, some systems of hydrophobic DP involve partial pore filling. These cases are obtained by the coalesce of polymer water-repellent films or globules or by the deposition of fine rubber particles. These systems combine water-repellency with partial pore filling mechanisms, which assists in reducing the permeation flow in concrete subjected to a hydrostatic pressure [6].

8.5.1 The chemical setting of organosilicon compounds

The reaction mechanism of organosilicon compounds is a multiple-step chemical process that involves a series of reactions. These include (1) hydrolysis, (2) formation of hydrogen bonds with the surface and among the organosilicon compounds, and (3) condensation mechanisms that involve releasing water molecules from the hydrogen bonds and thus converting them from (weak) physical bonds to (strong) covalent oxygen chemical bonds. These general steps are valid for silanes and siloxanes, which occur in alkaline conditions. The setting mechanism of alkali methyl siliconates is based on a similar chemical reaction but it requires reduced alkalinity conditions and hence it is catalyzed by the participation of carbon dioxide from air. These steps and the involved chemical reactions of setting organosilicon materials are described in the following subsections.

After condensation, silanol molecules form silicone (polysiloxane) molecules [11], creating hydrophobic films at the surfaces of the cementitious material. The resulting hydrophobic film is simply a nanomolecular poly siloxane lining that is established within the capillary pores [31], as illustrated in Fig. 8.6. It is bonded chemically to the siliceous content of the concrete while allowing the alkyl group (e.g., CH_3) to face outward from the internal surface (see Fig. 8.6). The types and structures of these organic groups and their distribution on the lining layer at the treated concrete surface govern the level of the hydrophobic performance and the chemical reactivity of the organosilicon compounds [47]. The DP effectiveness is also dependent on the rate of the setting reaction. Slow curing of DP materials can create setting difficulties caused by the escape of volatile silane before setting and can be associated with a carbonated surface [37].

The formation of such an organic hydrophobic layer is typically confirmed by the measurement of energy dispersive X-ray analysis (SEM/EDS), which indicates an increase in carbon content from the presence of the organic groups [20]. It is also confirmed by infrared (IR) spectroscopy as shown in Fig. 8.7, which compares results of IR spectroscopy for untreated, treated, and weathered concrete samples [20].

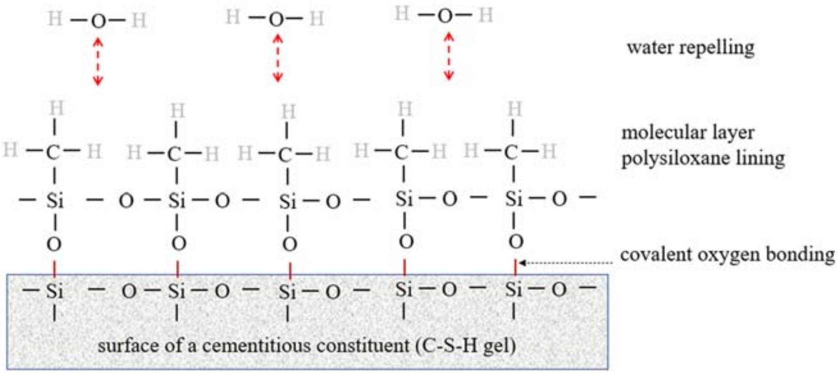


Figure 8.6 The structure of the hydrophobic layer adsorbed onto the siliceous content of the concrete with the alkyl group facing outward from the cementitious surface.

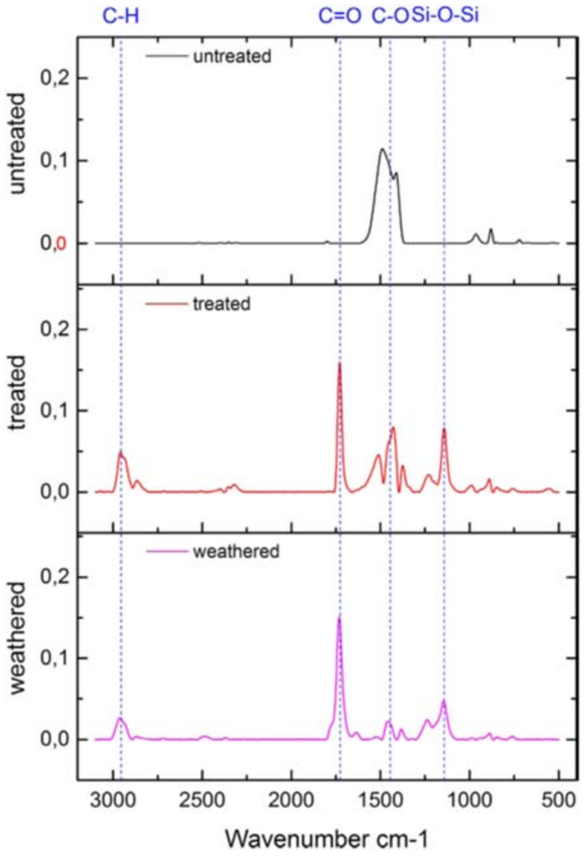


Figure 8.7 Results of IR spectroscopy for untreated, treated, and weathered concrete samples ([20]).

The formation of a hydrophobic layer is detected by an increase in the CH and SiOSi bonds for treated concrete surface compared to the spectroscopy of untreated surface [20]. The equivalent carbon contents from these spectroscopy results are 10.2 wt.% and 63.8 wt.% for untreated and treated concrete samples. The carbon content is decreased with weathering due to the degradation of the hydrophobic layer as described in Section 8.6.1 [20]. At the same time, Fig. 8.7 shows an increase in the Si OSi bonding.

8.5.1.1 *Alkaline catalyzed setting reactions of silanes and siloxanes*

The first step in the setting mechanism of silanes or siloxanes is the hydrolysis reaction, which produces silanol molecules [10]. Silanols are obtained when silicon atoms are attached to hydroxyl groups forming SiOH bonds, through replacing the organic R-group by a proton (H^+) as shown in Fig. 8.8A. This hydrolysis reaction is activated by the presence of moisture in the paste pores [31,33] and is catalyzed by the alkalinity condition in the pore solution [11]. Hence, silane and siloxane surface treatments may not perform well in carbonated concrete as carbonation reduces the required alkaline condition [3]. The produced silanol molecules are chemically unstable and thus they undergo further reactions through the participation of their active hydroxyl groups [11]. Consequently, the OH-groups on the produced silanols are capable through hydrogen bonding of (1) crosslinking among the silanols Fig. 8.8B and (2) bonding to accessible OH-groups on the cementitious substrate Fig. 8.8C. Condensation reactions transform the hydrogen bonds that are established within the silanols into oxygen bonds by releasing water molecules. The crosslinking among the silanols leads to the formation of polysilanols or poly siloxane molecules [11,31]. The crosslinked silanol molecules approach the surface and their OH-groups react with the accessible OH-groups on silicon sites on the cementitious surfaces (including CSH gel, ettringite, and calcium hydroxide and on fine aggregates) as shown in Fig. 8.8C. Then, polycondensation occurs by releasing water molecules from the hydrogen bonds established with the cementitious substrate [10,11]. Polycondensation transforms the hydrogen bonds into stable and strong oxygen bonds between the hydrophobe and the surface, as shown in Fig. 8.8C. These reactions lead to the formation of a continuous and self-oriented molecular hydrophobic layer at the surfaces of the cement hydration products and aggregates [10]. The net reaction of alkyl alkoxy silane with the silicon sites produces poly siloxane on the walls of the capillary pores [26]. The crosslinked poly siloxane lining develops as an integral part of the cementitious structure [31].

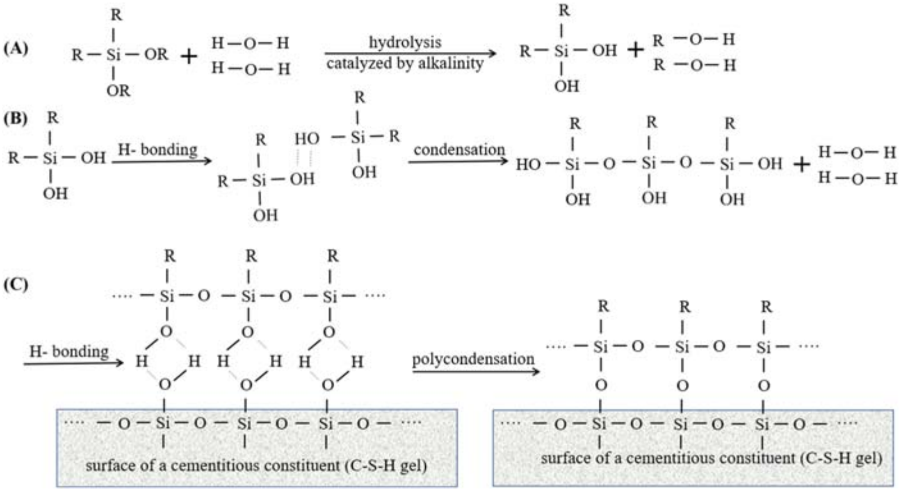


Figure 8.8 Illustrations of the reactions of silanes including (A) hydrolysis to produce silanols, (B) crosslinking among the silanols to produce polysilanols, and (C) bonding to accessible OH-groups on the cementitious substrate.

8.5.1.2 Carbon dioxide catalyzed setting reactions of siliconates

In the above chemical mechanism of setting of silanes and siloxanes, there is no required involvement of CO_2 from air in the setting mechanism, as it is an alkaline catalyzed mechanism. However, the chemical mechanism of setting an alkali methyl siliconate (e.g., sodium methyl siliconate) onto a concrete surface requires the presence of carbon dioxide (CO_2) as an essential catalyst for the hydrolysis (first) step in the setting mechanism. This setting mechanism on concrete surfaces is similar to the reported setting mechanism on wood surfaces as demonstrated elsewhere [21]. Fig. 8.9 illustrates the setting reactions of sodium methyl siliconate on concrete surfaces.

Carbon dioxide (CO_2) dissolves in water and drives water molecules to dissociate into hydrogen ions (H+) and hydroxide ions (OH) [Eq. (8.3)], forming carbonic acid [Eq. (8.4)]. The associated reduction in the pH of the pore solution promotes the hydrolysis of the sodium methyl siliconate to form silanol, as shown in Fig. 8.9A [48]. The rate of such a hydrolysis reaction is relatively slower than the rates of hydrolysis of other organosilicon compounds; as it is dependent on the availability of carbon dioxide within the pores. The availability of CO_2 is determined by its diffusion rate (and possibly advection rate, see Chapter 2) from the surrounding atmosphere (in which it exists in very small percentage). Also, there is a competition on carbon dioxide between this reaction and other reactions in alkaline concrete such as carbonation reactions with calcium hydroxide (see Chapter 3). Consequently, the bonding of sodium methyl siliconates to concrete surfaces is a slow process and thus some authors do not highly recommend them for concrete applications [5].

$$H_2O \overset{CO_2}{\rightarrow} H^+ + OH^- \tag{8.3}$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{8.4}$$

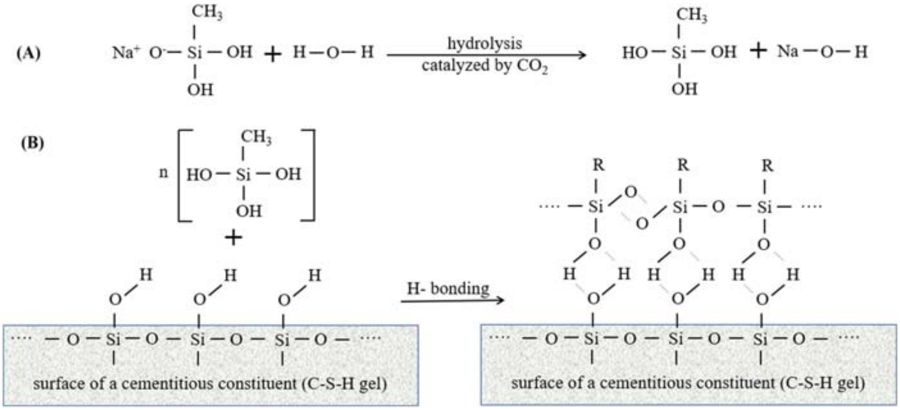


Figure 8.9 Illustrations of the reactions of sodium methyl siliconate showing (A) hydrolysis in the presence of CO_2 to produce silanols and (B) hydrogen bonding among silanols and with the accessible OH-groups on the cementitious substrate.

After the hydrolysis Fig. 8.9A, the produced silanol molecules react with OH-groups at the surface of concrete constituents and among themselves forming a hydrogen bond Fig. 8.9B, as in the cases of silanes and siloxanes (see Fig. 8.8). The third step of polycondensation for the formation of oxygen bonds is similar to that for silanes as already shown in Fig. 8.8C. This leads to the formation of poly methyl silsesquioxane lining that is chemically bonded to the cementitious surface.

8.5.2 Setting reactions of stearates and similar organic compounds

The setting reactions of stearates and similar organic compounds are based on neutralization reactions between the reactive fatty acid groups with calcium hydroxide (the by-product of cement hydration). The reactive stearate group (e.g., from stearate salts) can combine with available cations (mainly calcium ions) in pore solution. When the stearate salts are dissolved in water, they form a solution containing reactive stearate group, $(C_{18}H_{35}O_2)^1$, which combines with calcium ions according to Eq. (8.5). In some applications, stearic acid ($CH_3(CH_2)_{16}COOH$ or $C_{18}H_{36}O_2$) [1] is used instead of stearate salts; as it releases the same anionic group released by the other stearate compounds [1]. Stearic acid is insoluble in water at room temperature and hence it is used as a waterborne emulsion [1]. The stearic acid reacts with calcium ions producing insoluble calcium stearate as given by Eq. (8.4) [1].

$$Ca^{2+} + 2(C_{18}H_{35}O_2)^- \rightarrow Ca(C_{18}H_{35}O_2)_2 \tag{8.5}$$

This net setting mechanism is simply an ion exchange process as given by Eq. (8.6), leading to the deposition of a wax-like calcium stearate compound [4]. The reaction product is deposited as a hydrophobic layer that makes the concrete surface water-repelling [4]. Excellent hydrophobic characteristics are obtained from the long organic stearate chain [11]. When these compounds are used as admixtures, this ion exchange reaction consumes the by-product of the cement hydration and produces water. Consequently, it promotes the cement hydration process and decreases the setting time of the cement paste [1].

$$Ca(OH)_2 + 2CH_3(CH_2)_{16}COOH \rightarrow Ca(OOC(CH_2)_{16}CH_3)_2 + 2H_2O \tag{8.6}$$

Other fatty acids can produce hydrophobic characteristics through similar setting reactions of stearates in concrete. For example, oleates admixtures are reported to be effective water repellent by forming insoluble calcium oleate that is deposited as a hydrophobic layer within the capillary pores [31]. Fig. 8.10 shows the chemical structure of the hydrophobic DP surface treatment when stearate or oleate compounds are used [31].

The use of stearate compounds can be associated with other additional mechanisms and impacts on concrete. When ammonium stearate is mixed with cement, the reaction releases ammonia forming tiny trapped bubbles throughout the viscous

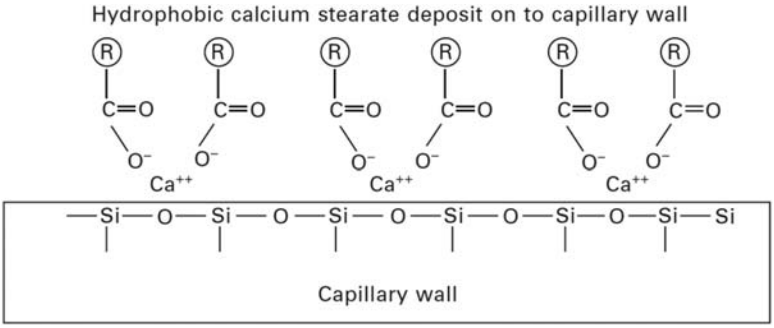


Figure 8.10 Chemical structure of the hydrophobic DP layer that is deposited with at the surfaces of pores obtained from stearate compounds ([31]).

mixture, which reduce the density of the cured concrete [40]. When butyl stearate is used, an additional thermal effect is possibly obtained as butyl stearate is considered as a phase change material that assists in managing thermal effects during hydration, for example, storing energy and reducing thermal conduction (as described in Chapter 2). In fact, the waxy nature of the produced calcium stearate from the addition of stearate compounds to concrete mixture may also be hypothesized to contribute in the thermal management of the concrete mixture; however, its melting temperature is relatively high (155°C). On the other hand, the melting temperature of stearic acid is 69.3°C [49]. These associated thermal effects deserve further analysis.

8.5.3 Setting of other hydrophobic systems

The setting mechanisms of systems of oils and polymer droplets are mainly physical. The setting mechanism of DP drying oils used for surface treatment is simply based on the evaporation of the carrying solvents (e.g., mineral spirits and kerosene). This is a slow process and hence treated concrete should be allowed 2 days for developing the treatment performance [5]. The setting mechanism of the DP polymer-emulsion admixtures is based on the formation of continuous polymeric film within the concrete pores. This is achieved through a physical mechanism of droplet/particle coalescence. The coalescence polymer droplets/particles reduce water penetration through concrete by a combination of water-repellency and pore blocking [17]. Other systems implement the concept of hybridization, combining the biomimetics (lotus effect) with the synthetic chemical effect and nanotechnology as in the use of nano-SiO_2 particles [12].

8.6 Requirements of hydrophobic dampproofing materials

The requirements for durable hydrophobic pore lining materials include requirements related to the application techniques (as described earlier in this chapter) and others related to the characteristics of the materials themselves as detailed below. The requirements for hydrophobic DP treatment can be summarized as follows.

1. *Penetrability* (when applied as solutions for surface treatment), which is dependent on the type, size, and structure of the hydrophobic group (see Section 8.4).
2. *Reactivity* with cementitious materials under the concrete conditions and surrounding conditions at a reasonably high rate. The reaction type and rate are dependent on the type of reactive groups on the organosilicon compounds (see Section 8.5.1).
3. *Bondability* of the produced hydrophobic molecular layer with the cementitious surfaces. This is usually based on chemical bonding for the case of organosilicon compounds. Other hydrophobic systems involve depositing precipitates or coalescence, which are just occupying part of the pores (see Section 8.5).
4. *High water repellency* indicated by a high WCA, which is dependent on the type, size, and structure of the hydrophobic group (see Section 8.3).
5. *Chemical stability* and resistance to alkaline conditions (see Section 8.6.1).
6. *Physicochemical stability* and resistance to UV radiation, as the thin hydrophobic layer may be degraded by UV exposure (see Section 8.6.1).
7. *Mechanical stability* and abrasion resistance, as the thin hydrophobic layer may be roughened away by the surface mechanical impacts (see Section 8.6.1).
8. *Breathability* of the DP by allowing vapor transmission [27] (see Section 8.8.4).
9. *Low toxicity or nontoxicity* of materials are required for environmental and public health purposes. The hydrophobic material must not possess a toxicity or cause environmental impacts from the emissions of the VOC. Solvent-based materials release VOC [11]. Typically, organic solutions may involve a level of toxicity. Health concerns of siloxanes have been expressed due to their long-term impacts on animals, although no acute toxic impacts of exposure to siloxanes have been reported on humans [11]. Siloxane compounds may possess acute effects such as irritation and respiratory symptoms due to the presence of silicone-hydrogen.
10. *Practicality* of material application such as its spray-ability, low volatility etc.

8.6.1 Stability of hydrophobic dampproofing materials

The durable performance of hydrophobic DP materials demands the stability of the hydrophobic layer. The review of Mundo et al. [11] indicated that the reported durability period of surveyed concrete applications with hydrophobic surface treatment was likely beyond 10 years and might exceed 20 years. However, Mundo et al. [11] also indicated that the long-term durability of various types of hydrophobic treatments requires a comparative investigation. Song et al. [10] indicated that the durability of super hydrophobic DP surface materials was considered insufficient as they can easily fall off [10].

The stability of a DP material is essential for the durability of the material itself and hence the durability of the treated concrete. The stability of hydrophobic DP materials is determined by the continuity of the bonding and degree of attachment of the hydrophobic layer onto the surfaces of the pores. The stability (indicated by the time-stability of the WCA) is governed by the types of interactions of the surface with the surrounding including chemical, physical, and mechanical attacks. These attacks are dependent on the service conditions and the level of water exposure including the cycles of wetting and drying and the level of hydrostatic pressure. Hydrophobic surface treatments do not make the concrete fully impermeable and hence, they are not adequate for water ponding conditions such as swimming pools and water retaining structures [11]. Silane's DP performance was reported to diminish under long-term immersion [3]. Increasing the pressure under a continuous wetting condition may cause a full or complete wetting of the surface textures and thus stops its nonwetting behavior (entrapped air pockets within the surface according to the Cassie state, see Chapter 5) [11].

The severity of the attacks is also dependent on contaminations: the types and level of chemical interactions at the surface govern the chemical stability of a hydrophobic layer. The above-described hydrophobic layers obtained from organosilicon compounds were found to be fairly stable when the hydrophobic surface is subjected to neutral or slightly acidic conditions. It can also resist slightly alkaline solutions. An excellent water-repelling material must be characterized with a high alkali resistance [27]. The hydrophobic layer can be disintegrated under strong alkaline attack. The chemical stability (or durability of the organosilicon hydrophobic layer) was found to decrease with increasing alkalinity (increasing pH) and with increasing time of exposure [21]. The molecular size and structure of the alkyl group governs the resistance of hydrophobes against deterioration in alkaline environments [9]. The chemical stability of silicone-based hydrophobic DP materials is governed by the chain length and degree of branching of the organic groups. Increasing the chain length and/or the degree of branching of the organic groups increases the resistance to degradation in alkaline conditions and enhances water repellency (however, it decreases its penetrability as described above). Silanes contain short alkyl groups and thus they have less alkaline resistivity than longer chained compounds. Siliconates have a very low alkali resistance [37]. Upon immersion in slightly alkaline conditions, a decrease in the WCA of surface treatment with potassium methyl siliconate (on a wood surface) was reported, although the surface remained hydrophobic [21]. However, when the same siliconate treatment was immersed in a highly alkaline solution (at a pH=12), a sharper decrease in the contact angle was reported with surface shift into hydrophilic characteristics [21]. Acidic conditions also reduced the WCA but without a shift into hydrophilic surface [21].

The stearate compounds form precipitated salts. However, it was also reported that the organic additions of fatty acids and their salts do not offer long-term durability, as they can be bio-degraded [31]. The oil-based and fat-based DP materials can be rehydrolyzed under strong alkaline conditions [31]. These natural hydrophobic DP admixtures can also be degraded by the biological attack under humid conditions (essential for the activity of the microorganisms).

The level of exposure to UV radiation is another controlling parameter in the physicochemical stability of the hydrophobic layer. Long time exposure to UV and natural weathering can destroy these materials with time [31]. When the penetration depth is short, the thin hydrophobic layer can be degraded when subjected to UV radiations [31]. The water absorption of silane-treated concrete was decreased by 50% after UV aging [2]. Hence, the durability of organosilicon compounds requires sufficient penetration depths into the concrete substrate. Kebao and Kagi [31] distinguished between UV impacts on the hydrophobic surface layer and that of the lining layer within the pores: the hydrophobicity of the surface layer may be decreased by disintegration due to interaction with UV radiations. However, they indicated that the poly siloxane hydrophobic molecular lining of the pores of rammed earth substrate was not affected by UV radiations, as the lining materials became an integral part of the structure through crosslinking (strong chemical bond). Basheer et al. [3] indicated that there was no difference in DP performance of hydrophobic treated concrete after 2-months exposure to UV radiation.

Extreme climate conditions such as high temperature or freezing impact the stability of the hydrophobic layer. The resistance of hydrophobic surface treatments (e.g., with silane and siloxane) decreases when the concrete is subjected to a high temperature, as the hydrophobic layer is not stable at a leveled temperature [16]. The resistance of silane against chloride ion ingress was decreased substantially when the concrete temperature reached 45°C [16]. The stability of hydrophobic treatment is also dependent on cyclic thermal impacts (e.g., freezing and thawing cycles). Fig. 8.11 shows the durability of hydrophobic concrete (treated with nanosilica particles), in terms of ice adhesion and as a function of number of icing-deicing cycles [14]. The treated concrete surface remained superhydrophobic with no notable increase of ice adhesion strength at a small number of icing and deicing cycles (<30) [14]. However, beyond 30 cycles, a significant decrease in hydrophobicity is observed.

The harshness of surface mechanical conditions can degrade the hydrophobic treatment by erosion effects. The abrasion action disintegrates the hydrophobic layer and the polishing action can remove part of the hydrophobic treatment [10]. Surface mechanical impacts such as traffic loads and vibrations may cause a full or complete wetting of the surface textures and thus stop the nonwetting

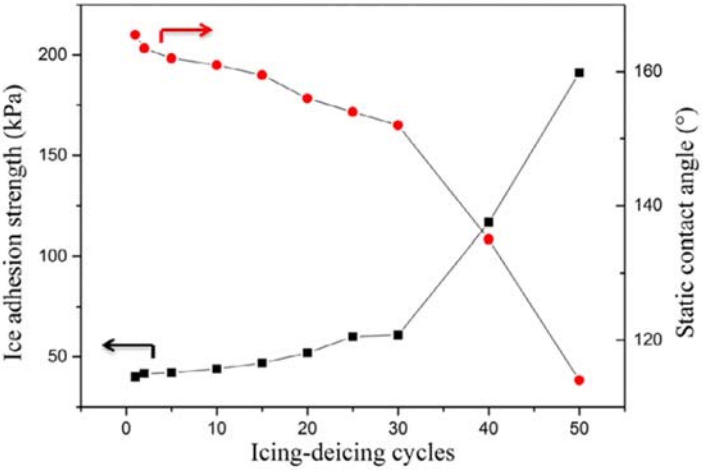


Figure 8.11 The durability of hydrophobic concrete (treated with nanosilica particle) in terms of static water contact angle and ice adhesion as functions of number of icing-deicing cycles ([14]).

behavior [11]. Hence, it was found that the WCA of the hydrophobic cementitious surface decreases when it is subjected to abrasion and wear actions [10]. As shown in Fig. 8.3, the WCA of weathered hydrophobic cementitious surfaces treated with silane/siloxane copolymer is lower than that of freshly treated surface [20]. In fact, the mechanical actions may not change the surface characteristics from hydrophobicity to hydrophilicity, but reduces the level of de-wetting by decreasing the WCA. This is because the hydrophobic treatment penetrates the surface into deeper depths below the surface that are not affected by the surface wear actions. Consequently, a part of the hydrophobic layer sustains even after surface polishing [50]. Total removal of hydrophobicity occurs when the WCA is relatively small (slightly >90 degrees), when the original hydrophobicity is low. The reported results in Fig. 8.3 indicate a characteristic shift from hydrophobic (with $\theta > 90$ degrees) into hydrophilic (with $\theta < 90$ degrees). Kebao and Kagi [31] distinguished between the mechanical stabilities of the hydrophobic surface layer and that of the lining layer with the pores. They indicated that the polysiloxane hydrophobic molecular integral lining layer was not affected by abrasion.

8.7 Durability performance of hydrophobic dampproofing

As described in Chapter 7, the performance of hydrophobic DP systems is commonly evaluated based on its reduction in wetting and water penetration, its durability enhancement, and its effect on the mechanical properties. The evaluation tests include direct and indirect methods [20]. Direct methods are structural-related tests such as IR spectroscopy and scanning electron microscopy (SEM), which are used to confirm the presence of organic groups and chemical bonding to hydration products [10,20,42] (see Section 8.5.1). In general, the level of reduction in wetting (hydrophobicity) is evaluated by measuring the static WCA while the efficiency in reducing water penetration is evaluated by measuring water absorption (percentage or coefficient) [11]. Tests for measuring the permeability under pressure are usually not valid for the hydrophobic DP systems. The main reported durability parameters for hydrophobic DP materials are resistances against chloride ion penetration, steel corrosion, carbonation, and freezing and thawing cycles. The tested transport characteristics of treated concrete include sorptivity, moisture and gas permeabilities (air, carbon dioxide, and oxygen), and ion diffusivity (e.g., diffusion of chloride ion). Other tested mechanical characteristics include compressive and flexural strength and abrasion resistance. The test methods and standard for these measurements are summarized in Chapter 7. The following subsections highlight the reported performance in the available literature.

8.7.1 Efficiency of water-repellency and de-wetting

The performance of hydrophobic DP materials is basically evaluated by testing the level of functionality of the resulting surface for de-wetting or hydrophobicity.

As indicated in Section 8.2.1, antiicing performance is a protection purpose that is also correlated to the level of hydrophobicity. These parameters are commonly evaluated by measuring the static WCA and sometimes by measuring the sliding contact angle of a water droplet with the surface (see Chapter 5). Increasing static WCA increases the level of hydrophobicity from hydrophobic to overhydrophobic and then to superhydrophobic [11,12], as shown in Fig. 8.1, and hence increases the efficiency of surface treatment. On the other hand, decreasing the sliding contact angle is an indication of an increase in the efficiency of hydrophobic DP [1]. The WCA of a surface is governed by (1) its characteristics (e.g., roughness, porosity, and structural nonhomogeneity), and (2) time-dependent interactions and surface conditions.

Liu et al. [21] found that the static WCA was increased with increasing the concentration of potassium methyl siliconate up to a certain limit. Similarly, Fig. 8.12 shows the effect of dosage of stearic acid emulsion added in a concrete mixture on the level of hydrophobicity of the concrete, indicated as contact angle (static and sliding). A minimum dosage of stearic acid emulsion is needed to obtain a hydrophobic surface. A very hydrophobic cement paste surface with a contact angle over 130 degrees was obtained when the stearic acid emulsion was added to the paste at a dosage of 1% of the cement weight [1]. Fig. 8.12 also shows that the sliding angle decreases with increasing the dosage of the stearic acid emulsion. In fact, the measurement of WCA is not very frequently used in evaluating the performance of cementitious materials because of practical difficulties in having a stable water droplet on the surface for sufficient time of measurement [11] (see Fig. 8.2 showing the instability of measurement of WCA).

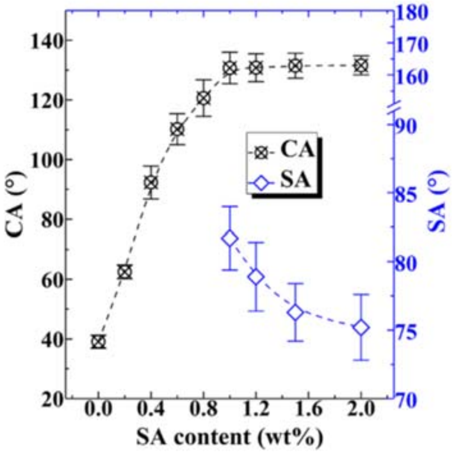


Figure 8.12 Effect of dosage of stearic acid emulsion in the concrete mixture on the static water contact angle (indicated in the figure as CA) and the sliding angle (indicated in the figure as sliding angle) of the produced concrete ([1]).

8.7.2 Reduction in water absorption

Water absorption is more commonly used for evaluating the performance of hydrophobic DP materials than measuring WCA, because of the above-mentioned practical difficulties in having a stable water droplet [11]. Water absorption is determined either by measuring the weight gain after immersing the concrete specimen in water for a given time or by measuring the rate of water penetration (or coefficient of water penetration), using Autoclam sorptivity test [3] or the Karsten tube penetration test. For concrete specimens with low porosity (highly dense structures), the Karsten tube penetration test is not believed to be applicable [10]. These tests are performed under a small water head (see Chapter 7). For example, 10 cm of a water head is used to measure the water absorption as a function of time. As indicated earlier, the hydrophobic DP systems can resist such a low value of hydrostatic pressure [6,16]. The cumulative water absorption per unit area (W_{cs}) is determined as function of time [3] and modeled by Eq. (8.1) to obtain the water absorption coefficient (S). Usually, water capillary absorption is accompanied by some reactions and binding with cementitious content of concrete. However, these reactions are slow and limited, hence, the amount of water absorption with time reasonably follows Eq. (8.1) [2].

Fig. 8.13 shows curves of the cumulative water absorption for untreated and treated mortar specimens using isooctyl triethoxy silane [10]. The hydrophobic surface

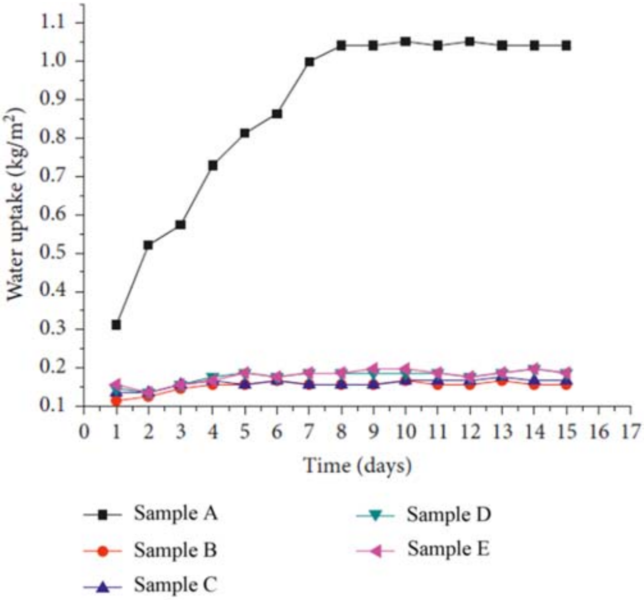


Figure 8.13 Curves of cumulative water absorption for untreated ordinary Portland cement mortar specimen with w/c=0.5 (A) and deeply treated specimen using isooctyl triethoxy silane (B). Also shown are results of water absorption after abrasion with 240-grit sandpaper for 0.3 mm (C), 5.3 mm (D), and 10.4 mm (E) ([10]).

treatment of concrete is usually very effective in reducing liquid water absorption [2]. In general, silanes and siloxanes have been found to be effective in reducing the water absorption of concrete [3,44]. The reduction in water absorption coefficient [S in Eq. (8.1)] for hydrophobic organosilicon DP systems is usually higher than 90% [11,2]. Hydrophobic surface treatment of nanoparticles of TiO_2 and SiO_2 mixed with silane was also found to reduce water absorption [11]. Feng et al. [1] reported a decrease of 86% in water absorption of a modified cement paste (with stearic acid emulsion addition at 1% of the cement weight). However, the review of Basheer et al. [3] highlighted that the percentage reductions in water absorption for some inefficient silane and siloxane treatments was as low as 16%, while for efficient treatment it approached 100% [3]. Always, a certain level of water absorption of hydrophobically modified concrete is obtained. This is because lining the pores cannot be complete and the large molecules of the hydrophobe cannot penetrate the nanopores in the cement paste [2], as described in Section 8.4. Also, capillary condensation explains why the reduction in water absorption for hydrophobic DP might be low [2]. The mechanism of capillary condensation includes three steps: (1) the transport of water vapor by permeation flow and diffusion, (2) capillary condensation, and (3) capillary absorption of the condensed water. On the other hand, as this capillary condensation effect is totally internal, it does not contribute in carrying and transporting harmful materials and ions (e.g., chlorides) from surroundings into concrete [2]. A limiting water absorption of 2.5% by mass and a reduction in water absorption by at least 50% are set for hydrophobic systems by The German Committee for Reinforced Concrete [3]. Basheer et al. [3] highlighted that according to the National Cooperative Highway Research Program, the acceptance criterion for hydrophobic surface treatments demands a reduction in water absorption of 75% or larger [3].

8.7.3 Reducing chloride ion penetration and corrosion

In a typical concrete, the diffusion of chloride ions can reach depths of 40100 mm when the concrete is exposed to a deicing salt or seawater for a few years [2]. Only free chlorides (about 94% of the total chloride ions in concrete) can cause threats for corrosion. A threshold concentration of chloride is used in the durability and reliability analysis. When the chloride content is lower than such a threshold concentration [e.g., in the range of 0.4%–0.7% by weight of cement [27]], no major durability issues are expected. The reduction in chloride ion penetration in concrete is an important durability parameter for hydrophobic DP materials. Evaluation of such a performance of hydrophobic WP materials is made by measuring the rate of chloride ion penetration through a section of concrete (diffusion test) or by measuring the profile or distribution of chloride ion concentration across a concrete depth after exposing the surface to a source of chloride ion for a given period of time. This is done with shallow immersion in salt solution, spraying, or bonding with saline solutions [3]. Chloride ion penetration is more frequently determined by rapid chloride ion penetration through measuring the total charge passage according to ASTM C1202 (see Chapter 7). It can be also tested by long-term chloride ponding according to ASTM C1543 (withdrawn 2019).

Hydrophobic WP materials are effective at reducing the ingress of chloride ion in concrete under nonhydrostatic conditions [27]. Fig. 8.14 shows the profiles of chloride ion content of a concrete specimen treated with various WP and DP

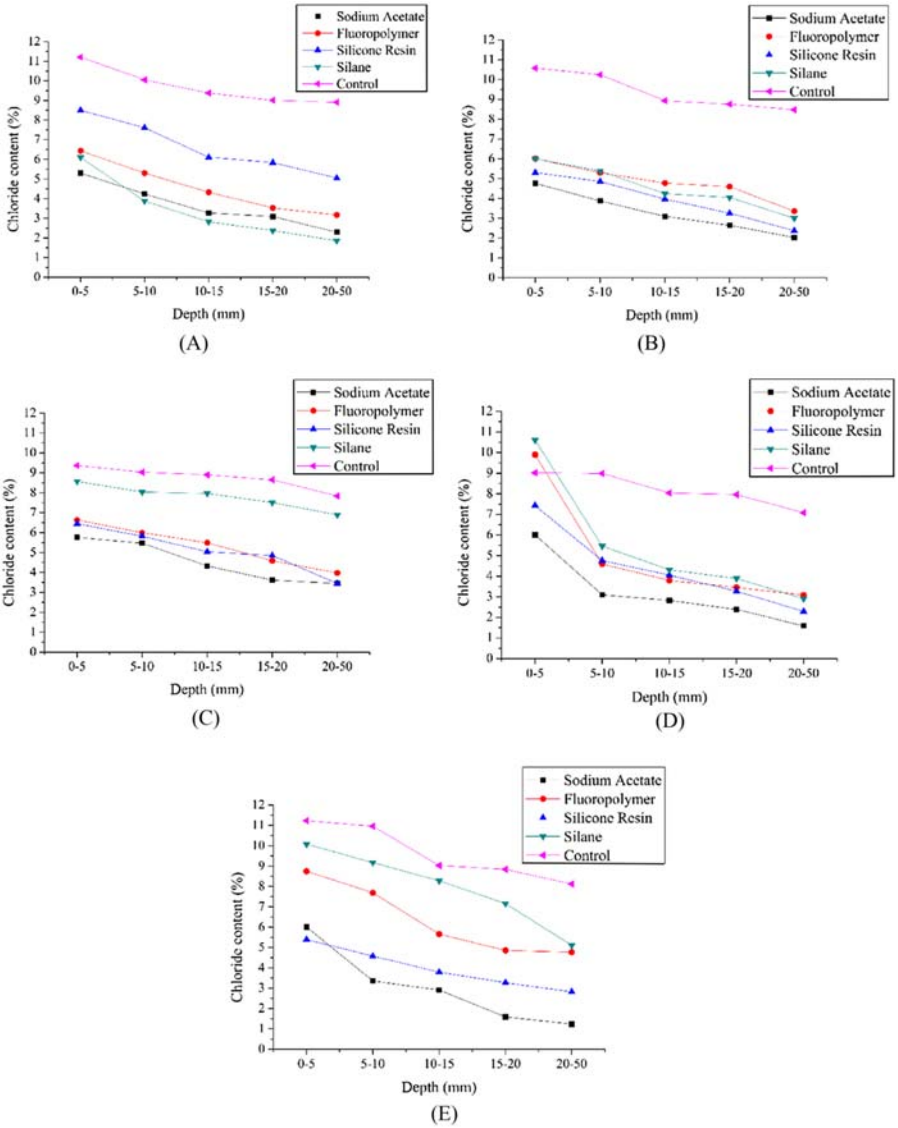


Figure 8.14 The profiles of chloride ion content in concrete specimens comparing nontreated and treated with various hydrophobic materials after they were ponded in a 5%-NaCl saline solution for 90 days at different levels of water saturation including (A) fully dry, (B) 2% moisture content, (C) 4% moisture content, (D) fully saturated (tested before drying), and (E) fully saturated (tested after drying) ([51]).

materials compared with the profile for nontreated concrete specimens after being ponded in a 5%-NaCl saline solution for 90 days [51]. An obvious decrease in chloride ion content is observed for all types of organic materials. Different levels of presaturation of the specimen with water yielded different performance. In general, increasing the saturation levels increases the levels of chloride ions in concrete [51]. This occurs because the diffusivity of chloride ions increases with increasing internal moisture content (see Chapter 2). Mundo et al. [11] and Basheer et al. [3] indicated that impregnation with silanes might be the most efficient system for reducing the ingress of chloride ions. However, Fig. 8.14 shows that the efficacy of saline is high for dry concrete specimens. Under water saturation conditions, other systems in Fig. 8.14 are much more efficient.

The penetration of dissolved chloride ions in water is hindered by reducing the capillary suction of chloride solution and by reducing the moisture content of concrete. In fact, a nearly linear correlation between the water absorption from immersion test and the content of chloride ion in concrete was reported [3]. In addition, it has been discussed in Chapter 2 that the diffusivity of chloride ions is strongly dependent on the moisture content of concrete. However, the review of Pan et al. [16] indicated different findings of the effect of silane on reducing chloride ion penetration: some of the reviewed studies indicated that silane failed to prevent the diffusion of chloride ion, but delayed the start-up time before achieving steady state diffusion [16]. In the review of Mundo et al. [11], the impregnation hydrophobic surface treatments were characterized with a uniform behavior of reducing chloride ion penetration by percentages higher than 85% [11]. Levels of concrete protection from chloride ion attacks vary among researchers, for example, reductions in chloride ion ingress is in the range of 25%95% [3]. In fact, the percentage reduction in chloride ion penetration is governed by the chemical and structural characteristics of the hydrophobic compounds and the structural and transport characteristics of the original concrete before treatment (e.g., porosity, liquid and gas permeabilities, and the presence of cracking). A sufficient penetration depth of DP materials is needed for effective protection of concrete against chloride ion penetration and a sufficient amount of the hydrophobic material is needed to provide larger coverage of the internal surface of concrete capillary pores [2]. The efficiency of hydrophobic DP materials for reducing the ingress of chloride ions in concrete is not enhanced significantly with installing the material in a multiple application [2] (see Section 8.4). A high percentage reduction in the diffusion coefficient of chloride ion was obtained when the original concrete had a high diffusion coefficient [16]. A reduction in the resistance of silane for chloride ion penetration was reported when the temperature was increased [16].

The efficiency of reducing the ingress of chloride ion is also correlated with corrosion protection of reinforcing steel. Reducing the corrosion of steel bars is also correlated with the reduction in the migration of other harmful ions such as sulfate ions. The use of silanes has been reported to reduce the corrosion current and reduce the formation of by-products of corrosion reactions [3]. The efficacy of hydrophobic DP materials can be obtained by comparing the macro-cell corrosion current and half-cell potentials of treated and nontreated concrete specimens [3].

The review of Pan et al. [16] indicated that although the effect of silane on the corrosion of steel has been widely investigated, an agreement on its impact has not been reached. Some hypotheses indicated that the increase in corrosion with silanes is attributed to the increase in the rate of diffusion of oxygen in dry hydrophobic capillary pores [16]. The corrosion of steel bars in concrete treated with silane was reduced by 50% in terms of reductions in corrosion current and by 37% in terms of the formation of corrosion by-products [16]. As in the analysis of chloride ion penetration, the level of corrosion protection is governed by the structure of the hydrophobic compounds and the original structure of the concrete before treatment (e.g., porosity and cracking). The long-term efficacy of hydrophobic surface treatment for inhabiting the initiation of corrosion in concrete depends mainly on the achievable penetration depth of the hydrophobic material within the concrete (required penetration depth >5 mm) [44].

Reductions in chloride ion penetration increase the time before the initiation of corrosion because of the decrease in soluble ions associated with the decrease in the moisture content [3]. The threshold chloride concentration for reliability analysis is performed for typical concentrations of 0.4%0.7% by weight of cement [27]. Then, the time required for a 50% probability of corrosion failure is estimated based on reaching the threshold chloride concentration at the interface with the steel reinforcement [27]. Hence, some silanes could extend the reinforcement corrosion time by almost four times [16]. Silane treatment of cracking concrete accelerated the corrosion of steel bars [16]. This can be attributed to the fact that silanes do not have the ability to heal or bridge cracks. However, Dai et al. [44] clarified that if cracks were present in concrete before the application of surface treatment, the hydrophobic treatment can still inhibit the corrosion of steel bars, with sufficient penetration depth [11].

Similarly, calcium stearate has been reported to enhance the corrosion resistance of reinforcement steel in concrete [46]. The percentage reduction in corrosion attack of self-compacting concrete was found to be dependent on the dosage of calcium stearate and the quality of the concrete mixture [46]. The corrosion attack of the reinforcing steel can be decreased by 30%–86% depending on the dosage of calcium stearate. The corrosion resistance of the modified cement paste can be increased significantly when a stearic acid emulsion is added to the paste at a dosage of 1% of the cement weight [1]. Such an enhancement is achieved by reducing the migration of chloride and sulfate ions through the capillary pores accompanying water as a carrier.

8.7.4 Reducing carbonation

Carbonation requires CO_2 permeation into the concrete pores where it reacts with calcium ions from the pore solution. Hence, concrete resistance against carbonation is associated with gas permeability. The evaluation of concrete resistance against carbonation is tested by measuring the depth of carbonation or the rate of diffusion of carbon dioxide [3]. As indicated in Section 8.2, gas permeability (similar to vapor permeability) is not affected by the formation of the pore lining hydrophobic layer, as the pores remain physically open. Gas and air permeabilities are correlated to vapor permeability or breathability of concrete [3,31]. In fact, as most of the hydrophobic DP systems are only pore liners, they are breathable [9]. Fig. 8.15 compares moisture transmission values of treated and untreated concrete specimens. The values are very close [20], although a small reduction in breathability with hydrophobic surface treatments at the initial stages are reported [3]. Basheer et al. [3] summarized the findings of several publications on the evaluation of breathability of various hydrophobic materials and highlighted that there were no significant differences between breathability of treated and nontreated concrete specimens (for silane systems).

Silane and siloxane can only control the moisture content of the concrete substrate by reducing capillary suction of liquid water; however, they do not decrease the diffusion of carbon dioxide through concrete [3]. Hence, concrete resistance against carbonation is not enhanced by hydrophobic DP treatment [3,27]. Pan et al. [16] reported that the carbonation of concrete could be decreased by most of WP coatings and surface treatments (e.g., polymeric barriers and hydrophilic materials such as silicates), but silanes and siloxanes had limited impact on the penetration of CO_2. Only about 20% reduction in carbonation depth was reported with silane and siloxane surface treatments [16].

8.7.5 Enhancing concrete resistance against freezing and thawing and scaling

Hydrophobic WP materials are effective in enhancing concrete resistance against damages from cycles of freezing and thawing. Evaluating the performance of hydrophobic WP materials is made by measuring reductions in the mass loss, length change, flexural strength, and/or compressive strength after subjecting the specimen to a certain number of freezing and thawing cycles [10] [according to ASTM C666

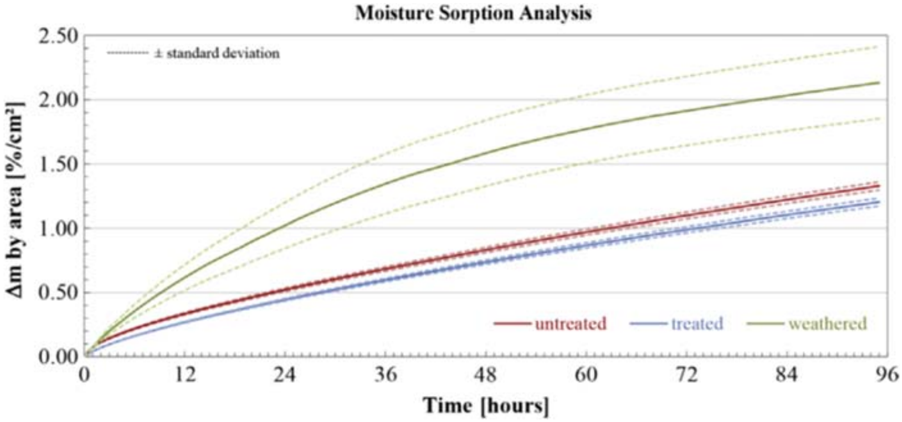


Figure 8.15 Percentage moisture absorption by area from the moisture-sorption test ([20]).

[26]]. Scaling resistance is measured by exposing the specimen to salt solutions at the surface under cycles of freezing and thawing.

Fig. 8.16 compares the percentage mass loss, flexural strength, and compressive strength for control and treated concrete specimens (using isooctyl triethoxy silane surface treatment) as functions of number of cycles of freezing and thawing [10]. It shows major reductions in the mass loss and in the loss of strengths for the treated specimen. The enhancement mechanism is mainly associated with the reduction in moisture content in concrete, because of the reduction of capillary absorption [16]. As mentioned above, the hydrophobic materials reduce the internal humidity in concrete, which in turn reduces capillary condensation, and hence reduces the availability of water within pores for phase change. In addition, reductions in thermal conductivity of mortar with siloxanes have been reported, which is because of the reduction in moisture content (see Chapter 2) [11]. Such a reduced conductivity minimizes heat loss, by internal conduction, during the freezing cycle. Silane cannot function well against cycles of freezing and thawing when the concrete is saturated before the treatment or when the resulting pressure during freezing and thawing cycles is larger than the hydrophobic repulsive force provided by silane lining [16].

In fact, [3] indicated that hydrophobic silane treatment could double the number of freezing and thawing cycles at which concrete began cracking by cycles of freezing and thawing. Some studies have reported that concrete with silane treatment degrades faster than untreated concrete under accelerated cycles of freezing and thawing [16]. Pan et al. reported that a number of studies confirmed that salt scaling

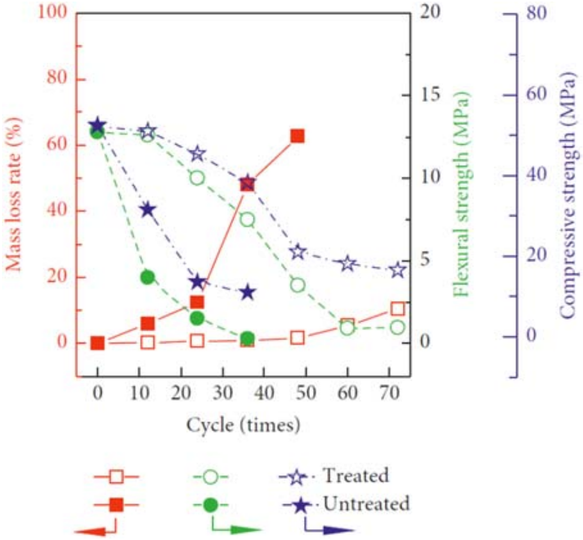


Figure 8.16 Percentage mass loss, flexural strength, and compressive strength for control and treated concrete specimen (using isooctyl triethoxy silane surface treatment) as functions of number of cycles of freezing and thawing ([10]).

was noticeably reduced (e.g., by 90%) using silane surface treatment [20]. This is attributed to similar mechanisms of reducing water penetration and thermal conductivity as discussed above.

Results of Basheer and Cleland [26] indicated that the hydrophobic surface treated concrete improved the freeze–thaw resistance even in the case of the porous concrete with high w/c ratio (e.g., w/c=0.65). However, treated concrete with high w/c ratio (poor pore structure and strength) withstands a lower number of freezing and thawing cycles than that of tight concrete [26]. Also, increasing the penetration depth of hydrophobic treatment increases the number of freezing and thawing cycles that can be withstood [26,16].

8.7.6 Strength parameters

The use of hydrophobic DP treatments has marginal effects on the strength and abrasion resistance of concrete. Some authors reported that silane treatment can enhance the surface mechanical properties and can assist in preventing and healing small cracks, although Pan et al. highlighted that there were no adequate experimental results to explain such an effect [9]. Shen et al. [25] reported experimental results showing that silane-based surface treatment improved the compressive strength of the treated historic concrete, specially, with cream applied material. This performance was associated with a compactness effect.

A slight enhancement of abrasion resistance was observed for the concrete treated with silanes, because the friction coefficient of the concrete surface could be reduced by silanes [16]. The hydrophobic surface treatment affects the surface skid resistance or frictional properties measured according to the BS EN 13036-4, by using the Pendulum test [13]. On the other hand, [25] concluded that strong hydrophobicity could generate tension and eventually could accelerate the concrete deterioration.

Some significant effects on the mechanical properties of concrete have been reported for hydrophobic materials when they are used as admixtures to the concrete mixtures. The resulting impacts depend on the chemical structure of the admixtures. In the case of stearate compounds, when calcium stearate is added to a mixture of self-compacting concrete, an increase in the compressive strength was reported [46]. On the other hand, when waterborne stearic acid emulsion admixture was added at a dosage of 1% of the cement weight to mixtures of mortars, the compressive and flexural strengths decreased by about 16% and 20%, respectively [1].

References

[1] Feng, Z., et al. (2019). Integral hydrophobic concrete without using silane. *Construction and Building Materials*, *227*, 116678.

[2] Zhan, H., Wittmann, F., & Zhao, T. (2003). Chloride barrier for concrete in saline environment established by water repellent treatment. *International Journal for Restoration of Buildings and Monuments*, *9*(5), 535−550.

[3] Basheer, P. A. M., et al. (1997). Surface treatments for concrete: Assessmentmethods and reported performance. *Construction and Building Materials*, *11*(7), 413−429.

[4] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI: American Concrete Institute.

[5] ACI. (2013). *Committee 515, ACI 515.2R-13. Guide to selecting protective treatments for concrete*. Farmington Hills, MI: American Concrete Institute.

[6] ACI. (2016). *Committee 212, ACI 212. 3R-16. Report on chemical admixtures for concrete*. Farmington Hills, MI: American Concrete Institute.

[7] de Souza Oliveira, A., et al. (2020). Crystalline admixture effects on crystal formation phenomena during cement pastes' hydration. *Journal of Thermal Analysis and Calorimetry*, *139*(6), 3361−3375.

[8] BSI. (2004). *EN 1504-2. Products and systems for the protection and repair of concrete structures—Definitions, requirements, quality control and evaluation of conformity—Part 2: Surface protection systems for concrete*. Brussels: European Committee for Standardization, Brussels.

[9] Pan, X., et al. (2017). A review on concrete surface treatment. Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578−590.

[10] Song, Z., Lu, Z., & Lai, Z. (2019). Influence of hydrophobic coating on freeze-thaw cycle resistance of cement mortar. *Advances in Materials Science and Engineering*, *2019*.

[11] Mundo, R. D., et al. (2020). Recent advances in hydrophobic and icephobic surface treatments of concrete. *Coatings*, *10*(5), 449.

[12] Muzenski, S., Flores-Vivian, I., & Sobolev, K. (2015). Hydrophobic engineered cementitious composites for highway applications. *Cement and Concrete Composites*, *57*, 68−74.

[13] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2019). Moisture evaluation of concrete pavement treated with hydrophobic surface impregnants. *International Journal of Pavement Engineering*, *21*, 1−9.

[14] Zhao, Y., et al. (2018). Icephobicity studies of superhydrophobic coatings on concrete via spray method. *Materials Letters*, *233*, 263−266.

[15] Aldred, J. (1989). The short-term and long-term performance of concrete incorporating dampproofing admixtures. In *Supplementary papers of 3rd CANMET/ACI international conference on superplasticizers and other chemicals in concrete*.

[16] Pan, X., et al. (2017). A review on surface treatment for concrete – Part 2: Performance. *Construction and Building Materials*, *133*, 81−90.

[17] ACI. (1999). *Committee 212, ACI 212.3R-91. Chemical admixtures for concrete*. Farmington Hills, MI: American Concrete Institute.

[18] Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C. (2002). *Design and control of concrete mixtures* (Vol. 5420). IL: Portland Cement Association Skokie.

[19] Shetty, M. (2005). *Concrete technology theory and practice*. New Delhi, India: S. Chand and Company LTD.

[20] Weisheit, S., et al. (2016). Assessment of test methods for characterizing the hydrophobic nature of surface-treated high performance concrete. *Construction and Building Materials*, *110*, 145−153.

[21] Liu, C., et al. (2011). Fabrication of superhydrophobic wood surfaces via a solution-immersion process. *Applied Surface Science*, *258*(2), 761−765.

[22] Cassie, A., & Baxter, S. (1944). Wettability of porous surfaces. *Transactions of the Faraday Society*, *40*, 546−551.

[23] van Oss, C. J. (2008). Chapter Eleven—The water–air interface. In C. J. van Oss (Ed.), *Interface science and technology* (pp. 149−160). Elsevier.

[24] Wenzel, R. N. (1936). Resistance of solid surfaces to wetting by water. *Industrial & Engineering Chemistry*, *28*(8), 988−994.

[25] Shen, L., et al. (2019). Performance of silane-based surface treatments for protecting degraded historic concrete. *Progress in Organic Coatings*, *129*, 209−216.

[26] Basheer, L., & Cleland, D. J. (2006). Freeze–thaw resistance of concretes treated with pore liners. *Construction and Building Materials*, *20*(10), 990−998.

[27] Schueremans, L., & Van Gemert, D. (1997). Service life prediction model for reinforced concrete constructions treated with water repellent compounds. In *Conchem Proceedings* (pp. 103–113). Dusseldorf.

[28] Beeram, P. S. R. (2017). *Characterization of ice adhesion strength over different surfaces pertinent to aircraft anti-/de-icing* (Graduate Theses and Dissertations) (p. 16073). Ames, IA: Iowa State University Capstones. https://lib.dr.iastate.edu/etd/16073.

[29] Ashworth, T., Tollefsen, B., & Weyland, J. (1979). Adhesion of ice to concrete surfaces—Preliminary results. *Transportation Research Board Special Report*, 185.

[30] Zhang, Y., et al. (2016). Effect of surface energy on freezing temperature of water. *ACS Applied Materials & Interfaces*, *8*(27), 17583−17590.

[31] Kebao, R., & Kagi, D. (2012). 10 - Integral admixtures and surface treatments for modern earth buildings. In M. R. Hall, R. Lindsay, & M. Krayenhoff (Eds.), *Modern earth buildings* (pp. 256−281). Woodhead Publishing.

[32] Wheeler, G. (2005). *Alkoxysilanes and the consolidation of stone*. Getty Publications.

[33] Zhang, W., et al. (2019). Study on unsaturated transport of cement-based silane sol coating materials. *Coatings*, *9*(7), 427.

[34] Liu, J., et al. (2019). Properties and hardening mechanism of alkali activated slag based hydrophobic coating at ambient curing condition. *Materials Research Express*, *6*(5), 055505.

[35] Li, F., et al. (2020). Investigation on waterproof mechanism and micro-structure of cement mortar incorporated with silicane. *Construction and Building Materials*, *239*, 117865.

[36] Franzoni, E., et al. (2014). Improvement of historic reinforced concrete/mortars by impregnation and electrochemical methods. *Cement and Concrete Composites*, *49*, 50−58.

[37] Jappie, L. (2019). *Literature review of the use of common protective coatings for concrete structures with experiences in the South African context.*, Engineering and the Built Environment.

[38] Chen, H., et al. (2020). The influence of surface treatment on the transport properties of hardened calcium sulfoaluminate cement-based materials. *Cement and Concrete Composites*, *114*, 103784.

[39] Yu, J., et al. (2019). Hydrophobic silane coating films for the inhibition of water ingress into the nanometer pore of calcium silicate hydrate gels. *Physical Chemistry Chemical Physics*, *21*(35), 19026−19038.

[40] Sanchez, M. A. (1992). *Lightweight concrete building product*. Google Patents.

[41] Muhammad, N. Z., et al. (2015). Waterproof performance of concrete: A critical review on implemented approaches. *Construction and Building Materials*, *101*, 80−90.

[42] Mora, E., et al. (2019). Control of water absorption in concrete materials by modification with hybrid hydrophobic silica particles. *Construction and Building Materials*, *221*, 210−218.

[43] Rahman, M., et al. (2016). Moisture efficacy of impregnant in concrete protection. In *Transportation Research Board 95th Annual Meeting*. Washington, DC, United States.

[44] Dai, J.-G., et al. (2010). Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: The role of cracks. *Cement and Concrete Composites*, *32*(2), 101−109.

[45] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. McGraw-Hill Education.

[46] Maryoto, A., et al. (2018). Corrosion resistance of self-compacting concrete containing calcium stearate. *Journal of Engineering Science and Technology*, *13*(10), 3263−3276.

[47] Tshabalala, M. A., et al. (2003). Surface chemistry and moisture sorption properties of wood coated with multifunctional alkoxysilanes by sol-gel process. *Journal of Applied Polymer Science*, *88*(12), 2828−2841.

[48] Piao, C., et al. (2013). Potassium methyl siliconate-treated pulp fibers and their effects on wood plastic composites: Water sorption and dimensional stability. *Journal of Applied Polymer Science*, *129*(1), 193−201.

[49] Haynes, W. M. (2014). *CRC handbook of chemistry and physics*. CRC press.

[50] Mascini, A., Cnudde, V., & Bultreys, T. (2020). Event-based contact angle measurements inside porous media using time-resolved micro-computed tomography. *Journal of Colloid and Interface Science*, *572*, 354−363.

[51] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2019). Fundamental interaction of hydrophobic materials in concrete with different moisture contents in saline environment. *Construction and Building Materials*, *207*, 122−135.

Hydrophilic crystallization waterproofing

9

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

9.1 Introduction

Protecting concrete from deterioration by water-related problems described in Chapter 3 demands prevention or minimization of water penetration through concrete pores. Water is transported through pores by permeation flow under a hydrostatic pressure (Chapter 2) and by capillary absorption or swelling (Chapter 5). Concrete durability is enhanced by reducing water permeability through waterproofing (WP) systems, which reduce the porosity of the cement paste. It is worth to recall that the objective of WP is usually to minimize water penetrability through concrete, which includes permeation, capillary absorption, diffusion, and combinations of these mechanisms [1]. However, pore blocking materials are used to reduce mainly the permeation flow under a hydrostatic pressure (see Chapter 2). Restricting the permeation flow of water through pores is a suitable WP solution for damped concrete, as encountered in below grade and water retaining concrete structures. On the other hand, dampproofing (DP) materials (which are described in Chapter 8) can only line the pores with a hydrophobic molecular layer that decreases water absorption but cannot resist the hydrostatic pressure. The mechanisms of water interactions with cementitious surfaces are described in Chapter 5. In general, the hydrophilic WP materials include active compounds that lead to precipitation of solid particles within the permeable pores, and thus reduce the water permeation rate under pressure, by increasing the flow resistance.

Based on the position of their WP action, WP systems are simply classified into surface applied systems (including membranes and coatings) and integral systems, which act from within the concrete structure [2] (see Chapter 6). The hydrophilic WP materials are categorized as internal WP systems, as they function from within the pore structure instead of creating an external barrier using membrane systems (see Chapter 6). They are referred to as integral WP systems as they become an integral part of the concrete mass [3]. Some researchers restrict the definition of integral WP to additions to concrete mixtures. Integral WP systems include solutions or emulsions, which are applied as a penetrating surface treatment that migrate into the concrete pores and admixtures that are added to the concrete mixture [4]. WP solutions are discussed in ACI 515.2R-13 [5]. WP additions to concrete mixture are also referred to as permeability reducing admixtures (PRA) (ACI 212.3R-10) [6]. PRA materials for nonhydrostatic pressure applications (PRANs) are typically

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00009-X

referred to as DP materials (see Chapter 8) and PRA materials for hydrostatic pressure applications (PRAHs) are referred to as WP materials [7]. Crystallization WP admixtures are considered among the types of PRAHs [8]. When the WP materials are added to the concrete mixture as an admixture or PRAHs, the pore blocking mechanism is achieved in the whole structure of concrete, while when these materials are applied as a penetrating surface treatment, a layer of concrete is waterproofed by the pore blocking mechanism. From a wide engineering perspective, integral WP approaches are considered in Chapter 7 to include (1) enhancing the cement hydration, (2) reducing the water demand for certain concrete mix design utilizing chemical admixtures, (3) blocking the capillaries through the filling effects of WP materials, or (4) a combination of these approaches [2]. Manipulating the mix design is discussed in Chapter 4 and using conventional chemical admixtures and supplementary cementitious materials (SCMs) are discussed in Chapter 7. This chapter covers the hydrophilic crystalline WP materials, which can be applied to concrete as solutions for surface treatments, powder, or liquid additions to concrete mixture at the time of batching. Powders of crystallization systems incorporated in the formulations of cementitious coatings and mortars are covered in Chapter 12. In this chapter, the types of the hydrophilic WP systems, their physicochemical backgrounds, and mechanisms are detailed. Then, the parameters of performance characteristics and durability enhancement are discussed.

9.2 Waterproofing by pore blocking

Pore blocking is achieved by creating obstacles in the flow path of water within cement paste. The basic idea behind the pore blocking WP system is to restrict (or ideally to prevent) the flow of water through plugging the capillaries of the cement paste and cracks in concrete and then transforms the overall concrete structure or a surface layer of it into water-tight system [9]. These obstacles are commonly solid particles with crystalline structure that are formed in situ through a chemical reaction (see Section 9.5) or inert fillers that deposit within the pores. In some cases, the flow restriction is created through the formation of hydrophobic polymer particles or oil droplets, which restrict the flow in addition to their water repelling effects (see Chapter 8). In fact, the deposition of the hydrophobic layer at the internal surfaces of the pores may reduce the available space for water flow and thus decrease the water permeability in concrete subjected to a hydrostatic pressure [6]. The typical hydrophilic DP materials (like silanes and siloxanes) can contribute to reducing the porosity of concrete through the formation of thin layer at the surfaces of the pores [10]. Some silanes have been reported to decrease the number of fine pores. For example, it has been reported that surface treatment with poly-methyl tri ethoxy silane resulted in a significant reduction in fine pores (with size $< 50\,\text{nm}$) in calcium sulfo aluminate mortars [10]. However, as described in Chapter 8, hydrophobic WP materials are commonly referred to as pore liners (according to EN 1504–2) [11] not pore blockers. Thus the two different mechanisms must not be mixed and this chapter deals only with hydrophilic pore blocking materials.

Concrete porosity and permeability are strongly dependent [1] (see Chapter 2). Porosity is a structural criterion that indicates how much of a concrete is an open space and is characterized by pore size, distribution, and connectivity [12,13]. On the other hand, permeability is an intrinsic property that specifies the rate of fluid flow into concrete [14]. The hydrophilic crystallization WP admixtures contribute in reducing the available space width by about 65% [15]. The total average porosity of the cement paste can be reduced by about 15% by their filling effect [16]. Concrete permeability increases exponentially with increasing the porosity in cement paste [17]. A small reduction in total porosity of the cement paste using hydrophilic crystallization WP admixtures can lead to a major reduction in concrete permeability [16]. Commonly, the formation of the crystals enables the modified concrete matrix to resist a hydrostatic pressure of 14 bars (or 200 psi) [6]. The capillary absorption (or wicking) [6] through fine pores in concrete is not driven by permeation flow and does not require an externally applied hydrostatic head (see Chapter 5). Consequently, creating flow obstacles may not reduce capillary suction [18]. In fact, the water penetration velocity by capillary absorption can be in the order of 10^6 m/s. Such a value is higher than that of typical water permeability coefficient in concrete. In some cases, reducing the porosity of concrete by pore blocking WP materials may increase water absorption due to pore refinement effect (see Section 9.3.1).

Only a part of concrete porosity creates the channels for fluid flow. According to ASTM C125–15b [19], concrete pores are categorized into impermeable pores and permeable pores. Only permeable pores are filled with water when the concrete is submerged in water for a sufficient time. As described in Chapter 2, the pores in cement past paste include (1) the gel pores (interlayer hydration space) with a size range of 0.5–2.5 nm and contribute by around 28% of the porosity of the cement paste [20] and (2) the capillary pores with a size range typically >10 nm. The capillary pores form irregular networks between the calcium silicate crystals (CSH gel) that are produced by cement hydration (see Chapter 1). The capillary pores include micropores with sizes in the range of 10–50 nm (medium capillary pores) and macropores that can have larger sizes up to 5 m for pastes with a large water/cement ratio, at early ages of hydration [14]. The molecular size of H_2O is approximately 0.3 nm (310^{10} m) [3]. Water in concrete exists in various forms in gel pores and capillary pores (see Chapter 2). The chemically bound water (or nonevaporable water as defined by ACI concrete terminology) [21] forms an integral part of the hydrated cement particles in the gel pores, thus it cannot be detached from paste, without thermochemical actions. Similarly, the adsorbed water by hydrogen bonding within the gel pores in the CSH structure is not flowable. Such a physically bonded water layer may extend up to six molecular levels of water (about 1.5 nm) [14]. Part of the weakly adsorbed water can be desorbed back into the bulk free water because of drying effects when the internal relative humidity decreases to less than 30% [14]. These two forms of chemically and physically bonded water do not play a role in concrete permeability. Water permeability in concrete is associated only with free bulk water [21] that can flow and can be removed without causing a volume change or shrinking [1]. Water permeation is promoted mainly within the capillary pores, which form microscopic channels. In fact, the connectivity of capillary pores are more crucial in water transport than just the capillary porosity [1]. In addition, macropores and cracks that result from durability problems (see Chapter 3) play more critical roles in water permeation. The pore blocking or clogging WP materials occupies the permeable capillary networks, which are established by the macropores and the cracks. Then, they create a flow resistance for water permeation. As mentioned above, gel pores (contributing by a significant fraction of concrete porosity) are very small and isolated, hence they do not contribute in providing a space for water permeation. Consequently, pore blocking mechanism does not target/involve precipitating materials within the gel pores. In general, the WP crystals were observed to fill pores within a size range of 20–200 m [3], which include medium and large capillaries (macropores) existing between CSH crystals and other hydration products.

In addition to the flow networks created by the macropores and the cracks, air voids may be thought to provide an additional contribution to concrete permeability [13]. As described in Chapter 2, air voids include entrained air voids with a size range of 10–1000 m [19] and entrapped air voids with sizes 1 mm). In principle, air voids are usually isolated and thus they are hypothesized to add a little contribution to water permeation through concrete. However, they may become interconnected through the networks of the capillary pores [22]. In fact, the porosity near the interface of air void-paste is approximately two to three times higher than that of the bulk paste region [1]. The involvement of intersecting capillary networks in connecting air voids may increase permeability in concrete [6]. However, according to another hypothesis, the use of air entrainment agents decreases the permeability of concrete as a consequence of their role in improving the workability of fresh concrete. In fact, air entrainment voids are essential for enhancing concrete durability by increasing concrete resistance against cycles of freezing and thawing. Thus they are incorporated in concrete intentionally and they are not intended to be blocked by crystallization WP materials. The unintentional air entrapped voids (e.g., from mixing of fresh concrete) [23] do not show visible differences from air entrainment voids [24]. Overall, pore blocking of the capillary networks will take care of the possible connectivity of air voids and thus it can be stated with reasonable confidence that pore blocking does not target to affect the air voids.

The porosity of aggregates that have a large capillary size (>10 m) may be thought to contribute to concrete permeability and hence it may be thought to demand pore blocking to reduce water permeation through concrete as a composite material. However, the aggregates are usually stronger and involve less total porosity than cement paste. The porosity of aggregates rarely exceeds 10% of the porosity of cement paste [14], and hence their permeability is lower than that of the typical cement paste. Overall, pore blocking targeted mainly resigning the porosity of cement paste rather than aggregates. However, the possible diffusion and penetration of WP materials within the pores of aggregates may lead to internal pore blocking of the aggregates. From another perspective, the addition of aggregates to concrete mixtures increases the permeability of the hardened concrete considerably. This is believed to occur due to the increase in the microcracks and the high porosity at the transition zone between the aggregate and the cement paste [14,25]. Thus the permeability of a concrete containing aggregates can be higher by an order of magnitude than the permeability of a corresponding cement paste [14]. Targeting the blocking of paste pores will again handle the effect of high porosity at the transition zone.

9.2.1 Swelling behavior of hydrophilic crystalline gels

The pore blocking particles themselves have a porous gel structure with tiny channels that allow swelling through capillary action into their internal structure causing a volume expansion, as illustrated in Fig. 9.1. Such a swelling behavior gives them the hydrophilic characteristics [9], which is different from the hygroscopic crystalline WP materials that suck water vapor by adsorption onto their surface (covered in Chapters 10 and 11). The capillary forces within the crystalline gel reduce the internal pressure and hence allows water penetration into the gel. The hydrophilic behavior of the crystalline gel is driven by its porosity: upon wetting, the fine capillary network system of the crystals sucks water through capillary absorption (see Fig. 9.1B). The existing literature does not offer experimental or theoretical analyses of the swelling kinetics of the crystallization WP gels. In general, the hydrophilic WP gel swells moisture from within cement paste through a similar kinetic process as that of concrete swelling kinetics. The swelling capacity is strongly dependent on the

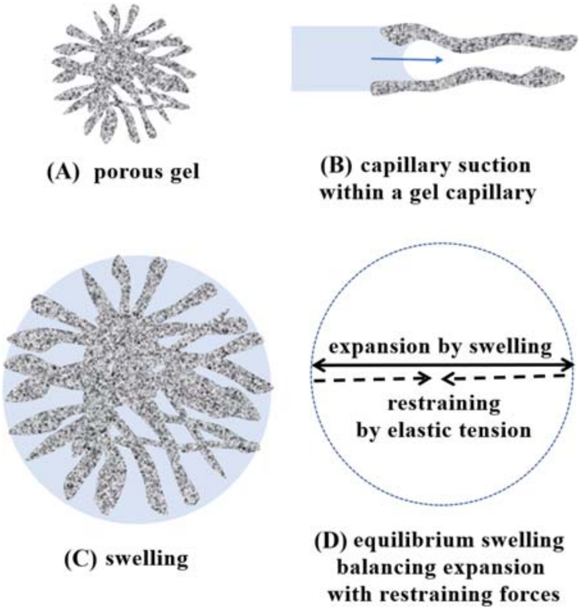


Figure 9.1 Illustrations of the mechanism of hydrophilic gel swelling, showing (A) a dry porous gel, (B) capillary action, (C) expanded gel, and (D) force balance at equilibrium swelling.

structural characteristics of the crystalline gel. These include the chemical composition and surface characteristics (e.g., surface groups), and crystal size, porosity and density. As described in Chapter 5, the driving force for capillary suction is the depression pressure [see Eq. (5.6)], which is inversely proportional to radius of the capillaries. Theoretically, decreasing the pore size increases the depression pressure and increasing the number of fine pores increases the sorptivity [18]. The structural parameters also include texture and the porosity of the hydrophilic crystalline material. Increasing the surface roughness of the hydrophilic material increases its hydrophilicity as explained by the Cassie model (see Chapter 5) [26]. Decreasing the porosity of the hydrophilic crystalline material can enhance the wetting conditions (Cassie model). Also decreasing the water contact angle of a hydrophilic crystalline gel increases its swelling capacity as it increases the level of hydrophilicity (as $<$ 90 degrees) [26]. The rate of swelling increases with decreasing the particle size of the gels due to the increase in the surface area subjected to water.

The hydrophilic crystals are composed of a very large number of small size internal capillaries (see Fig. 9.1C and Section 9.5.1); thus their swelling capacity (capillary suction) is much higher than that of concrete. There are no data on the effect of pore refinement within the hydrophilic crystals on their swelling behavior. However, a basic understanding of such a behavior can be gained by analogy with swelling kinetics in plyometric gels, for which the equilibrium swelling capacities and the rate of swelling increase with decreasing the particle size [27]. In general, the rate of the kinetic swelling process of hydrophilic materials is proportional to the square root of time (t). The cumulative water absorption per unit area (W_{cs} in g/m^2) is given by Eq. (9.1) (see Chapter 5).

$$W_{cs} = S\sqrt{t} \tag{9.1}$$

where S is the sorptivity of the hydrophilic material (kg/m^{2}s$^{0.5}$) [10]. Other empirical models were also used for describing the swelling kinetic for hydrogels including pseudo first and second-order models, which were frequently used for superabsorbent materials [27]. Such a water swelling may be enhanced by the capillary condensation (which occurs due to the penetration of water vapor and their subsequent condensation by cooling within the crystalline material). Capillary condensation increases the water content of the hydrophilic crystals. Some researchers state that the gel remains swelling as long as the moisture is available; however, swelling is an equilibrium reversible process. The kinetic swelling process continues until reaching an equilibrium capacity (W_e), through a mechanism that is well-described for polymeric gels [28]. Such an equilibrium mechanism is hypothesized to be valid for the crystalline gel. Hypothetically, the gel structure is elongated upon swelling and hence elastic stresses are developed within the gel structure during expansion (see Fig. 9.1D). These tensile stresses are opposed by the swelling or depression pressure contraction. Then, the gel attains an equilibrium swelling capacity when these two opposing forces are balanced, that is, when the expansion stresses overcome the depression pressure.

The volume expansion of the hydrophilic crystals within the pores of cement paste makes them occupy a larger fraction of the permeable pores and enhance their pore blocking efficiency. Such a volume expansion by water swelling may be enhanced by the capillary condensation that enlarges their expansion. A negative effect of the expansive swelling behavior of the WP crystalline gel on concrete structure is highlighted by some researchers. This is hypothesized to be caused by the potential generation of high internal stresses from expansion of crystals [29]. These stresses may affect the concrete structural integrity in a similar behavior encountered with the gel formation from the alkalisilica reactions (ASR) [29]. However, some silicate-based gels are not capable of exerting sufficient pressure to cause concrete cracking. For model systems of homogeneous amorphous sodium and calcium silicate gels, the pressure needed to prevent swelling was as low as 0.1 MPa, or it can reach up to 1 MPa (which exceeds the tensile strength of most concretes) [30]. Also, the swelling behavior is an equilibrium process that ends at a certain percentage swelling. The free-swelling of model systems of homogeneous amorphous sodium and calcium silicate gels were found to be as small as 0.5% and may reach up to 80% [30]. However, up to the author's knowledge at the time of preparing this chapter, no sufficient data or discussions are available in the literature on the swelling behavior of the WP crystals or on comparing their behavior with that of the gel produced by the ASR. These aspects deserve experimental investigation on hydrophilic gels of the crystallization WP materials.

When the concrete starts to dry again, the gel can release its moisture content by deswelling. The hydrophilic behavior of the crystalline gel is characterized by water swelling upon wetting and by water releasing upon drying, generating a continuous sink-source cycle. It is important to discuss the repeatability of cyclic swelling/deswelling behavior of the crystallization gel. Hypothetically, swelling is not expected to be completely reversible, that is, it will not achieve the same equilibrium swelling capacity every time it swells after a number of cycles. From the perspective of analogy, experimental results of swelling of polymeric superabsorbent gels indicated that the equilibrium swelling capacity was found to be lower in the second swelling cycle than that in the first swelling cycle [27]. For the case of crystallization WP gels, the swelling of water is not a simple physical process, as water is known to react with the active ingredients and cause further crystallization (see Section 9.5). Consequently, the process is not expected to be completely reversible particularly at early ages of crystallization formation. In fact, most of the industrial promoting materials highlight that the active ingredients remain dormant and can be activated for a further reaction with subsequent water absorption. This aspect of cyclic behavior also deserves experimental investigation.

The pore blocking mechanism is affected by the swelling capacity of the gels. In principle, the swelling behavior of water-absorbing materials or gels is generally governed by the time of contact with water [Eq. (9.1)], the surrounding conditions, and the gel structure. The physical and chemical parameters that affect the swelling rate and capacity of crystallization gel in concrete is believed to include temperature and pressure, pH and ionic strength as for the cases of other investigated hydrogels. Increasing salt concentration and ionic strength can lower the depression pressure and hence decrease the swelling capacity of the gel. However, no experimental studies are available on the performance of the crystalline gel in concrete as functions of pH or salinity.

From another perspective, swelling behavior of the crystals is one of the reasons for their low effectiveness in reducing water absorption of concrete [18] (see Section 9.6.2). At initial wetting of concrete containing hydrophilic WP crystals, a larger water absorption than reference concrete is obtained for two reasons: (1) the crystals suck water within their structure and expand and (2) the volume expansion of crystals refines the pores size of the paste through their filling effect and smoothens the surface of concrete making it more hydrophilic and thus causing more swelling. This occurs according to the Cassie model, which implies a decrease in the contact angle with smoothening the hydrophilic smooth surface, (see Chapter 5). It is worth to emphasize that the performance of the hydrophilic WP crystals is based on restricting the flow of water under a hydrostatic pressure and hence it targets at reducing the coefficient of permeability rather than reducing the capillary absorption and swelling.

9.3 Types of hydrophilic waterproofing materials

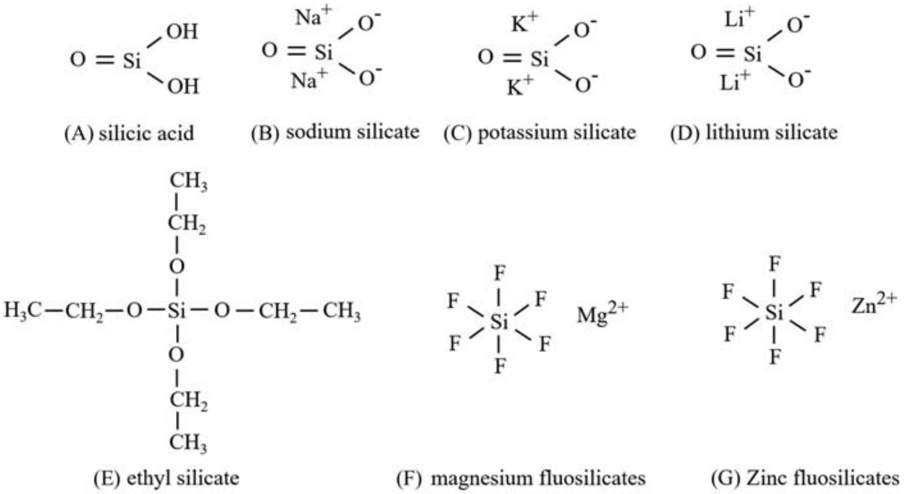
The chemical compositions of the industrial hydrophilic WP products are commonly proprietary; the manufacturers usually report part of the chemical and physical properties [16]. However, there are generic chemical families. In general, the internal hydrophilic WP systems include reactive and nonreactive materials. The reactive internal hydrophilic WP materials are compounds that have the ability to precipitate crystals through a chemical reaction with concrete constituents (see Section 9.5). The formed crystals have the ability to interact with moisture and grow by swelling so that it seals off the incoming water [4]. Systems of reactive hydrophilic WP materials include chemical solutions and mixtures of powders. Most of the literature focuses on powders when referring to crystallization WP. The nonreactive materials are inert particles that are physically deposited within the pores of the paste. They do have a swelling capacity but they do not react with water or other cementitious constituents.

Overall, the systems of hydrophilic WP can be categorized into the following families: (1) solutions of silicates and fluorosilicates, which are effective in blocking the capillaries in concrete surfaces [18,31], as detailed in Section 9.3.1, (2) powders of crystalline and/or natural hydrophilic particles incorporated in proprietary mixtures containing a carrier of cement and fine quartz sand [7,8,16], as detailed in Section 9.3.2, and (3) other pore filling systems as detailed in Section 9.3.3. The focus of this chapter is on the most popular types of these materials, which are the hydrophilic crystallization WP.

9.3.1 Hydrophilic crystalline waterproofing solutions

Reactive pore blocking silicate-based solutions include silicates and fluosilicate [10]. Sodium silicate (water glass) is the most commonly used pore blocking surface treatment material [10,18,31]. Potassium silicates, lithium silicate, and magnesium fluorosilicates are used at a much smaller extent [31]. Within this category, Chen et al. [10] provided a comprehensive comparison between sodium silicate, magnesium fluorosilicate, and tetra ethyl orthosilicate.

Silicate WP materials are alkali-silicon compounds, which are salts of a silicic acid [21]. They are formed through replacing the two hydrogen atoms in the silicic acid by two alkali atoms (see Fig. 9.2). The structures of the silicate compounds include a silicon atom bonded to a soluble alkali atom (e.g., lithium or sodium) and a reactive group that is capable of reacting and bonding with the calcium ion from the dissolution of calcium hydroxide, see Fig. 9.2. The use of sodium, potassium, or lithium alkalis solubilizes the silicate solution and promotes its penetration within concrete. Solutions of sodium silicate, potassium silicate, and lithium silicate are formulated with the addition of surfactants [32] and other ingredients that enhance their penetrability into concrete. ACI 515.2R-13 [5] lists sodium silicate, potassium silicate, lithium silicate among concrete protective treatments. These solutions are commonly categorized as floor hardeners and are stated to reduce water penetration in concrete. Their mechanism is based on their reaction with portlandite (calcium hydroxide) to form a water-insoluble precipitate or the development of additional silicate gel within concrete pores (see Section 9.5) [32]. ACI 515.2R-13 [5] states that “alkali silicates are widely used in the construction industry as water repellents, curing compounds, and set accelerators for concrete.” In fact, they are pore blocking materials not pore lining water repellents. Silicate materials include (1) solutions of reacting water soluble materials (sodium and potassium silicates), which react to form insoluble precipitates within pores [33], (2) solutions containing solidifying material (lithium silicate), which simply precipitate within the pores without a reaction [33], and (3) organic silicate compounds (tetra ethyl orthosilicate), which



(A) silicic acid (B) sodium silicate (C) potassium silicate (D) lithium silicate

(E) ethyl silicate (F) magnesium fluosilicates (G) Zinc fluosilicates

Figure 9.2 Structures of common silicate compounds.

are considered by some researchers as reactive hydrophilic crystallization agents. However, a further clarification on this issue is needed. Ethyl silicate or tetraethyl orthosilicate (TEOS) (see Fig. 9.2E) undergoes hydrolysis reactions for creating a hydrophobic layer (see Chapter 8) that has a secondary effect of pore filling. There is a hypothesis of a pozzolanic behavior of ethyl silicates [31]. The hydrolysis of TEOS is believed to release silicate ions that react with calcium hydroxide [10]. Some studies reported that ethyl silicate can produce more compacted concrete than sodium silicate [34]. However, it is a type of alkoxy silane compounds [35] and hence, it is mainly used as a hydrophobic DP material [31], with main characteristics that are not based on pore blocking effects as those of crystals [36]. The performance of this type of silicate will not be detailed in this chapter.

Fluorosilicate compounds include solutions of inorganic alkali salts that are used for surface treatment [37]. Similar to the silicate compounds, they react with calcium hydroxide [37] (see Section 9.5). Fluorosilicates can be obtained as by-products from the phosphate fertilizer industry. Their recycling in concrete application is a green practice that prevents pollution resulting from their release into the environment [38]. They include an alkali positive ion such as calcium, zinc, or magnesium combined with F_6Si^{2-} ions forming magnesium fluosilicate, zinc fluorosilicate, and calcium fluosilicate (e.g., F_6SiMg, F_6SiZn, F_6SiCa), respectively (see, e.g., Fig. 9.2F and G). There are other fluorosilicate compounds with a lengthy chemical formula that include more than one alkali ion such as sodium magnesium fluorosilicate ($F_{18}Mg_{16}Na_{10}O_{66}Si_{27}$). ACI 515.2R-13 [5] indicates that magnesium and zinc fluorosilicates are used separately or as mixtures combining both of them. Several patents have been registered on the use of fluosilicate compounds with concrete [see, e.g., Isador and Abraham [37]; Moraru [39], and Jones and Maxfield [40]]. They highlighted the protection of concrete against chemical and biological attacks through surface treatment [37].

9.3.2 Hydrophilic crystalline waterproofing powder admixtures

The main active materials in integral waterproofing admixtures include proprietary particulate materials incorporated in a fine cementitious mixture. The reactive materials in many crystalline powders are mainly silicate compounds [7]. Similarly, fluorosilicate compounds are used in powder form for use as admixtures [41,42]. In addition, reactive powders include calcium sulfo aluminate or aluminosilicate (e.g., in zeolite used in ultra-fine polarized proprietary powders) [43]. Powders of typical mineral admixtures (SCMs) such as slag and pozzolans may also be used in these formulations [7]. For more background on SCMs, readers can refer to Chapters 4 and 7.

The particles of crystalline admixture are irregular with a size range of 1–20 m [44], which is close to the size range of cement and fly ash. Some authors identified the presence of silica fume in the composition of crystallization powders by Fourier-Transform Infrared (FTIR) [7]. Ferrara et al. [44] found that the Energy Dispersive X-ray Spectroscopy (EDS) spectrum of commercial crystalline admixture was comparable with that of an ordinary Portland cement (OPC), but with slightly higher sulfur peak. Their results confirmed the presence of calcium, oxygen, silicon, magnesium, aluminum, and potassium. In addition, de Souza Oliveira et al. [7] provided the chemical composition of an organic-based commercial WP admixture, which was described by the manufacturer to be composed of cement, amino alcohols, and active chemicals. Table 9.1 compares the chemical composition of class G Portland cement and a tested crystalline admixture obtained by X-ray fluorescence [7]. The measured compositions indicate that there are significantly high portions of lime (CaO), loss on ignition (LOI), and high carbon contents. These observations indicate the presence of organic and/or inorganic carbon-based materials in the WP admixture composing a higher content than cement [7]. However, most of the crystalline admixture in powder form is mineral based. Table 9.1 shows in its third column the analysis of hydrophilic crystals [45] obtained from crystalline WP admixtures, which seems to be composed mainly of minerals. These types of crystalline materials are the focus of this chapter.

Inert hydrophilic particles include bentonite [4], talc, and other siliceous powders. Bentonite is a clay composed principally of minerals characterized by high water absorption and large volume expansion upon wetting (ACI concrete terminology) [21]. These particles are typically nonreactive. Their WP mechanism is simply based on pore filling. Reactive materials like sodium silicate are sometimes imprecisely included in the nonreactive internal hydrophilic WP materials [4]. Other particulate materials used for partial filling of the concrete capillaries include clay, hydrocarbon resins, and coal tar pitch.

9.3.3 Other pore filling waterproofing materials

Other pore filling WP materials include reactive and nonreactive organic materials. The reactive organic materials include reactive crystalline materials such as some salts of fatty acids that form precipitates such as calcium oxalate crystals [46] and sodium acetate [29,47,48,49], which is tested at the research level. Al-Kheetan, Rahman, and Chamberlain [50] labeled concrete treated with a sodium acetate

Table 9.1 Chemical compositions (%) of commercial crystalline admixture compared to that of class G Portland cement [7] and analysis of the crystals [45].

Compound	Class G cement [7]	WP admixture [7]	Analysis of the crystals [45]
CaO	63.5	44.0	85.3
SiO_2	20.5	7.6	9.71
Fe_2O_3	4.3	1.6	1.9
Al_2O_3	4.0	1.3	0.58
SO_3	4.3	1.5	
MgO	1.1	1.0	
K_2O	0.3	0.3	
Na_2O	0.3	3.3	1.49
Loss on ignition	1.2	36.9	
Carbon	0.2	13.1	

solution as a hydrophobic surface although they reported that the measured water contact angle was less than 90 degrees (see Chapter 5). In fact, these materials form different type of crystals from those obtained from hydrophilic crystallization WP materials, and they are beyond the scope of this chapter. Other organic pore filling WP materials include deposits of polymeric particles and natural particles that combine pore blocking WP with their hydrophobic DP function. As described in Chapter 8, these materials include precipitates of stearate compounds, coalescing of natural and petroleum oils, bitumen emulsions, and precipitates from suspensions of polymeric materials. Al-Kheetan et al. [50] indicated that the use of fluoropolymer resulted in the deposition of fine rounded particles with a size range $< 200\,\text{nm}$ [50]. The organic WP materials include modified lignosulphonate [51]. In addition, superabsorbent polymers (SAP) were studied as potential organic hydrophilic materials for crack healing [52].

There are pore filling WP materials, which are based on the use of nanoparticles such as nano-SiO_2 particles [53]. Functionalized nanoparticles with hydrophobic content are described in Chapter 8. Nano-SiO_2 particles with a size range of 5–100 nm can be produced through the sol-gel process [31]. The pozzolanic reaction with calcium hydroxide is a requirement for effective treatment using nanomaterials: driving pozzolanic nanoparticles into concrete reduces the $Ca(OH)_2$ content by approximately 8% [31]. As in the case of other pore filling WP materials, concrete treatment with nano-SiO_2 particles was reported to decrease the volume of pores larger than 50 nm [31].

9.4 Applications of hydrophilic waterproofing materials

For application as a surface treatment on fully cured concrete, surface preparation is essential for efficient performance in terms of bonding and penetration of the crystalline active ingredients into concrete. These surface requirements can be achieved by water jetting, sand blasting, or acid etching. For surface treatment of a carbonated concrete, it is recommended to start by conditioning the concrete surface with an alkaline solution in order to supply hydroxyl ions before the application of sodium silicate solution. Details are described in Chapter 6.

The surface application of WP solutions is normally performed using low pressure spraying, brushing, or rolling [29,32]. In reported cases, concrete surface was soaked in the surface treatment solutions for 10 minutes [10]. The soaking process was repeated three times [10]. These extensive treatments may not be comparable to practical applications and specific surface coverages. The method of curing after the surface treatment is an important parameter in determining the efficiency of pore blocking. Curing with water allows the reactive ingredients to penetrate within concrete and react with water and other cementitious constituents (as detailed in Section 9.5 [33]). For less encountered cases of solidifying types of surface treatment, curing at dry condition is required [33]. The penetration of WP material through concrete is achieved by capillary absorption, diffusion [3], and then by crystal growth through the chemical reactions (see Figure 7.3). The transport of active ingredients is governed by the hydrodynamic properties of the solution and the characteristics of the concrete surface. The presence of a surfactant in the solution formation improves penetrability of the material [32]. Absorption of the solution occurs by water suction mechanism, which is a time-dependent process that is governed by the same swelling models described in Section 9.2.1 [Eq. (9.1)] and as described for hydrophobic DP solution in Chapter 8. The actual penetration depth of reactive materials deviates from that predicted by the physical swelling kinetics of a nonreactive solution.

The practical coverage of materials is usually in the range of 2.55 m^2/L (100–200 ft^2/gal) (similar to hydrophobic surface treatment). In certain cases, lower application coverages (e.g., 1.8 m^2/L) [54] or higher application coverages (e.g., 10 m^2/L) [29] were reported. The solutions can be applied in two subsequent steps. Multiple applications of hydrophilic WP materials may yield a substantial enhancement in the penetration depth. In fact, refining the pore structure of concrete by the hydrophilic pore filling from the first application enhances its absorption capacity for a second application. This positive feature is in opposite to the case of multiple applications of hydrophobic damproofing surface treatment [18]. The timing of the second application of the solution is important, for example, Thompson et al. [32] reported the brushing of the surface by silicate solutions for a second was performed after 20 minutes of drying of the first brush.

The liquid penetration depth is dependent on the method of application, coverage, the level of wetting the surface, and the types and rates of the heterogeneous reactions. The penetration depth of the crystallization material has been measured by Scanning Electron Microscope (SEM) equipped with EDS [10], or using Inductive Coupled Plasma with Atomic Emission Spectroscopy (ICP-AES) [33]. A penetration depth of 5 mm is specified by EN 1504–2 [11]. The penetration depths of solutions of sodium silicate are reported to be within a few mm [31,33]. Other studies reported lower penetration depths in the range of 1–3 mm [5,35]. Chen et al. [10] reported that the penetration depth of sodium silicate solutions in calcium sulfo aluminate cement mortars was only around 60–85 m [10]. In addition to the aforementioned effects of solution characteristics, the surface quality and moisture content of the concrete surface have considerable effects on the penetration process. The penetration depth decreases with decreasing concrete porosity (increasing w/c ratio).

The hydrophilic WP admixtures can be added directly to the mixing water before mixing the other components [55] or added to the concrete mixer [56]. The hydrophilic WP admixtures are added to concrete mixture at a suitable dosage that is usually estimated as a fraction of cement or cementitious binder (including SCMs), similar to cases of other mineral admixtures. In many cases, the crystallization WP powders are added at 2% of the weight of cement [8,55,57]. Dosages recommended by the manufacturers are typically within the range of 1%–2% [9]. Choi et al. [41] added fluorosilicates at dosages within a range of 0.5%–2.0% (by weight). Teng et al. [56] reported that the dosage of crystallization WP admixtures for applications of antiflotation slabs was 0.8% by cement content mass. Takagi, Lima, and Helene

[58] utilized crystalline admixture at a dosage of 2.5% by weight of cement content for high performance concrete applications.

The addition of hydrophilic WP admixtures impacts the characteristics of fresh concrete: it reduces the slump [8] and increases air content [8]. The reduction in the slump had been interpreted by the tendency of the hydrophilic WP admixtures to swell water during the mixing process leading to lower workability [8]. However, the hydrophilicity starts to function after the formation of the crystals during concrete curing rather than in the plastic stage. The aforementioned interpretation is believed to be valid for the use of inert particles. An increase in slump and air content was reported for organic WP materials of modified lignosulphonate [51].

Dry shake application of the powders onto the surface of fresh concrete is also used [4]. The penetration and functioning mechanism are expected to be similar to the case of cementitious coatings (see Chapter 12). However, as this application method is done on fresh concrete, it possibly interferes with cement hydration and concrete curing. Hydrophilic materials for dry shake might be thought of as additives to concrete rather than just a surface treatment, although their function is restricted to a surface layer of the concrete.

For all application methods, the effectiveness of hydrophilic WP materials is dependent on the porosity of the reference concrete. It has been reported that increasing w/c ratio (increasing the porosity of reference concrete) increases the obtainable effectiveness of these materials in pore blocking and hence in enhancing the water resistivity of the capillary network [16]. Increasing the available pore space for crystal growth (or gel expansion by swelling) increases their capability of occupying a larger fraction of the permeable pores. Thus it might be better to use concrete with high w/c ratio in order to evaluate the WP performance of pore blocking WP materials.

9.5 Crystallization reactions of hydrophilic waterproofing systems

A series of physicochemical mechanisms are involved in hydrophilic crystallization WP. These include setting mechanism and water-hindering mechanism. The water-hindering mechanism is described in Section 9.2. The setting mechanism includes the physical processes of dissolution, penetration, diffusion of the active ingredients, and formation mechanism of the hydrophilic crystals within the pores. When the hydrophilic WP powders are added as admixtures to the concrete mixture, the active ingredients are first dissolved in water. They start the setting process after the creation of concrete pores and the formation of calcium hydroxide during the progress of the cement hydration process. When the hydrophilic WP materials are applied as powder dry shake on the surface of fresh concrete, the crystalline active ingredients are first dissolved in water from fresh concrete and then penetrate into concrete pores by diffusion. When the hydrophilic WP materials are applied as liquids on the surface, the solution is first penetrated into the concrete structure by capillary absorption (as described in Section 9.4). Then, the setting action starts when the solution occupies the pores. As mentioned in Section 9.3, the hydrophilic WP materials include solidifying materials, which are precipitated without chemical reactions and reactive water soluble materials [33]. For densifiers, the mechanism is based on using a stable filler that occupies the pores. In some formulations, the active ingredients are stated to have a catalytic function only [59]. This section details the chemical reactions involved in the setting of reactive crystalline WP materials. The silicate solution includes $SiO4^{4-}$ ions, which can react with soluble cations of Ca^{2+}, Mg^{2+}, and Al^{3+} in the pore solution of the cement paste forming insoluble colloid silicates [31]. The reaction occurs mainly with the by-product of cement hydration [calcium hydroxide or portlandite ($Ca(OH)_2$)]. Other reactions may involve the participation of mineral salts, CSH gel obtained from the cement hydration [33], partially hydrated cement particles [3,4], and cement components [7,59,60], such as tricalcium silicates (C_3S) [8]. The crystallization additives are also stated to react with sulfates and carbonates of calcium, sodium, and potassium [4]. These reactions are described below. Overall, these crystallization processes lead to the deposition of nonsoluble crystalline structures [4]. The crystals are integrally bonded to the cementitious structure [2] and cannot be dislodged from within the pores of the hardened paste [8,16]. This is the rationale behind the used terminology of integral WP, as mentioned above. These hydrophilic crystals grow with time to fill microscopic capillary pores and bridge the microcracks [2,45]. This is a kinetic process, the rate of which is dependent on material composition and surrounding conditions. Overall, the complete crystallization WP effectiveness was reported to become available within 12 days after the concrete casting [55].

In many silicate-based WP formulations (liquid and powders), the active mineral ingredients react with calcium hydroxide and moisture to produce calcium silicate hydrates or CSH gel, according to Eq. (9.2). The produced gel has the general formula of $n\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$, where n is the number of lime compounds in the hydrate (e.g., n=2 or 3). Specifically, for sodium silicate WP materials, the reaction is given by Eq. (9.3) [18,32]. This reaction is believed to be the main setting mechanism for many hydrophilic penetrating surface treatments and powder admixtures as proposed by many researchers [7]. The reaction given in Eq. (9.3) is generalized for other alkali silicates by Eq. (9.4), where M stands for Na, K, or Li [33]. These reactions result in a reduction in calcium hydroxide content of concrete [15]. The percentage reduction in CH is dependent on the age and the w/c ratio of concrete and the type (composition) of the admixture [15].

$$\text{active ingredients} + \text{Ca(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{nCaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O} \tag{9.2}$$

$$\text{Na}_2\text{SiO}_3 + \text{n}_1\text{Ca(OH)}_2 + \text{n}_2\text{H}_2\text{O} \rightarrow \text{n}_1\text{CaO}\cdot \text{SiO}_2\cdot \text{n}_2\text{H}_2\text{O(gel)} + 2\text{NaOH} \tag{9.3}$$

$$\text{M}_2\text{SiO}_3 + \text{n}_1\text{Ca(OH)}_2 + \text{n}_2\text{H}_2\text{O} \rightarrow \text{n}_1\text{CaO}\cdot \text{SiO}_2\cdot \text{n}_2\text{H}_2\text{O} + 2\text{M(OH)} \tag{9.4}$$

These reactions release alkali metal ions (e.g., sodium and potassium) that can be detrimental to concrete when reactive aggregates are used (i.e., through ASR, see Chapter 3) [5,31]. They may lead to efflorescence, which is more pronounced for sodium silicate than for potassium silicates. Lithium silicates lead to the lowest level of efflorescence among these alkali silicates. Mundo et al. [18] highlighted other hypotheses for setting of silicate compounds such as the precipitation of silicates (SiO_2) in addition to their reaction with portlandite leading to precipitating insoluble CSH gel as well as silicate reactions with other alkalis forming expansive swelling gel. These hypotheses were also summarized by Tran et al. [33]. Thompson et al. [32] indicated that the silicates involve a combination of these mechanisms. As mentioned earlier, the involved mechanism is dependent on the type of silicate compound: for example, the mechanism of lithium silicate is simply solidification [33], while the mechanism of sodium and potassium silicates involves a chemical reaction [33]. Tran et al. [33] indicated that even the solidifying type (lithium silicate) can also react with the CSH gel before its solidification, when it is soluble in water.

Similarly, fluorosilicates react with calcium hydroxide producing the pore blocking C–S–H hydrates [10]. Chen et al. [10] indicated that the magnesium fluorosilicate may lead to the formation of the silica gel and the precipitate of $KMgF_3$, which would contribute in filling the pores in the hardened cement pastes [10]. For example, magnesium fluorosilicate ($MgSiF_6$) reacts with calcium hydroxide according to Eq. (9.5) [18,42]. It can also react with calcium carbonate according to Eq. (9.6) [42]. Similar reactions are given for zinc fluorosilicate ($ZnSiF_6$) [42].

$$MgSiF_6 + 2Ca(OH)_2 \rightarrow 2CaF_2 + MgF_2 + SiO_2 + 2H_2O \tag{9.5}$$

$$MgSiF_6 + 2CaCO_3 \rightarrow 2CaF_2 + MgF_2 + SiO_2 + 2CO_2 \tag{9.6}$$

According to some studies [7,59,60], the active ingredients of the crystallization WP materials are considered to react with unhydrated cement particles, promoting further cement hydration and crystals formation [59,60]. The active ingredient, acting as a crystalline promoter, is given the symbol M_xR_x, where M refers to the alkali metal and R refers to the associated anion group. According to Azarsa et al. [8], the crystalline promoter reacts with tri calcium silicate ($3CaO{\cdot}SiO_2$) and water, according to Eq. (9.7).

$$3CaO \cdot SiO_2 + M_xR_x + H_2O \rightarrow Ca_xSi_xO_xR \cdot (H_2O)_x + M_xCaR_x \cdot (H_2O)_x \tag{9.7}$$

The reaction in Eq. (9.7) produces modified hydrates of calcium silicate [$Ca_xSi_xO_xR.(H_2O)_x$] and pore blocking precipitate [$M_xCaR_x.(H_2O)_x$] [8]. This reaction occurs without the involvement of calcium hydroxide [7]. Secondary crystallization materials (e.g., fly ash) may also be involved in such a general reaction [60]. On the other hand, de Souza Oliveira et al. [7] highlighted that calcium hydroxide was identified as the primary hydrate in mortars with WP admixtures. Consequently, they hypothesized that the more precise form of the reaction is given in Eq. (9.8), which involves the production of calcium hydroxide (CH) in addition to CSH hydrates and the pore blocking crystals, as also reported by Biparva & Gupta, [2].

$$\text{cement} + \text{water} + \text{crystalline admixture} \rightarrow C - S - H + \text{pore blocking crystals} + CH \tag{9.8}$$

Reiterman and Pazderka [61] indicated that the chemical mechanism involves the formation of disilicate and polysilicate anions leading to the formation of $3Ca2SiO_23H_2O$ and $3CaOAl_2O_3Ca(OH)_212H_2O$. Additional products of hydrated calcium aluminate ($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$) can be obtained from other reactions [60]. In the presence of carbon dioxide (from air in pores), sodium carbonates are hypothesized to be produced in addition to a similar CSH gel according to Eq. (9.9) [18].

$$Na_2SiO_3 + Ca(OH)_2 + CO_2 \rightarrow C - S - H + Na_2CO_3 + H_2O \tag{9.9}$$

Similarly, some nanoparticles involve pozzolanic activity, which can form additional calcium silicate hydrates (CSH) and calcium aluminate hydrates and reduce the $Ca(OH)_2$ content by approximately 8% [31]. The nonsilicate-based crystallization WP involves reactions with calcium hydroxide and lead to the formation of hygroscopic crystals as given by Eq. (9.10). WP systems involving hygroscopic WP are detailed in Chapters 10 and 11.

$$Ca(OH)_2 + \text{active ingredients} + H_2O \rightarrow \text{hygroscopic crystals} \tag{9.10}$$

9.5.1 Structure of hydrophilic crystallization waterproofing particles

The aforementioned differences in the crystallization processes of hydrophilic WP materials (e.g., physical solidification vs chemical reactions) and the differences in the compositions of WP materials lead to structural variations of the particles. The types of structures of hydrophilic WP particles include the following:

1. Insoluble hydrates, which include CSH gel ($n_1CaO{\cdot}SiO_2{\cdot}n_2H_2O$), hydrated calcium aluminate ($n_1CaO{\cdot}Al_2O_3{\cdot}n_2H_2O$) [60], $3CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}nH_2O$, and $CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}H_2O$.
2. Precipitates of silicon oxide (SiO_2).
3. Carbonates including sodium carbonate (Na_2CO_3) and calcium carbonate ($CaCO_3$) [18,33].
4. Fluorides such as calcium and magnesium fluorides (CaF_2 and MgF_2).
5. Deposited salts that involve hydrophobic groups such calcium stearates (covered in Chapter 8).

The insoluble calcium silicate hydrates or crystals are the most popular crystallization WP materials. Thompson et al. [32] reported that the surface treatment of cured concrete with sodium silicate led to the modification of the CSH gel that originally resulted from cement hydration but not the formation of new crystals.

The recent studies do not support the hypothesis of Thompson et al. [32]: Different types of silicate compounds can lead to different shapes of crystals [33]. Elsalamawy et al. [15] reported that the crystallization phases ranged from round particles to needle-like crystals. The results of Tran et al. [33] revealed that needles were obtained for systems with sodium silicates, rectangle-broken crystals were obtained for systems with potassium silicates, and irregular crystals for lithium silicates, as shown in Fig. 9.3 [33]. Mixtures of crystal shapes were obtained when mixtures of silicate solutions were used [33]. Tran et al. [33], reported that the shapes of the crystals were not altered when the crystallization occurred in a carbon dioxide-rich environment [see reaction in Eq. (9.9)]. In fact, both the gel from cement hydration and the obtained CSH gel from crystallization WP are porous and made of layers that are bonded by van der Waals forces. The estimated porosity of CSH gel from cement hydration can reach 28% [62] and the interlayer spacing is in the range of 0.5–2.5 nm.

The needle shaped crystals seem to be the most popular type [3,57,61,63]. Most of the reported structures for the commercial hydrophilic crystallization WP are branched needle-like crystals [16]. Needle-shape fine crystals (size $<$ 200 nm) were also observed with other types of nonsilicate-based WP systems such as sodium acetate [48]. The size of the hydrophilic crystals depends on the chemical composition of the crystalline WP material and the crystal shape. Bohus and Drochytka [3] indicated that the length of the needle crystals reached 13 m and their width was

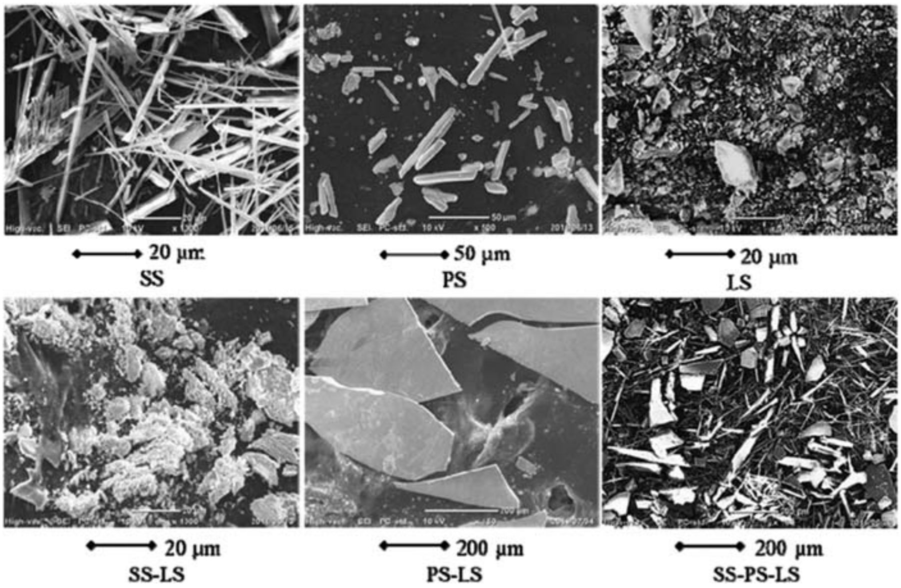
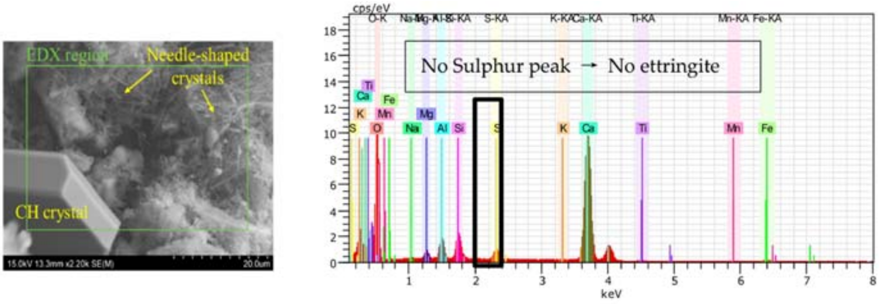


Figure 9.3 WP crystals used in the surface treatment of aqueous solutions of sodium silicate (SS), potassium silicate (PS), lithium silicate (LS), a mixture of sodium and silicate lithium silicate (SS-LS), a mixture of potassium silicate and lithium silicate (PS-LS), and product containing sodium potassium and lithium silicates (SS-PS-LS) [33].

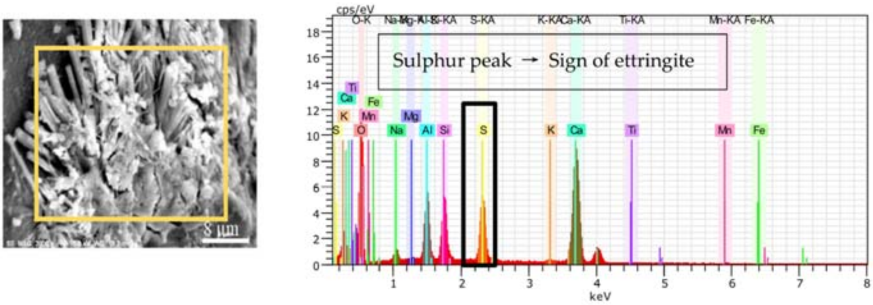
between 100 nm and 1000 nm. Azarsa et al. [57] reported that the lengths of needle crystals were in the range of 3–8 m [57]. Elsalamawy et al. [15] observed 30 nm rounded structure of C–S–H crystals in addition to the needle-like crystals.

The SEM micrograph of a cementitious mortar with needles of crystallization WP are shown in Fig. 9.4. They are quite similar to ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$)



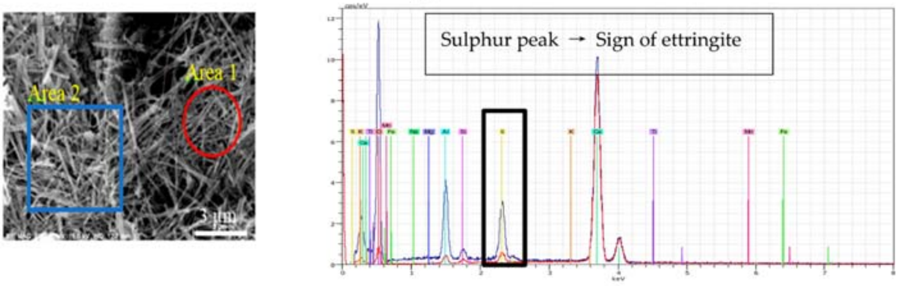
(i) (ii)

(A) O-K mix



(i) (ii)

(B) O-P mix



(i) (ii)

(C) O-X mix

Figure 9.4 (i) SEM micrograph and (ii) EDS spectrum of cementitious mixtures containing three types of crystalline waterproofing admixtures, labeled as (A) O-K mix, (B) O-P mix, and (C) O-X mix [16].

crystals [16,57] (i.e., acicular shape); this may create a confusion when identifying and labeling various cementitious constituents. As described in Chapter 1, the weak ettringite ($C_6AS_3H_{32}$) are produced from cement hydration and they make about 15%–20% of the paste volume [20]. The chemical composition (atomic percent) of ettringite includes 19.2% Ca, 4.3% Al, 7.66% S, and 63% O [57]. The hydrophilic WP crystals have been reported to have a different homogeneous chemical composition from that of the ettringite, particularly in terms of the sulfur content. Distinguishing between these two needle-like crystals was made by Azarsa et al. [57] through Energy Dispersive X-ray (EDX) analysis. They revealed a low sulfur peak for the hydrophilic WP crystals. On the other hand, de Souza Oliveira et al. [7] reported that the chemical analysis of the crystals obtained from some industrial hydrophilic crystallization WP admixtures revealed a high sulfur peak in the EDS spectra (similar to the spectra of ettringite) [7]. These differences in structural analysis could be due to the differences in the tested crystallization WP materials and the associated mechanisms in the two studies. This is revealed in Fig. 9.4(ii), which shows EDS spectrum of cementitious of three mixtures containing three different types of crystalline WP admixtures with different levels of sulfur peaks [16]. There are variations in the chemical compositions of the resulting crystals. Elsalamawy et al. [15] reported that the Ca/Si ratio in the produced crystals from three types of commercial crystalline WP admixtures ranged from 2.4 to 3.2 [15]. Increasing the Ca/Si ratio changes the structure of CSH gel from a loose fibril-like morphology to dense granular particles [15]. On the other hand, de Souza Oliveira et al. [7] reported that the ratio of calcium oxide to silicon oxide (C/S) for the crystals were 5.7, which was higher than that of CSH compounds from cement hydration (which had a ratio of 3.1) [7]. Nearly no differences in the compositions of crystals were detected between the rounded and needle crystals [7]. Both normal CSH gel and carbonate silicate gel (obtained in the presence of carbon dioxide [Eq. (9.9)] can coexist) [33].

9.5.2 Interaction with cement hydration

The cement hydration process is affected by the presence of mineral oxides and silicates that are incorporated in the formulations of the crystallization WP materials. In general, crystalline WP admixtures are compatible with cement compounds, mineral admixtures (SCMs), and typical chemical admixtures (e.g., air entraining admixtures, water reducing admixtures, and superplasticizers) [4]. The addition of crystallization WP materials mixtures are reported to cause positive effects on the early-age behavior of concrete [9]. The crystalline active ingredients participate in several physical and chemical interactions with cement causing additional improvements in concrete characteristics [7]. These improvements are basically the consequences of (1) the process modifications occurred in hydration reactions of cement constituents [7], and in the variations in the rate of nucleation and growth kinetics of the hydrates of produced silicates from cement hydration (see Chapter 1) and (2) the structural changes in the morphology of the phases of silicate hydrates [7].

Azarsa et al. [57] highlighted that the addition of crystallization WP admixtures to the concrete mixture affects its properties in the plastic stage (e.g., workability, pumpability, and finishability) and impacts the setting time [57]. Silicate-based admixtures are hypothesized to reduce the setting time of concrete. For example, the presence of silicates in the concrete mixture is known to accelerate the hydration of cement [32]. Pazderka and Hájková [55] reported that two types of well-known commercial crystalline admixtures caused a mild deceleration of the hardening of concrete during the first 28 days. In fact, some manufacturers formulate different versions of their crystallization WP products to make them more suitable to various practical applications in terms of setting time.

Although it had been known in the industry that sodium fluorosilicate can be added to Portland cement to reduce the setting time, however, experimental results showed that adding sodium fluorosilicate to cement had insignificant effect on the setting time [64]. In industrial practice, sodium fluorosilicate is believed to be formulated with other proprietary compositions, which work synergistically to reduce the setting time [64]. On the contrary, the use of other fluorosilicates as WP admixtures was found to cause a significant retarding effect [41,42]. These retarding effects are also known to occur for concrete mix designs involving mineral admixtures (e.g., fly ash and slag), but with different levels of delaying setting times. Fig. 9.5 shows results of determining the setting time as plots of needle penetration depth as functions of elapsed time from mixing cement with water for different dosages of fluorosilicate-based admixture [41]. Fig. 9.5 reveals a significant retarding effect that increases with increasing the dosage of the fluorosilicate [41]. Other nonsilicate-based WP admixtures were also reported to extend the setting time of concrete and the retarding effect increases with increasing the dosage of the WP

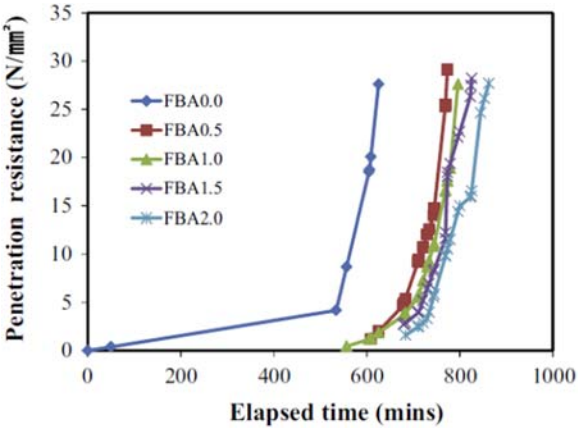


Figure 9.5 The penetration depth as function of elapsed time from mixing cement with water for determining the setting time at different dosages of fluorosilicate-based admixture added to the cement as an admixture (0%, 0.5%, 1.0%, 1.5%, and 2.0% of cement weight labeled as FBA0.0, FBA0.5, FBA1.0, FBA1.5, and FBA2.0, respectively) [41].

admixture [7]. It is worth mentioning that hydration acceleration may cause durability problems, particularly in hot weather applications, which already shorten setting time dramatically [2]. These conditions reduce the compressive strength and enhance the likelihood of shrinkage and cracking [2]. Thus the retarding effect of WP admixtures can lead to lower chance of cracking and reduces the premature moisture loss [2]. This effect is also associated with the curves of temperature development of hydration kinetics: WP admixtures commonly cause a shift in the temperature peak and extend the release of heat over a longer period of time. This thermal behavior assists in creating better conditions for cement hydration [2]. This hypothesis is in line with the quote from Choi et al. [41] "hindering the hydration inhibits the rapid increase of the cement hydration heat before hardening due to the thermodynamic heat-absorbing effect" [41]. Consequently, the retarding effect of WP admixtures can lead to lower chance of cracking and reduces the premature moisture loss, as indicated by Biparva & Gupta, [2].

9.5.3 Self-healing mechanism

The crystallization mechanism is considered to be a dynamic process: the manufacturers frequently state that when the concrete is under dry conditions, the crystallization system remains in a dormant state and then can be reactivated for further growth when encountering a new source of water [2]. This mechanism is considered to be the driving force for the so-called self-healing role of the crystallization WP materials of cracks in concrete structures. Cracks are caused by durability problems at an early stage of concrete curing and/or during the service life of concrete, as detailed in Chapter 3. They increase the rate of water permeation by creating larger channels than those created by the connected capillary networks. In fact, it is essential to distinguish between the crack healing through further crystallization reactions and crack filling through swelling behavior of previously formed crystals or inert hydrophilic particles. In principle, healing of concrete is a chemical process that leads to the formation of new filling material that is integrated with the cementitious structure in the cracks. The identified formed phases of crack filling materials are dependent on the types of the used healing materials [7] and the primary healing mechanism of the crystallization WP materials and other expansive additives. Cracks can be filled by the continuous generation of the silicates, carbonates, or other materials (e.g., ettringite, monosulphate, and crystals of calcium hydroxide) [58], which can bridge the cracks and bond to the cementitious surfaces [45]. These healing mechanisms densify the concrete and thus restore its mechanical properties and reduce its permeability [8], leading to enhancements in durability, structural serviceability, and sustainability [8]. These chemical reactions include the slow continuing hydration of unreacted cement constituents and crystallization reaction of the added reactive chemicals and crystallization promoters. These crack filling materials can be generated by (1) the continuing slow hydration reactions of the constituents of typical cementitious mixture, with the involvement of calcite ($CaCO_3$) nucleation [58], that occurs naturally (autogenous healing) [57], or (2) the reactions of active ingredients of WP materials (autonomous or engineered self-healing) [9,8,57]. More specifically, the mechanisms involved in autogenous self-repairing of cracks include (1) slow cement hydration, (2) formation of calcium carbonate ($CaCO_3$) as a result of the permeation of carbon dioxide into pores and cracks, (3) filling cracks by expansion by swelling behavior of the hydrophilic cementitious matrix, and (4) sedimentation of materials within the pores of the cement paste upon reactions [8]. The significance of each mechanism depends on the type and age of concrete. The healing capability of concrete can be enhanced by manipulating the typical concrete mix design through various additions [47], such as the use of shrinkage reducing admixtures [47,58] or the partial replacement of cement by SCMs (e.g., fly ash, slag, and silica fume) [47,58]. The autonomous healing mechanism is based on a chemical mechanism described in Section 9.5. In some literature, crystallization materials are referred to as autogenous healing stimulators [7], because of their role in promoting a further cement hydration of unhydrated compounds. In fact, both types of healing processes can coexist, the time required for self-healing can be reduced significantly with the presence of crystallization WP materials [57]. The efficiency of healing of cracks can be evaluated by measuring recovery indexes after the healing process of cracks [7].

The type of healing mechanism affects the width of the crack that can be healed. The natural autogenous healing is reported to have the ability to heal small cracks [$<$ 200 m [57] or ~200–300 m] [8,65]. The autonomous healing by crystallization WP materials can heal larger cracks [e.g., 250–400 m [57] or up to 600 m (0.6 mm)] [2]. However, Azarsa et al. [57] indicated that crystallization WP materials can seal cracks with a width less than 50 m at a high rate while they become inefficient for wider cracks. The hydrophilic crystalline WP admixtures were able to lead to 60% of crack sealing [44]. There are other studies on the use of SAPs through their filling of cracks by expansive behavior from swelling [52]. These types are beyond the scope of this chapter. A similar expansion mechanism for crack filling can be obtained by the use of bentonite as a swelling material benefiting from its hydrophilic characteristic.

9.6 Durability performance of hydrophilic waterproofing

The general requirements of hydrophilic crystalline waterproofing materials are similar to those listed for hydrophobic DP materials (see Section 8.6). These include requirements related to the application techniques and others related to the characteristics of the materials themselves. The characteristic requirements include penetrability of WP solutions, reactivity of the active ingredients, physicochemical stability, breathability, swelling characteristics, nontoxicity and practicality of material application, and having no negative impacts on the cement hydration reaction when used as admixtures or applied as onto green concrete. As in the case of other integral WP systems, evaluating the performance of hydrophilic WP systems is based on structural and property analyses. The test methods and standard for these measurements are summarized in Chapter 7. The evaluation tests include direct and indirect methods [66]. Direct methods are structural-related tests that are used to confirm the formation of crystals within the pores. The tested transport characteristics of treated concrete include water permeability and gas permeabilities (air, carbon dioxide, and oxygen) and ion diffusivity (e.g., diffusion of chloride ion). The reported durability parameters for hydrophilic WP materials are similar to those reported to hydrophobic DP materials (see Chapter 8). These include resistances against chloride ion penetration, steel corrosion, carbonation, and freezing and thawing cycles. The strength characteristics include compressive and flexural strength and abrasion resistance. The following subsections highlight reported performance of hydrophilic crystalline WP.

9.6.1 Performance investigation based on structural analysis

The performance of hydrophilic crystallization WP materials can be evaluated through tests that reveal the crystal structure, confirm the formation of the crystals, and identify the types of crystals (described in Section 9.5.1). Structural tests include SEM [32,48,50,57], XR-diffraction [48], EDS technique [16], combined SEM/EDS [7], FTIR spectra [48], and thermogravimetric analysis [7]. In some studies, the formation of crystals within the cementitious matrix may not be observed due to the possible damage of crystals during the harsh surface preparation steps required for typical polishing of the surface of concrete specimens [16].

Structural analysis commonly shows a reduction in the content of calcium hydroxide in the treated concrete compared to untreated concrete as consequences of the stoichiometry of crystallization reactions, as mentioned in Section 9.5. In addition, local variations in the content of calcium hydroxide within the cementitious matrix may be observed. For example, Wong et al. [22] reported less calcium hydroxide at the interface of air voids than that at the aggregate interface. Other structural analysis involves also measuring porosity and pore size distribution in the cement paste. Fig. 9.6 shows the porosity of hardened concrete paste at 28 days as a function of the dosage of fluorosilicate admixture [64]. Increasing the dosages of fluorosilicate causes a larger reduction in the porosity. The highest percentage reduction of 16.3% is obtained with 2% dosage [64].

Fig. 9.7 shows the pore size distribution as cumulative and differential (distribution) pore volume versus pore size for different treated and nontreated pastes. The treated systems include two hydrophilic systems (sodium silicate and magnesium fluorosilicate), two hydrophobic systems (tetraethyl ortho silicate and poly-methyl tri ethoxy silane) [10]. Fig. 9.6 reveals that all the surface treatments contribute to reducing the porosity. This is indicated by lowering the curves of volumes of cumulative pores due to pore blocking. The hydrophilic crystallization WP systems reduce the volume fraction of medium and large pores with sizes range of 50 nm1 m, while they increase the volume fraction of fine pores [10]. Both magnesium fluorosilicate and sodium silicate result in a similar pore refining effect [10]. Such a pore refining effect is attributed to two reasons, (1) partial occupation of permeable pores by the precipitation of C–S–H gel from crystallization reactions leading to more fine pores, (2) the contribution of the porosity of the produced C–S–H crystals, which themselves contain a high volume fraction nanopores [10]. A pore refining effect can be obtained

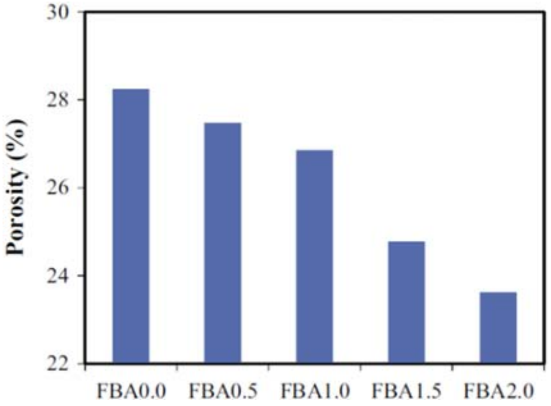


Figure 9.6 Porosity of hardened concrete paste at 28 days as a function of the dosage of fluorosilicate admixture for cases with 0%, 0.5%, 1.0%, 1.5%, and 2.0% of cement weight labeled as FBA0.0, FBA0.5, FBA1.0, FBA1.5, and FBA2.0, respectively [41].

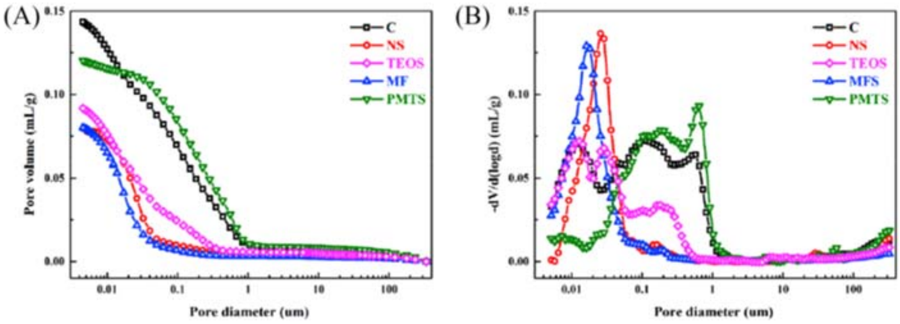


Figure 9.7 Pore size distribution as cumulative pore volume (A) and differential (distribution) pore volume (B) versus pore size in micrometer for hardened calcium sulfo aluminate paste treated with sodium silicate (NS), magnesium fluorosilicate (MFS), tetraethyl orthosilicate (TEOS), or poly-methyl tri ethoxy silane (PMTS) [10].

also by tetraethyl ortho silicate, but with a lower efficiency than that obtained from silicate compounds [10]. The hydrophobic DP system reduces the volume fraction of the fine pores (with sizes less than 50 nm) [10], whereas it has little effect on medium and large pores as expected. This is because the hydrophobic materials are simply pore liners that are based on the formation of a molecular thin layer (see Chapter 8). This is believed to support the hypothesis that silane molecules have the ability to penetrate into the gel pores of C–S–H gel and crease a hydrophobic molecular layer, which reduces the sizes of the gel pores [10,67]. Some studies indicated that ethyl silicates are believed to produce more compacted concrete structure than that obtained with sodium silicate [33,68,69]. However, Fig. 9.6 confirms that sodium silicate provides better pore refinement. The findings of Chen et al. [10] lead to the conclusion that combining hydrophobic WP materials with hydrophilic crystalline WP materials can provide better WP formulations [10]. Other additions (e.g., sodium acetate powder) were also reported to refine the pores and increase the concrete density [48,50]. Other studies indicated a reduction in porosity and in pores sizes with other hydrophobic surface treatments (e.g., using fluoropolymer) [50]. It is worth emphasizing that fine pores (<50 nm) are correlated with the gas permeability and diffusion (e.g., affecting carbonation) whereas medium and large pores (>50 nm) are correlated with the water penetration [10].

9.6.2 Reduction in water absorption and permeability by hydrophilic WP

The hydrophilic crystallization WP admixtures are categorized among PRAHs as they decrease concrete permeability under hydrostatic pressures [6,7,8]. This is achieved by reducing the total porosity (see Fig. 9.6) and refining the pores (see Fig. 9.6) and healing the cracks (as described in Section 9.5.3). Similarly, the surface floor hardeners partially block the pores and heal the cracks, and thus reduce the penetration of water and the accompanying harmful chemicals (ACI 515.2R-13) [5]. The level of WP improvement depends on the type, the dosage, and solid content of the WP materials as well as the quality of concrete (e.g., w/c ratio). Increasing the w/c ratio increases the effectiveness of hydrophilic WP materials in reducing water penetration [16]. It has been concluded by Elsalamawy et al. [15] that the effectiveness of hydrophilic crystalline WP admixtures for reducing concrete permeability is strongly dependent on availability of pores in concrete (i.e., high porosity with a high w/c ratio), as mentioned in Section 9.4. It is believed that the WP performance is related to the yield of the crystallization reaction, which is dependent on the availability of calcium hydroxide and the types of hydration products [10]. In general, evaluating the performance of the hydrophilic crystallization, WP materials may be based on direct measurement of reductions in capillary absorption or permeability [7]. However, different performances can be observed between these two methods.

Water absorption is determined by measuring the weight gain after immersing the concrete specimen in water for a given time or by measuring the sorptivity using Autoclam or Karsten tests under a small water head [70]. For measuring water absorption, Rahman and Al-Kheetan [48] used the initial surface absorption test according to BS 1881–208 and ASTM D 6489–99. Thompson et al. [32] used ASTM C 642, Chen et al. [10] used ASTM C1585–13 and the Chinese standard GB/T 17671–1999. Overall, the reduction in sorptivity for hydrophilic pore blocking materials is usually low due to the swelling behavior of the pore blocking crystals [18]. Hydrophilic WP materials can be associated with a high-water absorption at initial times of wetting (as described in Section 9.2.1). In addition, when the hydrophilic crystals suck water within their structure and expand, they refine the pores size and smoothens the surface of concrete making it more hydrophilic and thus causing more swelling (according to Cassie model). As described in Chapter 8 and in Section 9.2.1, decreasing the porosity and the pore size increases the capillary suction (Cassie model) and hence increases the sorptivity [18]. In addition, capillary condensation within hydrophilic gel [water vapor penetration, condensation, and then absorption within the gel capillaries [71]] contributes in increasing the water absorption of the hydrophilic WP systems. This issue might give hints on some statements of conflicting reports concerning the ability of silicate-based sealers to improve WP properties of concrete [35]. In fact, Song, Lu, and Lai [72] highlighted that the Karsten tube penetration test is not believed to be applicable for concrete specimens with low porosity [72]. Thus water absorption is not believed to be suitable and it is not frequently reported in industrial literature for evaluating the performance of hydrophilic crystallization WP materials. Despite that fact, data on sorptivity on hydrophilic WP systems are still reported in the studies showing a percentage reduction in sorptivity [that becomes higher when w/c ratio is increased [15]]. Fig. 9.8 compares the sorptivity of hydrophilic crystallization systems (sodium silicate and magnesium fluorosilicate) and hydrophobic systems (TEOS and poly-methyl triethoxy silane) for calcium sulfo aluminate cement-based mortars [10]. The hydrophilic materials (sodium silicate and magnesium fluorosilicate) reduced the sorptivity by 17.0% and 7.8%, respectively [10], while the hydrophobic material (poly-methyl tri ethoxy silane) reduced the water sorptivity by much higher percentage (94%) [10]. As discussed in Chapter 8, the percentage reduction in water absorption coefficient (*S*) with hydrophobic organosilicon DP materials is usually higher than 90% [18,71]. Similarly, Mirza, Abesque, and Bérubé [73] reported that the silicate sealers were not effective in reducing water absorption [at low temperatures application (4°C) [73]], while the hydrophobic sealers were effective. For soaking the surface with sodium silicate for 1 hour,

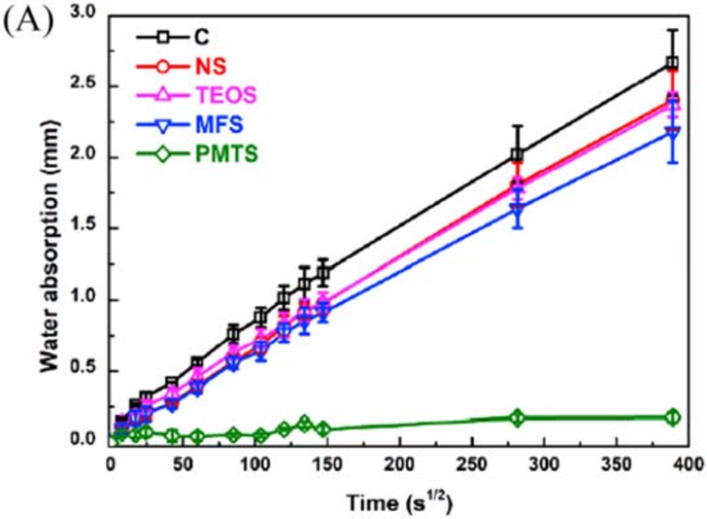


Figure 9.8 The water absorption in hardened mortars treated with sodium silicate (NS), magnesium fluorosilicate (MFS), tetraethyl orthosilicate (TEOS), and poly-methyl triethoxy silane (PMTS) [10].

Thompson et al. [32] reported a 30% reduction in water absorption. For hydrophilic crystallization admixture, the reported percentage reductions in water absorption were in the range of 4%–5% for 40 MPa concrete containing SCMs (fly ash or slag) [74]. Higher values were reported for commercial WP admixture on ordinary concrete: the reported percentages of reduction in sorptivity were 28%, 30%, and 50% for concrete mixtures with w/c of 0.39, 0.50, and 0.60, respectively, after 28 days curing [15]. Moreover, these percentages reached higher values of 34%, 63%, and 70% after 365 days curing [15]. No significant enhancement in sorptivity was reported for low permeable concrete (w/c ratio=0.39) with prolonged water curing.

Permeability tests at high hydrostatic pressures are better for evaluating the performance of pore blocking WP materials as their WP performance is based on restricting the flow under a pressure rather than reducing the capillary absorption. The coefficient permeability is commonly measured according to CRC C48 under a hydrostatic pressure of 1.38 MPa (200 psi). The hydrophilic crystalline WP materials increase the concrete resistance against such a water pressure [57]. It is well-reported that concrete with crystalline admixtures shows a significant reduction in the permeability at such a pressure [2]. This is commonly highlighted in industrial literature by simply stating that no leak can be observed when the treated specimen is tested according to CRC C48. More specifically, some industrial literature of hydrophilic crystallization WP materials indicate that the percentage reduction in the coefficient of permeability (according to CRC C48) is about 70%. Similarly, Azarsa et al. [16] reported a percentage reduction in the coefficient of permeability by more than 60%. Overall, Biparva & Gupta, [2] reported a percentage reduction in the permeability under pressure within the range of 57%–75% for crystallization WP materials.

Permeability at high hydrostatic pressures can be also done by measuring the depth of water penetration under a pressure of 0.5 MPa (72 psi) for 72 hours [8,16,57]. This is commonly done according to DIN 1048 “Water impermeability of concrete,” which is equivalent to EN 12390–8 (Depth of penetration of water under pressure) [2]. Concrete is considered a watertight for all practical purposes when the water penetration depth is less than 50 mm [57]. A concrete containing 2% of PRAH was reported to lead to a percentage reduction in water penetration under pressure by up to approximately 70% [56]. Biparva & Gupta, [2] reported a reduction of 62% in water penetration depth for crystallization WP materials (according to DIN 1048 Part 5). For 40 MPa concrete containing SCMs (fly ash or slag), lower values of percentage reduction (35%–45%) were reported for concrete with hydrophilic crystallization admixture (according to DIN 1048 Part 5) [74]. Bohus et al. [63] reported percentage reduction in the depth of water penetration for new crystalline WP admixtures to be the range of 40%–50%.

9.6.3 Reducing chloride ion penetration and corrosion by hydrophilic waterproofing

ACI 212.3R-16 highlights that integral WP materials can generally withstand aggressive environments with exposure to salt spray and some chemicals [6]. Typically, after exposing a typical concrete structure to a deicing salt or seawater for a few years, the penetration depth of chloride ion is in the range of 40100 mm [71]. In principle, the crystalline WP materials can reduce the rate of diffusion of chloride ions and their penetration depth in concrete by decreasing the porosity and the permeation flow of water contaminated with chloride ions. For ordinary concrete, a quadratic trend was obtained between the water penetration depth and the passage of electrical charge (as an indication of chloride ion penetration) [57]. However, no obvious correlation between water permeability and chloride ion penetration could be observed for concrete with hydrophilic crystallization WP materials [75]. Similarly, no significant linear relationship was observed between the electrical resistivity and the compressive strength (which is commonly highly correlated to water permeability) [75]. The diffusion coefficient of chloride ions is also reduced by decreasing concrete saturation as it is governed by the moisture content of concrete, as discussed in Chapter 2. Researchers use various types of test for evaluating the performance of WP materials for reducing chloride ion penetration. The direct tests are based on measuring the diffusion through a section of concrete or by measuring the distribution or chloride ion across a concrete depth (as described in Chapter 8) [70]. These tests include chloride permeability AASHTO T-277–83 [32], rapid chloride permeability test according to ASTM C1202 [8,57], chloride penetration according NCHRP 244 [32], surface/bulk electrical resistivity test according to AASHTO TP95 [8], bulk diffusion test according to ASTM C1556 [8], or long-term chloride ponding according to ASTM C1543 (Withdrawn 2019).

ASTM C1202, which is frequently used, usually indicates that the electrical charge passed (in Coulombs) through treated samples is less than that through reference samples [57]. Fig. 9.8 shows the total charge passage through two types of concrete mix designs comparing untreated and treated concrete with a commercial hydrophilic crystallization WP admixture [8]. The use of hydrophilic crystallization admixture causes a noticeable decrease in the charge passed through 28-days concrete but the decrease becomes insignificant after 56 days curing [8]. This is in the opposite of the expected trend, as late curing would enhance the formation of crystals; however, no definitive conclusion could be drawn by the authors [8]. In addition, the use of hydrophilic crystallization admixture causes somewhat higher charge passed through 28-days concrete with Portland limestone cement (PLC). According to classification in ASTM C1202 [75], Fig. 9.9 reveals that the chloride ion penetration in the reference concrete is classified as moderate and high and no major shifts in performance are obtained by using the hydrophilic crystallization admixture. These results indicate that the percentage reduction in chloride ion penetration is in the range of 20%–25% for OPC concrete, while it is less for PLC. Based on the commercial literature, the percentage reduction in chloride ion penetration of hydrophilic crystallization WP admixtures is stated to be as low as 10% for some products, while for other products it is stated to be up to 45% or within a higher range of 42%–53%. Azarsa et al. [57] reported a percentage reduction of 20% for a commercial product. Similarly, for an admixture based on fluorosilicate (combining a filling agent, a water reducing agent, and an expansion agent), the percentage reduction in chloride ion penetration was in the range of 27%38% [76].

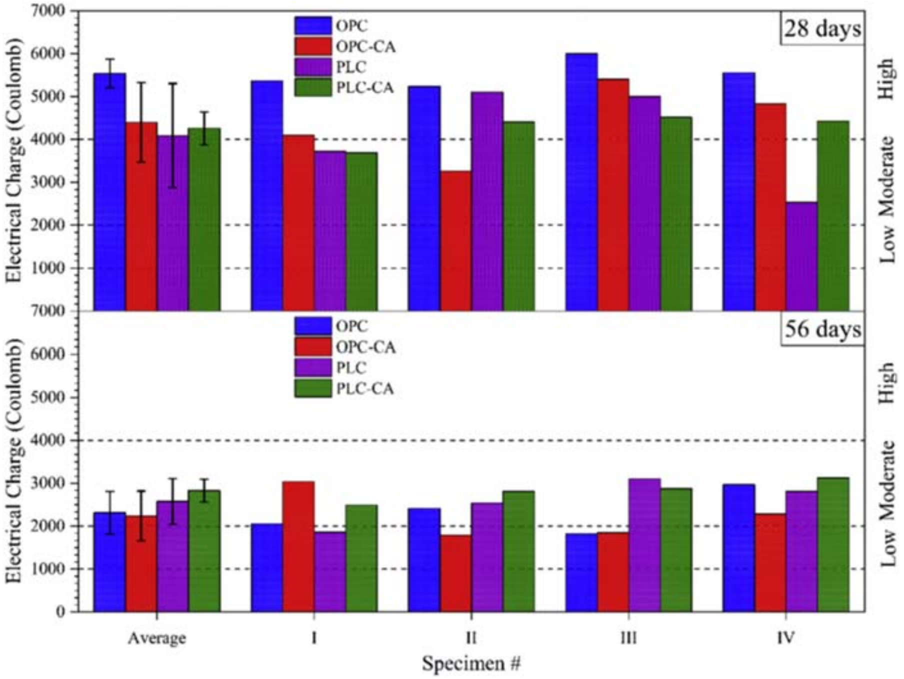


Figure 9.9 Total charge passage through two types of concrete mix designs [with ordinary Portland cement (OPC) and Portland Limestone Cement (PLC)] comparing untreated and treated with a commercial hydrophilic crystallization WP admixture [8].

The percentage reduction increased with increasing the dosage of the admixture [76]. The use of fluorosilicate as an admixture at 0.5% dosage led to an improvement in the resistance to chloride ion penetration by 37.5%, based on reducing the penetration depth of chloride ion [41].

Similarly, the penetrating surface treatment using silicate solutions can lead to minor reductions in chloride ion penetration (according to NCHRP 244) [54]. A percentage reduction in chloride permeability (according to AASHTO T-277–83) of about 20% was obtained when the sodium silicate solution was applied after 1 day of concrete curing. A higher percentage reduction (30%40%) was obtained when the sodium silicate was applied after 28 days of concrete curing [32]. Silicate sealers were reported by Thompson et al. [32] to be ineffective against chloride ingress. In general, it is common in literature that surface treatment by silicates is less effective than hydrophilic surface treatments (e.g., with silane) [54]. In fact, the penetration of chloride ions is better reduced by decreasing the capillary suction (using hydropic DP materials) than by using hydrophilic WP materials that reduces permeation flow under pressure.

The corrosion of steel bars is correlated with the migration of chloride ions and other harmful ions such as sulfate ions. Corrosion is affected by free chloride ions, which consists of about 94% of the total chloride ions in concrete. The efficacy of corrosion reduction can be determined by measuring the macro-cell corrosion current and half-cell potentials of treated and nontreated concrete specimens [70]. No major durability issues related to chloride ions are expected when their concentration, at depth equivalent to the depth of steel bars (i.e., at 120 mm from the exposed surface) [41], is lower than a threshold concentration. A wide range of threshold values have been set as limits for corrosion/deterioration problems. This is done by taking into account factors of concrete mix design such as w/c ratio, air content, and the type of reinforcement steel [77]. Typical threshold values for corrosion problems are in the range of 0.4%–0.7% by weight of concrete [78]. Much lower threshold values (0.03%) have been set in some analysis of the initiation of corrosion of black steel [79,80]. Then, Wells et al. [80] highlighted that the threshold is said to be 0.15% for epoxy-coated rebar and 0.64% for stainless rebar [80]. The time required for a 50% probability of corrosion failure is estimated based on reaching such a threshold [78]. Reducing chloride ions penetration increases the time required for initiating corrosion [70]. The hydrophilic crystalline WP admixtures can increase the time to corrosion by a factor of 5 [4], as they lead to fairly reduction in electrical current [57]. The penetrating surface treatment using silicate solutions are ineffective against corrosion [54]. Pan et al. [81] indicated that surface treatments with sodium silicate increased the time for corrosion by an insignificant period. Experimental results of Ibrahim et al. [54] indicated that the time to cracking of concrete treated with sodium silicate was almost similar to that for untreated concrete. The surface treatment with sodium silicate increased the time for corrosion from 10 years for nontreated concrete to 12 years for treated concrete, and the corrosion current density was decreased by about 13% [54].

9.6.4 Breathability and carbonation in concrete with hydrophilic waterproofing systems

Concrete resistance against carbonation is associated with gas permeability. Carbonation occurs as a result of permeation of CO_2 and its reaction with calcium ions in the pore solution (see Chapter 3). The performance of concrete resistance against carbonation is commonly evaluated by measuring the depth of carbonation or the rate of diffusion of carbon dioxide [70]. Gas and air permeabilities are correlated to vapor permeability or breathability [70,82]. The vapor transmission is measured using wet-cup and dry-cup absorption-desorption methods [70]. It is tested according to ASTM E96/E96M – 16. According to EN ISO 12572, the water vapor permeability of a building material is specified by the water vapor resistance factor.

Vapor can be transported through the connected pores of concrete by molecular diffusion in addition to permeation and advection (see Chapter 2). The transmission of water vapor is an essential characteristic to enhance concrete durability. Achieving a certain level of concrete dryness is essential for minimizing moisture-related problems (see Chapter 3). On the other hand, the transmission of water vapor from soil into concrete in submerged structures creates problems of damping and mildewed odors and reduces the quality of concrete and buildings. A low water vapor permeability in enveloping building structures may cause a surface condensation. In principle, the hydrophilic WP admixtures are not supposed to be vapor barriers as they only partially block the pores while the concrete pores remain reasonably open for the flow of vapor and gases. They only reduce the permeation of liquid water under a hydrostatic pressure [64]. Pazderka and Hájková [55] highlighted that "all producers of crystalline admixtures declare that their admixtures do not reduce the water vapor permeability of concrete." Then they indicated that a comparison of vapor transmission data with those for reference concrete are usually missing. The commercially available crystalline WP admixtures reduce the vapor permeability of concrete by a small percentage of 16%–20% [55]. Jalali and Afgan [4] reported that crystalline pore blocking WP reduced the vapor transmission in concrete by a percentage up to 50%. In fact, the interactions of crystals with water vapor may cause misinterpretations of the measurements of the vapor permeability. For example, the capillary condensation of the water vapor within the porous network of the hydrophilic crystals increases the water content of the crystals and hence leads to higher measurement of vapor inward flow.

The hydrophilic WP admixtures may be hypothesized to have insignificant effects on gas permeabilities, as they only reduce the permeation of liquid water under a hydrostatic pressure. However, some researchers believed that the WP enhances the resistance against CO_2 penetration [64]. Fig. 9.10 shows the percentage carbonation resistance of various silicate solutions [33]. The reactive silicate solutions (sodium and potassium silicates and their combinations) are more effective in reducing carbonation than the nonreactive solidifying type (lithium silicate). This is because the reactive silicate contribute to partial consumption of the penetrating carbon dioxide by binding through reactions to form silica gel [see Eq. (9.9)] [33]. Tran et al. [33] indicated that the mechanism of reducing carbonation is a combination of reaction and pore blocking. The result of Tran et al. [33] revealed that in the presence of carbon dioxide, the silicates react with carbon dioxide and immobilize it in addition to its reaction with calcium hydroxide. In such a

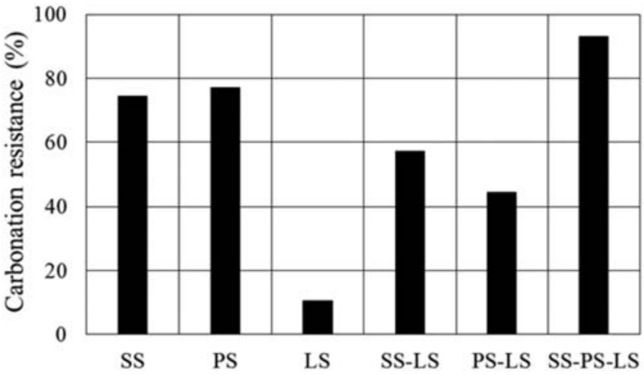


Figure 9.10 Percentage carbonation resistance of solutions of sodium silicate (SS), potassium silicate (PS), lithium silicate (LS), and other combinations of these silicates [33].

case, a carbonate-silicate gel can coexist. The detailed neutralization reactions between the different silicate compound and carbonic acid obtained from the dissolution of CO_2 in water can be summarized in Eqs. (9.11) and (9.12), in which M stands for Na, K, or Li. The precipitated calcium carbonate acts as additional pore blocking materials [18]. Choi et al. [64] reported that a fluorosilicate-based admixture led to percentage reductions in carbonation depth by 34.2% on the 7th day, 17.6% on the 28th day, and 22.9% on the 56th day.

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{9.11}$$

$$M_2O \cdot n_1SiO_2 + H_2CO_3 + n_2H_2O \rightarrow n_1SiO \cdot (n_2 + 1)H_2O \cdot M_2CO_3 \tag{9.12}$$

On the other hand, Chen et al. [10] found that surface treatment of calcium sulfo aluminate cement-based materials with sodium silicate and magnesium fluorosilicate could slightly reduce the carbonation rate within 7 days, then the carbonation depths of treated concrete were nearly equal to that of the control specimen after 28 days. Chen et al. [10] highlighted that specimens treated with hydrophobic materials of ethyl silicate resulted in a higher percentage reduction in carbonation (about 39%) [10].

9.6.5 Reducing concrete deterioration from freezing and thawing by hydrophilic waterproofing

The hydrophobic WP materials enhance the performance of concrete for resisting cycles of freezing and thawing by reducing moisture content and hence reducing its opportunity for freezing that creates internal stresses. In addition, the addition of hydrophilic WP admixtures increases air content (e.g., by about 10%) [8], which contributes in enhancing concrete resistance against cycles of freezing and thawing. The performance of hydrophobic WP materials is evaluated [according to ASTM C666 [83]]. This is done by measuring mass loss, length change, flexural strength, and/or compressive strength after subjecting the specimen to a certain number of freezing and thawing cycles [72]. According to promotional literature of manufacturers of crystalline admixtures, the strength loss of OPC mortar under cycles of freezing and thawing can be decreased by 38%. No sufficient experimental evidence could be found in the scientific literature. Durability studies of hydrophilic WP materials did not involve investigating the effect of freezing and thawing [8]. The review of Pan et al. [81] did not cover the effects of hydrophilic WP surface treatments on resisting cycles of freezing and thawing (it only discussed the performance of hydrophobic DP materials).

On the other hand, the effect of a fluorosilicate admixture on concrete resistance against freezing and thawing was investigated [64]. Overall, the resistance of fluorosilicate dosed concrete against freezing and thawing was enhanced by a percentage in the range of 20%–60% resulting from the pore blocking effect [64]. Fig. 9.11 shows the percentage reduction in the dynamic modulus of elasticity as a function

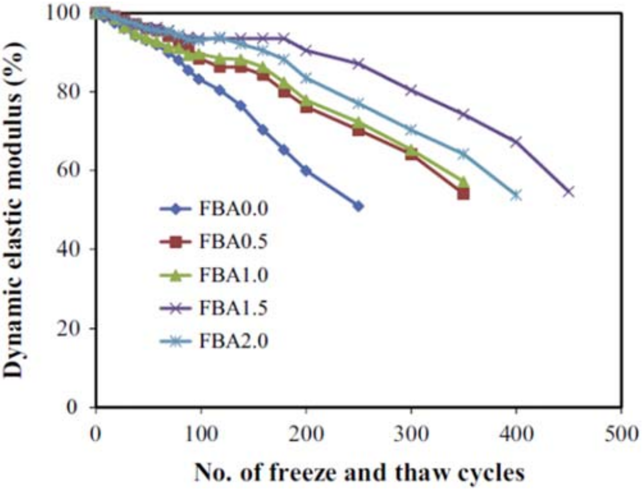


Figure 9.11 The percentage reduction in the dynamic modulus of elasticity as a function of the number of cycles of freezing and thawing for various dosages of fluorosilicate-based admixture (0%, 0.5%, 1.0%, 1.5%, and 2.0% of cement weight labeled as FBA0.0, FBA0.5, FBA1.0, FBA1.5, FBA2.0, respectively) [64].

of the number of cycles of freezing and thawing for various dosages of fluorosilicate-based admixture [64]. Increasing the dosage of fluorosilicates (up to 1.5% of cement weight) reduces the percentage reduction in the dynamic modulus of elasticity. However, when excessive fluorosilicate admixture was added ($> 1.5\%$), less effectiveness was obtained due to extra expansive effects from the formed gel.

9.6.6 Other durability and strength parameters

There are other durability effects of hydrophilic crystallization WP materials. The silicate surface treatment systems can help in reducing thermal movement associated with temperature fluctuations [35]. Similarly, the hydrophilic crystalline WP admixtures hinder the evaporation rate of water in concrete and thus retain larger moisture content in the mixture. These effects assist in delaying the initiation of cracking and in allowing a sufficient time for the fresh concrete to gain early-age strength [9]. The effects of crystallization WP materials on the early age cracking in concrete was investigated by Gupta and Biparva [9]. Overall, the hydrophilic crystalline WP admixtures provide a secondary advantage of acting as a shrinkage reducing admixture, particularly at early age [9]. They can resist the plastic shrinkage [9]. Also, it was reported that fluorosilicate-based admixture reduced free shrinkage strain of structural concrete significantly, and resulted in an effective reduction in shrinkage cracks [41]. The hydrophilic crystallization WP admixtures reduce drying shrinkage by about 20%–25% and restrained shrinkage cracking by 80% [2].

In addition, silicate surface treatment systems may assist in reducing the biological attack from the growth of fungus and algae and chemical attack [35]. ACI 515.2R-13 "Guide to selecting protective treatments for concrete" indicates that surface floor hardeners can reduce the chemical attack of concrete from mildly aggressive liquids, including weak acids [5]. According to other studies, silicate surface treatment systems cannot prevent chemical attack [35] or sulfate attack [54]. The crystalline WP admixtures may assist in protecting concrete against alkali aggregate reactions by reducing water penetration. However, there is no experimental evidence of such an effect. From another perspective, the crystallization mechanism [Eq. 9.3)] generates sodium hydroxide, which increases the chances for ASR [31]. Silicates can create a favorable environment for ASR by increasing the pH of the pore solution in concrete [80]. There is a little discussion in the literature on the possible impact of the released alkali ions from the general crystallization reaction [Eq. (9.4)] on the stability of aggregates [5,31]. The commercial literature of hydrophilic crystalline materials do not usually claim an enhancement in concrete resistance against ASR. Specialty admixtures (e.g., lithium compounds such as lithium hydroxide and lithium carbonate) are usually used for reducing ASR (as described in Chapter 7) [6,84]. This is achieved by increasing the stability of the reactive silica in aggregates and decreasing the formation of the expansive ASR gel.

The reactive hydrophilic WP materials can enhance the strength of concrete as its crystallization mechanism involves promoting cement hydration and the formation of additional CSH gel leading to a densifying effect [8]. The percentage enhancement in the compressive strength depends on the type, method of application, and dosage of the hydrophilic WP materials. Azarsa et al. [8] reported a peracetate strength enhancement of 11% for OPC concrete and 8% for concrete with PLC [8]. According to Jalali and Afgan [4], the crystalline WP admixtures increase the compressive strengths by a percentage in the range of 5%10% [4]. However, according to Pazderka and Hájková [55], the manufacturers usually promote that their admixtures slightly increase the compressive strength of concrete, while these statements might be based on the targeted strength from the mix design without a comparison with a reference concrete. Independent investigation of two commercially available hydrophilic WP admixtures indicated that there were no significant differences in compressive strength of dosed and nondosed concrete on 28 days [55,85]. Pazderka and Hájková [55] highlighted that such insignificant differences in compressive strengths are also believed to be valid for other crystalline admixtures due to chemical similarity [55]. On the contrary, the hydrophilic crystalline WP admixtures apparently caused a slight slowing down of the hardening process of concrete [55]. An enhancement of late compressive strength (after 28 days) could be more possible. A significant increase in the compressive strength of concrete was observed when a fluorosilicate admixture was used; resulting from the filling effect and the pozzolanic activity of the soluble silica obtained from fluorosilicate [64]. The percentage increase was found to be dependent on the dosage, at low dosages ($<1\%$) the compressive strength increased with dosages; however, adding fluorosilicate at a dosage above 1% reversed the trend. This reversed trend is believed to be due to creating excessive expansion pressure by the overfilling effect of the hydrophilic gel [64]. However, Appelbaum et al. [64] observed a significant decrease in compressive strength of cement paste incorporated with sodium fluorosilicate. It is worth mentioning that the types of dosed samples with WP admixtures (e.g., cement paste, mortar, or concrete) may affect the obtainable trend.

The surface hardness (or abrasion resistance) can be enhanced significantly by the surface treatments using sodium silicate and magnesium fluorosilicates and hence they are labeled as surface hardeners. ACI 515.2R-13 [5] stresses the role of fluosilicates treatment in increasing the abrasion resistance (according to ASTM C 418) and in reducing dusting. The level of improvement of surface hardness depends on the dosages and solid content and the quality of concrete (e.g., porosity). The level of enhancement in the abrasion resistance of surface-treated concrete with sodium silicate is higher than that treated with hydrophobic materials (ethyl silicate) [81]. Chen et al. [10] reported that surface treatments with sodium silicate and magnesium fluorosilicate significantly densifies the calcium sulfo aluminate cement-based materials; however, such a densifying effect has little effect on the compressive strength. These treatments could slightly increase the flexural strength [10].

References

[1] Ye, G., (2003). *Experimental study and numerical simulation of the development of the microstructure and permeability of cementitious materials*. Master of Engineering thesis, University of Technology, TU, Delft. Delft, The Netherlands.

[2] Biparva, A. & Gupta, R. (2010). Smart Waterproofing System: A Review. Proceedings of the International Conference on Future Concrete.

[3] Bohus, S., & Drochytka, R. (2012). *Cement based material with crystal-growth ability under long term aggressive medium impact. Applied mechanics and materials*. Trans Tech Publ.

[4] Jalali, U. H., & Afgan, S. (2018). Analysis of integral crystalline waterproofing technology for concrete. *International Research Journal of Engineering and Technology (IRJET)*, *5*(10).

[5] ACI. (2013). *Committee 515, ACI 515.2R-13 Guide to selecting protective treatments for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[6] ACI. (2016). *Committee 212, ACI 212. 3R-16 Report on chemical admixtures for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[7] de Souza Oliveira, A., et al. (2020). Crystalline admixture effects on crystal formation phenomena during cement pastes' hydration. *Journal of Thermal Analysis and Calorimetry*, *139*(6), 3361−3375.

[8] Azarsa, P., Gupta, R., & Biparva, A. (2019). Assessment of self-healing and durability parameters of concretes incorporating crystalline admixtures and Portland limestone cement. *Cement and Concrete Composites*, *99*, 17−31.

[9] Gupta, R., & Biparva, A. (2017). Do crystalline water proofing admixtures affect restrained plastic shrinkage behavior of concrete? *Revista ALCONPAT*, *7*(1), 15−24.

[10] Chen, H., et al. (2020). The influence of surface treatment on the transport properties of hardened calcium sulfoaluminate cement-based materials. *Cement and Concrete Composites*, *114*, 103784.

[11] BSI. (2004). *EN 1504-2: Products and systems for the protection and repair of concrete structures—Definitions, requirements, quality control and evaluation of conformity—Part 2: Surface protection systems for concret*. European Committee for Standardization, Brussels.

[12] Chindaprasirt, P., et al. (2008). Cement paste characteristics and porous concrete properties. *Construction and Building Materials*, *22*(5), 894−901.

[13] Van Breugel, K. (2004). Modelling of cement-based systems—The alchemy of cement chemistry. *Cement and Concrete Research*, *34*(9), 1661−1668.

[14] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. New York, USA: McGraw-Hill Education.

[15] Elsalamawy, M., Mohamed, A. R., & A.-l.E. Abosen. (2020). Performance of crystalline forming additive materials in concrete. *Construction and Building Materials*, *230*, 117056.

[16] Azarsa, P., Gupta, R., & Biparva, A. (2020). Inventive microstructural and durability investigation of cementitious composites involving crystalline waterproofing admixtures and Portland limestone cement. *Materials*, *13*(6), 1425.

[17] Ye, G. (2005). Percolation of capillary pores in hardening cement pastes. *Cement and Concrete Research*, *35*(1), 167−176.

[18] Mundo, R. D., et al. (2020). Recent advances in hydrophobic and icephobic surface treatments of concrete. *Coatings*, *10*(5), 449.

[19] ASTM. (2003). *C125-15b Standard terminology relating to concrete and concrete aggregates*. West Conshohocken, PA, USA: Annual Book of ASTM Standards.

[20] Bapat, J. D. (2012). *Mineral admixtures in cement and concrete*. CRC Press.

[21] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[22] Wong, H., et al. (2011). Effect of entrained air voids on the microstructure and mass transport properties of concrete. *Cement and Concrete Research*, *41*(10), 1067−1077.

[23] ACI. (2008). *Committee 201, ACI 201.2 R-08 Guide to durable concrete in* 2008, Farmington Hills, MI, USA: American Concrete Institute.

[24] Rashed, A. I., & Williamson, R. B. (1991). Microstructure of entrained air voids in concrete, Part I. *Journal of Materials Research*, *6*(9), 2004−2012.

[25] Sharma, A., et al. (2020). Characterization of paste microstructure for durability properties of concrete. *Construction and Building Materials*, *248*, 118570.

[26] Cassie, A., & Baxter, S. (1944). Wettability of porous surfaces. *Transactions of the Faraday Society*, *40*, 546−551.

[27] Shukla, N. B., & Madras, G. (2011). Reversible swelling/deswelling characteristics of ethylene glycol dimethacrylate cross-linked poly (acrylic acid-co-sodium acrylate-co-acrylamide) superabsorbents. *Industrial & Engineering Chemistry Research*, *50*(19), 10918−10927.

[28] Al-Jabari, M., Ghyadah, R. A., & Alokely, R. (2019). Recovery of hydrogel from baby diaper wastes and its application for enhancing soil irrigation management. *Journal of Environmental Management*, *239*, 255−261.

[29] Al-Otoom, A., Al-Khlaifa, A., & Shawaqfeh, A. (2007). Crystallization technology for reducing water permeability into concrete. *Industrial & Engineering Chemistry Research*, *46*(16), 5463−5467.

[30] Struble, L. J., & Diamond, S. (1981). Swelling properties of synthetic alkali silica gels. *Journal of the American Ceramic Society*, *64*(11), 652−655.

[31] Pan, X., et al. (2017). A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578−590.

[32] Thompson, J. L., et al. (1997). Characterization of silicate sealers on concrete. *Cement and Concrete Research*, *27*(10), 1561−1567.

[33] Tran, P. C., et al. (2018). Carbonation proofing mechanism of silicate-based surface impregnations. *Journal of Advanced Concrete Technology*, *16*(10), 512−521.

[34] Franzoni, E., Pigino, B., & Pistolesi, C. (2013). Ethyl silicate for surface protection of concrete: Performance in comparison with other inorganic surface treatments. *Cement and Concrete Composites*, *44*, 69−76.

[35] Jappie, L., (2019). *Literature review of the use of common protective coatings for concrete structures with experiences in the South African context*.Engineering and the Built Environment.

[36] Franzoni, E., et al. (2014). Improvement of historic reinforced concrete/mortars by impregnation and electrochemical methods. *Cement and Concrete Composites*, *49*, 50−58.

[37] Isador, S. & Abraham M., (1951). *Concrete hardening compositions of the metal salt type*.Google Patents.

[38] Li, W., et al. (2015). Research on using fluorosilicate for the enhanced performance of concrete. *Special Publication*, *303*, 293−300.

[39] Moraru, D. S. (1981). *Method for the protection of concrete in sea water*. Google Patents.

[40] Jones, J. W. & Maxfield P. (2002). *Method of hardening and polishing concrete floors, walls, and the like*.Google Patents.

[41] Choi, W.-C., Khil, B.-S., & Yun, H.-D. (2015). Characteristics of structural concrete containing fluorosilicate-based admixture (FBA) for improving water-tightness. *Construction and Building Materials*, *74*, 241−248.

[42] Gyu-Yong, K., et al. (2009). Evaluation of properties of concrete using fluosilicate salts and metal (Ni, W) compounds. *Transactions of Nonferrous Metals Society of China*, *19*, s134−s142.

[43] Pei, X., et al. (2017). Cementitious coatings for improved corrosion resistance of steel reinforcement. *Surface and Coatings Technology*, *315*, 188−195.

[44] Ferrara, L., Krelani, V., & Moretti, F. (2016). On the use of crystalline admixtures in cement based construction materials: from porosity reducers to promoters of self healing. *Smart Materials and Structures*, *25*(8), 084002.

[45] Žáková, H., Pazderka, J., & Reiterman, P. (2020). Textile reinforced concrete in combination with improved self-healing ability caused by crystalline admixture. *Materials*, *13*(24), 5787.

[46] Arvaniti, E. C., et al. (2010). Calcium oxalate crystallization on concrete heterogeneities. *Chemical Engineering Research and Design*, *88*(11), 1455−1460.

[47] Kushartomo, W., & Prabowo, A. (2019). *The application of sodium acetate as concrete permeability-reducing admixtures*. *IOP conference series: Materials science and engineering*. IOP Publishing.

[48] Rahman, M. & Al-Kheetan M. (2019). *Integration of anhydrous sodium acetate (ASAc) into concrete pavement for protection against harmful impact of de-icing salt*.

[49] Shi, X., et al. (2010). Freeze–thaw damage and chemical change of a portland cement concrete in the presence of diluted deicers. *Materials and Structures*, *43*(7), 933−946.

[50] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2019). Moisture evaluation of concrete pavement treated with hydrophobic surface impregnants. *International Journal of Pavement Engineering*, *46*(14), 1−9.

[51] Matar, P., & Barhoun, J. (2020). Effects of waterproofing admixture on the compressive strength and permeability of recycled aggregate concrete. *Journal of Building Engineering*, *32*, 101521.

[52] Lee, H. X. D., Wong, H. S., & Buenfeld, N. R. (2016). Self-sealing of cracks in concrete using superabsorbent polymers. *Cement and Concrete Research*, *79*, 194−208.

[53] Muzenski, S., Flores-Vivian, I., & Sobolev, K. (2015). Hydrophobic engineered cementitious composites for highway applications. *Cement and Concrete Composites*, *57*, 68–74.

[54] Ibrahim, M., et al. (1997). Effectiveness of concrete surface treatmentmaterials in reducing chloride-induced reinforcement corrosion. *Construction and Building Materials*, *11*(7), 443–451.

[55] Pazderka, J., & Hájková, E. (2016). Crystalline admixtures and their effect on selected properties of concrete. *Acta Polytechnica*, *56*(4), 306–311.

[56] Silva, E., et al. (2017). Case study of permeability-reducing admixture use in anti-flotation slabs: Building in Brasilia, Brazil. *Journal of Building Pathology and Rehabilitation*, *2*(1), 1.

[57] Azarsa, P., Gupta, R., & Biparva, A. (2018). Crystalline waterproofing admixtures effects on self-healing and permeability of concrete. In *1st International conference on new horizons in green civil engineering (NHICE-01)*. Victoria, BC, Canada.

[58] Takagi, E., Lima M., & Helene P. (2012). Contribution to study of the self-healing effect activated by crystalline catalysts in concrete structures when subjected to continuous exposure to water. In *Proceedings of the 3rd international conference of concrete repair, rehabilitation and retrofitting*. Cape Town, South Africa.Citeseer.

[59] Zhang, X. J., & Zheng, D. M. (2012). *Uniform design for preparation of cementitious capillary crystalline waterproofing coating*. *Advanced materials research*. Trans Tech Publ.

[60] Guo-Zhong, L., et al. (2014). The analysis on mechanism and application of cementitious capillary crystalline waterproofing coating. In *2014 international conference on mechanics and civil engineering (icmce-14)*. Atlantis Press.

[61] Reiterman, P., & Pazderka, J. (2016). Crystalline coating and its influence on the water transport in concrete. *Advances in Civil Engineering*, *2016*.

[62] Shetty, M. (2005). *Concrete technology theory and practice*. New Delhi, India: S. Chand and Company LTD.

[63] Bohus, S., Drochytka, R., & Taranza, L. (2012). *Fly-ash usage in new cement-based material for concrete waterproofing*. *Advanced materials research*. Trans Tech Publ.

[64] Appelbaum, K. S., Stewart, J. T., & Hartwell, G. R. (2012). Effect of sodium fluorosilicate on the properties of Portland cement. *Journal of Endodontics*, *38*(7), 1001–1003.

[65] Li, G., et al. (2019). Activated chemicals of cementitious capillary crystalline waterproofing materials and their self-healing behaviour. *Construction and Building Materials*, *200*, 36–45.

[66] Weisheit, S., et al. (2016). Assessment of test methods for characterizing the hydrophobic nature of surface-treated high performance concrete. *Construction and Building Materials*, *110*, 145–153.

[67] Yu, J., et al. (2019). Hydrophobic silane coating films for the inhibition of water ingress into the nanometer pore of calcium silicate hydrate gels. *Physical Chemistry Chemical Physics*, *21*(35), 19026–19038.

[68] Pigino, B., et al. (2012). Ethyl silicate for surface treatment of concrete – Part II: Characteristics and performance. *Cement and Concrete Composites*, *34*(3), 313–321.

[69] Sandrolini, F., Franzoni, E., & Pigino, B. (2012). Ethyl silicate for surface treatment of concrete – Part I: Pozzolanic effect of ethyl silicate. *Cement and Concrete Composites*, *34*(3), 306–312.

[70] Basheer, P. A. M., et al. (1997). Surface treatments for concrete: Assessmentmethods and reported performance. *Construction and Building Materials*, *11*(7), 413–429.

[71] Zhan, H., Wittmann, F., & Zhao, T. (2003). Chloride barrier for concrete in saline environment established by water repellent treatment. *International Journal for Restoration of Buildings and Monuments*, *9*(5), 535−550.

[72] Song, Z., Lu, Z., & Lai, Z. (2019). Influence of hydrophobic coating on freeze-thaw cycle resistance of cement mortar. *Advances in Materials Science and Engineering*, *2019*.

[73] Mirza, J., Abesque, C., & Bérubé, M.-A. (2011). Evaluation of surface sealers for concrete hydraulic structures exposed to low temperatures. *Materials and Structures*, *44*(1), 5−12.

[74] D'Souza, B., (2018). Watertight or waterproof concrete? In *The concrete NZ conference 2018*.Hamilton, New Zealand.

[75] ASTM. (2019). *C1202 - 19: Standard test method for electrical indication of concrete's ability to resist chloride ion penetration*. West Conshohocken, PA, USA: In Annual Book of ASTM Standards.

[76] Yu, Y., Yu, J., & Ge, Y. (2016). Water and chloride permeability research on ordinary cement mortar and concrete with compound admixture and fly ash. *Construction and Building Materials*, *127*, 556−564.

[77] Morse, K. L. (2009). *Effectiveness of concrete deck sealers and laminates for chloride protection of new and in situ reinforced bridge decks in Illinois*.Illinois Department of Transportation, Bureau of Materials and Physical Research.

[78] Schueremans, L. & Van Gemert D. (1997). Service life prediction model for reinforced concrete constructions treated with water repellent compounds. *Conchem Proceedings*, Dusseldorf, pp. 103–113.

[79] Wells, D., et al., (2014). *Sealants, treatments and deicing salt practices to limit bridge deck corrosion and experimental deck sealants and pier cap coating on interstate 471*.

[80] Wells, D., Palle S., & Hopwood II T. (2019). *Developing material specification and application criteria for sealing concrete bridge decks*.

[81] Pan, X., et al. (2017). A review on surface treatment for concrete – Part 2: Performance. *Construction and Building Materials*, *133*, 81−90.

[82] Kebao, R., & Kagi, D. (2012). 10 - Integral admixtures and surface treatments for modern earth buildings. In M. R. Hall, R. Lindsay, & M. Krayenhoff (Eds.), *Modern earth buildings* (pp. 256−281). Woodhead Publishing.

[83] Basheer, L., & Cleland, D. J. (2006). Freeze–thaw resistance of concretes treated with pore liners. *Construction and Building Materials*, *20*(10), 990−998.

[84] Thomas, M. D., Fournier, B., & Folliard, K. J. (2008). *Report on determining the reactivity of concrete aggregates and selecting appropriate measures for preventing deleterious expansion in new concrete construction*. United States: Federal Highway Administration.

[85] Pazderka, J. (2017). *The crystalline admixture effect on concrete and cement mortar compressive strength. Key engineering materials*. Trans Tech Publ.

Dual crystallization waterproofing topical treatment

10

Maher Al-Jabari[1], *Radi Al-Rashed*[2] *and Michael E. Ayers*[3]
[1]Chem-Crete Europe, Holic, Slovakia, [2]International Chem-Crete Corporation, Richardson, TX, United States, [3]Global Pavement Consultants, Inc., Fithian, IL, United States

10.1 Introduction

Water penetration within concrete and the associated chemical and physical interactions with cementitious materials cause various durability problems. They cause structural damages from alkalisilica reactions (ASR) [1–4], carbonation [5,6], freezing and thawing cycles [7], chemical attack [8,9], scaling and corrosion of embedded steel triggered by the penetration of chloride ions coming from deicing salts or sea water [10,11], and biological attack [12–14]. These problems are detailed in Chapter 3. Waterproofing (WP) assists in protecting concrete structures and minimizing these attacks. The function of internal (or integral) WP materials is established when WP active ingredients react with cementitious constituents resulting in products that become integral parts of the cement paste structure [15,16] (see Chapter 7). The terminology of integral WP started with permeability reducing admixtures [17] and extended for penetrating materials that modify the pore structure (see Chapters 6 and 7). The topically applied penetrating liquids are absorbed and then migrate through the concrete structure where they react and then function internally [15,16]. Internal and integral WP systems are also referred to as crystallization WP, pore filling, pore or capillary blocking [18], as well as pore lining [19]. According to ACI Concrete Terminology [20], penetrating solutions used for topical surface treatment of concrete are referred to as hardeners, densifiers, and sealers. Water permeation under a hydrostatic pressure is reduced only by the pore-blocking or filling mechanism [18], while pore lining mechanism can only reduce capillary suction under a condition of nonhydrostatic pressure [20]. Conditions of a nonhydrostatic pressure are encountered in above-grade structures exposed to a partial cyclic wetting with minor or no water head [17]. On the other hand, conditions of a hydrostatic pressure are encountered in water submerged structures including marine structures [21] and hydraulic structures [8]. In addition, conditions of a hydrostatic pressure can be encountered occasionally in wetted above-grade structures (e.g., pavements and walls) due to mechanical impacts from traffic loading or from pressure of wind currents [22]. Concrete treated with pore lining materials can withstand only a few centimeters of water head [17].

Advanced integral WP materials are based on combining more than one mechanism. This chapter introduces dual-crystallization waterproofing engineered (DCE) topical treatment that combines hygroscopic and hydrophilic crystallization with a

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00010-6

hydrophobic molecular layer. The originality of this WP approach has been registered as a patent [23]. Then, the DCE performance has been investigated in various recent research papers by the authors of this chapter [24,25] and by other authors [26–32] and in other official testing reports [33,34]. The available literature includes papers covering extensive performance and comparative analysis of the DCE material, which described the patented ingredients inaccurately [35–39].

This chapter presents the conceptual mechanism and describes the physicochemical functions of the DCE system. The chemical and physical actions of the DCE material and its water hindering mechanisms are defined. The DCE application onto freshly poured or hardened concrete pavements and other structures is highlighted. The application to fresh concrete is accompanied with the cement hydration process (see Chapter 1). Then, the chapter demonstrates the WP and durability parameters of DCE including pore size, density, permeability, water absorption, chloride ion penetration, concrete resistances to cycles of freezing and thawing, ASR, resistance against biological deterioration, and mechanical properties.

10.2 Concepts of dual crystallization waterproofing

The dual crystallization waterproofing material is a proprietary formulation of multiple reactive components in an aqueous solution [23] that is sprayed on freshly poured concrete [24], or on fully cured or old concrete [25]. The active ingredients of the DCE penetrate within the surface layer where they undergo a series of chemical reactions and physical interactions. Then, the produced crystalline material penetrates deeper within the concrete structure by crystal growth, as described in Chapter 7 (see Figure 7.2). The crystallization and molecular lining products combine hydrophilic and hygroscopic crystals with hydrophobic characteristics [25]. Then, they reduce water penetration through combined mechanisms of pore blocking with pore lining: The definitions and behaviors of hydrophobic, hydrophilic, and hygroscopic materials are presented in Chapter 5.

The DCE WP system is different from common sealers, which mainly produce a hydrophilic gel [40] (as detailed in Chapter 9) or form a hydrophobic molecular layer (as detailed in Chapter 8). The ACI Concrete Terminology [20] defines the sealer as “a liquid that is applied to the surface of hardened concrete, is colorless, is absorbed by the concrete, leaves little or nothing visible on the surface, and either prevents or decreases the penetration of liquid or gaseous media.” Sealers that are referred to as hardeners commonly aim at reducing dusting and increasing the surface abrasion resistance. Typical concrete hardeners include silicate solutions [6,20,40–42] and fluosilicate solutions [43–45]. On the other hand, the DCE material involves various types of active ingredients that lead to the formation of hygroscopic crystals that grow with moisture adsorption from air humidity and hydrophilic crystals, which expand upon swelling. These two types of crystals are formed within the pores of cement paste and hence reduce concrete porosity by pore blocking. The remaining open porosity is lined with a hydrophobic molecular layer that is formed from a third component of the active ingredients. Through these combined actions, the DCE performance is not restricted to one specific case of hindering water penetration, that is, reducing permeability under a hydrostatic pressure (as in the case of hydrophilic surface treatments for structures) [6,40−42] and reducing water absorption under a nonhydrostatic pressure (as in the case of hydrophobic surface treatments) [17,19,42,46−50]. The DCE system can reduce both the permeability and capillary absorption and thus hinders water penetration in damped concrete under a hydrostatic pressure (WP) and hinders capillary absorption through the water repellency property (dampproofing). Consequently, it can be applied for WP of damped structure and/or for dampproofing of partially wetted structures. Also, the DCE is applicable from positive and negative sides of concrete [28]. The chemical mechanism is detailed further in Section 10.4.

In some other publications, the concept of the dual WP system has been presented in a different way. For example, the term "dual effects" was used to refer to hydrophobic and crystallization effects (in cementitious coatings) [51]. Such a system involves a single typical hydrophilic crystallization system combined with the formation of a hydrophobic layer and hence it does not combine two types of hydrophilic and hygroscopic crystals. It is also worth not to confuse the concept of dual crystallization systems with sealers that include combinations of silicate compounds (e.g., sodium and potassium silicates) [52], as these material combinations remain based on the formation of hydrophilic gels. Table 10.1 lists industrial systems of aqueous dual crystallization WP, which include dual and triple functions. The available literature [24−39] deals mainly with the WP system involving triple functions.

10.3 Application and penetration of the dual crystallization waterproofing

The DCE solution is commonly applied onto concrete surfaces by spraying or brushing. Fig. 10.1 shows two types of spraying machines that are used in industry. When DCE solution is used among maintenance operations of pavements, the

Table 10.1 Types of dual crystallization materials.

System category	**Waterproofing interaction with water**	**Product phase and application**	**Waterproofing mechanism**
Dual functions	Hygroscopic and hydrophilic crystals.	Surface treatment of cured concrete flooring using an aqueous solution.	Pore blocking utilizing dual crystallization technology.
Triple functions	Hygroscopic, hydrophilic, and hydrophobic.	Surface treatment of fresh or cured concrete using an aqueous solution.	Pore blocking and water repelling utilizing dual crystallization technology.

Figure 10.1 Application of the DCE solution by spraying onto cured concrete for an airport runway (A) and a pavement (B).

shutdown of traffic is a crucial impact. The application of DCE by spraying is a rapid process and can be finished in a short period of time (see Fig. 10.1). Then, the DCE material penetrates the surface and starts its functions internally; meanwhile the pavement can be opened for operation without the need for curing times, which are commonly required by film forming coatings and membrane systems. The application of DCE is associated with a group of material characteristics such as sufficient penetrability, reactivity with cementitious materials, chemical and physical stability, and being environmentally friendly.

When DCE is applied to fully cured or existing concrete, typical surface preparation steps are commonly required in a similar fashion of other WP sealers (see Chapter 6): the surface must be clean, structurally sound, and with an open capillary system. Hence, it is required to remove dirt and residuals of curing agents by mechanical actions. Efficient surface cleaning promotes opening the surface capillary pores and hence enhances the penetrability of DCE solution. Subjecting the surface to a compressed air can assist in removing dust and loose particles from the surface. Flushing the surface with water can improve the cleaning process and it wets the surface creating a medium for DCE diffusion; however, the level of surface saturation impacts the penetration of the DCE solution as described in Figs. 10.4 and 10.5. If the surface has been previously treated with noncementitious WP materials or sealed with other polymeric agents, these materials must be removed by mechanical actions (e.g., sand blasting) before DCE application. For heavily contaminated surfaces, chemical surface treatment may be required to remove dirt, grease, and oil. Surface preparation steps may involve repairing and sealing joints, cracks, and voids greater than 1/16th inch (1.6 mm).

Usually, additional construction management activities are required for sealer application on fully cured concrete, and the sealer treatment requires the removal of curing compounds before application. In order to avoid such circumstances and costs, an alternative approach for DCE application on green concrete is possible [24,30]. This can be accomplished by spraying DCE on freshly poured concrete, after the initial set of concrete and when all bleed water has been dissipated from the surface [30] (see Fig. 10.2A). Then, a firm-forming curing compound can then be commenced immediately (see Fig. 10.2B). The active ingredients penetrate within the structure of green concrete by diffusion through the water phase. In such a case, the early formation of the pore-blocking DCE crystals and their interactions with water can assist in minimizing water loss from green concrete and thus enhance cement hydration (see Section 10.4).

The surface coverage of the DCE solution can be in the range of 2.5–4.9 m^2/L (100–200 ft^2/gallon) [24,25]. The commonly recommended coverage is 3.7 m^2/L (150 ft^2/gallon) while a higher surface coverage of 5 m^2/L has been tested [32]. The experimental study of Xiao et al. [34] showed that the coverage rate was not crucial. Materials of dual functions (hygroscopic and hydrophilic crystallization) can be applied in multiple subsequent applications. On the other hand, the DCE with triple functions (involving hydrophobicity) is usually applied as a one-coat application as after applying the DCE, the surface becomes hydrophobic and hence its absorption capacity is reduced making the absorption of a subsequent DCE application very low. This has been confirmed experimentally by Xiao et al. [34], as no

Figure 10.2 Application of the DCE by spraying onto freshly poured concrete pavement (A), followed by the application of a curing compound (B).

significant reduction in water absorption could be achieved with the subsequent application of the DCE: such a marginal benefit from subsequent applications had been also reported for typical hydrophobic surface treatments (see Chapter 8): no substantial increase in the penetration depth was observed when a typical hydrophobic penetrating sealer was applied to concrete surfaces in successive two-steps treatments [19].

The primary penetration of the DCE solution is achieved by capillary suction (as any other penetrating surface treatment, see Chapter 5). The capillary suction is governed by the physical and chemical properties of the solution including viscosity, volatility, density, and the molecular sizes of the active ingredients. This is a time-dependent process and hence the penetration of a sealer is governed by the contact time or the residence time on the wetted surface [46]. The penetration depth of DCE is governed by its physical and chemical properties and the surface characteristic of the concrete substrate. The active ingredients of the DCE include no volatile organic compounds and hence they cannot be lost to the atmosphere as encountered in the case of silanes and siloxanes. The DCE solution is a light liquid that has a specific gravity of about 1.1 with a low viscosity of 2.4 centipoise [25]. The active ingredients have short molecular structures (relative to the structures of silanes and siloxanes) and involve a penetration enhancer [23]. In addition, the penetration depth is governed by the physicochemical interactions of the DCE ingredients with the cementitious materials (see Section 10.4). In fact, after liquid penetration by capillary absorption mechanism, the soluble active ingredients can migrate deeper below the surface by diffusion and then the overall DCE penetration depth is further enhanced by crystal growth (see Chapter 6). These characteristics allow the DCE penetrability to be larger than that of typical hydrophobic materials, as reported by Xiao et al. [34]: Fig. 10.3 compares the penetration depths of cored samples from existing concrete pavements treated with various sealers (including the DCE, silanes, and typical hydrophilic silicate solutions) [34], showing the highest penetration depth for the DCE material (core#10). The penetration depth, from laboratory testing, is in the range of 2.5–6.4 mm [29]; however, crystal growth over time allows the penetration to reach about 12 mm as shown in Fig. 10.3 [34].

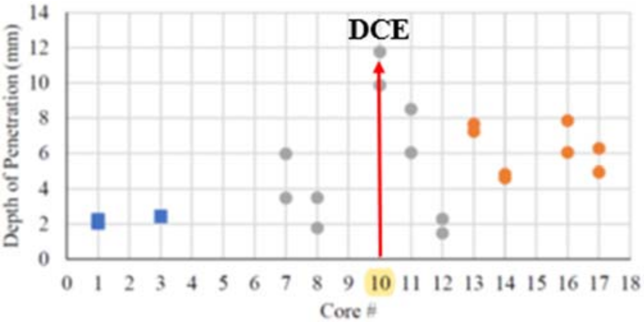
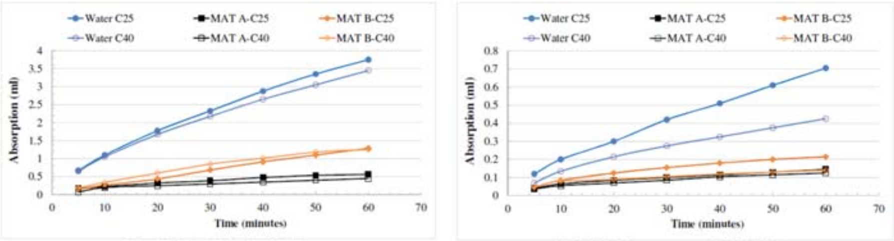


Figure 10.3 Depth of penetration of various sealers from cored samples in various highways projects in the United States (the DCE material is core#10) [34].

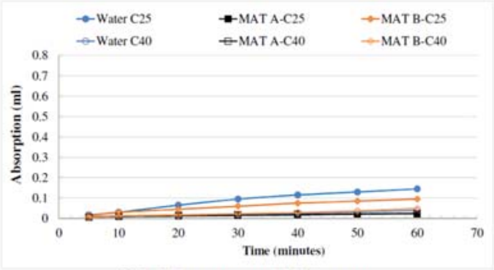
The initial penetration depth is affected by the temperatures of concrete substrate and the DCE solution: Decreasing the temperature increases the viscosity of the DCE solution and thus decreases its penetrability. In addition, the solubility of active ingredients in water decreases with temperature, hence a faster crystallization process of the DCE material may be promoted. This may cause the DCE crystalline materials to precipitate at shorter depths. The crystal growth is also dependent on temperature and humidity, and thus the rate of pore blocking can be reduced by decreasing the temperature. Usually, it is not recommended to apply the DCE solution when the temperature falls below 50°F (10°C). However, it still can be applied when the temperature is above the freezing point of water, but this condition can be associated with a lower penetration depth while the DCE WP mechanism will remain efficient.

The concrete characteristics that affect the penetration of the DCE solution include its porosity and level of water saturation. The porosity is governed by the mix design of the substrate and the curing conditions and age, as described in Chapters 2 and 4. The sealer penetration decreases with increasing the strength of the reference concrete (decreasing porosity), as shown in Fig. 10.4, which compares the penetration (uptake) of the DCE, distilled water, and a silane material in two types of concrete grades (C25 and C40) at different levels of saturation [32]. Rahman et al. [32] concluded that the DCE material achieved better uptake



(A) Fully dried (0%) case

(B) Half saturated (2.5%) case



(C) Fully saturated (5%) case

Figure 10.4 Material uptake per cube face (1010 cm) for distilled water, the DCE solution (labeled as MAT-B), and a silane solution (labeled as MAT-A), applied at a coverage rate of 5 m^2/L onto 28-days concrete cubic specimens of grades of C25 (25 N/mm^2) and C40 (40 N/mm^2) with w/c of 0.44 for dry (0% moisture) (A), half saturated (2.5% moisture) (B), and fully saturated (5% moisture) (C) [32].

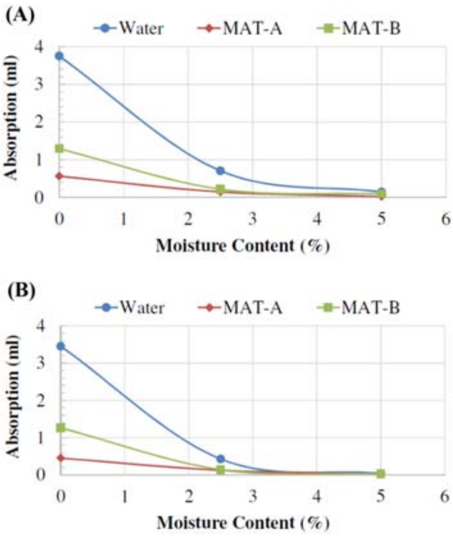


Figure 10.5 Total material uptakes within 60 minutes through 1010 cm as functions of concrete moisture concrete for distilled water, the DCE solution (labeled as MAT-B), and a silane solution (labeled as MAT-A), applied at a coverage rate of 5 m^2/L onto 28-days concrete cubic specimens of grades of C25 (25 N/mm^2) (A) and C40 (40 N/mm^2) (B) with w/c of 0.44 [32].

penetration than the tested silane sealer for all levels of concrete saturation. The sealer uptake declines significantly with increased moisture content as shown in Fig. 10.5 [32].

10.4 The dual-crystallization waterproofing engineered mechanisms

The DCE mechanisms involve (1) physical penetration of DCE within concrete structure by capillary action and diffusion (as described in Section 10.3), (2) setting of active ingredients through chemical reactions within concrete structures, and (3) the WP performance mechanism of the resulting WP materials, during concrete service life. A schematic representation of the parallel formation reactions of the active ingredients of the DCE and the performance mechanisms of the products of reactions are shown in Fig. 10.6 [25]. The DCE setting mechanism within concrete pores is mainly chemical. The reaction sites for each of the active ingredients of the DCE solution are presented in Fig. 10.6. During the DCE setting, the following simultaneous chemical reactions occur:

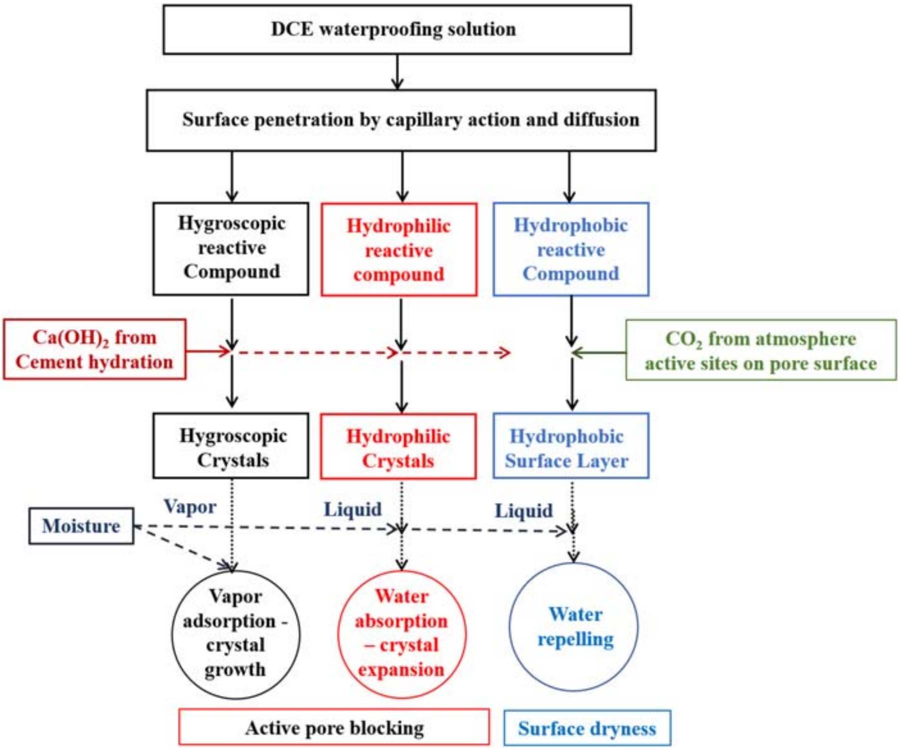


Figure 10.6 A schematic representation of the DCE mechanisms [25].

1. The formation of hygroscopic crystals through the reaction of hygroscopic active ingredients (DCE_{HG}) with calcium hydroxide ($Ca(OH)_2$) and their growth with water vapor adsorption, according to Eq. (10.1).

$$DCE_{HG} + Ca(OH)_2 + H_2O_{vapor}\text{hydrated hygroscopic crystals} \tag{10.1}$$

2. The formation of hydrophilic crystals through the reaction of hydrophilic active ingredients (DCE_{HPL}) with calcium hydroxide and water, according to Eq. (10.2).

$$DCE_{HPL} + Ca(OH)_2 + H_2O_{liquid}\text{hydrophilic crystals} \tag{10.2}$$

These two crystallization reactions [Eqs. (10.1) and (10.2)] are believed to take place on the surfaces of $Ca(OH)_2$ crystals where the calcium ions ($Ca^{2+)}$ ions are more available [25] (see Fig. 10.1). Their formulation consumes part of the undesired $Ca(OH)_2$ and produces a protective material. The presence of the hexagonal crystals of calcium hydroxide is reduced within the surface layer of concrete (treated with the DCE). The formations of these hygroscopic and hydrophilic crystals reduce the size of permeable capillary pores (see below).

3. The formation of hydrophobic molecular layer through the reaction of the reactive group of the hydrophobic active ingredients (DCE_{HPB}) with siliceous sites on the surfaces of the pores

in the presence of carbon dioxide from air, according to Eq. (10.3). The produced hydrophobic molecular layer is formed at the surfaces of CSH gel and ettringite crystals, where the siliceous sites are available. This reaction occurs at the external surface, which is accessible to atmospheric air (containing CO_2) and within the pores when they are filled with air.

$$\mathrm{DCE_{HPB}} + \mathrm{CO_2} + \mathrm{Si}_{\mathrm{site}s}\text{hydrophobic molecular layer} \tag{10.3}$$

All these reactions [Eqs. (10.1)–(10.3)] are triggered by the increase in the concentrations of the active ingredients, as a result of the evaporation of water of the DCE solution. When the DCE solution is applied onto the surface of fresh concrete, these reactions do not occur before a sufficient degree of cement hydration is achieved: The first two reactions [Eqs. (10.1) and (10.2)] are dependent on the availability of cement hydration by-product [$Ca(OH)_2$ crystals]. When the $Ca(OH)_2$ crystals become available and their soluble part forms the pore solution, the crystallization reactions of the DCE occur. Both reactions [Eqs. (10.1) and (10.2)] require calcium ions (Ca^{2+}) as a main reactant. Similarly, the third reaction is dependent on the establishment of the pore structure and air permeation from the surrounding. The development of the crystalline DCE system during the first 3 days after treatment of fresh concrete is shown in Fig. 10.7 [26]. With time, the formation of

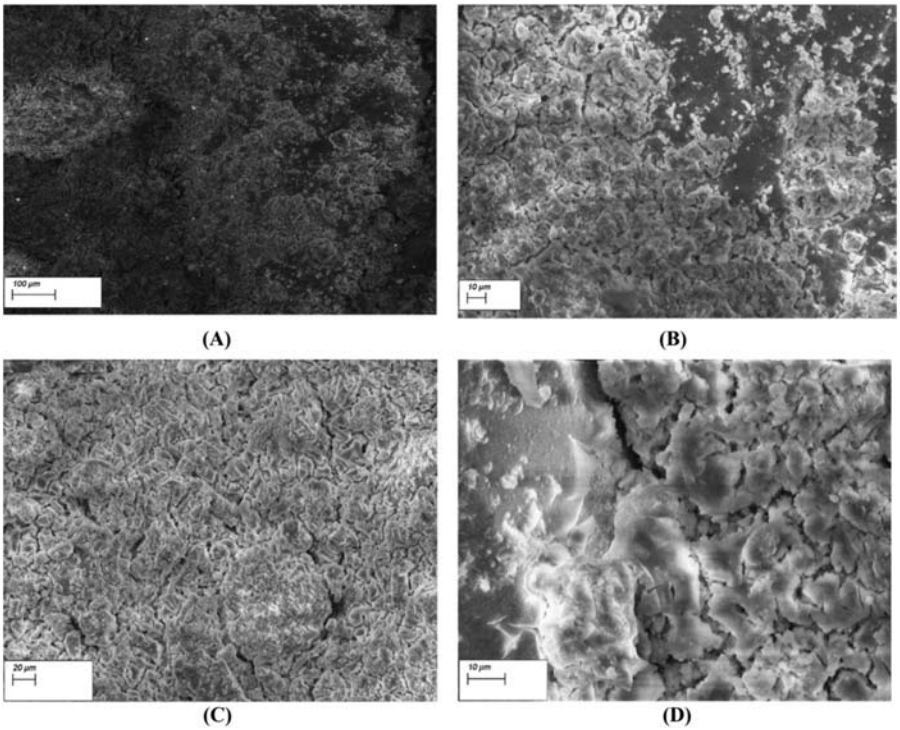


Figure 10.7 Crystal formation and development with time as observed under SEM after treatment: (A) 1 day (500), (B) 2 days (500), (C) 3 days (500), and (D) 3 days (5000) [26].

crystals progresses and they cover wider areas, until the whole surface of concrete is fully covered with the DCE crystals [26]. The spacing between the crystals is filled up progressively with time as shown in Fig. 10.7D (under 5000 magnification). The supply of CO_2 to the pores [needed for the third reaction Eq. (10.3)] occurs through air permeation within the established porosity of concrete. For cured concrete, carbon dioxide becomes available within the air phase in the pores. For green concrete, air from the atmosphere occupies the volume originally occupied by water (after its evaporation and/or consumption in the hydration reaction). As the kinetics of the third reaction is dependent on the availability of CO_2, hence its rate within the internal pores is believed to be slower than the rates of the two crystallization reactions [Eqs. (10.1) and (10.2)], due to the limited internal availability of CO_2. Carbon dioxide reaches the reactive site through a slow air permeation process and at a limited diffusion rate, from the surrounding atmosphere. However, carbon dioxide is available at the external surface of the substrate and hence the external surface becomes hydrophobic very quickly. This is why a subsequent application of DCE is not efficient because of limited surface wetting and capillary absorption as indicated in Section 10.3.

The size of the hygroscopic crystals from the first reaction [Eq. (10.1)] increases through crystal interaction with moisture vapor, benefiting from its hygroscopicity (see Chapter 5). This water adsorption process is believed to be mainly contributed by OH groups on the hygroscopic crystals and hence it is considered as a physicochemical process. The level of hygroscopicity is correlated well to the number of OH groups in common hygroscopic compounds [53]. The interaction of the hygroscopic crystal with vapor (adsorption) keeps the crystallization pore blocking mechanism in a dynamic state: the hygroscopic crystals remain active for further interaction with water vapor. For cured concrete, water vapor (from air humidity) is adsorbed onto these crystals. For green concrete, the evaporation of excess mixing water during cement hydration increases vapor availability. The growth process of the hygroscopic crystal has a rate and an equilibrium state (see Chapter 5): the kinetic behavior (the rate of crystal growth with moisture) is believed to be a mass transfer controlled mechanism; as described by Köhler theory [54]. Hence, it is dependent on the internal humidity of concrete. The vapor is consumed in crystal growth and it is retained within pores through a reversible adsorption/desorption process, instead of escaping outside concrete. The equilibrium crystal size (or growth factor) is exponentially dependent on the relative humidity of the surrounding air (see Chapter 5). The equilibrium crystal size can be described by a single hygroscopicity parameter (κ) [55] or by Freundlich adsorption isotherm [55] (see Chapter 5). Experimental curves of hygroscopic crystal size (usually expressed as mass-based hygroscopic growth factor) versus relative humidity are usually available for common hygroscopic materials. The active hygroscopic ingredients in the DCE solution are proprietary and hence their equilibrium behavior is described in generic terms. Fig. 10.8 shows a schematic representation of the relationship between the crystal size and the relative humidity of air in contact with the crystals (e.g., air in capillary pores): a minimal crystal growth is usually observed when the relative humidity is below certain limit (e.g., 30% or 40%). At such a low humidity

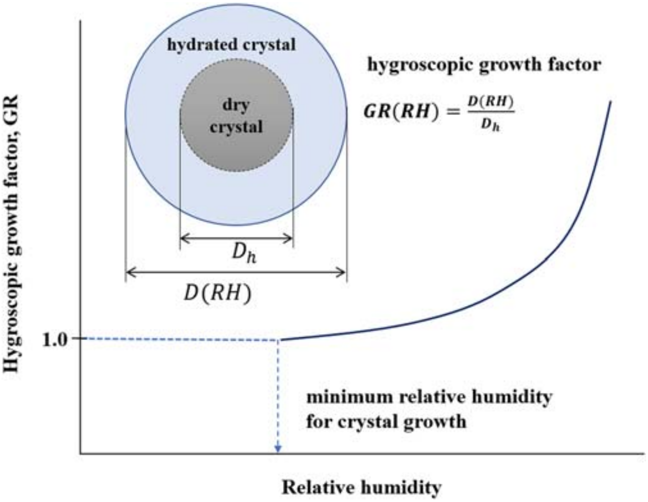


Figure 10.8 Schematic representation of the relationship between the equilibrium crystal size (expressed as hygroscopic growth factor) with relative humidity of air in contact with the crystals (based on definitions and equations detailed in Chapter 5).

condition, the crystal size is nearly equivalent to the size of the unhydrated crystals. This means that at equilibrium conditions of low humidity, the crystals can release most of the adsorbed moisture and retain its original size through the reversible desorption processes. Such a dynamic equilibrium process of water vapor interaction allows concrete breathing, which is an essential process for attaining an acceptable level of concrete dryness. The dependency of crystal size on air humidity creates a reasonably controlled capillary system for vapor permeability. Concrete breathing enhances concrete resistance against durability problems such as biological attacks, which is strongly dependent on air humidity (see Chapter 3) [14]. On the other hand, when a partial water penetration (during concrete service conditions) causes an increase in the humidity of internal air, the active hygroscopic crystals consume water vapor by its adsorption onto these crystals leading to their growth, which enhances pore blocking and prevents any further permeation of water.

The functioning mechanism of the hydrophilic crystals is simply physical swelling. Under damping conditions, the hydrophilic crystals (as porous gels) swell water by their physical interactions with water molecules. This occurs through van der Waals forces or hydrogen bonding. The absorbed water molecules arrange themselves at the internal hydrophilic surfaces of the crystals into layers. Swelling results in crystal expansion and leads to a further blocking of capillary pores and then prevents the subsequent permeation of water. As in the case of hygroscopic crystals, the swelling process has kinetic and equilibrium terms (see Chapter 5): the kinetic behavior is modeled by the Darcian flow of water through a porous medium under capillary suction. Based on flow analysis, the swelling process of the hydrophilic crystals is proportional to the square root of time of exposure to water. There are other empirical models for swelling kinetics reported for other types of hydrogels (e.g., pseudo first-order or second-order models). When the gel structure is elongated upon swelling, elastic stresses are developed within the gel structure and they resist or slow down its expansion under the effect of swelling pressure. Then, an equilibrium swelling behavior is achieved when the opposing depression (capillary) pressure balances the elastic stresses.

When the DCE solution is applied onto fresh concrete, the reversible mechanisms of vapor adsorption and water swelling assist in cement hydration [26,30]. Rahman and Chamberlain [30] highlighted that the DCE material provides a novel method to optimize concrete hydration at the curing stage when applied within about 3 hours following concrete casting: the application of the DCE solution on fresh concrete (grade C40 with w/c=0.45) achieved a strength gain of 5% over control concrete and led to no surface cracks, while the application of a curing compound (alone) achieved 4% [30]. The comparative analysis of Rahman and Chamberlain [30] indicated that the DCE material has a significant role in water retention and can have an additional role as a curing agent during normal curing. They also investigated the combined application of the DCE solution followed by a wax-based curing agent [30]: The combined application of the DCE solution and a curing compound achieved 9% strength enhancement under normal curing conditions [30]. However, under adverse curing conditions (when the specimens were subjected to forced air flux), the combined application of the two materials (the DCE solution and a wax-based curing compound) achieved 74% strength enhancement over control concrete, while the application of the DCE solution alone achieved 11% [30]. Different compressive strength trends were observed for combined treatments for cases with wax-based and liquid curing agents [26]. Protecting fresh concrete with the DCE treatment followed by applying a wax-based curing compound provides better improvement (in terms of concrete strength and resistance to water ingress) than the DCE treatment followed by applying a liquid curing agent. For water-based curing compounds, the application of the DCE solution on concrete (grade C40 with high w/c ratio of 0.48) reduced the percentage strength loss [26]. The DCE material has the ability to increase the level of defense against worse curing conditions and to enhance controlled hydration from the presence of its crystals, which assists in reducing strength loss (compared to control concrete) [26].

Under the service conditions of the DCE treated concrete, both crystals partially block the capillary pores in the cement paste and reduce the total porosity within the treated section. Consequently, the formation of these crystals decreases the fraction and the size of permeable capillary pores, which are responsible for water penetration (see Chapter 2). It has been demonstrated experimentally that treated concrete with the DCE solution has a higher density, a lower porosity, and lower permeable pores [25]. Table 10.2 compares structural characteristics for concrete treated with the DCE solution and nontreated control specimens [25]. The density of the DCE treated concrete is higher than that of untreated concrete by 6%–7%. This is because of the densifying effect of crystal formation and the pore filling mechanism by the precipitation of the products of crystallization

Table 10.2 Densifying effects and porosity reductions using DCE topical treatment on fully cured and old concrete.

Parameter	Percentage (%)
Percentage increase in the density of DCE treated concrete.	6.2−7.1
Percentage decrease in the fraction of permeable pore space.	44−61
Reduction in specific surface area.	7−11

Data from Al-Rashed, R. & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*, *13*, e00408.

Figure 10.9 Large surface cracks (> 1 mm) obtained in adverse curing conditions filled with the DCE crystals at 28 days (when the DCE solution is applied to fresh concrete) [30].

reactions, which occupy part of the empty capillary pores. Such a densifying effect is associated with a reduction in the volume of permeable pores by about 45%–60%. These characteristics lead to a major reduction in water penetration (see Section 10.5.1).

Due to their dynamic interactions with moisture, the two types of crystals can outspread within concrete structure toward any water source occupying the original porosity of concrete or filling developing cracks. The reactivity of the hygroscopic crystals with moisture vapor together with the swelling capacity of the hydrophilic crystals promotes the process of self-healing of cracks. Fig. 10.9 shows the sealing effect of the DCE material (when it is applied to fresh concrete): The large surface cracks (> 1 mm), which resulted at initial curing period under adverse conditions, were filled with the DCE crystals at 28 days of adverse curing regime, while similar cracks in the accompanying untreated concrete remained open [30]. The two types of crystals can occupy the permeable spaces (pores and cracks) and seal them off by crystal growth and expansion (through moisture adsorption and swelling). It is well-known that the rate of water penetration in cracks is much larger than its rate in capillary networks, thus sealing the cracks is more crucial for reducing permeability than just blocking the capillary pores. The dynamic crystallization process has the capability of healing typical

Figure 10.10 A picture of a concrete surface, part of it is treated with DCE materials (right) showing water repellency property, compared to untreated part (left).

concrete cracks that are created during concrete curing or during its service life (see Chapter 3 for types of cracking).

In addition to the aforementioned pore blocking mechanism, the DCE treated concrete repels water and hence assists in reducing capillary absorption. Fig. 10.10 shows a picture of a concrete surface of two sections, one section is treated with the DCE solution and the other section is not treated, displaying the water repellency property of the treated surface. For the nondamped conditions of concrete, the water-repelling layer ensures the dryness of capillary pores and prevents moisture buildup and hence enhances the concrete durability. The produced hydrophobic molecular layer turns out to be an integral constituent of the concrete structure through chemical bonding to the CSH gel and ettringite needles. Such a layer makes the surfaces of the remaining pores water-repellent. The hydrophobic layer is stable and insoluble in water. In fact, it repels water and resists acidic and alkaline solutions.

10.5 The dual-crystallization waterproofing engineered performance

In general, minimizing water penetration through concrete enhances concrete resistance against thermal, chemical, and biological attacks. Both pore blocking, by crystal formation and growth, and pore lining by creating a water-repellent layer decrease liquid water penetration by permeation flow and capillary absorption, which is then reflected in minimizing most of water-related problems in concrete. In addition, the dynamic interactions of the crystallization system provide an effective continuing solution to water-associated problems: evaluating the efficiency of the DCE system requires direct and indirect WP testing methods, as commonly demonstrated for other integral WP materials [56] (see Chapter 7). Direct methods include structural characteristics (such as porosity as given in Section 10.4) and measuring water absorption and permeability as described in Section 10.5.1. Indirect methods include measurements of other transport properties: some of which are considered as indirect tests of durability characteristics (e.g., ionic diffusivity). The following subsections describe the durability performance characteristics including resistance to penetration of chloride ions, salt scaling, ASR, cycles of freezing and thawing, and biochemical deterioration. In addition, the effect of the DCE treatment on the mechanical characteristics of concrete are described. These include compressive, tensile and flexural strengths, abrasion resistance, and skid resistance.

10.5.1 Waterproofing efficiency

The DCE system achieves major reductions in water penetration as a result of the structural modifications described in Section 10.4 (i.e., 6.2%–7.1% increase in the density and 44%–61% decrease in permeable pore space). The WP performance of the DCE treated concrete was tested by measuring water absorption according to ASTM 642 [57], ASTM D6489 [58], or Initial Surface Absorption Test (ISAT) BS1881–208 [59] or by determining the water permeability under a pressure of 14 MPa (200 psi) according to CRD-C 48-92 [60] or under a pressure of 0.5 MPa according to BS EN 12390 Part 8 [61]. The performance of the DCE was also tested using mortar specimens according to ASTM C1585 [62]. Table 10.3 lists the percentage reductions in water absorption and permeability with the DCE material obtained from these types of tests.

The percentage reduction in water absorption for the application of the DCE material on concrete tested according to ASTM C642 [57] is in the range of 60%–75%. A similar performance of reduction in water absorption was reported for DCE when tested according to ASTM D 6489-99 [37,39]. The effect of the DCE treatment on reducing the water absorption of treated mortar specimens tested according to ASTM C1585-13 is shown in Fig. 10.11 [34]. A lower percentage reduction in water absorption was obtained when the DCE solution was applied to mortar samples [34]. The higher performance for concrete application can be due to a significant densifying effect within the Interstitial Transition Zone between the coarse aggregate and the paste in concrete specimens. Xiao et al. [34] concluded that densification-based sealers (i.e. lithium silicate) and crystalline water proofer (referring to the DCE) were less sensitive to application rate and condition. Increasing the application rate did not provide a substantial reduction in the water absorption. The ranges of percentage reductions in water absorption using the DCE material are greater than those reported for traditional hydrophilic crystalline sealers; the reported decrease in the sorptivity was 17.0% for sodium silicate and 7.8% for magnesium fluorosilicate [52] (see Chapter 9). The ranges of the percentage reductions using the DCE material are even larger that the case for soaking the concrete surface with sodium silicate sealer for 1 hour, for which a 30% reduction in water absorption was reported [40]. The water absorption of concrete subjected to a water head of 7 cm, according to ASTM D6489–99 [58], is shown in Fig. 10.12 [37,39]. Fig. 10.12 compares the DCE treatment with other treatments of fluoropolymer and silicate sealers. The DCE treatment achieved 77% after 24 hours of immersion and 63% after 48 hours of immersion [37,39]. Nevertheless, after 48 hours of

Table 10.3 Waterproofing performance of the DCE treatment on fully cured and fresh concrete.

Parameter	Standard	Tested cementitious materials	Performance (percentage reduction, %)
Water absorption at normal temperature.	ASTM C642 [57]	Fully cured concrete beam and cylindrical specimens of hardened concrete with w/c = 0.5 [25].	60–75
Water absorption after immersion and boiling.	ASTM C642 [57]	Fully cured concrete beam and cylindrical specimens of hardened concrete with w/c = 0.5 [25].	47–64
Water absorption after 24-hour immersion.	ASTM D6489 [58]	Fresh concrete (grade C40 with w/c = 0.46) [37,39].	77
Water absorption after 48-h immersion.	ASTM D6489 [58]	Fresh concrete (grade C40 with w/c = 0.46) [37,39].	63
Water absorption in mortar.	ASTM C1585 [62]	Mortar specimens with various coverages and numbers of applications of the DCE solution [34].	37–56
Sorptivity after 1-hour exposure to a water head of 20 cm.	ISAT BS1881–208 [59]	Fresh concrete (grade C40 with w/c = 0.46) [37,39].	95
Permeability under a pressure of 0.5 MPa (74 psi).	BS EN 12390–8 [61]	Fresh concrete (grade C40 with w/c = 0.48): the water penetration depth for control specimens was 59 mm and 37 mm for adverse and favorably cured concrete, respectively, while no water penetration was detected for the DCE treated concrete in both cases of curing conditions [26].	About 100
Permeability under a pressure of 14 MPa (200 psi).	CRD-C 48–92 [60]	Fresh concrete (Iowa DOT C4) after standard curing for 24 hours then heat-curing at 150°F (66°C) till 28 days: the permeability coefficient for control concrete was 6.3410^{7} and that for treated concrete was $3.89\ 10^{9}$ (data from a certified testing report issued by CMT dated May 2021).	99.4

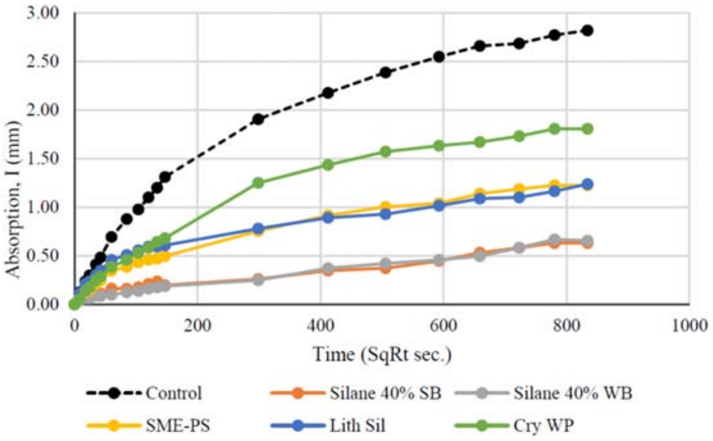


Figure 10.11 Water absorption for DCE treated mortar (green) compared to that of nontreated mortar (black) and to other types of treatments including silane and silicate sealers [applied to clean and dry mortar at 4.9 m^2/L (200 ft^2/gal) and tested according to ASTM C1585–13] [34].

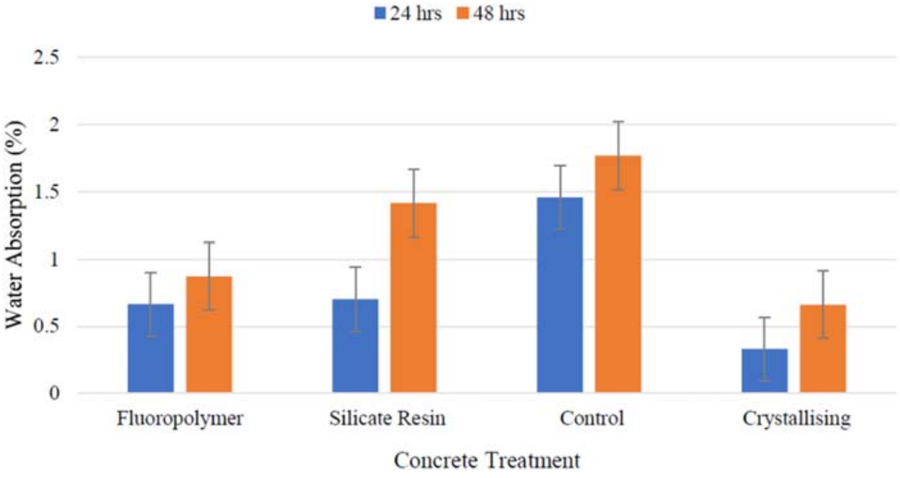


Figure 10.12 Water absorption of concrete subjected to a water head of 7 cm according to ASTM D 6489-99 after 24 and 48 h of immersion: comparing control concrete with concrete treated with the DCE material (labeled as crystallizing material), fluoropolymer, and silicate sealers [39].

immersion, fluoropolymer and silicate treated concrete achieved lower percentage reductions of 51% and 20%, respectively [37,39]. Results of sorptivity from ISAT according to BS 1881–208 are shown in Fig. 10.13 for control and DCE treated concrete subjected to a water head of 20 cm (also shown are results of

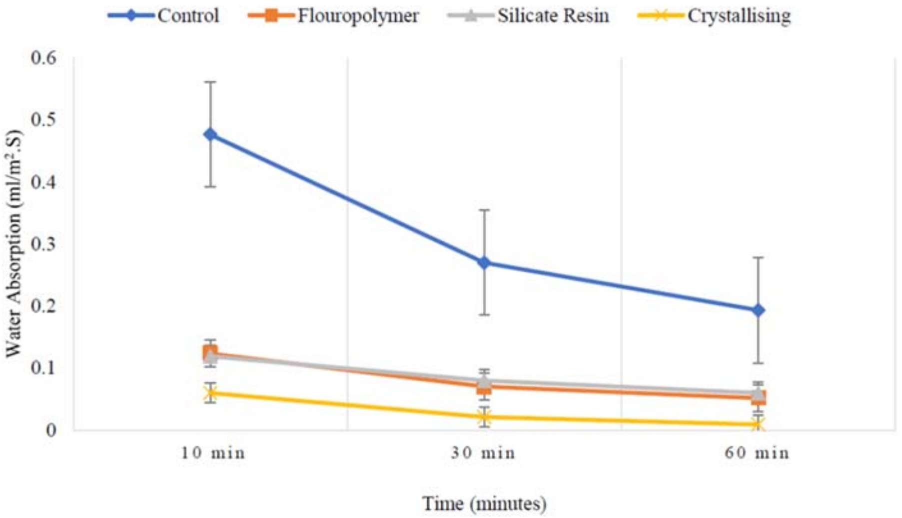


Figure 10.13 Water absorption rates (from ISAT according to BS 1881-208) for control concrete and concrete treated with the DCE (labeled as crystallizing material), fluoropolymer, and silicate resin [39].

fluoropolymer and silicate sealers). The DCE material achieved a 95% efficacy in reducing sorptivity after 1 hour from water exposure while fluoropolymers and silicate resins achieved about 69% [37,39].

For the purpose of comparison, it is worth recalling that the reduction in sorptivity with typical hydrophobic organosilicon sealers is usually higher than 90% [19,50] (see Chapter 8). However, the water absorption test is only suitable for evaluating the reduction in capillary action (under a none or a low hydrostatic pressure). In addition, some crystalline WP material can increase the water absorption in concrete compared to control samples as reported by Xiao et al. [34] for lithium silicate sealers. Under harsh curing conditions, the water absorption of the DCE treated concrete can outreach that of control concrete due to water interaction of crystals [26]. Hence, evaluating the WP performance based on testing water absorption does not provide accurate comparative measures for permeability-based performance as encountered in damped structures. Even in partially wetted structures such as pavements and building walls, a hydrostatic pressure can be encountered from tire loading and from wind effects (see Chapter 6). Consequently, the WP performance of pore-blocking crystalline materials must be evaluated based on permeability tests under a hydrostatic pressure (as their function is mainly restricting the permeation flow rather than reducing capillary suction). The DCE treated concrete tested under a pressure of 14 MPa (200 psi) according to CRD-C 48–92 [60] achieved over 99% reduction in the permeability coefficient. A similar high performance was reported for the DCE treated concrete when tested under a pressure of 5 bar (0.5 MPa) in accordance with BS EN 12390 Part 8 [61]: no water penetration was detected for the DCE treated concrete while an average water penetration depth of 59 mm and 37 mm were reported for adverse and favorably cured control concrete specimens, respectively [26].

10.5.2 Dual-crystallization waterproofing engineered enhancement of concrete resistance against chloride ion penetration

Reducing the permeability of the DCE treated concrete is associated with a major reduction in chloride ion penetration [25,29,32]. Chloride attack occurs by a combination of chemical reaction, mass transfer (diffusion), and water permeation [8]. Chloride ions come from deciding salts or from other natural sources such as sea water [21] or from aggregates that naturally contain chloride salts [63]. The formations of the DCE crystals and the DCE hydrophobic layer reduce the diffusivity of chloride ions and hence enhance concrete resistance for corrosion of steel bars and decrease chloride binding (adsorption on the C–S–H and ettringite crystals) [64]. The consequences of such a corrosion process include cracking, spalling, delamination, and bleeding [1]. The diffusivity of chloride ions in treated concrete was determined indirectly by measuring the passage of the electrical current (according to ASTM C1202) [65]. Chloride ion penetration was also determined by salt bonding experiments. The concentration profile of chloride was determined according to AASHTO T 259 and the chloride ion content is determined in accordance with AASHTO T 260. The reported results of DCE treatment reflects its role in improving the integrity of concrete and reducing porosity and water permeability in addition to diffusivity for chloride ions. The dynamic hygroscopic crystallization system consumes free moisture in the pores and thus eliminates the medium for the activity of chloride ions. In addition, the hydrophobicity of the DCE treatment maintains relatively dry concrete conditions, which also assists in preventing the continuity of the water medium. It has been reported that the ionic diffusivity of chloride ions is strongly dependent on the level of concrete saturation [8,66] (see Chapter 2). Decreasing the moisture content in concrete causes disconnections in the water-filled path within concrete capillaries. Table 10.4 lists the total charge passed and the estimated percentage reduction in chloride ion penetration in various concrete specimens (with the DCE applied to fully cured and to fresh concrete specimens) tested according to ASTM C 1202 [24,25]. Low values of charge passage provide an indirect indication of a low ionic penetrability and less susceptibility to chemical attack. According to ASTM C 1202 [65], negligible chloride ion penetration is classified when the total charge passage is <100 coulombs, very low chloride ion penetration is classified when the total charge passage is in the range of 100–1000 coulombs, and low chloride ion penetration is classified when the total charge passage is in the range of 1000–2000 coulombs (see Chapter 7). Table 10.4 includes results of reference concrete specimens with various levels of chloride ion penetrations: the DCE

Table 10.4 Total charge passed and the estimated percentage reduction in chloride ion penetration in concrete treated with the DCE material tested according to ASTM C 1202.

DCE application	Type of concrete specimen	Total charge passed (coulombs)		Percentage reduction in chloride ion penetration (%)
		Untreated concrete	Treated concrete	
On cured concrete [25]	High porosity—fully cured specimens.	4143	1927	54
On old concrete [25]	Low porosity cored specimens.	145	62.0	57
On freshly poured concrete [24]	Low porosity specimens with the DCE solution applied on NaCl or NaOH side.	646	13–8	9798
On freshly poured concrete [24]	Low porosity specimens with the DCE solution applied on NaCl and NaOH sides.	646	60	90

treatment on freshly poured concrete reduces the chloride ion penetration by more than 90% [24]. Lower percentage reductions (within the range of 54%–57%) were obtained when the DCE solution was applied on fully cured and existing old concrete (for cored samples from existing pavements) [25].

Direct tests of chloride ion penetration (according to AASHTO T 260) indicated that the percentage reductions in chloride ion concentration in concrete at two different depths was about 56% for the DCE treatment of cured concrete [25]. Rahman et al. [32] reported the profiles of chloride content after 60 days of salt ponding after the DCE is applied onto dry concrete of high porosity (grade C25) and low porosity (grade C40) as shown in Fig. 10.14. The percentage reduction in the total chloride content after 60 days of salt ponding are close for the two cases: 60% reduction was obtained for low strength concrete (grade of C25) and 59% reduction was obtained for high strength concrete (grade of C40) [32]. For the same types of concrete specimens (C25 and C40) treated with hydrophobic silane-based sealer, the reduction in the total chloride content was about 40%. This indicates that the DCE treatment can lead to better resistance against chloride ion penetration (and consequently better performance against the associated corrosion problems) than traditional hydrophobic sealers due to the combined pore blocking and lining mechanisms. Fig. 10.14 shows that at 25 mm depth, the DCE treatment leads to about 85% reduction in chloride ion concentration, while the silane-based sealer leads to about 50% [32].

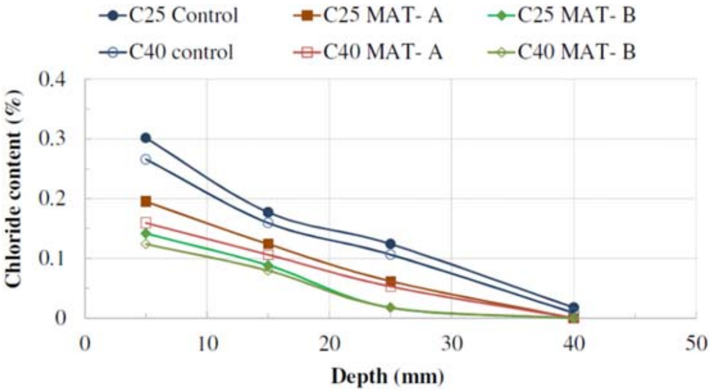


Figure 10.14 Profiles of chloride content after 60 days salt ponding for high porosity low strength concrete (grade of C25) and for low porosity concrete (grade of C40) [32].

10.5.3 Enhancement of concrete resistance against ASR

The DCE treatment has a significant role in reducing concrete deterioration by the ASR [24]. Generally, the DCE treatment leads to a high dimensional stability resulting from its pore blocking and lining effects, which reduce water penetration and moisture content in concrete. In saturated concrete, the ASR involve a group of lethal chain reactions between the solubilized alkalis and the reactive silica solubilized from the aggregates. The ASR lead to the formation of an expansive gel that endorses concrete cracking [1], causing a larger water suction and a further cracking with additional fatal ASR [67,68]. ASR are the most serious durability problems of concrete pavements [3]. The rate of ASR attacks is dependent on the alkalinity of the pore solution and the level of relative humidity (must be $>80\%$), as the water medium can serve as a diffusion medium for the solubilized alkalis and silica [1]. The DCE treatment can reduce the severity of these conditions, which are favorable for the ASR: The DCE performance against the ASR is primarily initiated by the reactivity of the DCE active ingredients, which partially consumes the calcium hydroxide (through the crystallization reactions 10.1 and 10.2). Furthermore, the DCE crystals reduce the availability of free water by consuming the moisture in crystal growth. Reducing the level of concrete saturation decreases the solvation of calcium hydroxide and hence the severity of the pore solution for ASR attacks. Consequently, the mechanism of ASR mitigation by the DCE treatment combines the reduction of reaction activities (reactants and medium) by (1) discontinuing the moisture phase (which is the vehicle for aggressive ions and the medium for ASR activities, (2) decreasing the alkalinity of the pore solution, and (3) the hydrophobicity of the DCE system that minimizes the wetting of the aggregates and thus reduces the contact of the alkaline pore solution with the silica content.

The level of enhancement of concrete resistance against the ASR is commonly evaluated by measuring the length change of mortar specimens in accelerating alkaline conditions according to aggressive tests of ASTM C1260 [69] or ASTM C1567 [70].

Fig. 10.15 compares the percentage length change for two types of aggregates (classified as reactive and nonreactive) [24]. According to ASTM C1567 [70], an allowable limit of 0.1% ASR expansion at 16 days (or 14 days according to some literature) [68,4] is set to indicate a low risk of deleterious expansion under field conditions. For concrete made with nonreactive aggregates (Ames Mine), Fig. 10.15A shows that the percentage length change (for both treated and untreated specimens) is lower than the allowable limit set by the ASTM C1567 (percentage expansion 0.1% at 14 or 16 days) [70]. However, significant reductions in the ASR expansion were obtained when the DCE was applied. On the other hand, for concrete made with reactive aggregates (Platte River gravels), Fig. 10.15B shows that the 14-days percentage length change of the untreated specimens is much higher than 0.1%, while that for the DCE treated specimens is close to 0.1%. When the percentage expansion falls within the range of 0.1%–0.2%, the ASTM C1567 test is considered inconclusive, and hence the

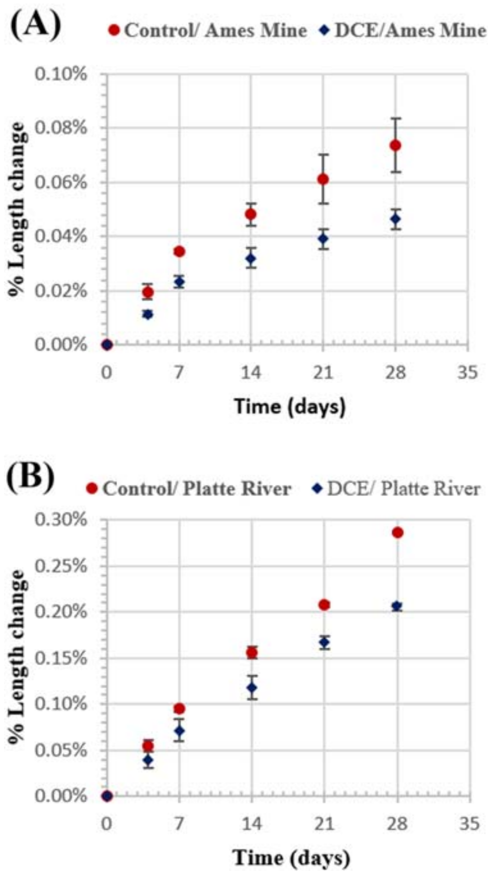


Figure 10.15 Percentage length change from ASR for two types of aggregates (from Ames Mine and Platte River) at w/c of 0.39, from tests according to ASTM C-1567 [24].

aggregates require further testing to finalize a conclusion whether or not they are reactive [67,68]. This is usually done using a 1-year testing according to ASTM C1293 [71]. However, previous records of the Platte River gravels confirmed their ASR reactivity.

Some researchers believe that the exposure period of 16 days is not sufficient for confirming the low risk of aggregates reactivity [3]. Hence, the use of 0.10% expansion limit at 28 days is recommended for indicating low ASR risk in the field condition [4]. Fig. 10.16 shows the percentage length change at 28 days as functions of w/c ratio for the aforementioned two types of aggregates [24]. Increasing the w/c

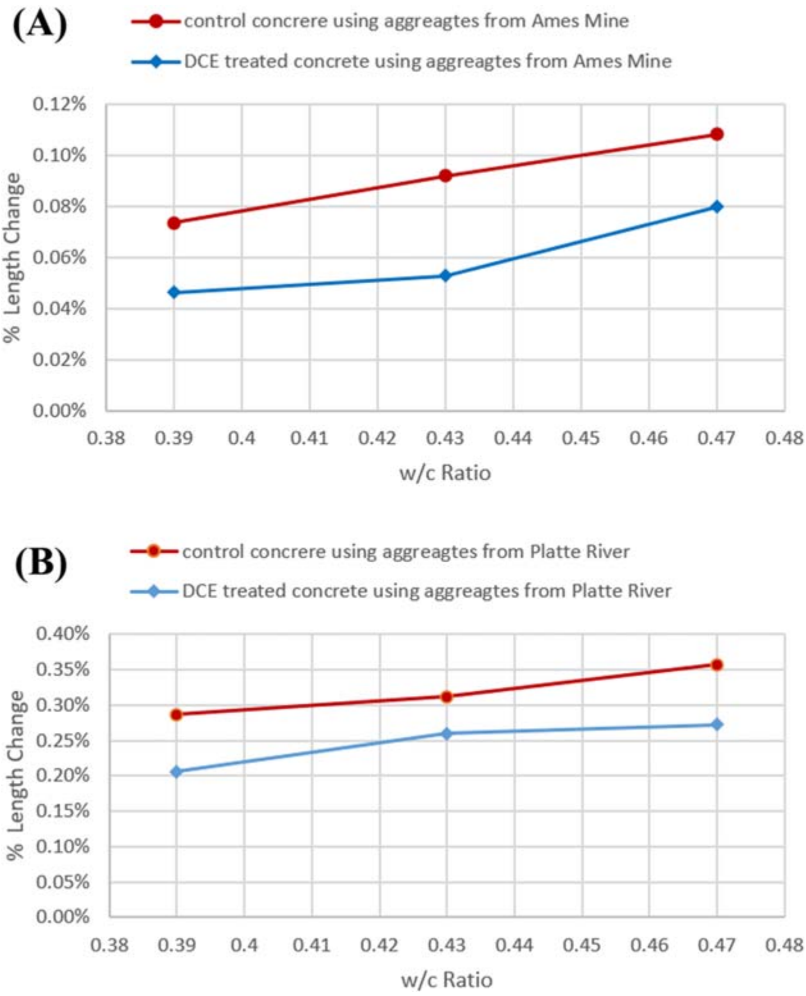


Figure 10.16 Percentage length change after 28 days exposure to ASR environment as functions of w/c ratios, for two types of aggregates (Ames Mine and Platte River), from tests according to ASTM C-1567 [24].

ratio increases the damages from ASR due to the increase in the porosity, as it is well-documented in literature (see Chapter 3). However, at all investigated w/c ratios, the DCE treatment reduces the ASR damage noticeably. The percentage reductions in the length change for the two types of aggregates were within the range of 20%–43%. This ability for ASR mitigation by crystalline WP is distinctively reported for the DCE treatment; no ASR testing was reported for hydrophilic or hydrophobic WP materials in the reviewed articles surveying the durability of concrete [41,42,72,73,74] or in recent research papers investigating the performance of crystalline admixtures [75−79] (see Chapters 8 and 9).

10.5.4 Enhancement of concrete resistance against cycles of freezing and thawing

The role of the DCE treatment in reducing water penetration and the active interactions of the dynamic crystalline system with moisture lead to major reductions in concrete deterioration under cycles of freezing and thawing [25,29,36]. The DCE mechanisms consume most of the available free moisture in concrete pores in a further crystal growth, and hence the availability of water for phase change into ice under freezing cycles is minimal. Hence, the harmful expansions and the severity of the associated internal stresses are decreased. The performance of the DCE treatment in increasing concrete resistance against cycles of freezing and thawing in water was tested according to ASTM C666 [80] and ASTM C1262 [81], and in the presence of deicing salts according to ASTM C672 [82].

Concrete deterioration under repeated cycles of freezing and thawing are shown Fig. 10.17 in terms of percentage length change and in terms of weight loss for the DCE treated and control concrete specimens [25]. The positive effect of the DCE pore blocking crystals starts to appear after 100 cycles in terms of reduced weight loss, while it starts to be more obvious after a lower number of cycles in terms of length change. After 300 cycles, the DCE treatment achieved 57% reduction in length change and about 100% percentage reduction in weight loss, as no change in the weight of the DCE treated specimen could be detected. Fig. 10.17 shows that the percentage length change of the untreated specimen at 300 cycles was close to the maximum allowable limit set by ASTM C666 (i.e., 0.10%) [80]. However, the DCE treatment reduced the percentage length change below the ASTM C666 limit significantly. The higher level of protection against cycles of freezing and thawing could be obtained when the DCE was applied to cured concrete with high moisture contents than when it is applied to a fully dry surface [36]. Fig. 10.18 compares the penetration depth of fluorescent sodium dye solution in the DCE treated and in the untreated extracted core buttons of concrete (grade C40) after 80 cycles according to ASTM C1262 [29]. It is apparent that a significant penetration depth can be seen in the control cored specimen while no noticeable penetration depth can be seen for the DCE treated cored sample. This provides a visual confirmation on the structural stability of the DCE treated concrete and the functional ability of the pore blocking crystals after the tested 80 cycles of freezing and thawing [29]. The stability of the

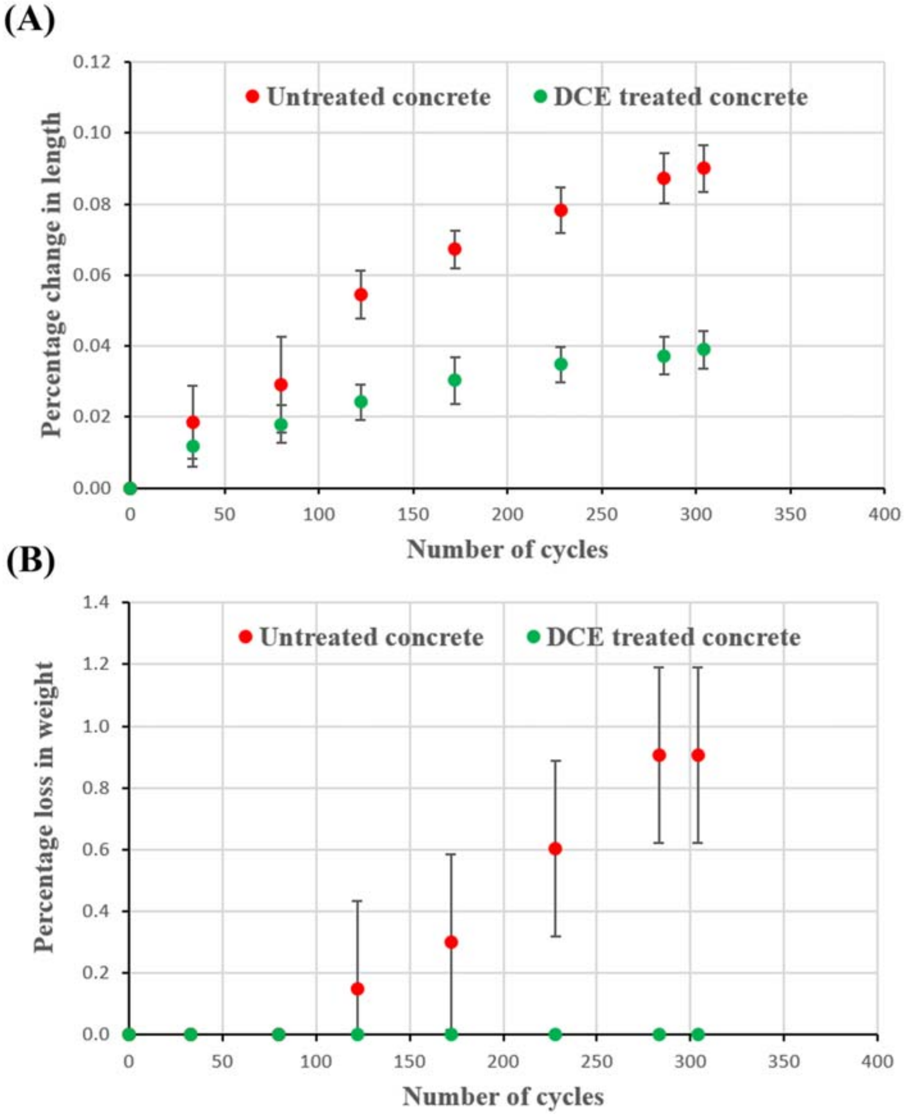


Figure 10.17 Percentage length change (A) and percentage weight loss (B) as functions of number of freezing and thawing cycles for the DCE treated and untreated concrete samples (the DCE was applied on fully cured concrete) from tests according to ASTM C666 [25].

DCE treated concrete (grade C40 with w/c=0.46) after freezing and thawing has been further confirmed by obtaining significantly low sorptivity (from ISAT experiment according to BS 1881–208) for the DCE treated concrete compared to untreated concrete [36]. ISAT experiments were done after subjecting the samples to harsh environmental impacts of a huge number of freezing and thawing cycles

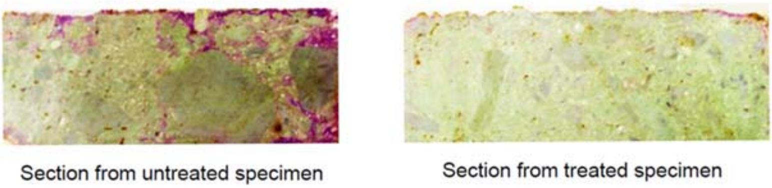


Figure 10.18 Penetration depth of fluorescent sodium dye solution in the DCE treated and untreated extracted core buttons of concrete (grade C40) after 80 cycles according to ASTM C1262 (after soaking in dye for 96 h) [29].

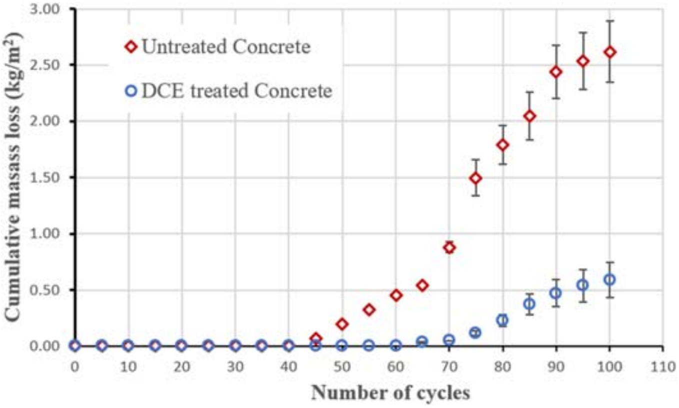


Figure 10.19 Cumulative mass loss as a function of number of freezing and thawing cycles in deicing salts from tests according to ASTM C672, for the DCE treated and untreated concrete samples (for the DCE application on freshly poured) [24].

(over 1000 cycles) in two approaches including air temperature alteration and water temperature alteration. Compared to other investigated systems (including silanes), the DCE treatment was shown to provide concrete with the highest level of protection when it was applied to saturated cured concrete [36]. After about 1000 cycles of freezing and thawing (in water), the estimated percentage reduction in sorptivity (at 60 minutes water exposure) was over 90%. These reported results confirm the stability of cement paste and the DCE crystalline structure under the tested harsh thermal impacts.

A similar role of the DCE treatment for enhancing concrete resistance against freezing and thawing in the presence of deicing salts was reported [29]. Fig. 10.19 shows results of scaling (as cumulative mass loss) of the DCE treated and control concrete surfaces exposed to freezing and thawing cycles in the presence of deicing salts from tests according to ASTM C672 [82]. A major percentage reduction in the cumulative mass loss for the DCE treated is obtained. The percentage reduction in mass loss increases with increasing the number of cycles. Treating the concrete surface with the DCE solution reduces the scaling damage by about 50% after 100 cycles. Again, this is mainly because of the reduction in water permeability of concrete from the surface as a result of the effective crystallization mechanism of the DCE and the reduction in chloride ion penetration, as discussed in Section 10.5.2. In addition, reducing water penetration reduces the impact of internal stresses by freezing.

10.5.5 Enhancement of concrete resistance against biological degradation by mold growth

Concrete treated with the DCE solution is reported to be resistant to mold growth with a zero growth rate [25]. The testing protocol (MIL-STD 810 G) classifies growth rating based on the level of mold growth (see Chapter 3). Trace growth may be defined as scattered, sparse fungus growth and assigned a rate of one. The fungal resistance of the DCE treated and control concrete specimens tested according to MIL-STD 810 G are summarized in Table 10.5 [25]. For the untreated control specimen, trace growth of fungus was given the rate of one, while a zero rate was given for the DCE treated specimen as it did not show any visible growth of fungus for both cases of treatments. This zero rating was obtained although the experimental conditions of temperature and relative humidity were confirmed to be conducive to mold growth [25]. Such a resistance to biological attack with the DCE treatment is believed to result from the major reductions in moisture content in the DCE treated surface and the lack of an available carbon source to provide nutrients for growth. Considerable reductions in the profile of internal humidity are reported for a similar crystallization WP technology (see data in Chapter 11). The relative dryness of the concrete pores through the dynamic hygroscopic crystal growth reduces the availability of water as the essential medium for the activity of mold and mildew growth. In addition, preventing moisture buildup on the subsurface of the concrete through the hydrophobicity of capillaries network assists in preventing hosting mold growth [25]. This capability of the DCE treatment for resisting biological attack of concrete is uniquely reported for the DCE material; no data for resistance of mold growth were reported for hydrophilic or hydrophobic materials in the review papers on the durability of concrete [41,42,72–74] or for the performance of crystalline admixtures [75–79] (see Chapters 8 and 9).

Table 10.5 Fungal resistance of the DCE treated concrete and control specimens tested according to MIL-STD 810 G [25].

Specimen	Inoculation	Fungus growth observation	Rating according MIL-STD 810 G
MCE treated concrete	After MCE treatment	None	0
MCE treated concrete	Before MCE treatment	None	0
Untreated	Control	Traces of growth	1

10.5.6 Effects of dual-crystallization waterproofing engineered treated on the mechanical characteristics and serviceability of concrete

The surface application of the DCE solution on fresh concrete shows no negative impacts on concrete mechanical properties as the DCE material does not interfere with the hydration reactions within the bulk of concrete [24]. The DCE setting reactions occur within the surface concrete layer. The crystallization reactions start to occur after a sufficient cement hydration has occurred and when the pore structure is established. In fact, the growth of hygroscopic crystals requires air-filled pores so that the crystals can suck the moisture from the pore space. In principle, the topical treatment of the fully cured concrete with the DCE solution is hypothesized to cause no noticeable difference in the compressive strength between treated and untreated concrete. Reported compressive strength for control and the DCE treated mortar specimen after 195 days were within less than 1% difference confirming that the partial utilization of water for crystallization does not interfere with the hydration process. On the other hand, when the DCE solution is applied to fresh concrete, the reversible water interaction behaviors of the crystals (vapor adsorption and swelling) assist in cement hydration [26,30] (see Section 10.4). For normally cured concrete (of grade C40 with w/c=0.45), the application of the DCE solution on fresh concrete achieved a strength gain of 5% over control concrete confirming the DCE role in water retention during curing [30]. In addition, the combined application of the DCE solution and a curing compound achieved 9% strength enhancement [30]. On the other hand, the DCE treatment was shown to reduce the percentage of strength loss under adverse curing conditions (forced air flux), as it increases the level of defense against worse curing conditions [26]. The combined application of the DCE solution and a wax-based curing compound under adverse curing conditions achieved 74% strength enhancement [30]. The combined application of the DCE treatment followed by the application of a curing compound assists in maintaining a suitable curing environment for concrete. Improving water retention assists in better hydration. The moisture retaining ability of fresh mortar specimens is improved by the application of the DCE solution and a curing compound by 37%–48% [24]. Retaining water in the fresh concrete is essential for enhancing the cement hydration process, and for attaining the required strength. This would prevent shrinkage, cracking, and the loss of abrasion resistance of the cured concrete. In addition, the water remains available for crystallization growth.

The effect of applying the DCE treatment on fully cured and old concrete on other mechanical properties was also demonstrated. It was found that there were no major differences in the pull-off strength for the DCE treated and untreated concrete. Concrete treated with the DCE solution showed no measurable loss in bond strength. This is because the mechanical strength of concrete results from its hydration reactions, while there is no involvement of crystallization treatment in this process. The DCE treated concrete has slightly higher abrasion resistance than the untreated concrete. The DCE treatment improves the abrasion resistance of concrete slightly due to its densifying effect and due to converting part of the calcium hydroxide into pore blocking crystals, which enhances concrete integrity and thus makes it harder. Under the same testing conditions of abrasion, the untreated concrete loses extra mass by about 7% [25]. In addition, the application of the DCE solution on old concrete causes no or little effect on the pull-off strength [25], while when applied on fresh concrete it can improve the surface adhesion strengths of treated concrete by about 13% (according to ASTM D7234) [83]. This is explained by the dryness of the surface as a result of the consumption of any available moisture content in crystal growth [24]. A small reduction in the coefficient of friction (5.3%) for the DCE treated concrete compared to that of untreated was reported (from horizontal-pull slipmeter test according to ASTM F609) [25,84]. Similarly, a minor reduction in the British pendulum number (7.3%) was observed for the DCE treated specimens. These slight reductions in the coefficient of friction, and in the British Pendulum number, are explained by the crystal growth and filling part of the surface roughness.

References

[1] Fernandes, I., & Broekmans, M. A. (2013). Alkali–silica reactions: An overview. *Part I. Metallography, Microstructure, and Analysis*, *2*(4), 257–267.

[2] Hobbs, D. W. (2015). *Alkalisilica reaction in concrete*. London, UK: Thomas Telford Publishing.

[3] Saha, A. K., et al. (2018). The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials*, *171*, 743–758.

[4] Thomas, M. D., Fournier, B. & Folliard, K. J. (2008). Report on determining the reactivity of concrete aggregates and selecting appropriate measures for preventing deleterious expansion in new concrete construction. United States. Federal Highway Administration.

[5] Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C. (2002). Design and control of concrete mixtures (Vol. 5420). Skokie, IL: Portland Cement Association.

[6] Tran, P. C., et al. (2018). Carbonation proofing mechanism of silicate-based surface impregnations. *Journal of Advanced Concrete Technology*, *16*(10), 512–521.

[7] Porras, Y., Jones, C., & Schmiedeke, N. (2020). Freezing and thawing durability of high early strength Portland cement concrete. *Journal of Materials in Civil Engineering*, *32*(5).

[8] Jianxia, S. (2012). 6.14 - Durability design of concrete hydropower structures. In A. Sayigh, (Ed.), Comprehensive renewable energy (pp. 377–403). Oxford: Elsevier.

[9] Mingyu, H., Fumei, L., & Mingshu, T. (2006). The thaumasite form of sulfate attack in concrete of Yongan Dam. *Cement and Concrete Research*, *36*(10), 2006–2008.

[10] Glass, G., & Buenfeld, N. (2000). Chloride-induced corrosion of steel in concrete. *Progress in Structural Engineering and Materials*, *2*(4), 448–458.

[11] Santhanam, M. & Otieno M., (2016). 5—Deterioration of concrete in the marine environment. In M.G. Alexander (Ed.) *Marine concrete structures*. Woodhead Publishing. p. 137–149.

[12] Javaherdashti, R., et al. (2009). On the impact of algae on accelerating the biodeterioration/biocorrosion of reinforced concrete: A mechanistic review. *European Journal of Scientific Research*, *36*(3), 394–406.

[13] Lence, A., et al. (2014). Best practices for maintenance of concrete bridge elements against mold and mildew growth. In *Proceedings of the construction research congress*: Atlanta Georgia, USA.

[14] Viitanen, H., et al. (2010). Moisture and bio-deterioration risk of building materials and structures. *Journal of Building Physics*, *33*(3), 201–224.

[15] Biparva, A., & Gupta, R. (2010). Smart waterproofing system: A review. *Proceedings of the International Conference on Future Concrete*.

[16] Jalali, U. H., & Afgan, S. (2018). Analysis of integral crystalline waterproofing technology for concrete. *International Research Journal of Engineering and Technology (IRJET)*, *5*(10).

[17] ACI. (2016). *Committee 212, ACI 212. 3R-16 Report on chemical admixtures for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[18] ACI. (1986). *Committee 515, ACI 515.1R-79 A guide to the use of waterproofing, dampproofing. Protective, and decorative barrier systems for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[19] Mundo, R. D., et al. (2020). Recent advances in hydrophobic and icephobic surface treatments of concrete. *Coatings*, *10*(5), 449.

[20] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[21] Mehta, P. K. (1991). *Concrete in the marine environment*. Boca Raton, FL, USA: CRC Press.

[22] Kubal, M. T. (2008). *Construction waterproofing handbook*. New York, USA: McGraw-Hill Education.

[23] Al-Rashed, R., (2008). *Aqueous chemical mixture to mitigate water associated problems in concrete pavements*. USA Patents.

[24] Al-Rashed, R., & Al-Jabari, M. (2021). Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete. *Case Studies in Construction Materials*, *15*, e00635.

[25] Al-Rashed, R., & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*, *13*, e00408.

[26] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2018). A novel approach of introducing crystalline protection material and curing agent in fresh concrete for enhancing hydrophobicity. *Construction and Building Materials*, *160*, 644–652.

[27] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2018). Development of hydrophobic concrete by adding dual-crystalline admixture at mixing stage. *Structural Concrete*, *19*(2).

[28] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2018). Remediation and protection of masonry structures with crystallising moisture blocking treatment. *International Journal of Building Pathology and Adaptation*, *36*(1), 77–92.

[29] Chamberlain, D.A. & Boswell, L.F. (2005). The use of pavix CCC100 as a reinforced concrete impregnate and as an alternative to silane. In *Performance based rehabilitation of reinforced concrete structures conference*. Prague, Czech Republic.

[30] Rahman, M., & Chamberlain, D. (2016). Application of crystallising hydrophobic mineral and curing agent to fresh concrete. *Construction and Building Materials*, *127*, 945–949.

[31] Rahman, M., & Chamberlain, D. (2017). Performance of crystalline hydrophobic in wet concrete protection. *Journal of Materials in Civil Engineering*, *29*(6), 04017008.

[32] Rahman, M., et al. (2016). Moisture efficacy of impregnant in concrete protection. In Transportation research board 95th annual meeting.Washington DC, United States.

[33] Wells, D., et al. (2014). *Sealants, treatments and deicing salt practices to limit bridge deck corrosion and experimental deck sealants and pier cap coating on interstate 471*.

[34] Xiao, D. X., et al. (2020). *Evaluation of penetrating sealers applied to saw cut faces in concrete pavement joints*. Wisconsin, USA: Wisconsin Highway Research Program.

[35] Al-Kheetan, M. J., et al. (2020). Development of low absorption and high-resistant sodium acetate concrete for severe environmental conditions. *Construction and Building Materials*, *230*, 117057.

[36] Al-Kheetan, M. J., et al. (2020). Resistance of hydrophobic concrete with different moisture contents to advanced freeze–thaw cycles. *Structural Concrete*, *22*, E1050−E1061.

[37] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2019a). *A-2–4 Comparative study of different hydrophobic materials in concrete pavement protection*.

[38] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2019b). Fundamental interaction of hydrophobic materials in concrete with different moisture contents in saline environment. *Construction and Building Materials*, 207, 122−135.

[39] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2019c). Moisture evaluation of concrete pavement treated with hydrophobic surface impregnants. *International Journal of Pavement Engineering*, 1−9.

[40] Thompson, J. L., et al. (1997). Characterization of silicate sealers on concrete. *Cement and Concrete Research*, *27*(10), 1561−1567.

[41] Pan, X., et al. (2017). A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578−590.

[42] Pan, X., et al. (2017). A review on surface treatment for concrete—Part 2: Performance. *Construction and Building Materials*, *133*, 81−90.

[43] ACI. (2013). *Committee 515, ACI 515.2R-13 Guide to selecting protective treatments for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[44] Gyu-Yong, K., et al. (2009). Evaluation of properties of concrete using fluosilicate salts and metal (Ni, W) compounds. *Transactions of Nonferrous Metals Society of China*, *19*, s134−s142.

[45] Jones, J. W. & Maxfield, P., (2002). *Method of hardening and polishing concrete floors, walls, and the like*. Google Patents.

[46] Basheer, P. A. M., et al. (1997). Surface treatments for concrete: Assessment methods and reported performance. *Construction and Building Materials*, *11*(7), 413−429.

[47] Dai, J.-G., et al. (2010). Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: The role of cracks. *Cement and Concrete Composites*, *32*(2), 101−109.

[48] Feng, Z., et al. (2019). Integral hydrophobic concrete without using silane. *Construction and Building Materials*, *227*, 116678.

[49] Song, Z., Lu, Z., & Lai, Z. (2019). Influence of hydrophobic coating on freeze-thaw cycle resistance of cement mortar. *Advances in Materials Science and Engineering*, *2019*.

[50] Zhan, H., Wittmann, F., & Zhao, T. (2003). Chloride barrier for concrete in saline environment established by water repellent treatment. *International Journal for Restoration of Buildings and Monuments*, *9*(5), 535−550.

[51] Lu, G., Zhao, W. & Dai, D. (2015). Study on preparation of cementitious capillary crystalline waterproofing coating. In 3rd *i*nternational *c*onference on mechatronics, robotics and *a*utomation. Atlantis Press.

[52] Chen, H., et al. (2020). The influence of surface treatment on the transport properties of hardened calcium sulfoaluminate cement-based materials. *Cement and Concrete Composites*, *114*, 103784.

[53] Chen, D. (2009). *Hygroscopicity of pharmaceutical crystals*. PhD Thesis, University of Minnesota, http://purl.umn.edu/47878.

[54] Liu, P., et al. (2018). Resolving the mechanisms of hygroscopic growth and cloud condensation nuclei activity for organic particulate matter. *Nature Communications*, *9*(1), 4076.

[55] Tang, M., et al. (2019). Water adsorption and hygroscopic growth of six anemophilous pollen species: The effect of temperature. *Atmospheric Chemistry and Physics*, *19*(4), 2247−2258.

[56] Weisheit, S., et al. (2016). Assessment of test methods for characterizing the hydrophobic nature of surface-treated high performance concrete. *Construction and Building Materials*, *110*, 145−153.

[57] ASTM. (2013). *C642-13, Standard test method for density, absorption, and voids in hardened concrete*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[58] ASTM. (1999). *D6489-99, Standard test method for determining the water absorption of hardened concrete treated with a water repellent coating*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[59] BS. (1996). *BS 1881-208, Testing concrete—Part 208: Recommendations for the determination of the initial surface absorption of concrete*. London, UK: BSI Standards Limited.

[60] CRD, C48-92. (1992). Standard test method for water permeability of concrete. U.S. Army Corps of Engineers.

[61] BS. (2000). *BS 12390-8:2000 Testing hardened concrete—Part 8: Depth of penetration of water under pressure*. London, UK: BSI Standards Limited.

[62] ASTM. (2020). *C1585-20, Standard test method for measurement of rate of absorption of water by hydraulic-cement concretes. In Annual Book of ASTM Standards*. West Conshohocken, PA, USA: ASTM International.

[63] ACI. (2008). *Committee 201, ACI 201.2 R-08 Guide to durable concrete in 2008*, Farmington Hills, MI, USA: American Concrete Institute.

[64] Mehta, P. K., & Monteiro, P. J. (2017). *Concrete microstructure, properties and materials*. New York, USA: McGraw-Hill Education.

[65] ASTM. (2019). *C1202-19: Standard test method for electrical indication of concrete's ability to resist chloride ion penetration*. West Conshohocken, PA, USA: In Annual Book of ASTM Standards.

[66] Zhang, Y., & Zhang, M. (2014). Transport properties in unsaturated cement-based materials—A review. *Construction and Building Materials*, *72*, 367−379.

[67] Agarwal, R., et al. (2017). Alkali silica reaction (ASR) mitigation in concrete by using lithium nitrate. *International Journal of Engineering and Applied Sciences*, *4*(3).

[68] Carlos Jr, C., et al. (2004). Accelerated laboratory testing for alkali-silica reaction using ASTM 1293 and comparison with ASTM 1260. California Department of Transportation.

[69] ASTM. (2014). *C1260-14: Standard test method for potential alkali reactivity of aggregates (mortar-bar method)*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[70] ASTM. (2013). *C1567-13: Determining the potential alkalisilica reactivity of combinations of cementitious materials and aggregate (accelerated mortar-bar method).* In Annual Book of ASTM Standards. West Conshohocken, PA, USA: AS TM International.

[71] ASTM. (2020). *C1293-20a, Standard test method for determination of length change of concrete due to alkalisilica reaction*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[72] Almusallam, A. A., et al. (2003). Effectiveness of surface coatings in improving concrete durability. *Cement and Concrete Composites*, *25*(4), 473−481.

[73] Berndt, M. L. (2011). Evaluation of coatings, mortars and mix design for protection of concrete against sulphur oxidising bacteria. *Construction and Building Materials*, *25* (10), 3893−3902.

[74] Muhammad, N. Z., et al. (2015). Waterproof performance of concrete: A critical review on implemented approaches. *Construction and Building Materials*, *101*, 80−90.

[75] Azarsa, P., Gupta, R., & Biparva, A. (2019). Assessment of self-healing and durability parameters of concretes incorporating crystalline admixtures and Portland limestone cement. *Cement and Concrete Composites*, *99*, 17−31.

[76] Azarsa, P., Gupta, R., & Biparva, A. (2020). Inventive microstructural and durability investigation of cementitious composites involving crystalline waterproofing admixtures and Portland limestone cement. *Materials*, *13*(6), 1425.

[77] de Souza Oliveira, A., et al. (2020). Crystalline admixture effects on crystal formation phenomena during cement pastes' hydration. *Journal of Thermal Analysis and Calorimetry*, *139*(6), 3361−3375.

[78] Reiterman, P., et al. (2020). Reduction of concrete surface permeability by using crystalline treatment. *Revista Romana de Materiale*, *50*(1), 69−74.

[79] Žáková, H., Pazderka, J., & Reiterman, P. (2020). Textile reinforced concrete in combination with improved self-healing ability caused by crystalline admixture. *Materials*, *13*(24), 5787.

[80] ASTM. (2015). *C666/C666M-15, Standard test method for resistance of concrete to rapid freezing and thawing*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[81] ASTM. (2018). *C1262/C1262M-18, Standard test method for evaluating the freeze-thaw durability of dry-cast segmental retaining wall units and related concrete units*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[82] ASTM. (2003). *C672/C672M-03, Standard test method for scaling resistance of concrete surfaces exposed to deicing chemicals*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[83] ASTM. (2019). *D7234-19, Standard test method for pull-off adhesion strength of coatings on concrete using portable pull-off adhesion testers*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

[84] ASTM. (2013). *F609-05, Standard test method for using a horizontal pull slipmeter (HPS)*. In Annual Book of ASTM Standards. West Conshohocken, PA, USA: ASTM International.

Multicrystallization waterproofing enhancer for concrete mixtures

11

Maher Al-Jabari[1], *Radi Al-Rashed*[2] *and XinbaoYu* [3]
[1]Chem-Crete Europe, Holic, Slovakia, [2]International Chem-Crete Corporation, Richardson, TX, United States, [3]Civil Engineering Department, University of Texas at Arlington, Arlington, TX, United States

11.1 Introduction

Most durability problems are caused by water penetration through the capillary networks in concrete structure. This is normally associated with various physicochemical interactions with the cementitious structure. The mechanisms of durability problems are associated with water penetration, vapor movement, and other transport mechanisms through concrete (see Chapters 2 and 3). Water in saturated concrete is the vehicle for the transport of many deleterious reactants. Other concrete problems are related to the phase changes of water that cause various thermo-mechanical effects on concrete. Common durability issues include concrete deterioration from water expansion–contraction during the cycles of freezing and thawing [1], scaling and steel corrosion by the penetration of chloride ion [2,3], chemical attack [5,4], carbonation [6,7], alkali–silica reactions (ASR) [8–11], and biological attack [12–14]. The wetting conditions of concrete govern the rate of water ingress and the severity of water contaminations determines the type and the rate of attacks. Waterproofing (WP) of concrete structures can provide an effective protection for concrete through reducing moisture permeation (under a hydrostatic pressure) by blocking the concrete pores [15] and reducing capillary absorption (under a nonhydrostatic pressure condition) by lining the pore with water repelling layer [16]. Integral WP materials develop their protection function upon their reactions with the cementitious constitutes [17,18]. These include admixtures and liquid penetrating surface treatments that migrate within the concrete structure and react within the pores [17,18] (see Chapters 6 and 7). The terminologies that describe these materials include permeability reducing admixtures, crystalline WP, pore blocking, capillary blocking [15], and pore lining [19]. The internal WP admixtures are defined as “a chemical which is added to the cement matrix that promotes the development of additional gel or other precipitate within concrete voids, after its diffusion to the pore water” (ACI 515.2R-13 [20]). Typical hydrophobic admixtures are described in Chapter 8 while typical hydrophilic powder admixtures are described in Chapter 9. Chapter 10 already describes the dual-crystallization waterproofing engineered (DCE) topical treatment that combines the mechanisms of hygroscopic and hydrophilic crystallization with hydrophobic function. The DCE is applied onto the surface of cured concrete [21] or

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00011-8

fresh concrete after the disappearance of bleeding water [22]. This chapter describes the multicrystallization enhancer (MCE) as a new integral WP system that is added to the concrete mixture and combines the aforementioned WP mechanisms. The MCE is a patent bending technology that is based on a similar previous patented WP technology [23]. The WP mechanisms and performance of the MCE has been investigated in recent research papers [24–26]. Furthermore, the MCE system was investigated in other extensive papers [27–30] that inappropriately identified the proprietary ingredients based on interpreting the Fourier-Transform Infrared (FTIR) spectra of concrete and crystalline composite systems; without having information about the patent bending formulation.

Evaluating integral WP technologies commonly takes into account the impacts of integral WP materials on (1) the characteristics of fresh concrete (such as workability, slump retention, set retarding effect, plastic shrinkage etc.), (2) the mechanical properties of fully cured concrete such as compressive and flexural strengths and abrasion resistance, (3) the WP efficiency such as permeability and water absorption, (4) the durability characteristics of fully cured concrete (e.g., resistances against chloride ion penetration and freezing and thawing cycles), and (5) other capabilities such as self-healing of cracks. There are other important parameters that are related to the effective management of the moisture and the thermal effects that are rarely discussed for typical hydrophilic crystalline WP materials. In this chapter, the physicochemical and water hindering mechanisms of the MCE and their role in improving the durability parameters are presented. In addition, the effects of MCE on concrete curing, structure, and strength development as well thermal management are discussed. The MCE efficacy in reducing permeability, water absorption, and enhancing concrete resistances against cycles of freezing and thawing, chloride ion penetration, and ASR are detailed.

11.2 Mechanism of waterproofing by multicrystallization enhancer

The MCE is a proprietary formulated aqueous solution composed of multiple reactive components that produce pore blocking and lining effects in a similar way as that presented in Chapter 10 for the DCE topical treatment. The MCE solution is simply added to the concrete mixture either at the concrete mixing plant or at the job site. It can be added to the mixing water or directly to the concrete mixture. The MCE solution is commonly dosed at 2% of the cement weight, but other investigated dosages were in the range of 1%–4%. Increasing the MCE dosages can increase the concentration of the active ingredients in the concrete mixture, which increase their availability for reactions and their impact on the concrete curing process.

The addition of the MCE to the fresh concrete mixture assists in dispersing the cement particles and promotes the stability of the cementitious slurry so that the particles behave as individual dispersed particles for a sufficient time. Consequently, the

MCE improves the flowability of the fresh concrete and increases its workability by promoting the formation of a homogeneous mixture. This is achieved through the plasticizing role of the hydrophobic ingredients [24]. The slump of fresh concrete using ordinary Portland cement (OPC) was found to increase by about 33% [24]. The level of enhancement in slump is dependent on the mix design; larger enhancements in the slump can be obtained with other mixes. Increasing the dosage of the MCE in the concrete mixture was found to increase its consistency and flowability [27,29]. Hence, a mix design targeting a certain slump value can be obtained with a lower water to cement (w/c) ratio when the MCE is added. The consequence of reducing the water content in the fresh concrete mixture enhances the mechanical and durability characteristics of fully cured concrete. Upon mixing, the MCE is homogeneously dispersed among the concrete mixture and hence achieves a full coverage throughout the cured concrete structure (i.e., no variations in "penetration depth"). The MCE mechanisms involve the curing process of its active ingredients, which is associated with the cement hydration reactions and the performance of the produced WP materials during concrete service life.

The MCE setting mechanism within the concrete pores is a chemical process that involves similar chemical reactions as described in Chapter 10. The active ingredients undergo a sequence of chemical reactions and physical interactions with water and the cementitious materials. The schematic representation of the formation reactions of the active ingredients of the MCE and the performance mechanisms of the products of reactions are similar to those shown in Fig. 10.7 (see Chapter 10): two of the active ingredients of the MCE system (the hydrophilic and the hygroscopic constituents) react with the by-product of cement hydration (calcium hydroxide, CH) as reported for other hydrophilic crystalline powder admixtures (see Chapter 9). These reactions form crystals that partially block the capillary pores. The remaining porosity (after the partial pore blocking effect of the crystals) is lined with a water-repelling layer, which is produced from the hydrophobic content of the MCE ingredients. The hydrophobic active ingredient reacts with silicon sites at the cementitious surface and produces a hydrophobic molecular layer. The layer bonds to silicone sites of the calcium silicate hydrates (C—S—H gel) and other constituents of the cement paste in a similar mechanism as described in Chapter 8. Then, the products of reactions including the crystals and the hydrophobic layer become integral parts of the pore structure in concrete by adhering to the walls of the pores [27].

The associated structural changes in this mechanism were revealed by analysis and comparison of the FTIR spectra of the concrete structure, the MCE structure, and concrete integrated with the MCE system [27]. The reported FTIR spectra of the MCE and its interaction with concrete are shown in Fig. 11.1. The analysis of these FTIR spectra revealed a significant increase in the transmittance of peaks at 2881 cm^{-1}, 2969 cm^{-1} corresponding to —OH, —CH stretching vibrational bonds, respectively, and an increase in the transmittance of the peak 875 cm^{-1} corresponding to $-\text{CO}_3$ bond. The levels of these bonds remained nearly the same for the MCE system and the MCE interacted with concrete [28]. These spectral similarities confirm the association of the active ingredients (involving these bonds)

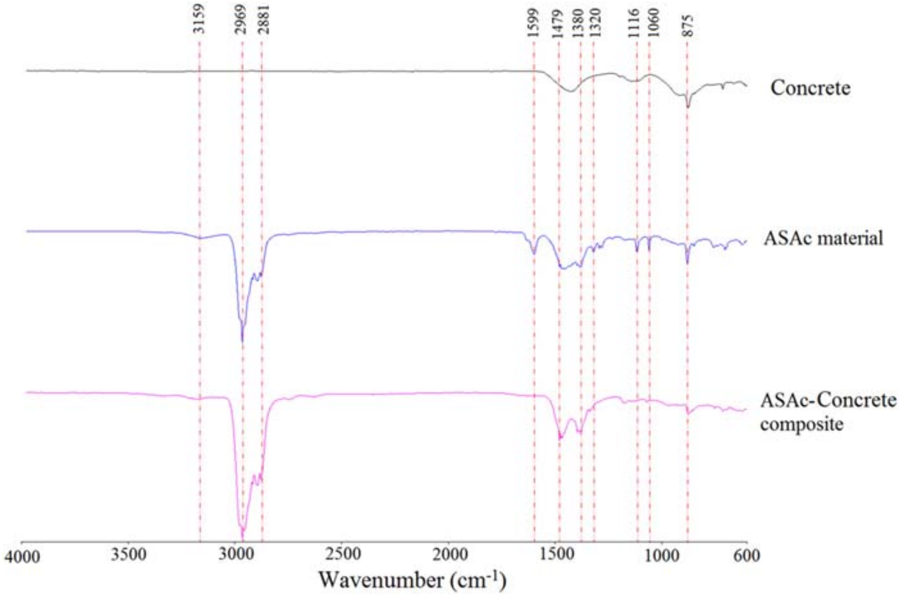


Figure 11.1 The FTIR spectra of concrete, the MCE (labeled in the figure as ASAc), and its interaction with concrete [30].

with the concrete structure: The increase in the $-CO_3$ bond in the MCE-dosed concrete is attributed to the formation of the hygroscopic crystals. Moreover, the increase in the $-OH$ bonds in the MCE-dosed concrete indicates an increase in the hydrogen bond, which is interpreted by the crystal growth through the interaction with water and the formation of the hydrophobic molecular layer (see Chapter 5) (this was imprecisely interpreted in references Al-Kheetan et al. [28] and Rahman and Al-Kheetan [27]) due to the inappropriate identification of the proprietary ingredients of the MCE system as indicated in Section 11.1. On the other hand, the increase in the $-CH$ bond in the MCE-dosed concrete is attributed to the attachment of hydrophobic ingredient (containing the $-CH_3$ groups) onto the silicon cites at the cementitious surfaces forming the hydrophobic organosilicon bonds as reported in previous publications [27,28].

The SEM analysis of the MCE-dosed concrete revealed needle-like crystals (hygroscopic) as shown in Fig. 11.2. Fig. 11.2 compares the produced microstructure from the self-crystallization of the MCE system and from the interaction between the MCE with the cementitious surfaces in cured concrete [27]. The formation of silica gel that adhered to the walls of the pores and developed into solid crystals (hydrophilic) was also highlighted by Rahman and Al-Kheetan [27]. The crystals are very small (<200 nm) and well-distributed within the paste structure. Consequently, their implantation and integration inside the capillary pores were facilitated [27,28]. Their partial occupation of the pores reduces the pores size and refines it as well as densifying the concrete [27].

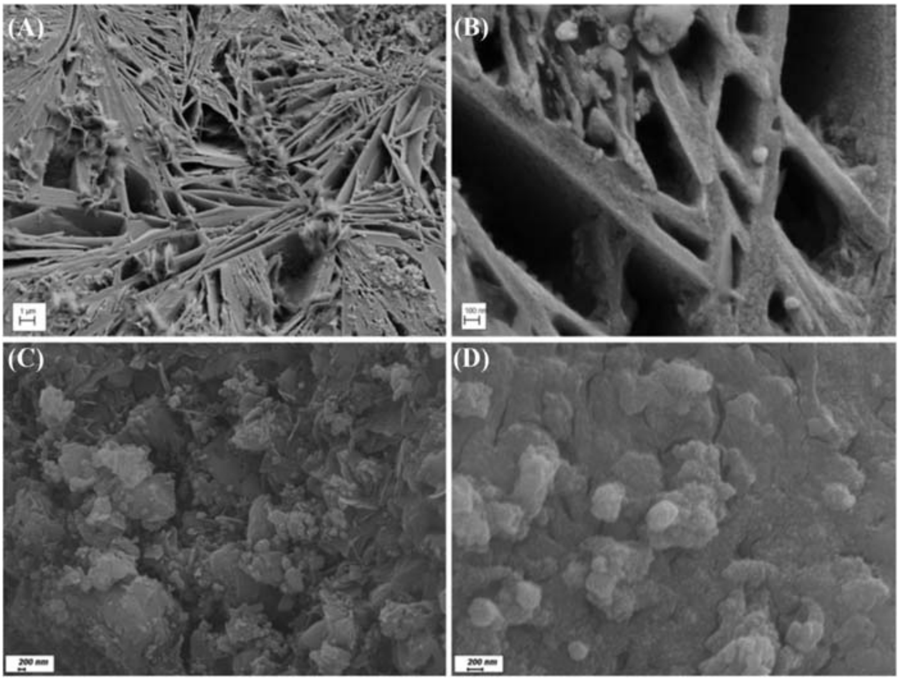


Figure 11.2 SEM micrographs of the crystallization of the MCE without mixing with concrete at a magnification of 910,000 (A) and 9,100,000 (B), and the interaction between the MCE and the cementitious surfaces in cured concrete at a magnification of 920,000 (C), and 950,000 (D) [30].

From the perspective of the kinetic mechanism, the partial consumption of CH by the MCE reactions enhances the cement hydration process. A further enhancement in the cement hydration is obtained as a result of the ability of the MCE to manage moisture through its reversible interaction with water (as detailed below) and through its ability to manage thermal effects as detailed in Section 11.4. During a typical concrete curing process, the water content in the concrete mixture is reduced by its consumption in (1) the cement hydration reactions, (2) the water evaporation due to the exothermic heat of hydration reactions, and (3) the water physical bonding within gel pores (adsorbed water molecules), as detailed in Chapter 1. With the progress of cement hydration, the concentrations of the active ingredients within the formed pores increase and the CH becomes more available; thus the MCE reactions are promoted and accelerated [24]. The produced crystals start to precipitate within the concrete capillary network after the initial cement hydration process.

Furthermore, the kinetic mechanism of the formation of hydrophobic layer demands the availability of carbon dioxide from the air. The rate of the supply of CO_2 is faster at the external surface (which is already exposed to air) than that at the internal surfaces: the supply of CO_2 to the internal structure starts to happen after the establishment of the concrete pores and when the atmospheric air is allowed to occupy the volume of pores after water evaporation and/or consumption in the hydration reactions. This occurs through air permeation and CO_2 diffusion (see Chapter 2). The reaction of the hydrophobic ingredients can occur internally after the availability of CO_2 and the generation of active sites at the cementitious surfaces for reactions. For these reasons, the kinetics of the reaction of the hydrophobic constituent occurs at a slower rate than those of the other two reactions of hygroscopic and hydrophilic ingredients. The precipitated and deposited products of the MCE reactions are characterized with combined internal triple functions of hydrophilic and hygroscopic crystals and a hydrophobic molecular layer. The physical behaviors and water interactions of the hydrophilic, the hygroscopic, and the hydrophobic materials are described in Chapter 5.

The performance mechanism of the integrated MCE system is a physicochemical process that is based, first, on the interactions of the crystals with water: The hygroscopic crystals grow with the moisture adsorption by sucking the humidity from the air in the pores while the hydrophilic crystals expand upon water swelling. These two types of crystals formed within the pores of cement paste reduce the concrete porosity by pore blocking effect. The growth of the MCE crystals with moisture exposure provides the concrete with a self-healing mechanism for hairline and thermal cracks and then achieves regenerated WP functions. These combined functions provide the MCE the ability to hinder water penetration driven by permeation flow and/or capillary suction. Hence, the MCE can be applied for WP of hydraulic structures and/or for dampproofing of partially wetted structures.

When the MCE-dosed concrete is subjected to high internal humidity, the hygroscopic crystals attract and suck water vapor from air. The crystals utilize the internal moisture in the hygroscopic process of crystal growth, which enhances the MCE pore blocking efficiency. The vapor adsorption onto hygroscopic crystals reduces the moisture content within concrete. Fig. 11.3 compares the internal relative humidity in control and MCE-dosed concrete blocks at 4-inch depth from the surface (plotted based on data from Al-Rashed and Al-Jabari [24]). Fig. 11.3 shows that a significant reduction in the internal humidity is obtained after the first few days of curing. Similar trends were reported at other depths of 2 and 3 inches, achieving reductions in internal humidity ranging between 13% and 22% at 28 days [24]. On the other hand, at the early stages of curing (e.g., the first 7 days), the internal humidity of the MCE-dosed concrete is similar to or higher than that of the control concrete. This indicates that the interaction of the MCE system with water vapor does not interfere with the cement hydration reactions and the MCE does not compete with hydration reactions on liquid water at the first few days. This was also confirmed by the strength development curves (see Section 11.2.1) [24]. Such an adsorption process of moisture on the hygroscopic crystals is reversible. This thermodynamic reversibility maintains the MCE system in a dynamic process driven by the potential of the crystals to attain an equilibrium with the internal humidity in pores. As described in Chapter 10, the equilibrium size of the hygroscopic crystals (commonly indicated by a defined

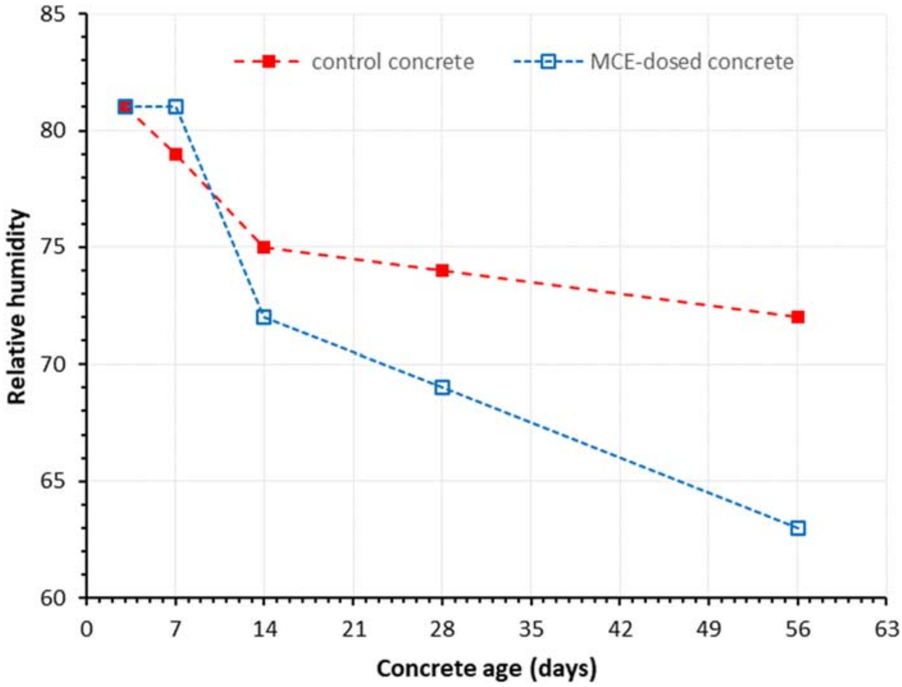


Figure 11.3 Internal relative humidity at a 4-inch depth within control and MCE-dosed concrete blocks (121212 inches) as functions of curing age with w/c ratio of 0.42, from testing according to ASTM F2170 and with the concrete temperature kept constant at 25°C (77°F).
Source: Plotted based on data from Al-Rashed, R. & Al-Jabari, M. [24].

growth factor) is dependent on the relative humidity of the surrounding air. The relationship between the equilibrium crystal size and the relative humidity is given by an exponential function, as described by simplified Köhler theory using the hygroscopicity parameter (see Chapter 5). A schematic representation of the equilibrium relationship between the crystal size (or growth factor) and the relative humidity is already shown in Fig. 10.9 (see Chapter 10). The hygroscopic crystals have negligible crystal growth when the relative humidity is below 30% or 40%. At such low humidity conditions, the crystal size is almost equivalent to that of the unhydrated crystals (no water adsorption).

On the other hand, when the concrete is subjected to an excessive liquid water penetration under a hydrostatic pressure, the hydrophilic crystals swell and expand, and hence they create larger flow obstacles and consequently minimizes any further water penetration. Similar to the hygroscopic crystals, the swelling of the hydrophilic crystals is a reversible equilibrium process (see Chapter 5). Thus they maintain the ability to release the moisture and shrink when the moisture content in concrete drops again. By these pore blocking and moisture interaction mechanisms, the hygroscopic and the hydrophilic crystals are effective in reducing water permeation under a hydrostatic pressure. Parallel to that, water penetration by capillary absorption under a condition of nonhydrostatic pressure is retarded by the water-repelling function of the adsorbed hydrophobic layer. The WP mechanisms of the hygroscopic and the hydrophilic crystals is reflected in reducing the water permeability while the mechanism of the hydrophobic layer is reelected in reducing the water sorptivity.

11.2.1 Enhancement of mechanical characteristics of concrete by multicrystallization

The progress of the crystallization process is associated with a strength development. Rahman and Al-Kheetan [27] highlighted that "the presence of crystals within the concrete structure in such a dense and well-distributed way would give the treated concrete rigidity and strength." The effects of the MCE on the compressive strength and hardness of concrete has been reported by Al-Rashed and Al-Jabari [24]. Fig. 11.4 compares curves of development of the compressive strength with curing time for control and 2% MCE-dosed concrete with three different mix designs, including 100% OPC and fly ash modified Portland cement [24]. Fig. 11.4 shows that the addition of the MCE to fresh concrete increases the compressive strength after the first few days. In fact, the type and level of the interference of the MCE in the process of strength development depend on the type of mix design, the w/c ratio, the curing conditions, and the dosage of the MCE. Fig. 11.4 shows that the addition of the MCE to concrete mixtures modified with fly ash (Iowa DOT C4-WRC20) enhances the compressive strength at all curing ages. In some cases, a minor slowdown in the strength development at the early stage of about 7 days [24] or up to 14 days can be observed [27]. Rahman and Al-Kheetan [27] observed that the delay of the strength development with the addition of the MCE can extend beyond that initial period due to the delay of the hydration process. However, they reported that after curing for 28 days, significant increases in the compressive strength with low w/c ratios (0.32 or 0.37) were observed (in the range of 13%−42%), while they observed a reduction in the 28-days compressive strength with the addition of the MCE for high w/c ratios of 0.4 and 0.46 [27]. In most cases, the strength enhancement appears more significantly after 28 days but in other cases it becomes more obvious after 56 days.

Table 11.1 lists the percentage enhancement of the compressive strength of various concrete mix designs using MCE at 2% dosages obtained from a previous publication [24] and other testing reports submitted to the authors. Table 11.1 indicates that the final compressive strength of MCE-dosed concrete is higher than that of control concrete in most of the reported cases. Overall, the addition of the MCE at a dosage of 2% can achieve enhancements in the compressive strength at 28 days and 56 days by different percentages within a wide range of 3%–13%. This strength enhancement indicates that the MCE promotes more hydration reactions at late stages and densifies the concrete. The value of the percentage enhancement depends

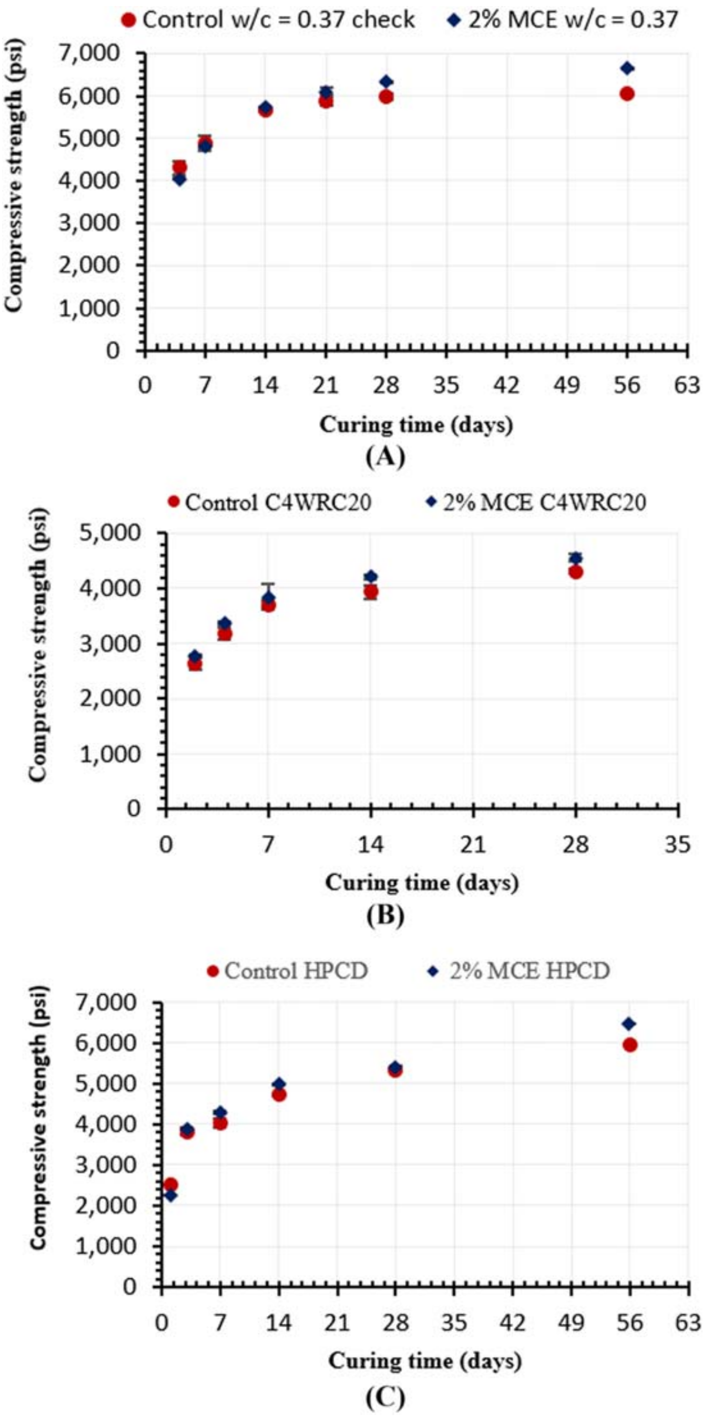


Figure 11.4 Curves of compressive strength as functions of curing time for control and 2% MCE-dosed concrete of various mix designs, including: (A) ordinary Portland cement using Iowa DOT C4 with a w/c ratio of 0.37; (B) a blend of 80% Portland cement and 20% fly ash modified Iowa DOT C4-WRC20 with a w/c ratio of 0.4; (C) high performance concrete using Iowa DOT HPC-D ready mix concrete [24].

Table 11.1 Percentage enhancement of the compressive strength of concrete using the MCE in various mix designs.

Mix design	Binder	w/c ratio	Compressive strength at 28 days	Compressive strength at 56 days
			Enhancement	Enhancement
Iowa DOT C4	OPC	0.42	− 1.2%	5.2%
Iowa DOT C4	OPC	0.37	5.9%	9.6%
Iowa HPC-D	OPC	0.42	5.8%	—
Illinois pavement mix design	OPC	0.5	12.7%	9.8%
Iowa C4WRC20	OPC modified with fly ash	0.4	1.4%	8.4%
Illinois pavement mix design with 20% fly ash	OPC modified with fly ash	0.42	2.7%	2.8%
Iowa C4WRC20—curing under freezing for 90 days	OPC modified with fly ash	0.42	—	19.5%
Illinois pavement mix design with slag	OPC modified with slag	0.42	17.9%	7.0%
Mass concrete using Iowa DOT C4-WRC20 (35 days)	OPC modified with fly ash	0.37	10.4%	—

on the curing age and the mix design. This percentage enhancement is within the range reported for typical commercial hydrophilic crystalline WP powder admixtures for which the crystallization mechanisms also promote cement hydration and produces additional C−S−H gel that densifies the concrete [31,32]. The compressive strength enhancements of OPC concrete using a commercial hydrophilic crystalline admixture was reported to be in the range of 5%–10% (see Chapter 9). Table 11.1 indicates that the addition of MCE to OPC concrete can achieve a higher percentage enhancement than that for concrete mix with fly ash. This might be due to the competing roles of fly ash and the MCE system on reactions with calcium hydroxide (the by-product of cement hydration) and the common effects on managing the heat of hydration (see Section 11.4). In some cases (for Iowa DOT C4 at 28 days), the percentage enhancement is slightly negative (−1.2%) but then it becomes positive at 56 days at a value of 5.2% that is within the typical strength enhancement range. This may indicate that the enhancement in some cases can appear at a much late stage (after 2 months). A much higher percentage enhancement is obtained for the case of slag modified cement at 28 days (18%) but then it achieves a typical percentage enhancement at 56 days. This might be due to kinetic effects during the hydration process. In fact, a slight deceleration of the concrete hardening during the first 28 days was reported for hydrophilic crystalline powder admixtures [33].

This strength enhancement using the MCE is obtained because (1) the MCE enhances the dispersion of cement particles in plastic stage and minimizes the encapsulation of cement particles during early hydration (as per the aforementioned plasticizing role of the MCE in Section 11.2, (2) the ability of the MCE crystals to hold moisture through their reversible water interactions, (3) the MCE crystallization process manages the thermal effects in fresh concrete by storing a fraction of the evolved heat from the cement hydration reactions and releasing it back at a later stage (see Section 11.4), and (4) the MCE reactions consume part of the produced CH and hence drives the hydration reactions forward [24]. Furthermore, Al-Kheetan et al. [28] reported that the MCE material increased the compressive strength of the concrete when cured under hot conditions. Their results showed an enhancement of 64% in the 28-days compressive strength when the MCE was added at 4% of the cement weight with w/c ratio of 0.32 and cured at a temperature of 60°C [28]. Moreover, adding 2% MCE to concrete with w/c ratio of 0.46 preserved its 28-days compressive strength when cured at a freezing temperature of −25°C and increased its by 8% when cured at a high temperature of 60°C [28].

The enhancement in the compressive strength is associated with a surface hardening effect of the MCE. Fig. 11.5 compares curves of wear depth for fully cured MCE-dosed concrete specimens for two dosages of 1% and 2% MCE additions [24]. The wear depth is increased with elapsed time for the two cases; however, increasing the MCE dosage increases the wear resistance significantly as indicated

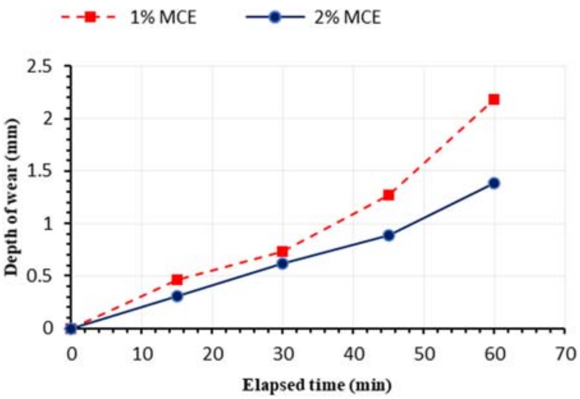


Figure 11.5 Curves of wear depth for fully cured MCE-dosed concrete specimens for two dosages of 1% and 2% MCE additions, determined from testing according to ASTM C779, Procedure B, using Iowa DOT C4-WRC20 design mix at w/c ratio of 0.54 [24].

by lowering the wear depth due to the additional enhancement of concrete integrity and the filling effect of MCE crystals with 2% MCE compared to 1% [24]. Similar trends were reported for other w/c ratios of 0.44 and 0.49; however, the rate and the level of wear increase with increasing the w/c ratio due to the increase in the concrete porosity. The reductions in the wear after 60 minutes, for increasing the dosage of the MCE from 1% to 2%, were in the range of 28%–37%. The percentage reductions in the wear were higher at higher w/c ratios. This MCE enhancement of the abrasion resistance is similar to that reported for the similar crystallization system (DCE) used for topical treatment [21] (see Chapter 10).

11.3 Reducing porosity and permeability of concrete with multicrystallization enhancer

The morphology of concrete incorporated with the MCE system was reported in previous publications and revealed the formation of highly distributed and strongly bonded crystals within the paste pores [27,28] (see Section 11.2). The formation of the crystals inside the pores and their distribution increase the rigidity of the pores [28]. As a result of the aforementioned role of the MCE in densifying concrete and enhancing its integrity, a significant decrease in the porosity is attained. The crystallization was also reported to increase the interfacial bonds between the cement hydration products and aggregates in the cured concrete [27,28]. Rahman and Al-Kheetan [27] reported that the formation of the crystals within the concrete structure acted to improve its density and reduce the size of pores, making them finer [27]. Increasing the dosage of the MCE (from 1% to 2%) leads to about 4% increase in the concrete density and about 50% decrease in the fraction of permeable pores (for concrete with w/c in the range of 0.44−0.54) (from tests according to ASTM C642) [24]. The density increase and the porosity reduction are achieved from the increase in the reaction yield of the MCE crystallizations with the increase of the MCE dosage from 1% to 2% [24]. These differences were reported for two dosages (1% and 2% MCE); however, larger differences can be obtained between control concrete and 2% MCE-dosed concrete. A similar densifying effect was also reported for the topical surface treatment of the DCE [21] (see Chapter 10). This could be achieved from the pore blocking and filling effects resulting from the precipitation of the hygroscopic and the hydrophilic crystals within the permeable pores. Furthermore, the addition of the MCE to the concrete mixture enhanced the rigidity of the cured concrete and occupies a noticeable volume of the large capillaries or macropores (> 1 m), most of the capillary pores (100–1000 nm), and some of the fine pores (10–100 nm) [28]. Incorporating the MCE system in concrete mixtures led to an improved morphology of concrete [27], even when it was cured under extreme environmental conditions [28] (see Section 11.4). Al-Kheetan et al. [28] showed microstructures that revealed the bonds at the interfaces between the MCE products and concrete matrix and a reduction in the crack propagation when concrete was cured under freezing conditions. The decrease in the fraction of permeable pores leads to a major reduction in water penetration through concrete as detailed below:

The percentage water absorption for 2% MCE-dosed concrete was found to be lower than that for 1% MCE–dosed concrete by about 50% (from tests according to ASTM C642) [24,34]. Again, larger differences in the water absorption can be obtained between control concrete and 2% MCE-dosed concrete. In fact, the level of changing water absorption by the addition of the MCE system was found to be dependent on the w/c ratio, the curing conditions, the concrete age, and the dosage of the MCE. Fig. 11.6 compares the water absorption rates for control, 2% MCE, and 4% MCE-dosed concrete specimens after curing in a water bath at 21°C for various periods [27]. The water absorption rate of the 2% MCE-dosed concrete was reduced significantly (compared to that of control specimen) for concrete at various w/c ratios (with a range of 0.32–0.46). However, for MCE-overdosed concrete (4%), the reduction was obtained only for cases with low w/c ratios (0.32 and 0.37) [27]. The percentage reduction in water absorption rate reached about 64% for concrete with w/c of 0.37 dosed by 4% MCE. The decrease in water absorption rate in the MCE-dosed concrete was explained by the formation of sufficient organosilicon bonds at the surfaces of the pores making them hydrophobic and reducing the capillary absorption (see Section 11.2 and the FTIR analysis). In addition, Al-Kheetan et al. [28] observed that the water absorption rate decreased by about 79% when 2% of the MCE solution was added to concrete with w/c ratio of 0.32 and cured at 60°C for 28 days. Furthermore, the impact of subjecting the MCE-dosed concrete to cycles of freezing and thawing on the absorption rate is explained in Section 11.4.2.

In fact, the water absorption of concrete may be increased with the addition of integral crystalline WP systems as the crystals interact with water through the crystal growth as explained for typical hydrophilic crystalline WP powders (see Chapter 9). This can be more obvious at short-term curing or for cases with high porosity (e.g., high w/c ratio) and with more crystalline material (e.g., overdosages at 4%) that is associated with large demands on water for crystal growth: for curing in a water bath at 21°C for 7 days [27], the addition of the MCE (2% or 4%) decreased the water absorption for concrete with low w/c ratio (0.32 and 0.37) while it increased that for concrete with high w/c ratio (0.4 and 0.46). On the other hand, for curing under freezing conditions or at a high temperature at 60°C for 7 days [28], a dosage of 4% of the MCE increased the water absorption rate. The increase in water absorption at the early stages of curing was explained by the demand of water for the growth of the crystals [28] (for the hygroscopic crystal growth).

The reduction in the water absorption is the consequence of the reduction in the capillary suction (under a condition of no hydrostatic pressure). This is mainly achieved by the hydrophobic behavior. On the other hand, the role of the pore blocking crystals is commonly tested under a hydrostatic pressure condition. With the addition of the MCE, the permeability coefficient of concrete can be reduced by three orders of magnitude [25] when tested at a pressure of 1.4 MPa (200 psi)

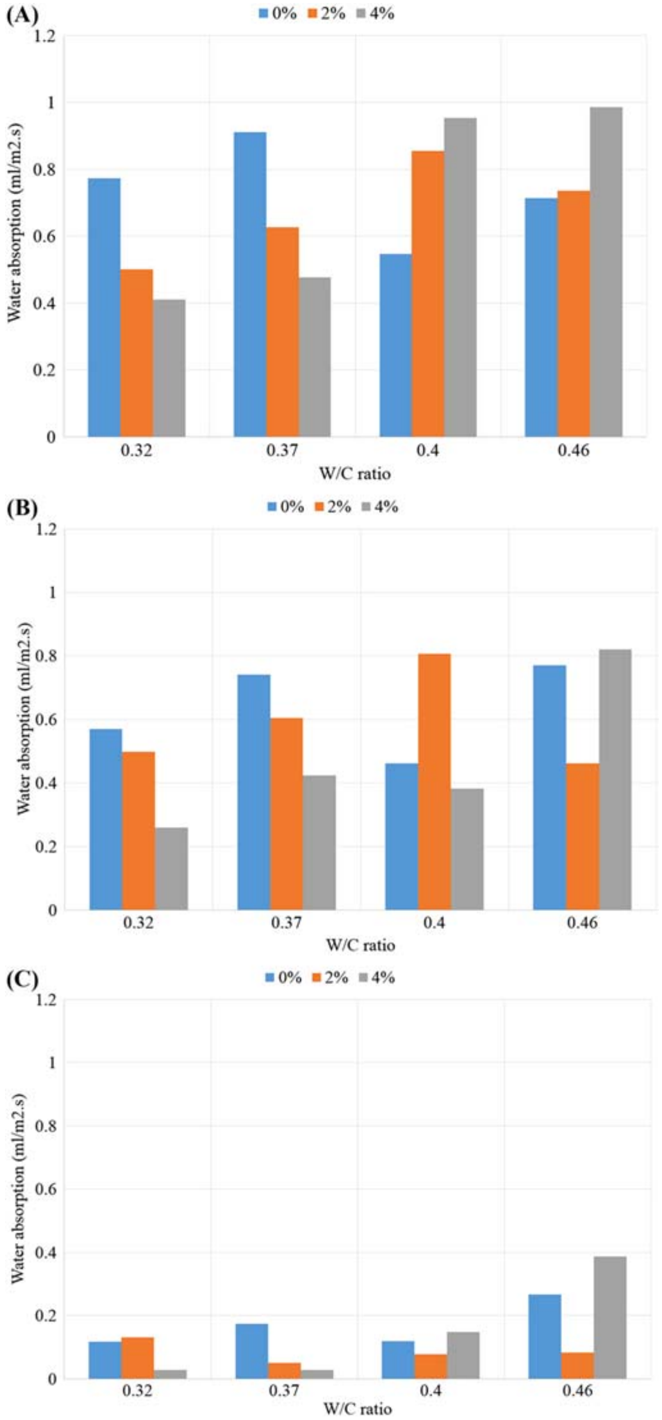


Figure 11.6 Water absorption rates for control, 2% MCE, and 4% MCE-dosed concrete specimens after curing in a water bath at 21°C for 7 days (A), 14 days (B), and 28 days (C) [30].

according to the United States Corps of Engineering method specified in CRD-C 48–92 [35]. This reduction in the permeability under 1.4 MPa pressure is similar to the reported performance for some hydrophilic crystalline powder admixtures [18,36]. However, lower reductions in the permeability coefficient were also reported for other hydrophilic powder admixtures. This is because the combined effect of the hygroscopic and the hydrophilic crystals exceeds the single effect of hydrophilic crystals. The reported percentage reduction in the permeability coefficient of concrete enhanced with hydrophilic powder admixtures is about 70% or more than 60% [37] or reported to be within the range of 57%–75% [18] (based on tests according to CRD-C 48–92) [35].

Furthermore, the MCE reduces the vapor emission from concrete as shown in Fig. 11.7 from tests using the nondestructive electronic moisture meter according to ASTM F2659 [24]. This is attributed to the adsorption of water vapor on the hygroscopic crystals, which is then reflected in a reduction in the free moisture content (see Fig. 11.3). Fig. 11.7 shows that the difference in moisture emission (between the control and the MCE-dosed concrete specimens) is small at the initial stages of curing. This indicates a lower availability of the hygroscopic crystals at the early stages and hence a lower impact of the hygroscopic crystallization mechanism on the cement hydration reactions at the initial stages. Then, the difference becomes much larger at a late curing stage as crystal growth becomes more active when the availability of water decreases during the progress of concrete curing. Then, the hygroscopic crystals grow at a larger growth rate (indicated by major reductions in moisture emissions at 14 and 28 days). These results

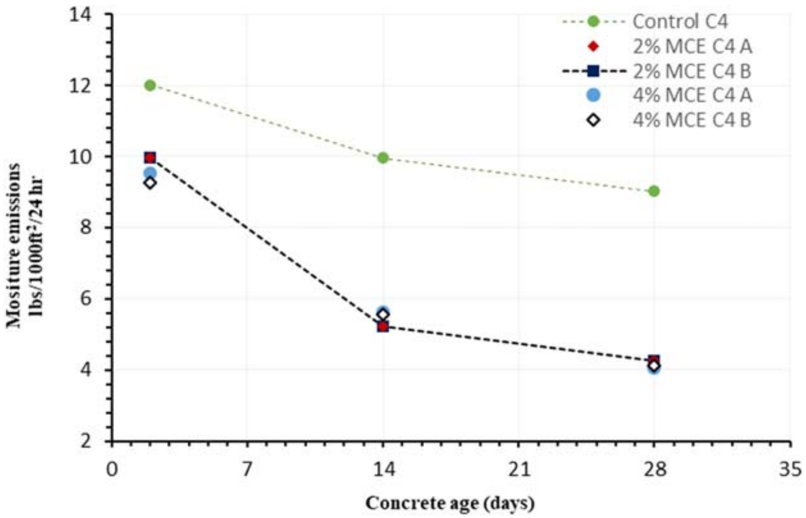


Figure 11.7 The rate of moisture vapor emission from concrete (for slabs of 11.59.5 inches and 2 inches thick with the mix design of Iowa DOT C4 with w/c ratio of 0.42) comparing that for control and two MCE-dosed concrete (2% MCE and 4% MCE), determined according to the standard procedures of ASTM F2659 [24].

were also supported with other results from testing similar concrete specimens according to ASTM F1869 [38], which involves the measurements of moisture emission as well as weight gain as a result of moisture absorption. Comparing the results of the MCE-dosed concrete with those of control concrete specimens after a period of 40 days indicates that the rate of moisture vapor emission is reduced by 37% and the moisture absorption is increased by about 106% [24]. This is because the MCE-dosed concrete captured a larger fraction of moisture than the control concrete. This was associated with a 47% increase in the slab moisture weight gain as a result of the process of the hygroscopic crystal growth by absorbing the free moisture within the crystalline structure and leading to an increase in concrete density [24]. This interaction with vapor was not reported for other integral hydrophilic WP systems (see Chapter 8).

The reduction of the hydraulic conductivity is also associated with reductions in the mass and thermal diffusivities of concrete (see Sections 11.4 and 11.5).

11.4 The role of multicrystallization enhancer in managing thermal effects in concrete

The MCE has the ability to manage the thermal effects during the concrete curing and during the service life of concrete [26]. These effects result from the heat release from the exothermic cement hydration reactions or from concrete curing under severe cold conditions, or from the exposure of concrete to cycles of freezing and thawing. The ability of the MCE to manage these thermal effects is based on its capacities for (1) the reversible adsorption of the free moisture through the growth of the hygroscopic crystal, (2) the reversible storing of the thermal energy within the crystals, and (3) the WP performance as described in Section 11.3 [26]. These capabilities reduce the availability of water and the possibility of its freezing within the paste pores and also hinder the adhesion of ice onto the cementitious surface, as icephobicity is correlated to hydrophobicity [19]. Al-Jabari et al. [26] listed and detailed the hypotheses that explain the thermal performance of the MCE system in concrete. These included (1) reducing conduction heat transfer, (2) managing the water phase change within the concrete pores, (3) managing the moisture content though a combined heat transfer and mass transfer process, (4) preventing freezing in fresh concrete through heat generation and storage, and (5) minimizing ice adhesion by thermodynamic and heat transfer mechanisms. The addition of the MCE to concrete mixture reduces the thermal conductivity of the concrete and hence reduces the rate of conduction heat transfer. The addition of 2% MCE enhances the thermal resistivity of fully cured concrete by about 19% as a result of its pore blocking mechanism and by the reduction of the internal moisture [26].

The nonmanaged thermal effects in concrete can lead to internal thermal stresses that cause cracking and then increase the concrete porosity. This will then lead to increasing concrete thermal, mass, and hydraulic conductivities, the consequences of which are major durability problems. These issues are reflected in measurements of the rate of heat release, temperature profiles, and the associated changes in the thermal and mechanical characteristics during cement hydration and concrete curing at various conditions (Section 11.4.1) and when the cured concrete is subjected to cycles of freezing and thawing (Section 11.4.2).

11.4.1 Managing thermal effects during concrete curing using multicrystallization enhancer

Managing the thermal effects during cement hydration is crucial in the analysis of mass concrete applications and is important for concrete durability as the rapid temperature rise followed by a subsequent cooling within the first period of 3 days creates thermal stresses and causes concrete shrinkage and cracking (see Chapter 1). In fact, the concrete tensile stress is governed by the heat of cement hydration [16]. In addition, it is essential in evaluating the technical feasibility of concrete curing under severe cold conditions. The MCE system assists in managing the thermal effects in these cases. Fig. 11.8 compares the rate of the heat release from an OPC paste as a function of time with that from a similar OPC paste with 2% MCE [26]. The characteristic shape of the differential heat evolution curve shown in Fig. 11.8 [commonly reported for various cementitious binders [39,40] as discussed in Chapter 1] reflects the overall cement reaction kinetics and the various hydration mechanisms. After the initial slow heat release within the first hours (induction stage), the heat release is accelerated progressively toward a maximum value (acceleration stage), then it slows down at a decreasing rate for the remaining period (as detailed in Chapter 1). Managing the thermal effects by the MCE occurs primarily by decreasing the initial rate of heat release and extending the induction period while maintaining nearly the same total heat release during the 48 hours of the calorimetric test period [26]. Similar characteristic behaviors were also obtained

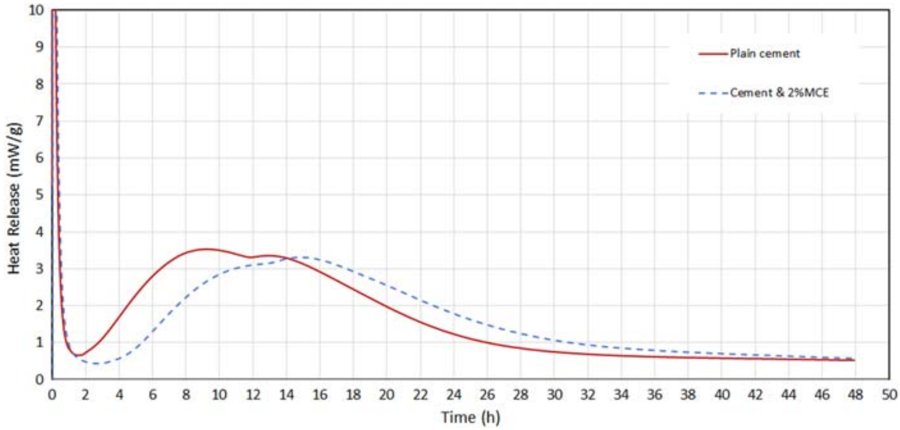


Figure 11.8 Calorimetric heat release from ordinary Portland cement paste for control and MCE-dosed specimens with a w/c ratio of 0.4 (unpublished work) [26].

for pastes containing supplementary cementitious materials (SCMs) such as fly ash and slag [26]. A similar heat evolution curve, with a similar rightward shift of the temperature peak, was reported in previous literature for the addition of a hydrophilic crystalline WP powder admixture [18]. Such a similar thermal effect was also considered to assist in creating better conditions for cement hydration [18].

The addition of the MCE and/or SCMs causes a slight retarding effect on the cement hydration as indicated by shifting the thermal peaks rightward. This is commonly obtained by measuring the needle penetration resistance according to ASTM C403/C403M-16 [41]. Such a behavior has been also reported for hydrophilic crystalline WP powder admixtures as the active ingredients participate in the physicochemical interactions with cement particles [42]. For example, the use of zinc and magnesium fluorosilicate as hydrophilic WP admixtures led to a significant set retarding effect [43] (see Chapter 9). The addition of minor amounts of such admixtures (0.5% dosage) led to a delay in the setting time for about 2.5 hours [44]. In addition, nonsilicate-based WP admixtures were shown to cause similar retarding effects [42]. The length of the retarding period is governed by the w/c ratio and the types and doses of the WP additives. This effect promotes process modifications of hydration reactions (e.g., variations in the rate of nucleation and growth kinetics of the hydrates) and induces structural changes in the phases of the hydration products [42]. It has been documented that "hindering the hydration inhibits the rapid increase of the cement hydration heat before hardening due to the thermodynamic heat-absorbing effect" [44]. These effects can explain the mild deceleration of the hardening process of concrete during the initial curing period in some cases [33]. Furthermore, the retarding effect of the MCE and other crystalline WP admixtures can decrease the moisture loss at early stages and then reduce the possibility of the thermal cracking and shrinkage and lead to a more durable concrete structure [18].

The aforementioned ability of the MCE to mitigate the heat release from the cement hydration reactions during the initial stage promotes its use for mass concrete, which is normalty associated with a temperature rise of nearly 4.6°C for each 100 kg of cement content [45]. As explained in Chapter 4, temperature rises and temperature gradients within structures involving mass concrete cause major durability problems [46,47]. The subsequent cooling stage after the high temperature rise within the first 3 days generates thermal stresses and causes shrinkage problems and cracking. Fig. 11.9 compares the temperatures at the centers of large specimens (1.51.5 m) of control and MCE-dosed mass concrete as functions of time [26]. The maximum temperature of mass concrete, which occurs at the center is characteristically set at 57°C ((135°F) [48]) and the maximum temperature difference within the structure is set at 19.4°C to prevent thermal cracking [47]. Fig. 11.9 shows that the maximum temperature for both cases were less than 57°C (135°F). This is because the mix design for the control specimen already involves fly ash as a replacement of the cement, the early heat contribution of which is much lower than that of OPC (see Chapter 4). It has been reported that the addition of fly ash to mixtures of mass concrete can reduce the temperature peak by about 2°C for each 10% replacement of cement [45]. Even though, Fig. 11.9 indicates that the temperature peak is reduced by about 6.6°C (12°F) with 2% MCE addition. This level of

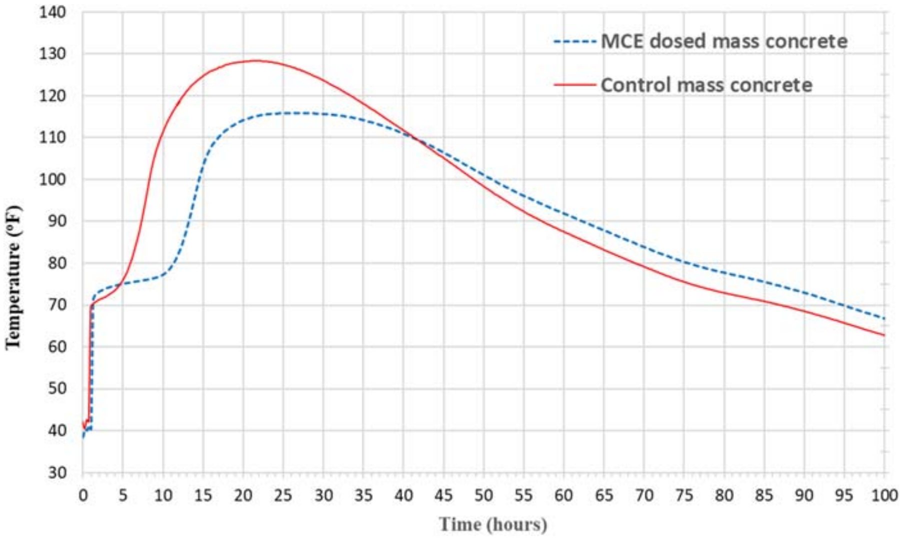


Figure 11.9 Temperatures at the centers of control and MCE-dosed mass concrete specimens (1.51.5 m cylinders), using Iowa DOT C4-WRC20 mix design at w/c ratio of 0.37 (unpublished work) [26].

decrease of the maximum temperature can permit increasing the cement content in mass concrete while maintaining low maximum temperatures [45].

Fig. 11.9 also shows that dosing the mass concrete mixture with the MCE flattens the temperature curve and causes a rightward shift of the temperature peak by about 7 hours, which is crucial for controlling the rate of heat evolution at early stages. In addition, the rate of the subsequent cooling stage in the MCE-dosed mass concrete is lower than that in the control mass concrete. This provides a further contribution in reducing the potential for thermal cracking. In fact, the thermal management of the MCE in mass concrete does not appear only in lowering and delaying the temperature peak but also in reducing the internal temperature gradients. Al-Jabari et al. [26] showed that the MCE can reduce the maximum temperature gradient by about 25%. The maximum temperature gradient in the MCE-dosed mass concrete was about 10°C (18°F) while that for the control mass concrete was about 13°C (23.8°F). The temperature gradient in the MCE-dosed mass concrete composes only about 50% of the set maximum temperature gradient in mass concrete. This effective thermal management is attributed to the role of the MCE in decreasing the rate of heat generation and delaying the initial cement hydration (extending the induction period as explained above section) and reducing the loss of water (as explained in Section 11.2). Managing the thermal effects in mass concrete by the addition of the MCE is also reflected in an enhancement in the compressive strength by 10% [26].

The MCE has another unique thermal role of managing concrete curing under severe cold conditions [26,28]. These extreme frost curing conditions were reported to negatively affect the control concrete specimen through generating microcracks [28]. Subjecting the concrete mixture to freezing conditions at the early stages of the cement hydration results in the freezing of the available water required for hydration reactions. Such a freezing within the weakly established pore structure causes expansion and then leads to increasing the crack propagation rate within the pores in addition to retarding the hydration reactions [28]. This would then create delicate cement-aggregate bonds [28]. In addition, curing at low temperature leads to sharp thermal gradients through the concrete structure, which in turn causes internal stresses and the propagation of microcracks [28]. Curing MCE-dosed concrete under freezing conditions was enhanced by preventing the freezing of water in fresh concrete [26]. Maintaining water in the liquid phase for a sufficiently long time is crucial for promoting the cement hydration reactions. Fig. 11.10 compares the temperatures of control and MCE-dosed freshly casted concrete specimens (at 1.27 cm below the surface) exposed to surrounding freezing conditions. The specimens were placed in a freezer at −45°C for 90 days after allowing the concrete specimen to cure for 24 hours in a moist condition at a temperature of −18°C [26]. Fig. 11.10 shows that the temperature of the MCE-dosed concrete remains higher than the freezing temperature for a month or two while that of the control specimen drops sharply below the freezing temperature within a couple of days. Then, the temperature of the MCE-dosed concrete remains above that of the control concrete by about 5.5°C (10°F) during the subsequent stages. Similarly, the role of the MCE in managing the concrete curing under less severe conditions (−25°C) was reported in another previous publication [28]. Overall, for the control specimen under surrounding freezing conditions, the cement hydration reactions cannot proceed

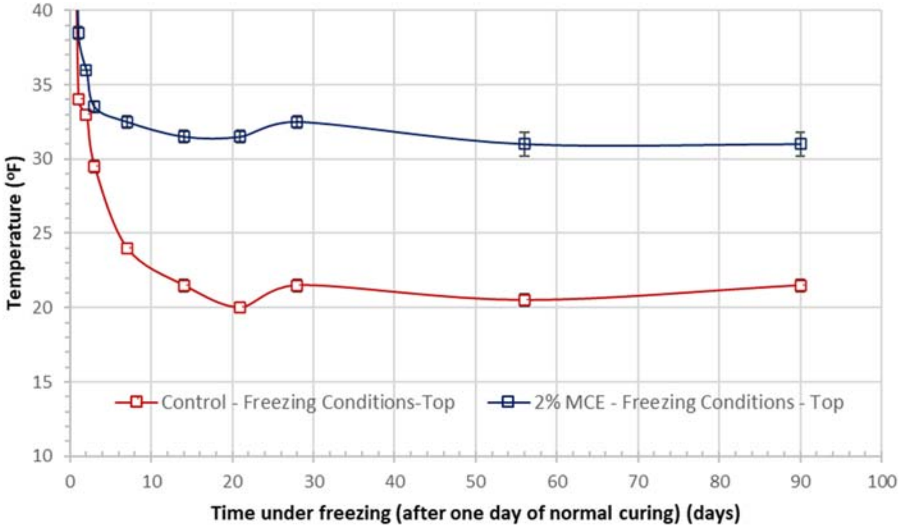


Figure 11.10 Temperatures at 1.27 cm below the surface of control and MCE-dosed concrete specimens, using C4-WRC20 at w/c ratio of 0.4 cured under continuous freezing surroundings at 45˚C (50˚F), after allowing the concrete specimen to cure for 24 h in a moist condition at a temperature of 18˚C (0˚F) (unpublished work) [26].

effectively after water freezing that occurs within the first 2 days. On the other hand, by maintaining the water in a liquid phase for 1 or 2 months, the cement hydration reactions are maintained and permit curing to achieve a sufficient compressive strength. These thermal effects were reflected in increases in the compressive and the flexural strengths and in the relative dynamic modulus for the MCE-dosed concrete [26]. Al-Kheetan et al. [28] also reported that the use of MCE can increase the compressive strength of the concrete (over that of the control specimen) when cured under freezing conditions. The presence of the MCE crystals led to development of a denser microstructure than that of the control concrete specimens when concrete was cured under severe cold conditions [27,28].

This thermal role is attributed mainly to (1) the availability of a sufficient internal energy within the MCE-dosed concrete specimen to account for the heat loss to the surrounding and (2) the reduced rate of heat conduction. The internal energy is secured by maintaining additional sources of heat generation from the MCE mechanism. In addition to the heat release from the promoted cement hydration, these heat sources include (1) the exothermic crystallization reactions (i.e., from the MCE precipitation and hydration mechanisms), and (2) the latent heat released from the vapor condensation during the growth of the hygroscopic crystals. However, the evolution of these heat sources needs the specimen to be under less severe conditions to pass the induction and accelerating stages of the cement hydration process, otherwise water freezing cannot be prevented and the MCE cannot promote the hydration process. This was observed when the two specimens were subjected immediately to surrounding conditions at −45°C [without allowing the initial cure for 24 hours at a temperature of −18°C (0°F)] [26]. In such a case, the two concrete specimens froze within 90 minutes showing water crystals at the surfaces of both control and MCE-dosed specimens.

Furthermore, the investigated severe curing conditions included curing at a relatively high temperature (e.g., at 60°C). Curing concrete at a high temperature of 60°C leads to drying effects and higher water losses at an early age, which then slows down both the hydration process and the formation of the crystals [28]. The MCE has a role in managing moisture content and maintaining an appreciable amount of water for subsequent hydration as explained in Section 11.2. As mentioned in Section 11.3, when concrete with w/c ratio of 0.32 was cured at 60°C, the water absorption rate was decreased by about 79% after the addition of 2% of the MCE solution to the concrete mixture [28]. Also, the addition of 4% of the MCE solution to the concrete mixture cured at 60°C with w/c ratio of 0.32 increased the 28-days compressive strength by more than 64% (compared to control), while the addition of 2% MCE at the same conditions but with w/c ratio of 0.46 increased the 28-days compressive strength by 8% [28].

11.4.2 Enhancing concrete resistance to cycles of freezing and thawing using multicrystallization enhancer

The aforementioned abilities of the MCE to control the thermal effects also assist in reducing concrete damages resulting from cycles of freezing and thawing. Such a frost performance was shown experimentally by subjecting control and MCE-dosed fully cured concrete specimens to cycles of freezing and thawing in water [26,29,30] or in air [29,30] and then determining the changes in length, mass, rate of water absorption, and/or selected mechanical characteristics of the tested specimen. Fig. 11.11 compares percentage relative dynamic modulus as a function of number of freezing and thawing cycles for control and MCE-dosed concrete [26], from standard testing in water (according to ASTM C666 [49]) but by cycling between more extreme temperatures of −53°C to 22°C instead of −29°C to 4°C specified by the ASTM C666. Fig. 11.11 shows that the percentage relative dynamic modulus of the MCE-dosed concrete is much higher than that of the control concrete indicating a higher dimensional stability [26]. Adding the MCE to concrete was found to decrease the percentage mass loss after 300 cycles of freezing and thawing by 92% and decrease the percentage length change by 15% [26]. This enhancement of frost resistance is attributed to the ability of the MCE-dosed concrete to prevent water freezing during the freezing cycles. Al-Jabari et al. [26] confirmed that during the freezing cycles, the internal temperature of the MCE-dosed specimen remained above freezing temperature (nearly >40°F) while that of the control specimen dropped significantly below freezing (by about 12°F−18°F).

The effectiveness of the MCE in protecting concrete against frost actions was demonstrated in other studies [29,30] by subjecting control and MCE-dosed concrete specimens for a longer number of freezing and thawing cycles in water (1080 cycles). Each cycle alternated between −10°C and 6°C for a duration of 4 hours, and the test continued for a continuous time period of 6 months. Moreover, such an effectiveness

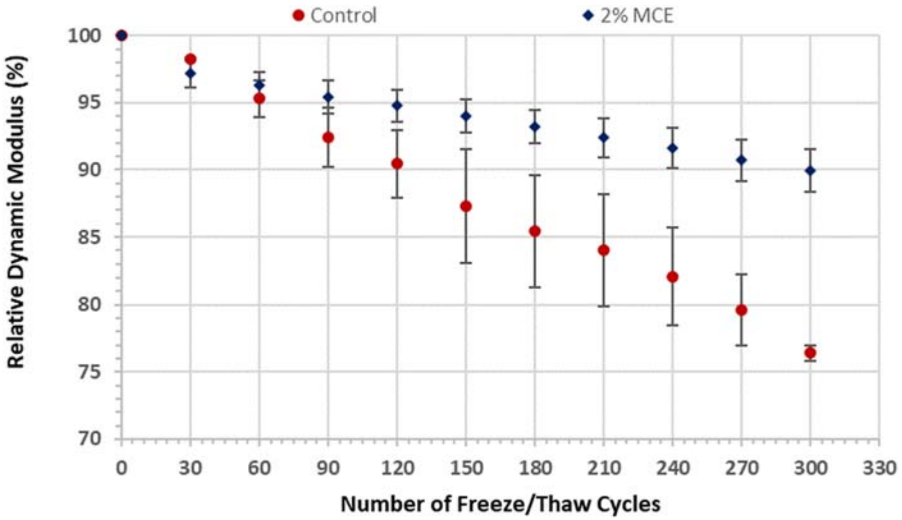


Figure 11.11 Percentage relative dynamic modulus versus number of freezing and thawing cycles using modified ASTM C666 (i.e., cycling under more extreme temperatures of 64˚F to 72˚F) for specimens of control concrete 2% MCE-dosed concrete (Iowa DOT C4WRC20 at w/c of 0.40) (unpublished work) [26].

was also demonstrated by subjecting similar specimens to cycles of freezing and thawing in air for a similar testing time period of 6 months. In this second type of test, each cycle was alternated between −20°C and 20°C for a duration of 24 hours, and thus the time period of 6 months resulted in a net number of 180 cycles [29]. Then, the resulting mass loss, rate of water absorption, and compressive strength of the tested specimens were compared for control, 2% MCE, and 4% MCE-dosed concrete at various w/c ratios [29]. The results revealed that the level of the long-term frost performance of the MCE-dosed concrete was dependent on the w/c ratio and the dosage of the MCE. Fig. 11.12 compares the water absorption rate after 6 months of

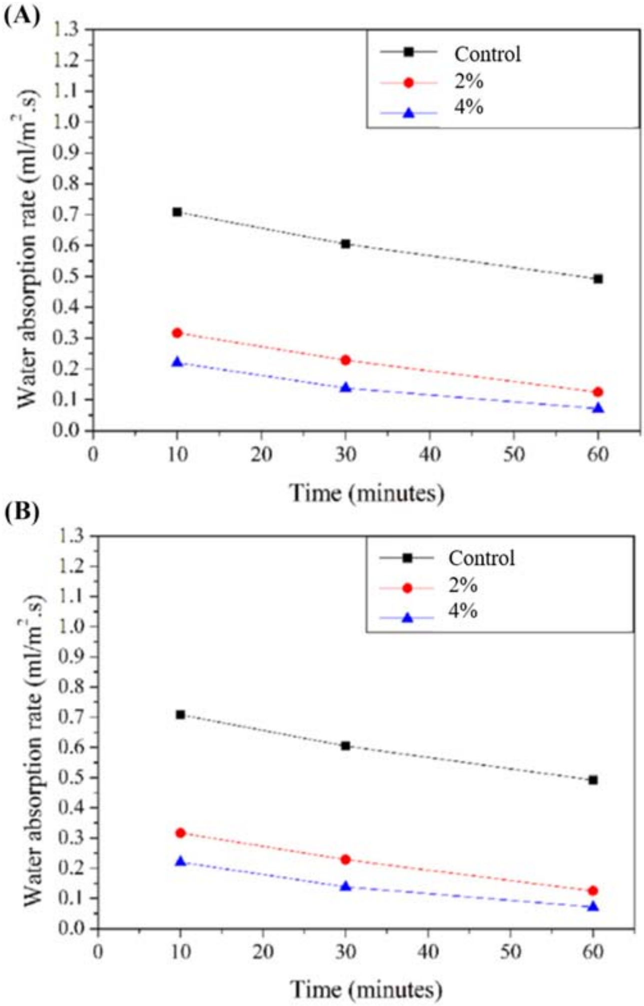


Figure 11.12 Water absorption in control, 2% MCE, and 4% MCE-dosed concrete specimens (with w/c ratio of 0.37) after being subjected to 6 months of freezing and thawing 1080 6-h cycles in water (A) and 180 24-h cycles in air (B) [27].

freezing and thawing in water and in air for control, 2% MCE, and 4% MCE-dosed concrete with w/c ratio of 0.37 [29]. Fig. 11.12 shows a significant reduction in water absorption rate in 2% MCE and 4% MCE-dosed specimens. A nearly similar performance was obtained for specimens with a lower w/c ratio (0.32). After the 1080 cycles, the percentage reduction in the water absorption rate for the dosage of 2% MCE was 78% and 85% for mixtures with 0.32 and 0.37 w/c [29]. Larger reductions were observed when these low w/c ratio's specimens (0.32 and 0.37) were subjected to freezing and thawing in air [29]. However, for specimens with higher w/c ratios (0.4 or 0.46), the 2% MCE-dosed specimens maintained its significant performance in reducing the water absorption rate after the 6-month periods of freezing and thawing in water or in air, while the overdosed MCE specimens (4%) did not perform well, as they increased the water absorption rate over that of the control specimens. On the other hand, the performance of the overdosed MCE (4%) concrete at low w/c ratios (0.32 and 0.37) surpass that of the normal dose of 2% MCE [29]. Fig. 11.13 compares curves of mass loss as functions of number of freezing and thawing cycles in water for control, 2% MCE, and 4% MCE-dosed concrete with a w/c ratio of 0.37 [29]. The trends of effects of MCE dosages and w/c ratio on the percentage mass loss were similar to the aforementioned trends of the effects on water absorption rate [29]. For freezing and thawing in air, an increase in the mass of the specimen was observed due to the absorption of humidity. The trend of effects of the MCE dosage and w/c ratio for freezing and thawing in air was similar to that based on the mass loss after cycles of freezing and thawing in water, while the quantitative behaviors were different. Furthermore, a nearly similar performance was obtained when the specimens were evaluated based on the compressive strength. The MCE-dosed

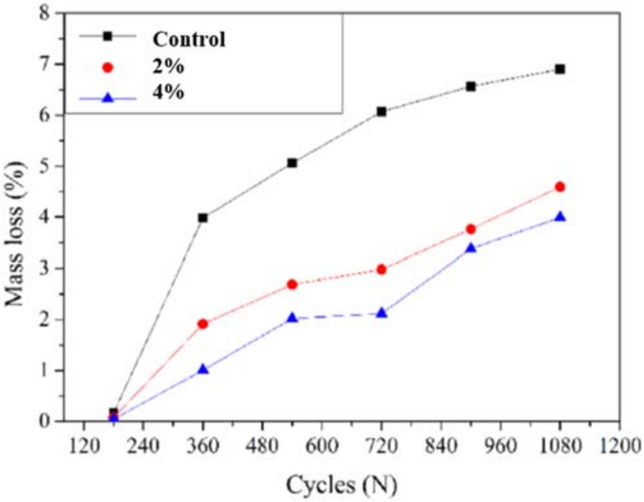


Figure 11.13 Comparative curves of mass loss as a function of number of freezing and thawing cycles in water for control, 2% MCE, and 4% MCE-dosed concrete with w/c ratio of 0.37 [27].

specimens maintained higher compressive strengths after freezing and thawing in water or in air only at low w/c ratios (0.32 and 0.37) [29].

11.5 Reducing chloride ion penetration in multicrystallization enhancer-dosed concrete

The decrease in water penetration is associated with a decrease in the chloride ion penetration as obtained through the indirect test of the electrical indication to resist chloride ion penetration according to ASTM C1202 [50]. The addition of the MCE to concrete mixture (Iowa C4-WRC20 concrete at a w/c of 0.4 tested after 7 days of curing) led to reduction in the total charge passage of 90.7% [25]. A similar performance (from a similar test) was obtained with the similar crystalline WP solution (the DCE) used as a topical surface treatment [22].

Furthermore, significant reductions in the chloride ion content in concrete dosed with MCE were obtained from direct tests from chloride ponding [27]. The level of reduction in the chloride ion content in concrete depends on the w/c ratio, curing conditions, and the dosage of the MCE. Fig. 11.14 compares the profiles of chloride

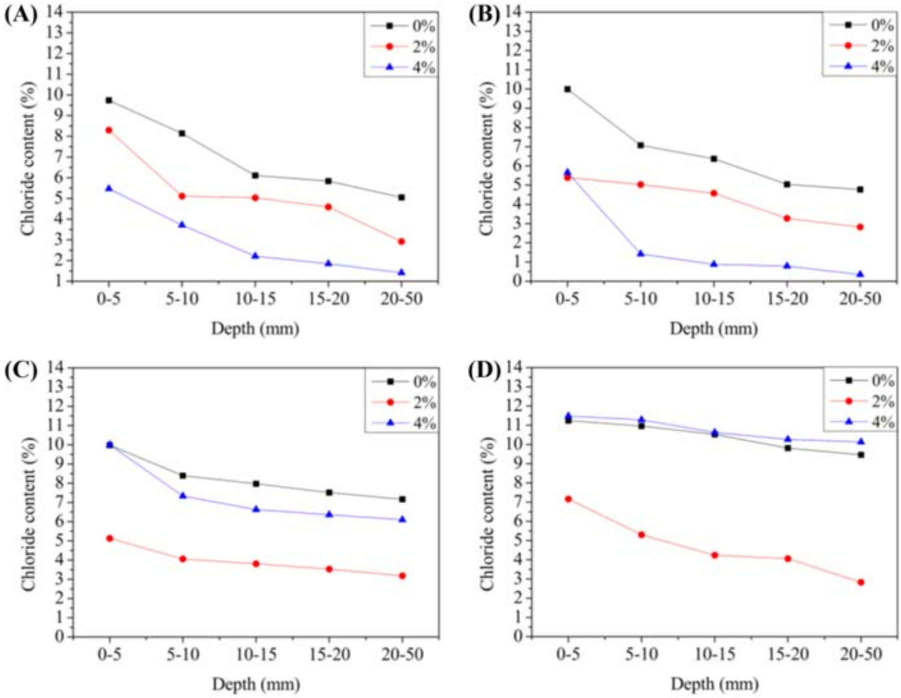


Figure 11.14 The profiles of chloride content in control, 2% MCE, and 4% MCE-dosed concrete specimens after curing in a water bath at 21°C for 28 days for various w/c ratio of 0.32 (A), 0.37 (B), 0.40 (C), and 0.46 (D) [30].

ion content in control, 2% MCE, and 4% MCE-dosed concrete specimens (fully cured) for various w/c ratios [27]. For the full range of the investigated w/c ratios (0.32–0.46), the addition of 2% MCE reduced the chloride ion content at all depths significantly. Larger percentage reductions were obtained when the MCE was dosed in porous concrete (e.g., with w/c ratio of 0.4 and 0.46) as the role of the MCE crystalline system and hydrophobic layer became more pronounced. For 4% MCE-dosed concrete, the penetration of chloride ions was reduced by more than 90% in the depth range of 20–50 mm for concrete with a w/c ratio of 0.37, and by more than 70% for concrete with a w/c ratio of 0.32. At high w/c ratios, the overdosage of the MCE loses its effectiveness.

11.6 Enhancement of concrete durability against alkali–silica reactions by multicrystallization enhancer

The role of the MCE in reducing concrete porosity, water permeability, and the diffusivities of aggressive ions hinders the rate of ASR. This is also associated with its role in decreasing the moisture content in concrete (see Fig. 11.3). In fact, there is no noticeable discussions on mitigating ASR in literature handling the impacts of WP materials on the durability of concrete [51–55] or in papers presenting crystalline powder admixtures [31,37,42,56,57]. The ASR are shown to be mitigated by the DCE topical surface treatment [22] and by the addition of the MCE [25]. The efficacy of mitigating ASR is commonly evaluated by laboratory testing of aggregates casted in mortars and placed under accelerating conditions involving aggressive thermal and chemical environment according to the procedures of ASTM C 1260 [58] or ASTM C1567 [59]. These ASTM standards specify an allowable limit of percentage length expansion of 0.1 at 16 days for low risk of deleterious ASR (or innocuous behavior). A potentially deleterious ASR deteriorations under field conditions are assumed valid when the 16-days percentage length expansion exceeds 0.2%. When the percentage length expansion is between 0.1% and 0.2%, these short-term tests are considered inconclusive, hence a long-term test according to ASTM C1293 is then required [60]. When the 1-year percentage expansion (according to ASTM C1293) is above 0.04%, the aggregates are potentially reactive.

The addition of the MCE to concrete mixtures leads to mitigating ASR and to significant dimensional stability. The activity of ASR is based on the dissolution of the reactive silica from aggregates, a process that requires a sufficient moisture in concrete (e.g., >80% relative humidity) [11]. The hygroscopic and hydrophilic crystals of the MCE causes major reductions in the internal humidity of concrete by vapor adsorption and swelling, as indicated in Section 10.2 [24]. In addition, the curing reactions of the ingredients of the MCE system consume part of the calcium hydroxide and hence reduce the severity of the alkaline pore solution. Furthermore, the mechanism of mitigating ASR involves (1) discontinuing the water phase (which is the vehicle for aggressive ions and the medium for ASR process), (2) reducing the alkalinity and the severity of the pore solution, and (3) creating an internal hydrophobicity that minimizes the wetting of the aggregates and thus reduces the contact area between the alkaline pore solution and the active silica content of the aggregates.

The percentage reduction in the percentage length expansion by the addition of the MCE is affected by the types of the aggregates and the porosity of concrete or w/c ratio [61]. The ability of MCE to reduce ASR was tested experimentally for aggregates from five different sources in North America [25]. The curves of the percentage length expansion for control and MCE-dosed specimens are compared in Fig. 11.15 for reactive aggregates of the North Platte NE type. Similar curves are shown in Fig. 11.16 for another reactive aggregates composed of New Brunswick Stone. Figs. 11.15 and 11.16 show that for these two types of reactive aggregates, the percentage length expansions at 16 days for MCE-dosed specimens are lower than the allowable ASTM limit of 0.1%, while that for control specimens are much higher than the 0.2% limit. For these cases, the use of the MCE shifts the ASTM classification of these aggregates from reactive to nonreactive. This is achieved regardless of the use of 16- or 28-days expansion as a classification criterion. For other cases of highly reactive aggregates (e.g., Texas aggregates), the use of the MCE can shift the ASTM classification of the aggregates from reactive to inconclusive ASTM classification [25]. The percentage reductions in the length expansion

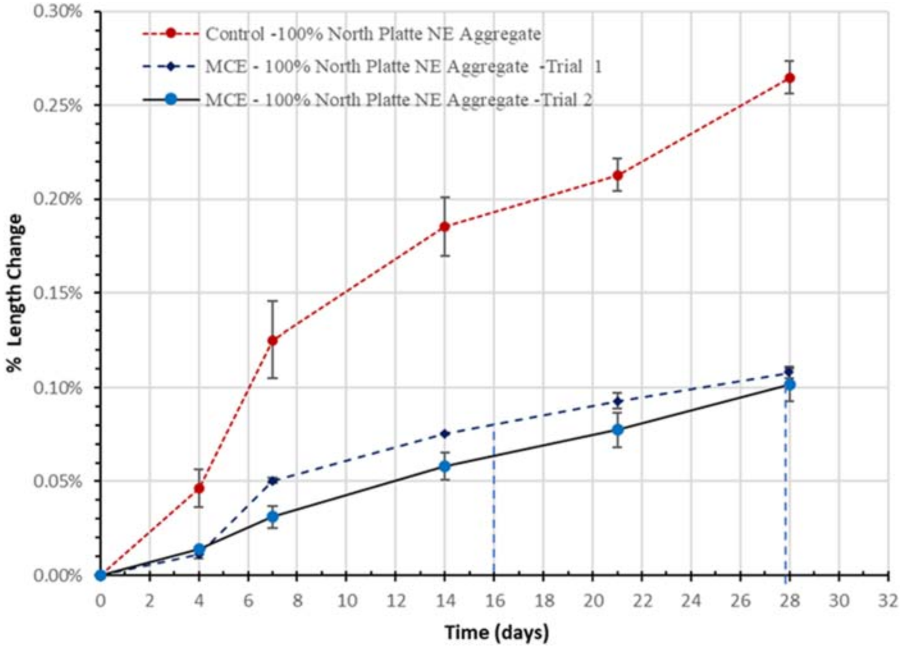


Figure 11.15 Curves of percentage length expansion as functions of time for control mortar specimens made with North Platte NE aggregate and for two duplicates of similar specimens made with the addition of 2% MCE, all with 100% coarse aggregates at w/c 0.47, (unpublished work) [25].

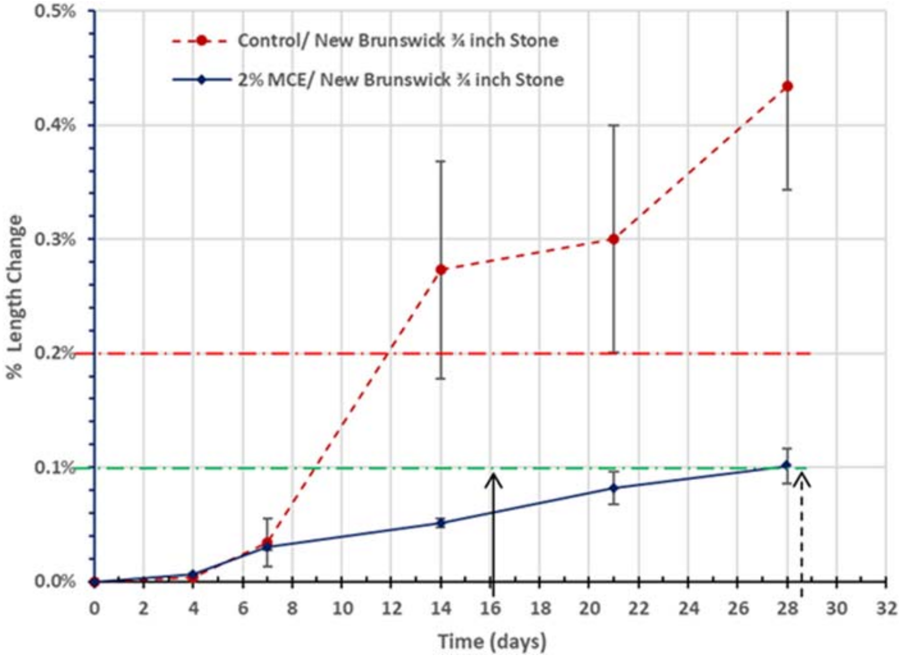


Figure 11.16 Curves of percentage length expansion as functions of time for control mortar specimens made with New Brunswick Stone aggregates (100% coarse aggregates), at w/c 0.47, compared to similar specimens made with 2% MCE obtained from separate trails, (unpublished work) [25].

Table 11.2 Percentage reduction in length of expansion by ASR after 28 days at w/c = 0.47, (unpublished work) [25].

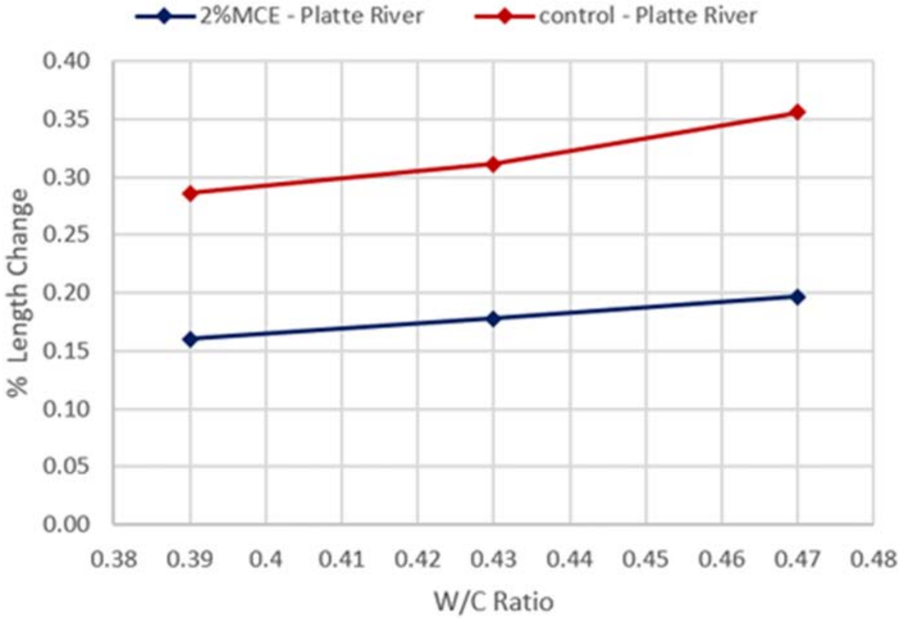
Aggregate source	ASTM classification	Percentage ratio of fine/coarse aggregates	% reduction in ASR expansion
North Platte, NE, United States	Reactive	0/100	61%
New Brunswick Stone, Canada	Reactive	0/100	77%
Texas, United States	Highly reactive	0/100	63%
Platte River, west of Omaha, Nebraska, United States	Reactive	50/50	44.7%
Ames Mine, United States	Nonreactive	50/50	32.7%

after 28 days for the five different aggregates are listed in Table 11.2 [25]. Table 11.2 indicates that a percentage reduction in the length expansion within the range of 61%–77% can be obtained for the reactive limestone aggregates [22]. This obtained efficacy of the MCE is higher than the reported efficacy when SCMs are used, for example, replacing 10% of the cement weight by silica fume achieved 50% reduction in ASR expansions [9]. For highly reactive gravels (of Platte River type), a lower percentage reduction in the length expansion (45%) was reported from testes involving equal proportions of the gravels and nonreactive sand. In fact, a decrease in the efficacy of the MCE for mitigating the ASR can be expected with lowering the level of the ASR attacks through decreasing the amount of reactive aggregates in the mixture. Furthermore, for nonreactive aggregates of Ames Mine type, the percentage reduction in the length expansion was 33%. This low percentage is believed to be obtained as these aggregates already had a minimal ASR reactivity coming from the stability of their structure and the silica content.

Furthermore, the effects of w/c ratio on the percentage length expansion (at 28 days) of control and MCE-dosed mortar specimens are shown in Fig. 11.17 for two types of aggregates (Ames Mine and Platte River). The level of the ASR deterioration increases with increasing the w/c ratio due to the increase in concrete porosity and other transport properties. However, the MCE remains active for mitigating ASR at all w/c ratios. Table 11.3 compares the percentage reductions in ASR after 28 days for two types of aggregates. Within the investigated range of w/c (0.39–0.47), the percentage reductions in ASR expansion for the reactive aggregates were within the range of 43%–45%. A larger percentage reduction was obtained for nonreactive aggregates at low w/c ratios (Table 11.3).

In the study of Al-Jabari et al. [25], the efficacy of mitigating ASR by a new approach of prewetting the aggregates with MCE was established experimentally. Fig. 11.18 compares the curves of the percentage length expansion for control and MCE-wetted gravel (of Platte River type mixed with equal amounts of nonreactive sand) [25]. Fig. 11.18 shows that wetting the reactive aggregates with the MCE can achieve a reasonable reduction in the percentage expansion at all days. Based on the 16-days ASTM criterion, prewetting the combined aggregates of reactive gravels and nonreactive sand (50/50) shifts the ASTM classification of the reactive aggregates from reactive to inconclusive. This performance is attributed to the pore-blocking effect of the reactive aggregates by the absorbed MCE within their structure. This effect decreases the rate of water penetration into the aggregates and then hinders the leaching of the reactive silica from the aggregates structure. In addition, the growth of the produced MCE crystals with moisture promotes their expansion from within the aggregates toward the adjacent paste layer. This crystal growth can lead to a significant densifying effect of the Interstitial Transition Zone, which is normally more porous and more permeable than the paste bulk (see Chapter 2). Prewetting the reactive aggregates with the MCE can achieve a percentage reduction in 28-days ASR expansion by about 27%. This efficacy is lower than that for the case of the direct addition of the MCE to the mixture (45%) but slightly above that for the DCE topical surface treatment (24%) (see Chapter 10) [22]. For the purpose of comparison of these treatment approaches, Fig. 11.18 compares the

(A) reactive aggregates



(B) Non reactive aggregates

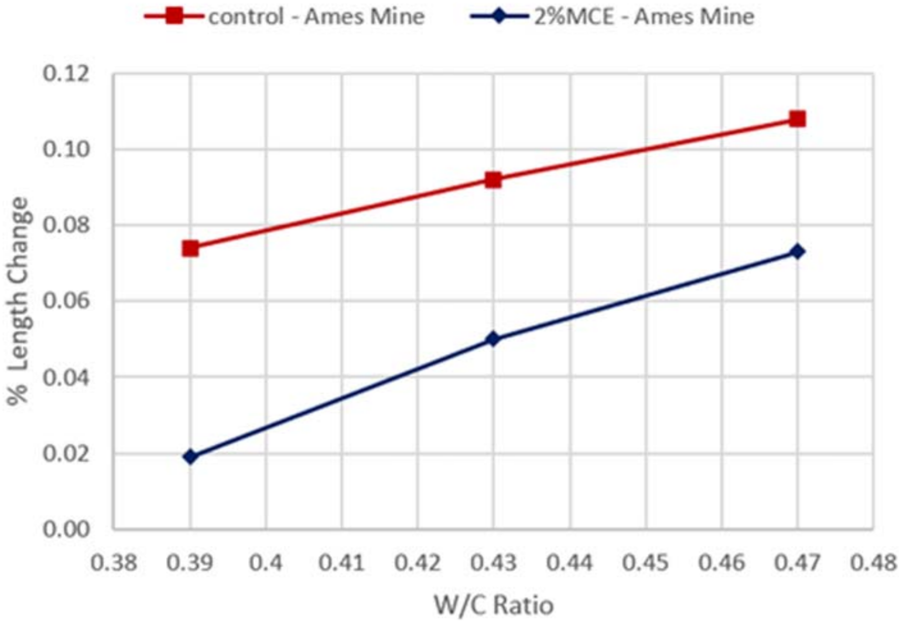


Figure 11.17 Percentage length expansion at 28 days as functions of w/c ratios, for mortar specimens made with Ames Mine aggregates (A) and Platte River aggregates (B) with 50/50 proportions, (unpublished work) [25].

Table 11.3 Percentage reduction in ASR after 28 days at various w/c ratios, for two types of aggregates of Ames Mine and Platte River, (unpublished work) [25].

w/c	**Percentage reduction**	
	Platte river gravel (reactive)	**Ames mine (nonreactive)**
0.39	44.0%	73.7%
0.43	42.9%	45.4%
0.47	44.7%	32.7%

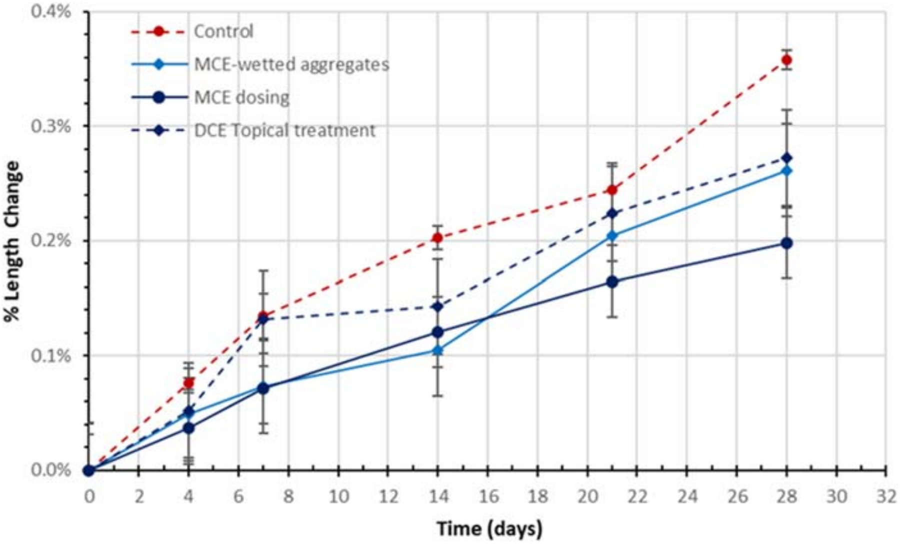


Figure 11.18 Curves of percentage length expansion as functions of time for control mortar specimens compared to those for MCE-dosed specimen, MCE-wetted aggregates, and DCE topical treatment, all made with Platte River gravels at w/c of 0.47 and the same proportions of 50/50.

Source: Data from Al-Rashed, R. & Al-Jabari, M. [22] and Al-Jabari, M. & Al-Rashed, R. [25].

curves of the percentage length expansion for MCE-dosed concrete, MCE-wetted aggregates, and DCE topical treatment. Fig. 11.18 shows that the three approaches lead to a similar trend of reducing the ASR attacks. Based on the 16-days ASTM criterion, the three approaches shift the classification of the reactive aggregates from reactive to inconclusive. The differences in the performance of MCE application methods could be attributed to variations in the net amounts of the MCE that is made available in each method of application within the paste.

References

[1] Porras, Y., Jones, C., & Schmiedeke, N. (2020). Freezing and thawing durability of high early strength Portland cement concrete. *Journal of Materials in Civil Engineering*, *32*(5).

[2] Glass, G., & Buenfeld, N. (2000). Chloride-induced corrosion of steel in concrete. *Progress in Structural Engineering and Materials*, *2*(4), 448−458.

[3] Santhanam, M., & Otieno, M. (2016). 5—Deterioration of concrete in the marine environment. In M. G. Alexander (Ed.), *Marine concrete structures* (pp. 137−149). Woodhead Publishing.

[4] Mingyu, H., Fumei, L., & Mingshu, T. (2006). The thaumasite form of sulfate attack in concrete of Yongan Dam. *Cement and Concrete Research*, *36*(10), 2006−2008.

[5] Jianxia, S. (2012). 6.14—Durability design of concrete hydropower structures. In A. Sayigh (Ed.), *Comprehensive renewable energy* (pp. 377−403). Oxford: Elsevier.

[6] Anon. (2002). Chapter 3: Fly ash, slag, silica fume, and natural pozzolans. *Design and control of concrete mixtures, EB001* (pp. 57−72). Portland Cement Association.

[7] Tran, P. C., et al. (2018). Carbonation proofing mechanism of silicate-based surface impregnations. *Journal of Advanced Concrete Technology*, *16*(10), 512−521.

[8] Hobbs, D. W. (2015). *Alkali-silica reaction in concrete*. London: Thomas Telford Publishing.

[9] Saha, A. K., et al. (2018). The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials*, *171*, 743−758.

[10] Thomas, M. D., Fournier, B., & Folliard, K. J. (2008). *Report on determining the reactivity of concrete aggregates and selecting appropriate measures for preventing deleterious expansion in new concrete construction*. United States: Federal Highway Administration.

[11] Fernandes, I., & Broekmans, M. A. (2013). *Alkali–silica reactions: an overview*. Part I. *Metallography, Microstructure, and Analysis*, *2*(4), 257−267.

[12] Viitanen, H., et al. (2010). Moisture and bio-deterioration risk of building materials and structures. *Journal of Building Physics*, *33*(3), 201−224.

[13] Javaherdashti, R., et al. (2009). On the impact of algae on accelerating the biodeterioration/biocorrosion of reinforced concrete: A mechanistic review. *European Journal of Scientific Research*, *36*(3), 394−406.

[14] Lence, A., et al. (2014). Best practices for maintenance of concrete bridge elements against mold and mildew growth. In *Proceedings of the construction research congress*: Atlanta Georgia, USA.

[15] ACI. (1986). *Committee 515, ACI 515.1R-79. A guide to the use of waterproofing, dampproofing. Protective, and decorative barrier systems for concrete*. Farmington Hills, MI: American Concrete Institute.

[16] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI: American Concrete Institute.

[17] Jalali, U. H., & Afgan, S. (2018). Analysis of integral crystalline waterproofing technology for concrete. *International Research Journal of Engineering and Technology (IRJET)*, *5*(10).

[18] Biparva, A., & Gupta R. (2010). Smart Waterproofing System: A Review. Proceedings of the International Conference on Future Concrete.

[19] Mundo, R. D., et al. (2020). Recent advances in hydrophobic and icephobic surface treatments of concrete. *Coatings*, *10*(5), 449.

[20] ACI. (2013). *Committee 515, ACI 515.2R-13. Guide to selecting protective treatments for concrete*. Farmington Hills, MI: American Concrete Institute.

[21] Al-Rashed, R., & Jabari, M. (2020). Dual-crystallization waterproofing technology for topical treatment of concrete. *Case Studies in Construction Materials*, *13*, e00408.

[22] Al-Rashed, R., & Al-Jabari, M. (2021). Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete. *Case Studies in Construction Materials*, *15*, e00635.

[23] Al-Rashed, R. (2008). *Aqueous chemical mixture to mitigate water associated problems in concrete pavements*. USA Patents.

[24] Al-Rashed, R., & Al-Jabari, M. (2021). Multi-crystallization enhancer for concrete waterproofing by pore blocking. *Construction and Building Materials*, *272*, 121668.

[25] Al-Jabari, M., et al. (2022). Mitigating alkali silica reactions in concrete by waterproofing using multi-crystallization enhancer. International Chem-Crete Co., Richardson, Texas, USA.

[26] Al-Jabari, M., et al. (2022). *Managing thermal effects in waterproofed concrete with multi-crystallization enhancer*. Richardson, Texas: International Chem-Crete Co.

[27] Rahman, M., & Al-Kheetan, M. (2019). Integration of Anhydrous Sodium Acetate (ASAc) into Concrete Pavement for Protection against Harmful Impact of Deicing Salt. *JOM, 71*, 4899–4909.

[28] Al-Kheetan, M. J., et al. (2020). Development of low absorption and high-resistant sodium acetate concrete for severe environmental conditions. *Construction and Building Materials*, *230*, 117057.

[29] Al-Kheetan, M. J., et al. (2020). Comprehensive investigation of the long-term performance of internally integrated concrete pavement with sodium acetate. *Results in Engineering*, *6*, 100110.

[30] Mazen, A.-K., Rahman, M., & Ghaffar, S. (2020). Advanced freeze-thaw assessment of internally integrated concrete with sodium acetate. In *International conference on civil infrastructure and construction (CIC* 2020).

[31] Azarsa, P., Gupta, R., & Biparva, A. (2019). Assessment of self-healing and durability parameters of concretes incorporating crystalline admixtures and Portland limestone cement. *Cement and Concrete Composites*, *99*, 17−31.

[32] Matar, P., & Barhoun, J. (2020). Effects of waterproofing admixture on the compressive strength and permeability of recycled aggregate concrete. *Journal of Building Engineering*, *32*, 101521.

[33] Pazderka, J., & Hájková, E. (2016). Crystalline admixtures and their effect on selected properties of concrete. *Acta Polytechnica*, *56*(4), 306−311.

[34] ASTM. (2013). *C642-13. Standard test method for density, absorption, and voids in hardened concrete*. In Annual Book of ASTM Standards. STM International: West Conshohocken, PA.

[35] CRD. (1992). *C48–92*. *Standard test method for water permeability of concrete*. U.S.: Army Corps of Engineers.

[36] Azarsa, P., Gupta, R., & Biparva, A. (2018). Crystalline waterproofing admixtures effects on self-healing and permeability of concrete. In *1st International conference on New Horizons in Green Civil Engineering (NHICE-01)*. Victoria, BC, Canada.

[37] Azarsa, P., Gupta, R., & Biparva, A. (2020). Inventive microstructural and durability investigation of cementitious composites involving crystalline waterproofing admixtures and Portland limestone cement. *Materials*, *13*(6), 1425.

[38] ASTM. (2016). *F1869. Standard test method for measuring moisture vapor emission rate of concrete subfloor using anhydrous calcium chloride*. In Annual Book of ASTM Standards. ASTM International: West Conshohocken, PA.

[39] Bullard, J. W., et al. (2011). Mechanisms of cement hydration. *Cement and Concrete Research*, *41*(12), 1208−1223.

[40] Mounanga, P., et al. (2004). Predicting Ca $(OH)_2$ content and chemical shrinkage of hydrating cement pastes using analytical approach. *Cement and Concrete Research*, *34* (2), 255−265.

[41] ASTM. (2016). *ASTM C403/C403M–16. Standard test method for time of setting of concrete mixtures by penetration resistance*. In Annual Book of ASTM Standards. West Conshohocken, PA: ASTM International.

[42] de Souza Oliveira, A., et al. (2020). Crystalline admixture effects on crystal formation phenomena during cement pastes' hydration. *Journal of Thermal Analysis and Calorimetry*, *139*(6), 3361−3375.

[43] Gyu-Yong, K., et al. (2009). Evaluation of properties of concrete using fluosilicate salts and metal (Ni, W) compounds. *Transactions of Nonferrous Metals Society of China*, *19*, s134−s142.

[44] Choi, W.-C., Khil, B.-S., & Yun, H.-D. (2015). Characteristics of structural concrete containing fluorosilicate-based admixture (FBA) for improving water-tightness. *Construction and Building Materials*, *74*, 241−248.

[45] Chen, Y.-Y. (2019). Effects observed in temperature rise evaluation tests for mass concrete. *Technical journals*, *34*(2), 81−94.

[46] de Matos, P. R., et al. (2020). Effectiveness of fly ash in reducing the hydration heat release of mass concrete. *Journal of Building Engineering*, *28*, 101063.

[47] Han, S. (2020). Assessment of curing schemes for effectively controlling thermal behavior of mass concrete foundation at early ages. *Construction and Building Materials*, *230*, 117004.

[48] Gajda, J., & Vangeem, M. (2002). Controlling temperatures in mass concrete. *Concrete International*, *24*(1), 58−62.

[49] ASTM. (2015). *C666/C666M-15. Standard test method for resistance of concrete to rapid freezing and thawing*. In Annual Book of ASTM Standards. West Conshohocken, PA: ASTM International.

[50] ASTM. (2019). *C1202–19. Standard test method for electrical indication of concrete's ability to resist chloride ion penetration*. In Annual Book of ASTM Standards. ASTM International: West Conshohocken, PA.

[51] Almusallam, A. A., et al. (2003). Effectiveness of surface coatings in improving concrete durability. *Cement and Concrete Composites*, *25*(4), 473−481.

[52] Pan, X., et al. (2017). A review on surface treatment for concrete – Part 2: Performance. *Construction and Building Materials*, *133*, 81−90.

[53] Pan, X., et al. (2017). A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578−590.

[54] Muhammad, N. Z., et al. (2015). Waterproof performance of concrete: A critical review on implemented approaches. *Construction and Building Materials*, *101*, 80−90.

[55] Berndt, M. L. (2011). Evaluation of coatings, mortars and mix design for protection of concrete against sulphur oxidising bacteria. *Construction and Building Materials*, *25* (10), 3893−3902.

[56] Reiterman, P., et al. (2020). Reduction of concrete surface permeability by using crystalline treatment. *Revista Romana de Materiale*, *50*(1), 69−74.

[57] Žáková, H., Pazderka, J., & Reiterman, P. (2020). Textile reinforced concrete in combination with improved self-healing ability caused by crystalline admixture. *Materials*, *13*(24), 5787.

[58] ASTM. (2014). *C1260-14. Standard test method for potential alkali reactivity of aggregates (mortar-bar method)*. In Annual Book of ASTM Standards. ASTM International: West Conshohocken, PA.

[59] ASTM. (2013). C1567-13. *Determining the potential alkali–silica reactivity of combinations of cementitious materials and aggregate (accelerated mortar-bar method)*. In Annual Book of ASTM Standards. West Conshohocken, PA: ASTM International.

[60] ASTM. (2020). *C1293-20a. Standard test method for determination of length change of concrete due to alkali–silica reaction*. In Annual Book of ASTM Standards. West Conshohocken, PA: ASTM International.

[61] Chamberlain, D. A., & Boswell, L. F. (2005). The use of Pavix CCC100 as a reinforced concrete impregnate and as an alternative to silane. In *Performance based rehabilitation of reinforced concrete structures conference*. Prague, Czech Republic.

This page intentionally left blank

Waterproofing coatings and membranes

12

Maher Al-Jabari
Mechanical Engineering Department, Palestine Polytechnic University, Hebron, Palestine

12.1 Introduction

Concrete is subjected to various aggressive conditions that cause water penetration and lead to several types of water-related problems and durability issues, as discussed in Chapter 3. The waterproofing (WP) barrier can provide a protective treatment for extending the service life of concrete structures and a method for retaining water within a structure. The performance and durability characteristics are governed by the surrounding conditions, which include level water exposure, types of contaminations, climate conditions, possible phase change, and mechanical conditions (e.g., abrasion). Damped concrete structures (e.g., hydraulic structures [1] and marine structures [2]) are subjected to a hydrostatic pressure that creates water permeation flow (see Chapter 2) and needs WP materials. On the other hand, concrete surfaces that are subjected to cyclic wetting (e.g., unsaturated building walls and roofing) promote capillary absorption (see Chapter 5) and needs dampproofing [3]. Dampproofing and WP terminologies are included in ASTM D449/D449M [4]. Typically, cementitious WP coatings are applied for underground concrete structures such as basements, and for water retaining structures such as in swimming pools.

Chapter 6 covers the various categorizations of WP approaches: WP techniques are categorized, according to ACI 515.1R [5], into membranes, dampproofing, and capillary blocking. The European categorization of WP materials (EN 1504-2) [6] categorizes surface treatments into coatings, pore liners, and pore blockage. In fact, some authors categorize the WP materials simply into organic and inorganic materials [7]. Other categorization approaches combine physical structure, chemical composition, and WP approach, in which the WP materials are categorized into film forming organic coatings, cementitious layers, pore-lining hydrophobic treatments, and pore filling treatments [8]. In the two review papers of Pan et al. [7,9], WP of concrete surfaces were categorized into coatings, hydrophobic impregnation, and pore blocking treatment. These categorizations include materials that function externally and others that function internally after penetration into concrete structure. Hence, WP approaches are categorized in this book (Chapter 6) mainly into (1) external WP barriers that prevent or reduce the incoming water flux to the concrete and (2) internal WP systems that redesign the pores (by pore blocking and/or pore lining), making the whole concrete structure or a surface section water-resistant (Chapters 7–11). This chapter is devoted to the first WP approach that includes polymeric barriers

Integral Waterproofing of Concrete Structures. DOI: https://doi.org/10.1016/B978-0-12-824354-1.00012-X

(PB) and nonpolymeric barriers. It covers the backgrounds and applications of polymeric and cementitious WP coatings. The generic formulations, structures, and the chemical and physical mechanisms are discussed and the performance and durability parameters are presented.

12.2 Terminologies and categories of external waterproofing barriers

In principle, the "coating" term covers any liquid or semisolid material applied onto a concrete surface. However, the terminology of WP coatings includes some overlap between external barriers and nonfilm penetrating solutions, which are used for surface treatment (see Chapter 6). For example, the ACI Concrete Terminology [10] refers to penetrating surface treatment under coating terminology. Similarly, the two review papers of Pan et al. [7,9] combined the coatings with liquid penetrating materials under "surface treatment." As indicated earlier, the terminology of coating is restricted in this book to the formation of a continuous external surface layer. It is hard sometimes to distinguish between the terminologies of coating systems and liquid membranes. Hence, the membranes and coatings are grouped, in this book, under external barriers, while reactive solutions applied to concrete surfaces (covered in Chapters 7–10) are labeled under surface treatment. Table 12.1 lists the types, compositions, and the main mechanisms of WP barriers, which include PB, cementitious coatings (CC), and combined polymer-cementitious systems. These types of WP barriers are covered in various international standards and guides such as ACI 515.1R [5], ACI 515.2R [11], and EN 1504-2 [6]. Fig. 12.1 illustrates the main types and mechanisms of WP barriers. Overall, the PB are considered totally external as they have limited penetration depths ($<400\,\mu m$) [7] with no significant effect on concrete pores (see Fig. 12.1A). On the other hand, most of the CC involve major penetrations of active ingredients within the concrete structure and hence they redesign the pores' structure (see Fig. 12.1C and D). Consequently, crystalline or hydrophobic CC are considered integral WP materials. Although cement-based coatings and mortars typically include pore penetrating integral WP materials, they are covered in this chapter because they form a continuous surface layer. This topic coverage is in line with previous literature: for example, Nair and Gettu [12] categorized the external WP systems into membranes, coatings, and modified cement mortars. Similarly, Pan et al. [7] categorized the external layers into polymer coatings, clay-nanocomposite polymer coatings, and CC. The cementitious WP layers include motors in addition to thin coatings. The crystalline CC are used in water retaining structures such as reservoirs, water tanks, swimming pools, and as a protective system for reinforced concrete for improving its durability [13]. The cement-based WP systems include polymer-modified cementitious coatings (PMCC), which combine polymeric compounds with cementitious materials for improving the mechanical properties of coatings (e.g., strength, resilience, adhesion) and water resistances [7]. PMCC typically have low penetration depths similar to PB (see Fig. 12.1B). There are other types of WP barriers such as bentonite

Table 12.1 Types, composition, and mechanism of WP barriers.

Main WP category	Generic formulations	Functional water interactions	Active ingredients	Main mechanism
Cementitious coatings and mortars	Cementitious dry powder blends including active ingredients, cement, fine sand, and other additives that require only the addition of water upon application.	*Water swelling crystalline gel*	Silicate and fluorosilicate compounds.	Formation of external rigid barrier with diffusible pore blocking reactive materials that form hydrophilic crystals that expands by swelling within the cementitious layer and concrete pores.
		Vapor adsorbing crystals.	Proprietary alkali organic compounds.	Formation of external rigid barrier with diffusible pore blocking reactive materials that form hygroscopic crystals that expands by moisture adsorption within the cementitious layer and concrete pores.
		Water repellents.	Alkali salts and fatty acid derivatives (e.g., stearate compounds).	Formation of external rigid barrier with diffusible pore lining reactive materials that form hydrophobic molecular layer on surfaces of the pores of cementitious layer and concrete.
		water repellents and inert fillers.	finely divided inert fillers.	formation of external rigid barrier with water repelling surfaces based on the deposition of hydrophobic particles (with partial pore blocking) within the pores of the cementitious coating.

(*Continued*)

Table 12.1 (Continued)

Main WP category	**Generic formulations**	**Functional water interactions**	**Active ingredients**	**Main mechanism**
		Other ingredients.	Supplementary cementitious materials and chemical admixtures such as lignosulphonate compounds.	Formation of external rigid barrier with pore refinement mechanism of the cementitious coating, which is based on the use of mineral and chemical admixtures (as described in Chapters 1 and 7).
Polymer-modified cementitious coatings	One-component dry powder blends of cement, fine sand with polymeric additives (and fibers) that require the addition of water upon application.	*Flexible cementitious barriers*.	Redispersible polymer powders [e.g., poly (styrene-acrylic ester)].	Formation of external flexible impermeable cementitious barrier with pore blocking effects.
	Two-component system of blends of cement, fine sand, and fibers that require the addition of polymeric emulsion at the job site.	*Flexible cementitious barriers*.	Fibers and polymers (e.g., acrylic polymer).	Formation of external flexible impermeable cementitious barrier with pore blocking effects.
Polymeric barriers	Preformed sheets and liquid-applied membranes that are adhered to the concrete surface (with possible fibrous reinforcement).	*Bituminous membrane*.	Bituminous materials and coal tar emulsion with possible modification with polymers (e.g., styrene-butadiene-styrene copolymer).	Formation of external flexible barrier (dampproofing).

		Polymeric coatings	Polymeric compounds (e.g., acrylic, epoxy, polyurethane etc.).	Formation of external barriers with good adhesion to concrete and minimum blistering and cracking.
		Elastomeric membrane.	Polymeric compounds (e.g., styrene-butadiene-styrene, ethylene propylene diene monomer).	Formation of external elastomeric barrier with good adhesion to concrete and high resistance to UV and thermal effects.
		Thermoplastic membranes.	Polymeric compounds (e.g., polyvinyl chloride, high density polyethylene).	Formation of external thermoplastic strong barrier that resists hydrostatic pressure.

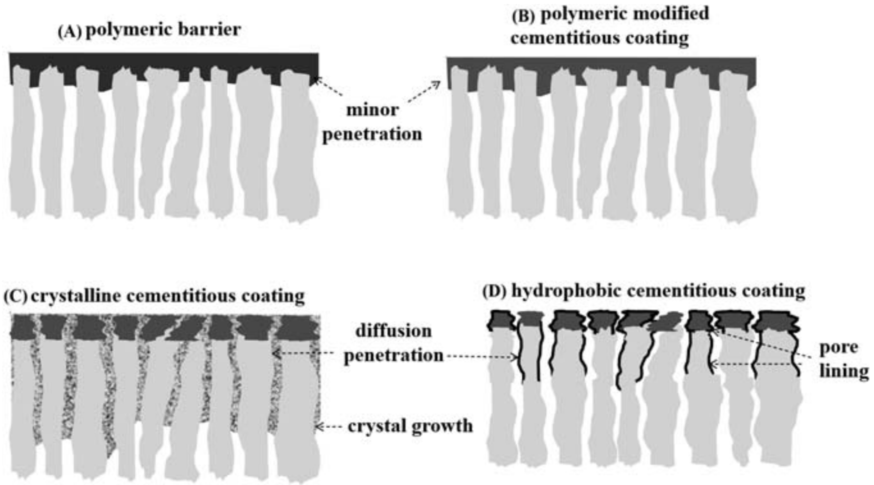


Figure 12.1 Main types of waterproofing barriers illustrating the levels of penetrations.

carpet or membrane [14]. The granules of bentonite compounds (e.g., sodium bentonite) are thixotropic with a high swelling capacity and thus they are transformed into a gel phase when immersed in water and create a barrier. They can absorb 12−15 times of its dry mass. These systems are not detailed in this chapter.

The PB include liquid membranes (constructed-in-place) such as bituminous and resinous systems and preformed sheets such as polymer, elastomer, and asphalt-laminated board systems [15]. The PB systems may make only one component of a full WP system consisting of several components and layers. Built-up systems are usually composed of multiple layers of mats or glass fabric mopped with bitumen or coal tar emulsion [16]. The "membrane is a barrier placed on top of the concrete and then protected by another material that functions as the riding surface" [17]. The types of PB include a wide range of systems that can be grouped into bituminous membrane, thermoplastic membranes, elastomeric membrane, and typical polymeric coatings (see Table 12.1). In fact, there is no unified terminology or standard categorization for PB. ASTM D 4071−84 [18] covers liquid-applied membranes, preformed sheets, and built-up membrane systems. The review of Wells, Palle, and Hopwood [19] categorized the systems for bridge decks into four groups: (1) liquid membranes, (2) sheet membranes, (3) friction polymers or thin overlays (laminates), and (4) polymer asphalts or thick impermeable overlays [19]. In the United States, some governmental institutions may use their own terminology for the barrier systems. For example, Virginia Department of Transportation (DOT) specifies five types of membrane systems [17]: three of them are for prefabricated fiber reinforced membranes that require the use of a primer and two hot-applied liquid membranes with protective covering. Massachusetts DOT specifications [17] include: (1) sheet systems of reinforced rubberized asphalt or reinforced tar and resin, (2) coal tar emulsions with glass fiber reinforcement, and (3) rubberized asphalt membranes that are hot-applied. The PB are also used for bridge decks in 60% of US state agencies, most Canadian provinces, and in many European countries [17]. However, there was a decrease in use of PB for new bridge decks in the United States since 1974 from 74% to 26% for the year 2011 [17].

WP can be applied to the negative or the positive side of water pressure on the concrete surface (see Chapter 6). The side of WP application governs the accessibility of moisture to concrete. Negative side application may cause a sandwiching effect of moisture (see Chapter 6). This can allow moistening the concrete structure (ACI 515.1 R) [5] and minimize drying shrinkage and cracking. On the other hand, moistening concrete increases deterioration by thermal attack under cycles of freezing and thawing and by chemical attack from penetration of harmful contaminants within moisture (e.g., chloride ions). For new below-grade structures, the WP barriers are typically applied to the positive side before backfilling. This application limits the accessibility of the WP side for repair and maintenance. In the common practices, most polymeric sheets and film forming materials are applied to the positive side. The CC are typically applicable to negative and positive sides. The PB are used for below-grade and above-grade concrete structures and roofing [17].

12.3 Types of materials for waterproofing barriers

12.3.1 Cementitious waterproofing coatings

The chemical composition of crystalline CC and mortars include blends of cement, fine sand, fibers, and WP active ingredients packaged in a dry powder form ready for mixing with water [13,20,21]. Selecting suitable grading of fine sand (e.g., using two different particle sizes) assists in reducing the porosity of the coating [22]. The typical formulations of CC include Portland cement ($40\% - 70\%$), quartz sand ($5\% - 10\%$), and active chemicals ($10\% - 30\%$) (weight percentages) [23]. In some CC, the dosage of the crystalline admixture is just at 2% [24]. Some formulations are further modified by adding supplementary cementitious material (SCMs) such as fly ash, slag, and silica fume [24–26]. SCMs are added as partial replacements of cement, for example, fly ash can be added at a dosage of 10% by weight [24]. The characteristics of fresh and hardened coatings might be further improved by the addition of water reducer admixtures and other additives [20], such as superplasticizer of polycarboxylate base [24,25].

The active ingredients in the CC and mortars are typical WP admixtures (see Chapter 7) [27–29]. These include hydrophilic and hygroscopic crystalline ingredients and hydrophilic materials. In less frequent applications, inert densifiers are also used. The main chemical families of additives include organic-polymeric, organometallic, inorganic compounds (see Chapter 6). In some applications, the adhesion and flexibility of the CC are enhanced through the addition of polymeric materials, leading to a category known as PMCC [8]. In other types, the formulations of CC combine crystalline materials with polymer compounds [22,24,29,30]. Table 12.2 lists

Table 12.2 Types of cementitious integral waterproofing coatings and mortars.

Type of integral cementitious coatings	Waterproofing mechanism	Application	Sample references
Hydrophilic crystallization	Pore blocking and crystal growth by swelling.	Waterproofing—resist hydrostatic pressure.	Al-Kheetan et al. [13]; Li et al. [20]; Saricimen et al. [21]; Zhang and Zheng [31].
Hygroscopic crystallization	Pore blocking and crystal growth by moisture adsorption.	Waterproofing—resist hydrostatic pressure.	Industrial literature.
Densifying materials	Pore refinement by filling pores with inert particles that increase the density.	Waterproofing—resist hydrostatic pressure.	Yang et al. [32].
Hydrophobic materials	Pore lining with water repellent molecular layer.	Dampproofing—do not resist hydrostatic pressure.	Li et al. [27,28]; Liu et al. [33]; Zhang et al. [34].
Polymer-modified cementitious coating	Combining pore lining and polymer networking.	Dampproofing.	Pan et al. [7]; Diamanti et al. [8]; Al-Kheetan et al. [13]; Jalal et al. [35]; Jappie [36].
Combine crystallization—polymer-modified cementitious coating	Combining pore blocking and polymer networking.	Waterproofing—resist hydrostatic pressure.	Bohus et al. [27]; Drochytka et al. [24]; Li et al. [29]; Lu et al. [22]; Qin et al. [30].

these types of WP cementitious materials. The performance mechanisms of CC are similar to those of other integral WP systems. These include (1) pore blocking through the formation of hydrophilic or hygroscopic crystals by chemical reactions with cementitious constituents, (2) pore lining through the formation of water repelling molecular layers from chemical reactions with the active sites at the cementitious surfaces, (3) pore refinement mechanism using mineral and chemical admixtures. In fact, these types of materials are essentially integral WP materials as the active ingredients penetrate into the concrete structure where they undergo chemical reactions or deposit within the pores of concrete and become an integral part of the cementitious structure. Upon curing, they harden and form a watertight coating that hinders the water penetration into concrete by minimizing water permeation or capillary absorption. Many CC are mainly based on crystallization [37]. The active ingredients in the crystalline CC are usually proprietary powders incorporated in Portland cement and fine sand [38,39]. The active chemicals in many industrial formulations of hydrophilic CC are silicate-based substances [23]. The activated chemicals in other formulations of CC include aluminosilicate (zeolite), sodium carbonate, sodium aluminate, tetrasodium EDTA, and glycine [20]. The proprietary particulate materials used for forming CC with hygroscopic crystallization systems are not unfold. The active ingredients in the hydrophobic coatings and mortars include powders of silane methyl [28], tri methoxy silane [33], -(methyl propylene oxy) propyl tri methoxy silane [27]. The water repellent admixtures (silane powders) are also added in the formulations of WP cement-based mortars for the surface protection of bricks, blocks, masonries, and cladding panels [28]. Also, white Portland cement was incorporated with silicone rubber (as a hydrophobic agent), and titanium dioxide as a solar reflective filler to obtain hydrophobic self-cleaning coating [40]. Materials used in formulating the PMCC are described in the following subsection.

12.3.2 Polymer-modified cementitious coatings and mortars

The PMCC and latex-modified mortars are made of dry blends of cement and fine sands with the addition of polymeric material that participate in the curing process of the cementitious materials [8,13]. The generic types of polymers that are mixed with Portland cement include (1) elastomeric polymers (e.g., natural rubber, synthetic latex, styrene-butadiene, and neoprene), (2) thermoplastic polymers (e.g., polyacrylic ester, styrene-acrylic, and polyvinyl acetate), (3) thermosetting polymers (e.g., epoxy resins, bituminous asphalt, rubberized asphalt, and coal-tar), and (4) mixed systems [36]. The polymer addition can be as dry polymeric powders blended within the cementitious powders (e.g., at a dosage of 10% of the cement weight) [7], or as liquid emulsions or solutions, which come as separate components and mixed with the cementitious powders at the job site. In formulations of dry blends of PMCC, reemulsifiable polymeric particle with particle size in the range of 1–10 μm are used [35]. The redispersible polymer powders include ethylene-vinyl-acetate, poly(styrene-acrylic ester), poly (acrylic ester), polyvinyl acetate [35]. The two-component powder and liquid systems involve the use of emulsions of elastomeric, thermoplastic, thermosetting, and bituminous latexes, which are prepared by emulsion polymerization of polymer particles dispersed in water. These include polyethylene, polypropylene, acrylics, styrene-butadiene rubber, acrylonitrile rubber, and styrene-acrylic ester [35]. The water-soluble polymers that can be added to the cement mortar as powders or as solutions include cellulose derivatives, polyvinyl alcohol, and polyacrylamide. The selection of the polymer is dependent on its physical properties (e.g., viscosity, glass transition temperature, and minimum film forming temperature), its compatibility with cementitious materials, and the required minimum dosage in the mix (or polymer/cement ratio) [35]. A detailed comparison between the properties of PMCC of various polymer additions is available elsewhere [36]. Overall, the PMCC can achieve the following four purposes [7]: (1) pore refinement of the coating structure by decreasing the number of pores larger than 100 nm and increasing the number of pores smaller than 100 nm, (2) forming a polymeric matrix within the coating structure, which increases the toughness of the paste and reduces the surface microcracks, and (3) polymer elasticity that mitigates shrinkage and provides the PMCC with a crack-bridging capability. The polymer particles reduce the formation of microcracks during the curing process [29]. The addition of polymers also improves the characteristics of the green slurry, by enhancing the workability and by decreasing the water/cement ratio (w/c) for a certain required consistency. This leads to high-strength coatings and reduces the permeability of the coatings [41], while maintaining good breathability [7].

There are various types of investigated formulations that combine crystallization materials with polymer compounds [22,24,29,30]. A proposed formulation of PMCC with crystalline materials includes a basic cementitious mixture that contains 270 kg of cement, 700 kg silica sand, and fly ash at a dosage of 10% of the binding material [24]. Then, a commercial crystalline admixture is added at a dosage of 2% of the binding material together with 10 kg of carboxymethyl cellulose and 5 kg of defoaming agent of synthetic copolymer base [24]. These powders are mixed with 700 kg of styrene-acrylate dispersion and 300 kg of water together with 8 kg of silica fume dispersion (5% solid content) [24]. Investigated polymeric systems included polymer redispersible powders of vinyl acetate and ethylene base (e.g., at a dosage of 3.5% of the powders), or styrene-acrylate dispersion powder with carboxymethyl cellulose [24]. Other formulations were based on sulphoaluminate cement, modified with lime stone powder, crystalline powders (about 4% of the binding material), silica fume (about 5% of the binding material), and hemihydrated gypsum (about 3% of the binding material) with vinyl acetate−ethylene copolymer redispersible powders [29]. The polymer dosage was at 6%−7% of the cementitious materials. In addition, lithium carbonate was added as a coagulant and naphthalene was added as a superplasticizer [29]. In these cases, the polymer particles occupy a fraction of the fine pores, form a hydrophobic layer, and reduce the formation of microcracks during the curing process [29]. At the same time, the crystallization WP mechanism was confirmed to cofunction with such a polymer functionality [24]: Similar crystals were observed in pores as those obtained with typical crystalline CC [26]. The presence of the crystalline active chemicals improves the secondary water impermeability and thus the self-healing characteristics of the polymer-modified waterproof mortar [29].

12.3.3 Polymeric barriers

The chemical formulations of PB are based on polymeric compound(s) in a carrier of organic solvent or emulsified in water and formulated with other additives for improving their characteristics. The additives include viscosity reducing materials, fillers, and/or reinforcing fibers. The phases of the PB at the time of application include semisolid materials, polymeric liquids, dispersions, and emulsions. They form membranes and sheets with a wide range of physicochemical characteristics and mechanical properties (e.g., adhesion, strength, elasticity). The quality and the performance of PB depend on their chemical structure and formulations. Table 12.1 lists the range of generic polymeric compounds that are used in PB. The survey of Russell [17] identified 23 types of proprietary PB that are used for WP application on pavements in the United States, Canada, and European countries. The following subsections describe selected polymeric membranes and coatings.

12.3.3.1 Sheet systems

The preformed sheet systems are factory-precured polymeric materials that are formed by calendaring or extrusion. They are cast to the required thickness and widths and are cured in sheet making factories and then packaged in rolls. The sheet membranes are typically made of thermoplastics, vulcanized rubbers, or rubberized asphalts, which harden during the manufacturing process. The formulation of high-quality flexible WP membranes requires the use of elastomers of macromolecular materials that can accommodate a reversible stretching. They include bituminous and asphalt systems, asphalt-impregnated fabric, polymer, and elastomer membranes [16]. The identified sheet materials in Russel survey [17] included rubberized asphalt, bituminous membrane, polymer-modified asphalt, modified bitumen, and polymeric membrane. The identified sheets in the review of Xi et al. [15] included bituminous membrane, modified bitumen, coal tar emulsion reinforced with two plies of coated glass fabric, reinforced tar and resin, polymer-modified bitumen, styrene-butadiene-styrene (SBS), polymeric membrane, and nonwoven polyester. The types of sheets for roofing included bitumen, SBS polymer-modified bitumen, self-adhesive membrane made of polymer film (300-high density polyethylene), self-adhesive bitumen rubber layer, synthetic polyvinyl chloride (PVC) membrane [42]. The following are descriptions of commonly used WP sheet systems:

Bituminous sheets

The bituminous WP sheets are made of mixtures of asphalt or coal-tar with fillers (e.g., limestone and sand) formulated using organic solvents. They include cold and hot-applied sheet membranes [10]. Asphalt is obtained from natural sources or from petroleum processing [10]. Coal tar is obtained from residues from the distillation of coal. For adhering cold-applied bituminous sheets, asphalt emulsions or solvent cut-back mastics are used. Cold-applied bituminous sheets may be used as dampproofing of nonsubmerged concrete. Asphalt membranes are not suitable for WP application when they are continuously subjected or damped in water as they may degrade by reemulsification. Hot-applied bituminous WP systems pose little strength; thus they may be reinforced by the addition of fabrics and felts. Reinforcing bituminous membranes with fibers improve their mechanical characteristics and increase their resistance for cracking from thermal and mechanical stresses.

Polymer-modified bitumen sheets

Bituminous membranes are not recommended for exposure to sunlight unless they are modified with flexible polymers. Polymer-modified bitumen sheets are made using bitumen and fillers (e.g., limestone and sand) with the addition of other polymeric materials. Flexible polymers such as polyurethane or acrylic-based polymers are added to improve the sheet quality such as mechanical characteristics and UV resistance. These types of polymer modifications include (1) atactic polypropylene, which gives the sheet rigidity and tear resistance, (2) SBS, which improves the sheet elasticity, and (3) rubberized asphalt sheet with a small fraction of styrene-butadiene polymer. The third type is the common WP system used in Canada for bridge decks [16]. These sheets are self-adhesive that bonds to the concrete surface from the effects of the adhesion characteristics of asphalt and polymers. They may involve the addition of some resins and oils to improve adhesion. New bituminous membranes are continuously developed such as the bituminous system modified with polyurethane [43]. The incorporation of polyurethane enhances the percentage elongation of the sheets, and hence improves their ability for accommodating structural movements and loads [14]. In addition, the polyurethane polymer enhances the WP characteristics of the membrane and shortens its curing time [14]. These sheets are typically installed on the positive side of the water pressure.

Rubber sheets

The typical rubber sheets include (1) chlorinated rubber coatings used for WP of swimming pools, (2) neoprene membranes, which are made of polychloroprene and have intermediate resistance to oil exposure, (3) butyl rubber sheets, which are made from a copolymer of isobutylene with a small amount of isoprene (they resist UV radiation but do not have good bonding with concrete), (4) ethylene propylene diene monomer sheets, which are made from the polymerization of ethylene and propylene (breathable and UV-resistant with low permeability), and (5) poly isobutyl sheets, which are manufactured from polyisobutylene and other synthetic rubbers and have the characteristics as the composing materials [12].

Polyvinyl chloride sheets

The PVC sheets are widely used thermoplastic membranes for durable roofing and tunnel lining applications. The PVC sheets can be reinforced with glass or polyester fibers. They are joined using hot air welding. They have the advantages of low temperature flexibility, high temperature tolerance, and fire resistance. Reinforced PVC sheets have higher strength, dimensional stability, and WP performance than the nonreinforced PVC sheets [12]. They are high resistant against indentation and impact [12].

12.3.3.2 Liquid membranes systems

Liquid membranes are referred to as constructed-in-place systems as they cure on concrete surface to produce an impermeable flexible solid barrier. They are formulated using water-based emulsions or solvent-based materials including bituminous materials or resinous liquid systems [17]. They come as a single-component or multiple-components: The single-component liquid membranes cure and harden through the evaporation of the volatile solvents, or through the interactions with surroundings (reaction with moisture or thermal interactions). The modified polymeric membranes of water-based emulsions cure and solidify by the evaporation of water. The two-components liquid membranes come in two separate liquid parts that are mixed at the job site and then the polymeric compounds cure and harden through a catalytic reaction. These include modified bitumens, polyurethane, epoxy, and acrylics [17]. According to Xi et al. [15], the materials used in successful liquid membranes included reinforced asphalt-based membrane, hot rubberized asphalt, polymer-modified asphalt, rubberized bitumen, reinforced rubberized asphalt, resins of epoxy or polyurethane, two-component polymer, methyl methacrylate, rubber polymer, and polypropylene. The types of membranes for roofing included polyethylene, ethynyl vinyl acetate/ethynyl ethyl acrylate, [42]. The following are descriptions of commonly used liquid membranes:

Bituminous liquid membranes

The materials of bituminous liquid membranes are similar to those in bituminous sheet systems but they are packaged in liquid form. Cold-applied bituminous membranes are made of asphalt emulsions or solvent cut-back mastics and are reinforced with fabric. Asphalt emulsions are not usually recommended for applications on below-grade structures, as they may degrade by reemulsification, particularly when they contact water before full curing. They may be used as dampproofing materials when the concrete is subjected to partial wetting. Hot-applied bitumen systems require preheating the material in order to obtain certain consistency, then it is applied to the concrete substrate. Bitumen membrane systems are not UV-resistant and cannot withstand pedestrian traffic [44].

Polyurethane liquid membranes

Polyurethane compounds are expensive and very versatile materials. They are used for WP of flat roofs and surfaces exposed to weathering conditions. They include aliphatic and aromatic isocyanate polyurethanes. Aromatic polyurethanes have better resistances (against water, chemical, and abrasion) than aliphatic polyurethanes but they have lower flexibility and resistance to UV radiations [36]. Polyurethane membranes include single-component systems that are cured by reaction with moisture and two-component systems that are mixed at the job site and cure through a chemical reaction among the system ingredients [44]. For moisture-cured single-component polyurethanes, the film thickness must be less than a maximum set value (e.g., within a range of ±100–200 μm). This is essential to prevent the accumulation and entrapment of bubbles of carbon dioxide that are by-products from the curing reactions, which can reduce the bond strength and durability [36]. Polyurethane compounds also involve the reaction of an isocyanate (which is harmful to human health) [7] with hardeners utilizing active hydrogen groups. The installation of reactive polyurethane requires monitoring the moisture content of the concrete surface before application, in order to prevent peeling or debonding of membranes. The spray-applied polyurethane systems for bridge decks can be applied horizontally, vertically, and overhead with consistent thickness [45]. The polyurethane systems act as vaporproofing membrane. In fact, it is hard to generalize the characteristics of polyurethane membranes, particularly when the chemical description of the types of polyurethanes are not given [36]. In general, polyurethanes are suitable for applications on concrete surfaces subjected to traffic and exposed to deicing salts, as they are characterized with excellent mechanical properties, bonding, crack bridging, and resistance to chemical and biological attacks [14]. However, they do not resist high alkaline surroundings [7].

Epoxy coatings

Epoxy systems are two-component liquid membranes made from a thermosetting polymer formed from the reaction of resin with a suitable hardener [10]. The epoxy systems used for concrete applications are based on bis-A epoxy resins, which are solvent-free systems with low molecular weights (about 380) [36]. The curing of epoxy systems is associated with possible problems resulting from the involvement of water and carbon dioxide, which can react with the uncured epoxy and produce carbonic acid. This leads to defects in the film and reduces adhesion, strength, and chemical resistance of the membrane. Compared to other PB, the epoxy membranes commonly have a high performance in terms of WP, reducing chloride ion penetration, electrical resistivity, and chemical resistance [36]. Epoxy systems are usually recommended for applications requiring enhanced adhesion, low shrinkage, and chemical resistance [7,36]. However, they have low levels of fracture energy, hydrophobicity, and thermal stability [7]. As in the case of polyurethanes, variations in the performance of different epoxy membranes are usually reported [36].

Acrylic membranes

Acrylic liquid membranes come mostly as single-component polymeric solutions or emulsions [44], which are cured through physical drying of the solvent [7]. The acrylic emulsions are the most common WP systems for practical, economic, and environmental parameters [44]. They are commonly used in internal wet areas. They can be formulated to obtain UV-resistant membranes for external use. Methyl-methacrylate's flooring or decking system is an advanced acrylic system that is based on two components, which are mixed at the job site and rapidly cure to form flexible and tough coating. It can be installed in sites that need to be accessible quickly [44]. Acrylic membranes are breathable and resistant to degradation under alkali, oxidation, and weathering conditions [12]. However, they have low adhesion strength and they are not suitable for long-term immersion in water or under soil [7].

12.4 Applications of waterproofing barriers

The effective application of WP materials is governed by surface characteristics of the concrete substrate, application methods, and surface coverage [7]. The application requirements include proper ambient conditions and surface preparation. The governing ambient conditions include moisture contents and temperatures of concrete and surroundings. Usually, a minimum substrate and/or ambient temperature is specified for applying the WP barriers [17]. Commonly, the surface temperature must be larger than 2°C or 4°C [17]. The ambient temperature affects the level of concrete dryness. For the case of PB, the ambient temperature affects the status of entrapped air within concrete pores, which may then impact bonding. Surface preparation is essential for ensuring sufficient bonding and structural integrity (for the case of crystalline CC) [6]. In fact, most of the failures of barriers are due to improper surface conditions and inadequate surface preparations [6]. It is essential to ensure a sound and nondefected concrete surface with no residuals of debonding materials. Usually, there is a series of surface preparation steps that are set by the manufacturers. For the application of PB, the surface must be smooth, dry, structurally sound, free of protrusions, rough edges and cracks, clean and free from oil, laitance, curing compounds or any other contaminants [17]. ACI 515.1R [5] recommends the following preconditioning methods: (1) typical cleaning methods for removing oils and dirt, (2) mechanical actions (e.g., sandblasting) for deep cleaning, and (3) chemical treatments (e.g., acid etching) for opening the pores to have a better penetration. Surface cleaning involves the use of brooms or compressed air to remove loose materials and contaminations (e.g., residuals from the previous coatings) [17]. The PB cannot be applied on saturated surfaces otherwise debonding problems are faced, hence, water must not be used for surface cleaning. No differences in bonding between air blasting and abrasive blasting were reported experimentally [17]. The application of CC requires conditions of clean, structurally sound, crack-repaired, and open capillary system (for allowing the penetration of the crystalline chemicals). Smooth surfaces (e.g., resulting from the use of steel forms) may require light sand-blasted for better bonding of CC and opening the structure for penetration. ACI 515.1R [5] does not recommend the use of curing compounds on fresh concrete that is supposed to receive a WP barrier, unless they are completely removed before the WP application. On the other hand, the surfaces must be saturated as CC demands a wet concrete surface for better curing conditions [7]. Commonly, the industrial literature specifies a “saturated surface dry condition” to enhance the diffusion of the active ingredients and the formation and growth of the crystals. In this case, water blasting is preferred as it provides mechanical cleaning and roughening effects as well as moistening the surface. There is also a group of surface repairing methods for defected concrete before placing the membrane, the selection of which must be compatible with WP materials [17]. Usually, for repairing existing leaking structures, cementitious rapid setting plug mortars (which may include integral WP materials) are used to stop the water leaks. Cracks and joints must be routed out to sound concrete using cementitious mortars. The application-related features of WP materials include brushing and spraying characteristics, penetration of WP ingredients, thickness of WP barrier, adhesion to wet concrete. The following two sections describe the applications of cementitious and PB.

12.4.1 Application of cementitious waterproofing coatings

The powders of CC are mixed with water on the job site to obtain slurry consistency. Typically, crystalline WP coating materials are mixed at a volume ratio of 2.5−3 parts powders to one part water [13,46]. The powder water mixing ratio may be dependent on the application methods and equipment. For the two-parts systems of PMCC, the powders are mixed with a specified polymer emulsion. The system is mixed thoroughly, for example, using a slow speed drill equipped with a mixing paddle or using a mortar mixer. In general, it is important to mix quantities that can be applied within 20−30 minutes from the time of mixing to avoid cement setting before application [13]. The mixture shall be stirred frequently to restore workability without adding extra water. The slurry is applied onto a wet concrete surface substrate by brushing [30], spraying [38], troweling, or rolling [24]. The system is usually applied in two coats [23,39]. The second coat is applied after initial setting of the first coat (which is typically within 2−3 hours depending on the surrounding conditions) [46] and before the first coat is dried (i.e., within less than 48 hours) [23,38]. Ensuring a saturated surface dry condition before application of the second coat and curing by misting with water are essential between the two coating applications in order to ensure good bonding and integrity between the two layers of CC. It is recommended to avoid the application of CC in hot and windy conditions as the CC may dry out prematurely. The crystalline CC must be moist cured for a minimum period of 2 days to promote cement hydration and allow crystallization reactions. This is typically done by spraying water three to four times per day, starting after the initial set of the coating, or at a larger spraying frequency in warmer and windy climates. Deficient curing [13], with a low level of moisture content during the first 2−3 days, reduces the WP performance of CC [38]. For below-grade structures, the backfilling materials must be moistened in order to maintain coating wetness during the remaining curing period.

The coating thickness, powder-water mixing ratio, and slurry coverage are dependent. The reported coverages of powders are within a range of 1.0−1.25 kg/m^2 [46] or within a wider range of 0.9−1.4 kg/m^2, as per commercial literature. Spraying application may require larger water/powder mixing ratio than the brushing application. For brushing application with 1/2.5 water to powder volume ratio the coverage is in the range of 0.65−0.8 kg/m^2, while a 1/3 water to powder ratio yields a coverage of about 1.0 kg/m^2. For spraying application with 3/5 water to powder ratio, the coverage is in the range of 0.65−0.8 kg/m^2. The thickness of one layer of CC is in the range of 0.5−1.0 mm [13]. According to some standards (e.g., China construction code), the CC thickness must be within the range of 0.8−1.0 mm [22]. Typically, a CC at coverage rate of 1.3 kg/m yields a thickness of 0.75 mm. When more than one coating application is used, the net layer thickness is commonly 2 mm [13]. For a screed system, the thickness is in the range of 3−5 mm [24]. According to the survey of Shell [47], the net coating thickness of cementitious systems in the United States had a range of about 3−6 mm. The reported average thickness in experimental investigations included 1 mm [39], a range of 1−1.5 mm [38], a range of 1.5−2 mm [24], or up to 3 mm [25]. A wider range of thicknesses for mortars was reported: from a few millimeters to less than 10 mm [8]. For PMCC, 2 mm for epoxy-modified cementitious mortar and about 3 mm for the latex-modified cementitious mortar were reported [48]. Overall, the thickness of a cementitious barrier system can be in the range of 2–10 mm [7]. These thickness ranges are usually larger than those of typical PB [48].

The active ingredients of the CC migrate with moisture through a penetration process that is dependent on the porosity and transport properties of concrete, as described in Chapter 7. The active ingredients can reach depths of 10 mm within 4 weeks of coating applications [24,39], and up to 190 mm in 132 days, as highlighted in commercial literature. In fact, a much larger penetration depth of more than 300 mm (12 inches) [46] was claimed (e.g., for concrete with w/c ratio of 0.65), without sufficient experimental evidence. Overall, reasonable penetration depths were reported to be in the range of 5–50 mm from the concrete surface [49]. On the other hand, the penetration depths of the polymeric systems within the concrete substrate are usually low (e.g., less than a few millimeters).

12.4.2 Installation of polymeric waterproofing barriers

In a precise technical terminology, it is better to use installation term for preformed sheets and application term for liquid membranes. If the installation/application is not made properly, water penetration under the PB creates major damages. ASTM D 4071 describes the standard practice for the PB systems for concrete bridge deck [18]. For surfaces subjected to mechanical impacts, such as traffic on pavements and backfilling for below-grade structures, a protective layer is essential to protect the PB. The use of primers is recommended by most manufacturers in order to enhance bonding [17]. The full PB system for bridge decks usually includes the application of a primer to concrete surface, an adhesive, a tack coat, a protection board, and bituminous concrete layers. The application of liquid membranes may involve the installation of a reinforcing fabric [17]. In such a case, a first coat of liquid is sprayed, on which the fabric is placed, then a second layer of liquid membrane is applied [17].

As mentioned earlier, ensuring a dry concrete surface is essential for the application of PB, as increasing moisture content decreases the adhesion strength [41] and leads to bubble formation or blistering of the PB. A limit of moisture content of concrete for the application of PB is specified at 4% [41], 5% [45], or 6% by mass of concrete [17]. Hence, a sufficient curing age (above 28 days) is essential for the efficient adhesion of the PB. It is recommended by ACI 515.1 R [5] to apply PB in the afternoon for lowering the surface moisture after allowing the concrete to be exposed to sun and air for 6 hours [50]. In addition, this allows the exposed concrete to reach its maximum temperature, and thus no further air expansion occurs after PB application, which can result in peeling off of the membrane.

It is essential for liquid membranes (applied by spraying or brushing) to ensure the formation of a continuous membrane with the control of membrane thickness. These criteria are more crucial than liquid penetrability within concrete. In fact, the penetration depth of a polymeric membrane is low (less than a few millimeters) and has a minor contribution to the membrane performance [7]. In fact, the WP functions of polymeric coatings are not based on redesigning the concrete pores and hence their limited penetration depths are usually accepted. The use of liquid membranes was discontinued in some countries due to difficulties in ensuring uniform thickness [17]. The dry film thickness of a fully cured membrane should meet a minimum value. The thicknesses of typical polymeric membranes can be within the range of 0.1−1 mm [7] or within a wide range of 0.1−5 mm [51]. A too thin membrane will not have sufficient integrity and elastomeric properties. Increasing the membrane thickness enhances its adhesion to the concrete substrate [44]. Several values are set as minimum required thickness. For example, a minimum required thickness is set for rubberized asphalt barriers at 1.65 mm (65 mil) according to AASHTO, and 1.78 mm (70 mil) according to some state agencies in the United States [15]. Shell survey [47] highlighted that the thicknesses of the liquid membranes in the United States was in the range of 1.27−1.52 mm (50−60 mil). The results of Berndt [48] indicated that the thickness of an epoxy liquid coat by brushing was in the range of 0.35−0.45 mm. This thickness of PB is commonly less than that of a PMCC [7,48].

Sheet membranes are installed onto concrete surface by one of the following three mechanisms: (1) using self-adhesive sheets, which are made sticky from one side (covered by a protective paper layer in the factory), (2) bonding the membrane to the surface by heating, or (3) adding a pressure-sensitive adhesive material for sticking the sheets to the concrete surface [17]. For application with seam overlaps, the sheets are installed upward in a concrete vertical structure starting from the lowest part and overlapping on the top of each other by about 5 cm (2 inches). Then, seams and termination ends are sealed using a mastic for sufficient bonding. Finally, they are rolled by a hand-propelled machine for adhesion. The reported thicknesses of sheets (polyethylene, asphalt/polyethylene, polymer-modified bitumen) can be within a narrow range of 0.15−0.25 mm (6−10 mil) or within a wider range of 0.51−3.0 mm (20−120 mil) [47].

12.5 Mechanisms of waterproofing barriers

The setting mechanisms of external barriers range from polymerization in organic membranes to hydration reactions in cementitious layers. Combinations of these two mechanisms are also encountered with PMCC. The kinetics of the setting processes are dependent on the compositions and the surrounding conditions. Specifying a minimum curing time is essential for reaching a required level of performance in terms of strength and WP effectiveness [17]. A typical cementitious curing process is involved in CC in which the strength develops with time. Fig. 12.2 shows the strength development curve for a hygroscopic crystalline CC. Normally, the application of CC does not influence the compressive strength of concrete substrate itself [23]. There are no set or standard strength values for the

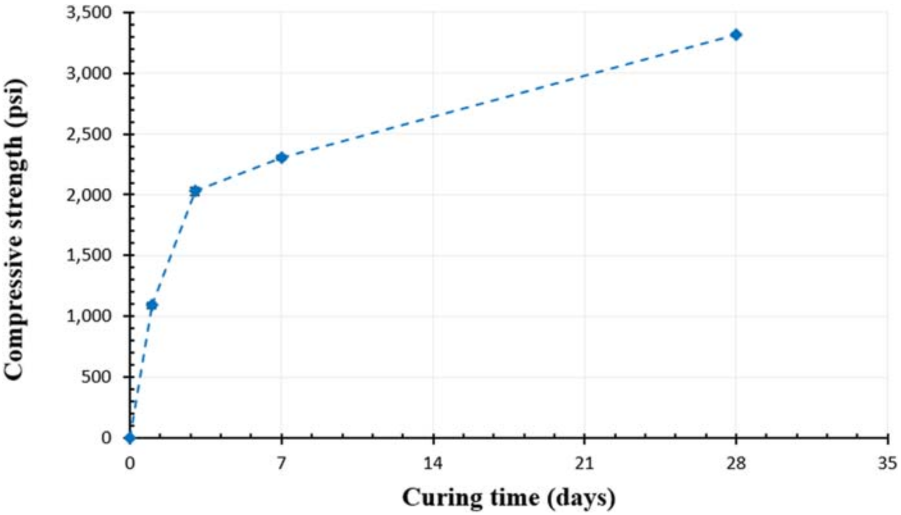


Figure 12.2 Typical development of compressive strength of hygroscopic crystalline cementitious coating obtained according to ASTM C109 (data from a testing report submitted to the author).

Table 12.3 The percentage development of compressive strength and adhesion strength of crystalline cementitious coatings (data from a testing report submitted to the author).

Days	**Percentage development of 28-day value**	
	Compressive strength	**Pull-off strength**
1	32.8%	—
3	61.1%	79.2%
7	69.5%	87.7%
28	100.0%	100.0%

cured crystalline CC. The 28-days compressive strength values of crystalline CC can be in the range of 21−28 MPa (about 3000−4000 psi). The compressive strength depends strongly on the powder to water volume ratio (which can be chosen from a range of 2−3). It depends on the chemical formulation of the CC (e.g., the use of SCMs and other admixtures). The CC adheres to the concrete surface mainly through a cementitious bonding, which progresses with proceeding hydration reactions. Table 12.3 compares the percentage development of compressive strength and the percentage development of the pull-off strength (relative to 28-day values), for the same type of crystalline CC in Fig. 12.2. The adhesion strength seems to develop faster than the compressive strength, possibly because of the contribution of the crystallization networks and their entanglement between the coating and the concrete structures. The manufacturers of CC usually recommend protecting the coatings until they gain sufficient compressive strength. The protection from light mechanical impacts (e.g., traffic) should be for 2 days and from heavy traffic or loading for at least 5 days (see Fig. 12.1). For below-grade structures, a sufficient curing time is needed before backfilling in order to enable the CC to withstand the mechanical impact. This is typically specified at 7 days, at which the strength gain reaches about 70% and the bond strength gain reaches about 90%, as listed in Table 12.3.

The growth of WP performance of the CC is more important than strength development. It is dependent on the physicochemical setting mechanisms of the crystalline active ingredients. After setting the slurry on the surface, the active ingredients of the WP material migrate with moisture from the coating structure into the concrete structure through the capillary pores (see Fig. 12.1). The dissolved active ingredients are carried into concrete structure deeper than the coating thickness by infiltration, capillary action, and diffusion (see Section 12.4.1). Then, the active ingredients commonly react with the products of cement hydration in presence of moisture [37]. The crystalline CC works on the same principle as the WP admixtures (as detailed in Chapter 9), as similar active ingredients are typically used [38]. The types of reactions and the structures of produced materials depend on the types and amounts of active ingredients. Their setting reactions and the formation mechanisms are similar to those detailed in Chapters 8–10. In most cases of crystalline CC, the water-soluble active ingredients react with water and calcium hydroxide (CH) in the paste matrix according to Eq. (12.1) [20,21,23] or Eq. (12.2). These reactions are initiated at the surfaces of cement hydration products, particularly the portlandite (CH). The active ingredients are also claimed to react with unhydrated cement particles, and promote further hydration to produce crystals [31,49]. Other chemical reactions occur also with mineral salts, mineral oxides, and partially hydrated cement particles [25]. The chemical reactions of CC involving zeolite are given by Eqs. (12.3–12.5) [39]. The reactions produce calcium silicate hydrates (C–S–H) gel, the structure of which can be confirmed through measuring XRD patterns as shown in Fig. 12.3. Fig. 12.3 shows an increase in the intensities of the peaks characterizing the produced C–S–H gel and a reduction in the intensities of the peaks characterizing the consumed CH [20]. The XRD pattern of specimens with crystalline CC shows more ettringite, which contributes in the compactness effect and self-healing ability of the CC. The crystalline CC have the ability to form crystals after 2 days, then, their sizes and complexity develop with curing time [37]. Based on experimental findings, the crystalline CC require a period of 5–10 days (120–240 hours) for optimum curing [13], while the PMCC needs less time (3 days for optimum curing) [13]. A significant low WP effectiveness is expected at the early stages (24–72 hours) [30]. The ultimate efficacy of WP of crystalline CC is commonly approached after 12 days of curing [52]. In fact, the effectiveness of crystals formation and growth is strongly dependable on the availability of water in capillary pores and cracks [37]. When no sufficient water is available, no crystal growth can be obtained even after 12 days [37]. With sufficient water

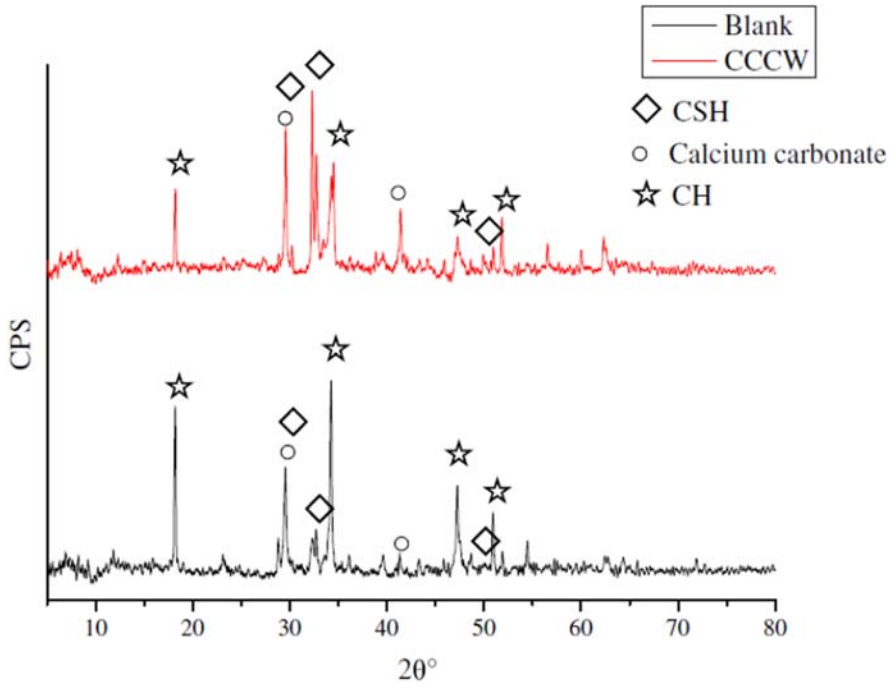


Figure 12.3 XRD patterns of capillary crystalline cementitious coatings compared to those of blank cementitious material [20].

content during the first 12 days, the size and structure of crystals are developed and their shape becomes more complex [31].

$$\text{active ingredients} + Ca(OH)_2 + H_2O \rightarrow \text{hydrophilic } C-S-H \text{ gel} \qquad (12.1)$$

$$\text{active ingredients} + Ca(OH)_2 + H_2O \rightarrow \text{hygroscopic crystals} \qquad (12.2)$$

$$SiO_2 + n_1Ca(OH)_2 + n_2H_2O \rightarrow n_1CaO \cdot SiO_2 \cdot (n_3 + 1)H_2O \qquad (12.3)$$

$$Al_2O_3 + n_1Ca(OH)_2 + n_2H_2O \rightarrow n_1CaO \cdot Al_2O_3 \cdot (n_2 + 1)H_2O \qquad (12.4)$$

$$Al_2O_3 + 2SiO_2 + 3Ca(OH)_2 + nH_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot (n + 1)H_2O \qquad (12.5)$$

$$Al_2O_3 + CaSO_4 + Ca(OH)_2 + H_2O \rightarrow CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 2H_2O \qquad (12.6)$$

The aforementioned setting and hydration mechanisms control the microstructure of the crystalline CC. The chemical composition of the produced crystals includes tobermorite gel ($3Ca2SiO_23H_2O$) together with hydrated calcium aluminate

$3CaOAl_2O_3Ca(OH)_212H_2O$ [24,37]. Also, some systems are associated with the formation of insoluble particles of CaF_2 [26,37]. The types of crystalline products depend on the types of the active ingredients. Fig. 12.4 shows the crystallinity of hygroscopic crystalline CC [38]. These rounded crystals seem to have a different structure than those reported for hydrophilic crystals shown in Fig. 12.5, which form insoluble fibrous crystals [21]. The hydrophilic crystals are described in many publications [24,25,30,37,38] as needle shaped crystals, or as acicular crystals [20] or more specifically as branched needle-like crystals [24]. The produced crystals are combined with concrete structure and block its pores. The size of the hydrophilic crystals are typically in the range of $10^{-7} - 10^{-4}$ m [37]. The dimensions of crystalline structure are in the range of 20–200 μm [20,26]. For acicular shape, the length of a single crystal can reach up to 13 μm [25,26] or 15 μm [24] or up to about 20 μm [24] and their width can be in the range of 100–1000 nm [25,26]. In

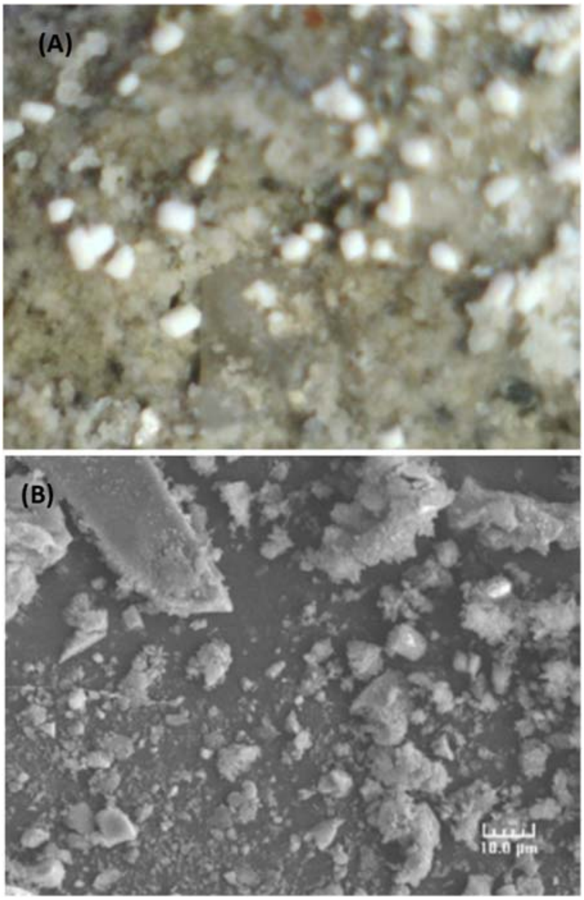
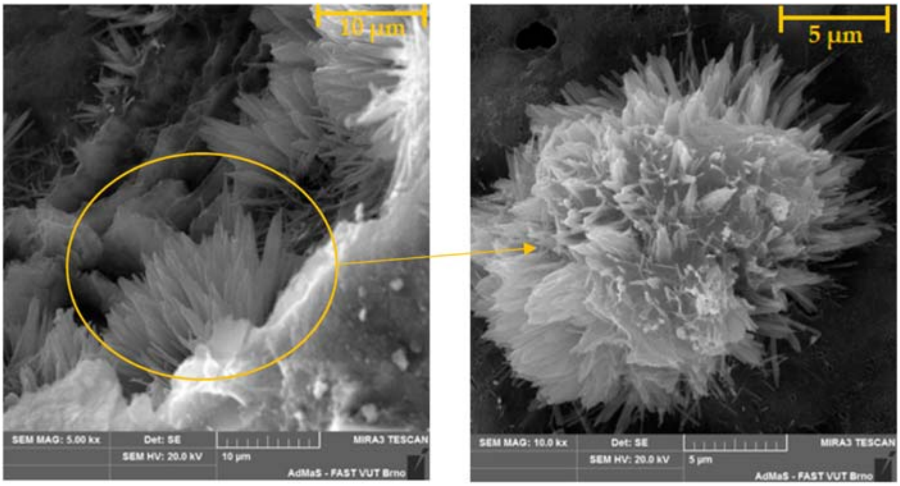


Figure 12.4 Crystallinity of hygroscopic cementitious coating after 30 days of curing. (A) 800 magnification (white crystals) and (B) under SEM 1000 magnification [13].



(A) (B)

Figure 12.5 SEM photomicrographs of crystals formed in the pore of a mortar (a) and detail of the formed crystals (b) (Hodul, Žižková et al. 2020).
Hodul, J., N. Žižková and R. P. Borg (2020). "The Influence of Crystalline Admixtures on the Properties and Microstructure of Mortar Containing By-Products." Buildings 10 (9). https://www.mdpi.com/buildings/buildings-10-00146/article_deploy/html/images/buildings-10-00146-g013.png.

commercial literature a larger crystal length in the range of 20–25 μm and a diameter in the range of 1–4 μm are reported.

The growth of these crystals in the presence of moisture provides the concrete with a self-healing ability to seal cracks up to 0.4 mm (0.015 inch) [39]. The self-healing mechanism is similar to the above-mentioned pore bocking crystallization mechanism. It involves the consumption of $Ca(OH)_2$ and the production of C–S–H gel, calcium carbonate, and ettringite were observed through XRD and SEM analysis [20]. This effect is obtained as the crystallization system is usually in a dynamic state and thus can be perpetual. When concrete gets in a dry state, the crystallization system remains in a dormant state. The crystallization system can be dynamic and thus capable of reactivating the growth mechanism when encountering a new source of water from wetting or penetration. Upon the development of cracks and fractures due to any durability problem (discussed in Chapter 3), water penetration into concrete promotes further crystal growth. This is accomplished by further hydration reactions producing additional crystals. These reaction products can close the cracks and hence block them against further water penetration [39]. This mechanism is usually referred to as self-repairing or self-healing [53]. In fact, the crystallization reaction must reach an ultimate (equilibrium) yield as discussed in Chapter 9. Then, the self-healing effect can be obtained from the swelling and expansion of the hydrophilic gel, as detailed in Chapter 9.

The setting mechanism of PMCC combines the cement hydration and the polymerization and yields an interpenetrating network of polymeric and cementitious matrices as demonstrated by ACI 548.3 [36]. The polymerization mechanism is believed to start after the formation of a joint dispersion of polymer and cement particles upon system mixing. After the initial cement hydration and when water is partially consumed by hydration and evaporation, the polymer molecules become concentrated in the established pores of the cement paste. Consequently, polymer coalescing starts to occur. This leads to the deposition of polymer particles on the surfaces of the hydration products (e.g., C—S—H gel) and unhydrated cement particles leading to pore lining. Eventually, a solid layer of polymer particles (or network) coats and covers the cementitious particles leading to co-matrix formation. With polymeric solutions, polymer bridging is developed between the crystals of the by-products of cement hydration (CH), which strengthens the cementitious structure. However, such a bridging mechanism decreases the flexural strength of the cementitious structure. The kinetics of polymerization reactions are governed by the temperature, humidity, and wind conditions as well as the saturation level of the concrete substrate prior to coating applications [36]. The hydration of the cement is retarded by the presence of dispersed polymer molecules due to their cement encapsulation effect. If polymer coalescing is initiated before enough cement hydration is accomplished, shrinkage problems are encountered in the cement paste before it builds a sufficient tensile strength to resist cracking.

The PB set and harden through polymerization reactions and/or molecular crosslinking, entanglement, and adhesion to the concrete substrate. Some of these mechanistic aspects are discussed in Section 12.3.3. For the single-component liquid membranes, the setting mechanisms involve (1) the evaporation of the carrier solvent (organic or water) and (2) the thermal and moisture interactions with surroundings. The two-components liquid membranes (such as epoxy and polyurethanes) cure and harden through a catalytic reaction between resin and hardener components of the system, utilizing active hydrogen groups. Xi et al. [15] demonstrated the development of bond strength with curing time. The early bond strength is crucial for allowing traffic on the coated concrete in order to prevent the risk of shearing failure. This topic is further detailed in the following subsection.

12.5.1 Bonding of external waterproofing barriers

The membranes and coatings are required to have sufficient adhesion strengths in order to ensure durable performance. The adhesion of barrier systems is dependent on their chemical structure, setting mechanism, quality of concrete substrate (e.g., its strength and the levels of surface roughness and dryness), the application of the membrane, and the use of a primer [7]. The minimum bond strength of barriers is typically set at 1 MPa (145 psi) [17] [or 0.7 MPa (or 100 psi)] [44]. Insufficient adhesion between the PB and the concrete deck is a prime defect that causes water wetting at the interface and leads to sheet blistering and reemulsification of the asphalt [17]. The bond strength (or tensile adhesion strength) for liquid membranes is typically tested using nondestructive field test [17] (pull-off strength test according to ASTM D4541). For pavement application of polymeric membranes, the tensile bond strength between the membrane and the asphalt overlay is tested using the pull-out test according to ASTM C900 [17].

The CC are bonded to the concrete surface through cementitious bonding and crystal networking, which develops with curing. Fig. 12.6 shows the development of bonding strength with curing time for crystalline CC and PMCC [30]. A larger bond strength is usually obtained for PMCC due to contribution of the adhesion characteristics of the polymer networking and its elastic nature. The typical threshold value of the pull-off strength (1 MPa) can be exceeded for the PMCC before 120 hours (5 days) of curing. On the other hand, a more than doubled time period (more than 10 days) is required to achieve the 1-MPa limit for crystalline CC, as shown in Fig. 12.6. However, the bond strength of the crystalline CC develops faster than that of PMCC within the first 2 days. This is hypothesized to be due to a reduction in the elastic properties of the polymer from its viscous nature in wet condition [30]. The 28-days value of pull−off adhesion strength is 2.2 MPa for PMCC and 1.6 MPa for crystalline CC [30]. Some commercial literature reports that the tensile bond strength for crystalline CC (according to EN 1542) is 1.23 MPa. Similarly, the bond strength of polymer-modified cementitious mortars is commonly within the range of 2.2−3.3 MPa (320−480 psi) [48]. The adhesion strength of CC and PMCC decreases when the coating is applied onto a smooth surface [30] (without sandblasting) [13]. The percentage reduction in the 28-days adhesion strength can be in the range of 20% − 25%.

For PB, the liquid membranes have better bonding strengths than the preformed sheets [15]. According to a review of Pan et al. [7], the adhesion strength of

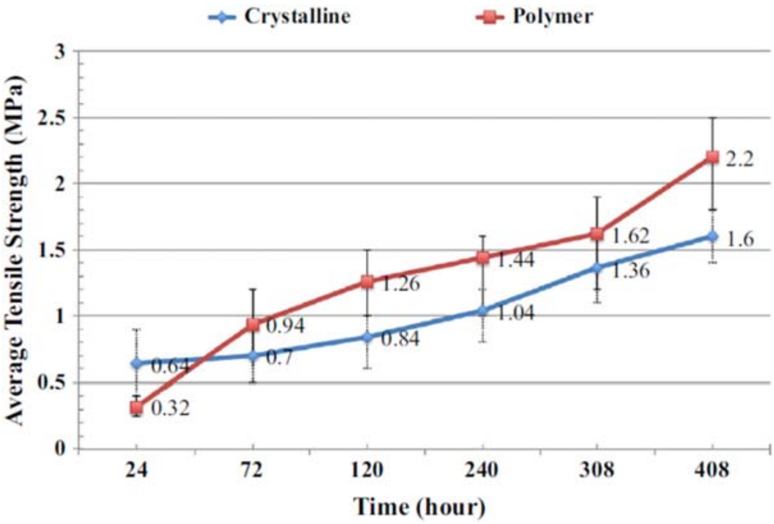


Figure 12.6 The bond strength of crystalline cementitious coating and polymer-modified cementitious coatings applied on rough cementitious substrate [13].

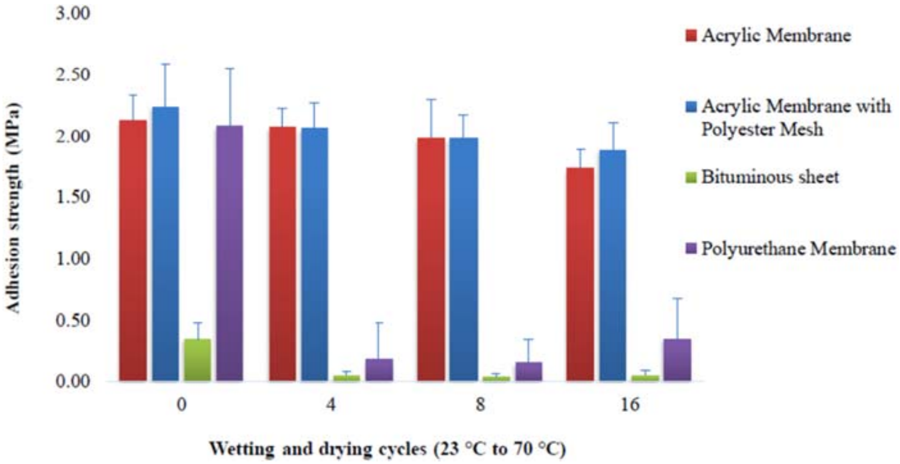


Figure 12.7 The adhesion strength of membranes with concrete for bituminous, polyurethane, and acrylic with and without polyester mesh and at different number of wetting and drying cycles [54].

polymeric membranes are typically larger than 1.4 MPa (200 psi) [i.e., > the set minimum bond strength of 1 MPa (145 psi)] [17]. Fig. 12.7 shows that the adhesion strength of polyurethane and acrylic are around 2 MPa while the adhesion strength of bituminous is much less (<0.4 MPa). Polyurethane membranes are characterized with excellent bonding [14]. Berndt [48] reported higher bond strength values of epoxy systems [2.9–4.0 MPa (420–580 psi)]. Acrylics are reported to have a lower adhesion strength than epoxy resin [7,55]. Fig. 12.7 shows that the bond strength decreases with wetting and drying cycles [54]. A less significant decrease is observed for acrylic membranes subjected to wetting and drying cycles. For pavement application, the minimum tensile bond strength between the membrane and the asphalt overlay (ASTM C900) is typically set at 0.7 MPa (100 psi) [17]. The reported values in bridge decks applications were in the range of 150–772 kPa (22–112 psi) [17]. As mentioned above, the level of vapor transmission governs the adhesion strength of the membranes and coatings [7].

12.6 Stability of external barriers

Concrete durability is governed by the durability of the WP materials itself and it is strongly dependent on the type of the barriers and their mechanical and bonding characteristics as well as WP efficiency (see Chapter 6) [7]. The external barriers may be attacked by the surrounding chemical, physical, thermal, and mechanical impacts and then the concrete structure becomes subjected again to water-related problems. The failure of polymeric coatings appears as sections of cracking, blistering, peeling, bubbling, and pin-holes resulting from the entrapment of moisture and air bubbles under the membrane [7,44]. Cracking is a failure in the barrier itself resulting from its shrinkage (from temperature change) or from the movement of the concrete substrate [7]. On the other hand, the blistering and peeling are associated with partial losses of adhesion due to penetrations of moisture and aggressive substances, respectively [7]. The signs of failure include the appearance of bubbling and mold growth on the membrane and wetting or ponding on the surface [44]. The failure of WP barriers may be attributed to several factors. These include improper surface preparation, application failure, ignorance of the environment conditions, and unsuitable material selection [44]. The application-related failures arise from unsuitable liquid characteristics, improper control of the thickness of the barrier, surface wetness (for PB) or dryness (for cementitious barriers), unsuitable application temperature, uncontrolled process kinetics (polymerization or cement hydration) [44,56]. The durability of PMCC is also influenced by other controlling parameters such as w/c ratio, polymer−cement ratio, type of the polymer, moisture content, and curing conditions [41]. The durability of materials used in cementitious barriers is commonly similar to that of concrete. The stability of WP barriers is governed by its resistance to disintegration and debonding by thermal and physicochemical actions (physical, chemical, and biological attacks). The main instability problems of the PB are related to their exposure to water, chemicals, temperature, and UV radiations.

In general, the selection criteria of the WP materials include economic and technical parameters. These parameters are used as attributes in the selection approaches (e.g., using multiattribute decision making methodology) [42]. The economic parameters include service life (which is governed by material durability) in addition to cost and availability [17]. The technical parameters include surrounding/environmental conditions and physicochemical properties of the barrier materials [44]. These include material stability, bondability to the concrete surface, and resistance to mechanical, thermal, and physicochemical impacts from surroundings. The durability-related characteristics of barrier materials include resistance against water and chemicals penetrations, abrasion resistance, UV stability, adhesion, elasticity, toxicity, dirt pick-up, and color retention [56]. Ideally, the WP system for bridge decks should be impermeable to water with crack-bridging capability, good adhesion, tolerance of deck roughness, and resistant to traffic before application of the riding surface [17].

The stability and bondability of PB are impacted by environmental conditions such as temperature cycle, drying and wetting cycle, UV radiations [9]. Fig. 12.7 shows that the bond strengths of various PB decrease with increasing the number of cycles of wetting and drying. The PB degrade with aging that leads to a decrease in the bond strength by breaking the intermolecular bonds in the polymers; and hence it reduces the quality of the barrier itself [7,57]. In acrylic coatings, aging leads to the break of O−CH and C−N bonds [9]. In epoxy membranes, aging decreases the intensity of C−C and C−O groups and increases the intensity of C=C and COO groups [9]. In polyurethane membranes, aging decreases the intensity of C−H and C−O bonds [9]. Xi et al. [15] reported that the bond strength of the WP membranes declined at a rate of about 15% per year. The continuity of the bond is more crucial than the adhesion strength in order to avoid blistering [17]. On the other hand, the review of Pan et al. [9] revealed that the effects of aging (by temperature, UV radiations, and other factors) on the performance of acrylic, epoxy, and polyurethane membranes were limited. The acrylic liquid membranes are resistant against UV radiation, hydrolysis, and alkali [7]. Polyurethane and epoxy liquid membranes have low resistances against degradation at high temperatures [7]. Exposure to UV radiations for a long time causes instability problems of bitumen-based WP materials due to the loss of ductility (they become fragile). Hence, as mentioned in Section 12.3.3, they are modified by the addition of flexible polymers such as polyurethane or acrylic-based polymers to improve their stability against UV exposure. Furthermore, water exposure affects the stability of bituminous WP membranes that are obtained from emulsions, since they undergo reemulsification upon water immersion [12]. Coal tar membranes are more resistant to degradation by water than asphalt materials. Also, vapor transmission from within concrete and its accumulation under the membrane causes blistering and peeling of the PB and leads to a loss of adhesion. The adhesion strength of a membrane is decreased significantly when the rate of vapor emission is larger than 283 μg/s [7]. The polymer-modified mortars are also characterized with high chemical resistance and UV resistance [7]. Increasing the molecular size can enhance the WP performance and strength of the PB.

The chemical stability and bondability is affected by the surrounding chemicals. Epoxy systems have high chemical resistance and anticorrosion characteristics [36]. Polyurethane liquid membranes have excellent chemical resistance against degradation from deicing and against carbonation, and they resist acid attack, chloride ions, and biological attack [14]. However, polyurethane liquid membranes are unstable in high alkaline conditions [7]. Acrylic membranes are stable in alkali and oxidation conditions [7], and they resist degradation in corrosive environments [12]. Chloride ion penetration reduces the bondability of various PB [15]. It has reported that chloride ponding reduces the adhesion strength by 20%–27% for self-adhering preformed rubberized asphalt sheets and by about 14% for liquid membranes of auto-catalytic polyuria [15]. For the case with strong bonding (e.g., epoxy system), chloride ponding reduces the adhesion strength by only 3.4% [15].

The mechanical stability demands that the WP barriers must absorb and accommodate mechanical impacts arising from structural instability, thermal cycles, or surface actions in order to prevent or minimize cracking. Thermal stresses are caused by the cyclic temperature changes during service (e.g., expansion-contraction under cycles of freezing and thawing). Mechanical stresses may be generated from structure vibration or building movement. They are also required to have indentation/puncture resistance [17], as any resulting holes or localized failure may lead to the failure of the entire membrane system [57]. This is required to resist puncturing damages from the surface erosion effects [57] or during backfill of below-grade structures [46]. A high resistance to indentation at the maximum possible installation temperature (no penetration) is also required in order to prevent puncture by aggregates during application and rolling of the hot mix asphalt wearing surface [17].

Cracking resistance is a crucial mechanical property of the membranes [7]. This requires having a sufficient flexural strength to absorb concrete shrinkage effects and having a suitable coefficient of thermal expansion to absorb stretching from temperature variations. According to ASTM D882, the preformed polymeric sheets are required to have a minimum tensile strength of 345 kPa (50 psi) for rubberized asphalt and 276 kPa (40 psi) for modified bitumen. In addition to strength, the flexibility and elasticity of PB are crucial for providing them with the ability to expand or bridge any moving or developing cracks during the service life of concrete structure [17]. In fact, elongation rather than strength is a more proper characteristic for the membrane ability to accommodate cracks [17]. The membranes must have elastic properties to be able to bridge a crack width of 150 μm (0.06 in.) at 0°C [17]. Crack-bridging ability of membranes is tested according to ASTM C1305/C1305M-16 or CSN EN 1062-7. The polymer membranes can have the ability to protect concrete containing possible cracks with a maximum width of 0.06 mm [7]. Preformed polymeric sheets are required to have a minimum percentage elongation, at breach at 73.4°F, of 10% and 15% for bitumen and rubberized asphalt, respectively [17]. Hence, some formulations of polymeric membranes include elastic polymers and/or they are reinforced with fibrous materials for increasing its elasticity and elongation. For this purpose, the bitumen WP sheets are incorporated with polyurethane to enhance their elasticity, and improve their ability for accommodating mechanical impacts [14]. The epoxy membranes have poor cracking resistance [7]. Polyurethane membranes are characterized with excellent mechanical properties (e.g., high strength, abrasion-resistant, and flexibility) [14]. They also have good characteristics of self-healing, crack bridging, and no shrinkage [7].

The crystalline CC are rigid, but they have the crack healing ability and they can seal cracks up to 0.4 mm (0.015 inch) in the presence of moisture [39], as described in Section 12.5. The addition of polymers to CC enhances their mechanical properties [7] (e.g., flexural and tensile strengths, adhesion strength, flexibility, resilience, crack-bridging ability). It also increases the toughness of the paste and reduces the surface microcracks [7]. The presence of polymers in the CC improves their resistances against abrasion, cycles of freezing and thawing, chloride ion penetration [36]. For this purpose, some researchers had investigated the performance of combined crystalline and polymeric CC [22,24,29,30].

12.7 Durability performance of waterproofing barriers

The evaluated durability characteristics of the coated concrete include resistances against the ingress of water, chloride ions, chemicals, carbonation, freezing and thawing, and biological attack [7,15,19,41]. The evaluated mechanical properties include tensile strength, compressive strength, abrasion resistance, puncture resistance, crack bridging, skid resistance, and thermal expansion characteristics [7,19]. The relevant testing methods, ASTM and EU standards for evaluating the WP membranes are listed by Russell [17] and by Nair and Gettu [12]. The nondestructive testing methods used by US agencies include electrical resistance, ground-penetrating radar (e.g., measuring thickness and voids), chain drag or hammer sounding (e.g., detecting delaminations), and leak testing [17]. Other field testing methods include visual inspection, ultrasonic method, air permeability method [17], and infrared thermography (thermal signal to identify defects such as blisters) [19]. The following subsections discuss the main durability characteristics.

12.7.1 Effectiveness of waterproofing

The WP performance of the barriers is related to their permeabilities for water, vapor, and gases. Water penetration through coatings and membranes occurs at the molecular level mainly by diffusion and possibly by capillary action. In CC, the capillary absorption is the main transport mechanism in the absence of pressure. The diffusion in polymeric networks is governed by their structural and physical characteristics. The structural parameters include microstructure, level of crosslinking bonding, and morphology, which control the molecular-sized pores in the polymer phase [7]. These structural parameters are governed by hardening process and stoichiometry, stiffness of the polymeric molecular chain, and cohesive energy density of the membrane [7]. The physical characteristics are related to the types of water polymer interactions (i.e., water affinity), which is also dependent on structural parameters (e.g., the availability of sites for hydrogen bonding along the polymer chains) [7]. The effectiveness of WP performance of barriers is commonly determined by measuring rate of water absorption according to ASTM C1585−20 and/or measuring the percentage water absorption according to ASTM D6489−99 (2020). However, for WP application on pavements, the cyclic actions from traffic loading on pavements pump water into the structure [19] (see Chapter 6). Pressures from tire loading applied by heavy trucks can reach a value in the range of 90 − 130 psi [19]. Hence permeability testing of membranes under pressure is frequently done according to ASTM D5084. In addition, the coefficient of permeability through CC under a hydrostatic pressure of 1.38 MPa (200 psi) is measured according to CRD-C48−92 "Standard test method for water permeability of concrete" [58]. Due to variations in the formulations of WP barriers, it is hard to give precise trends of WP performance or detailed comparisons of durability properties. In fact, the test methods for water penetration documented by manufacturers are almost as varied as the commercially available materials [19]. For example, the applied pressures in WP tests ranged from 4.3 psi to 3600 psi. Wells et al. [19] identified the necessity to develop a single WP test method to compare WP characteristics of the various membranes available [19].

Significant variations in the WP performance are reported for PB with the same chemical family (same generic type) but from different manufacturers [55]. Table 12.4 lists the WP characteristics for acrylic, epoxy, polyurethane chlorinated rubber, and polymer emulsion coatings, including two different commercial products for each generic type [55]. Fig. 12.8 shows the percentages of water absorption as functions of time for these coatings as coded in Table 12.4, and compared to uncoated mortar [55]. The estimated percentage reductions in water absorption

Table 12.4 Waterproofing and durability characteristics of various polymeric membrane systems [55].

Liquid membrane coatings	Code of the tested product	Weight gain 56 hours immersion (%)	Absorption rate (g/m^2/hour)	Sorptivity (mm/hour$^{0.5}$)	Charge passed (coulombs)	Classification ASTM C1202	Chloride diffusion coefficient (10^{-8} cm^2/second)	Time to initiation of corrosion (years)
Specimen		**Mortar**	**Mortar**	**Mortar**	**Concrete**	**Concrete**	**Concrete**	**Concrete**
Acrylic coating	AC1	0.23	4.4	0.03	163.67	Very low	2.08	9.96
Acrylic coating	AC2	1.46	30.6	0.23	69.71	Negligible	3.49	5.94
Epoxy coating	EP2	0.27	4.9	0.04	159.93	Very low	2.59	7.99
Epoxy coating	EP1	1.3	26.9	0.2	7.32	Negligible	7.67	2.7
Polyurethane coating	PU1	0.21	3.4	0.03	39.09	Negligible	1.83	11.3
Polyurethane coating	PU2	1.83	36.6	0.27	6.36	Negligible	0.7	29.59
Chlorinated rubber coating	CR1	0.76	16.1	0.12	49.83	Negligible	9.56	2.17
Chlorinated rubber coating	CR2	1.04	22.6	0.17	38.7	Negligible	8.4	2.47
Polymer emulsion coating	PE1	3.42	55.6	0.4	703.4	Very low	8.4	2.47

(*Continued*)

Table 12.4 (Continued)

Liquid membrane coatings	Code of the tested product	Weight gain 56 hours immersion (%)	Absorption rate (g/m^2/hour)	Sorptivity (mm/hour$^{0.5}$)	Charge passed (coulombs)	Classification ASTM C1202	Chloride diffusion coefficient (10^{-8} cm^2/second)	Time to initiation of corrosion (years)
Specimen		**Mortar**	**Mortar**	**Mortar**	**Concrete**	**Concrete**	**Concrete**	**Concrete**
Polymer emulsion coating	PE2	3.32	59.7	0.45	514.67	Very low	15.94	1.29
None coated concrete	CON	4.78	63.4	0.47	975.47	Low	19.18	1.08

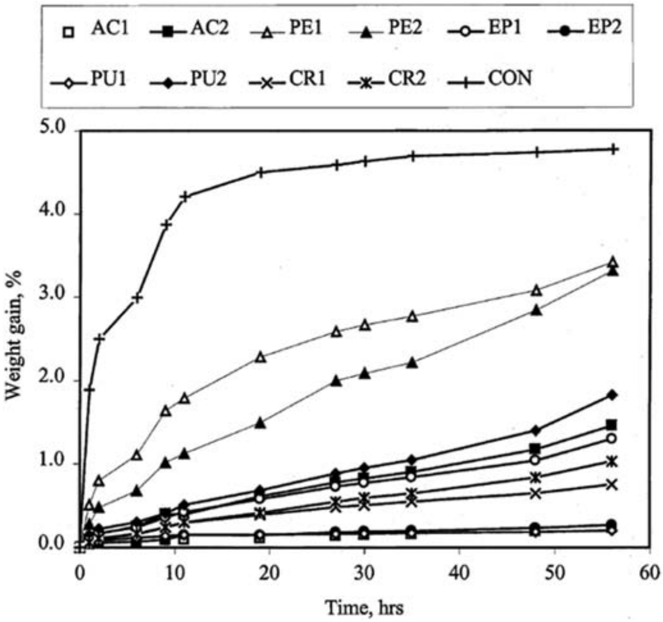


Figure 12.8 Water absorption as functions of time for coated mortar (with various polymeric membranes as coded in Table 12.4) compared to uncoated mortar (CON) [55].

(percentage, rate, and sorptivity) are listed in Table 12.5. Table 12.4 shows that the sorptivities of these PB are in the range of 0.03–0.45 mm/hour$^{0.5}$ and the absorption rates are in the range of 3.4–60 g/m^2/hour, while the equivalent values for control uncoated mortar specimens are 0.47 mm/hour$^{0.5}$ and 63 g/m^2/hour, respectively. These values indicate that the percentages reduction in absorption rate and sorptivity are within a wide range of 5%–95% (see Table 12.5). Despite the fact that significant variations are observed within membranes of the same generic type, the polyurethane and epoxy membranes are highly effective in reducing water penetration. Overall, they have better WP performance than other types as indicated by the percentage reductions [55]. Table 12.5 shows that the reductions obtained by polyurethanes, epoxies, and acrylics can exceed 90%. This is also indicated by lower absorption curves in Fig. 12.8. For the uncoated cement mortars water absorption occurred at a very rapid rate and the percentage absorption at 56 hours was about 5% by weight, while for mortars coated with polyurethane and epoxy membranes water absorption occurred at a very slow rates and the percentages of water absorption were in the range of 0.21%–1.83% and 0.27%–1.3% for polyurethane and epoxy membranes, respectively [9]. Similar behaviors were obtained for acrylic and chlorinated rubber membranes with percentages of water absorption of 0.23%–1.46% and 0.76%–1.04%, respectively [9]. However, coatings with polymer emulsions allow a larger water absorption (in the range of 3.3%–3.4%) [9]. Based on a

Table 12.5 Estimated percentage reductions in water absorption parameters and chloride ion diffusions for systems listed in Table 12.4.

Liquid membrane	**Code of the tested product**	**Percentage reduction in the listed parameters**				
		Water absorption	**Water absorption rate**	**Sorptivity**	**Charge passed**	**Chloride diffusion coefficient**
Polyurethane	PU1	95.6	94.6	93.6	96.0	90.5
	PU2	61.7	42.3	42.6	99.3	96.4
Epoxy	EP2	94.4	92.3	91.5	83.6	86.5
	EP1	72.8	57.6	57.4	99.2	60.0
Acrylic	AC1	95.2	93.1	93.6	83.2	89.2
	AC2	69.5	51.7	51.1	92.9	81.8
Chlorinated rubber	CR1	84.1	74.6	74.5	94.9	50.2
	CR2	78.2	64.4	63.8	96.0	56.2
Polymer emulsion	PE1	28.5	12.3	14.9	27.9	56.2
	PE2	30.5	5.8	4.3	47.2	16.9

full review of various WP systems, Pan et al. [9] used the term relative water absorptions (= 100% percentage reduction) for normalizing various results. They ranked the WP performance of epoxy resin, polyurethane, chlorinated rubber, and acrylic to be closely similar and equivalent to that of hydrophobic surface treatment (silane/siloxane). They are better than PMCC or the hydrophilic sealers (e.g., sodium silicate or magnesium fluosilicate) [9].

For crystalline CC, the produced crystals occupy a significant fraction of the capillary pores and cracks [24]. The crystals cannot fully block the whole pore structure [26]. This is explained by some authors to be because of the limitation of water availability or the full consumption of the available free moisture in crystallization [26]. Eventually, the crystals can lead to about 40% reduction in the porosity of permeable pore and cracks (size range 7.5 nn − 7.5 μn). The crystals lead to pore refinement of pores less than 100 nm. According to commercial literature, the percentage reduction in the volume of permeable pores (> 100 nm) can reach about 73%. Similarly, the presence of polymers in PMCC allows a reduction in the porosity of the coating and an increase in its hydrophobicity [8]. The percentage water absorption in PMCC decreases with increasing polymer/cement ratio [7]. Overall, the water absorption of PMCC is in the approximate range of 2%−2.5%, which is larger than the aforementioned values of PB (<2%) [7]. The water absorption of hygroscopic crystalline CC is in the approximate range of 1%−1.82%. In general the WP performance of hygroscopic crystalline CC is better than that of PMCC [13]. When the PMCC are applied onto smooth surfaces (no sandblasting), a less effective WP performance is obtained (a larger water absorption) [13]. This effect is less pronounced for crystalline CC as the soluble active ingredients can efficiently penetrate smooth surfaces as well as rough surfaces.

In fact, the level of WP effectiveness is dependent on time. The WP performance of CC evolves with the progress of hydration and setting reactions during curing [38] (see Section 12.5). More pronounced networks of crystals are formed with curing time [13]. This can be indicated by a decrease in the measured water absorption with curing time [38]. Fig. 12.9 shows the percentage water absorption as a function of curing time for hygroscopic crystalline CC and for PMCC. The initial water absorption of the crystalline CC (measured after 24 hours from application) is reduced by about 80% after final curing [13]. Similarly, it is reduced by about 87% for the PMCC after final curing [13]. It is worth recalling here that some studies indicated that silicate-based (hydrophilic) crystalline active ingredients lead to an increase in the water absorption in concrete (when added as an admixture) compared to the reference concrete due to the increase in fine pores [23]. The same silicate-based crystalline CC was found to lead to a small reduction in water absorption (about 10% reduction at 28 days testing). Similar to hygroscopic CC, the water absorption of coated concrete with silicate-based crystalline CC was not noticeably affected by sandblasting the concrete surface before the application of the CC [23]. This is because in both cases, the active ingredients can penetrate smooth surfaces by diffusion and capillary absorption.

For permeability testing (according to ASTM D5084), the transportation agencies commonly adopt a maximum limit of the hydraulic conductivity or permeability

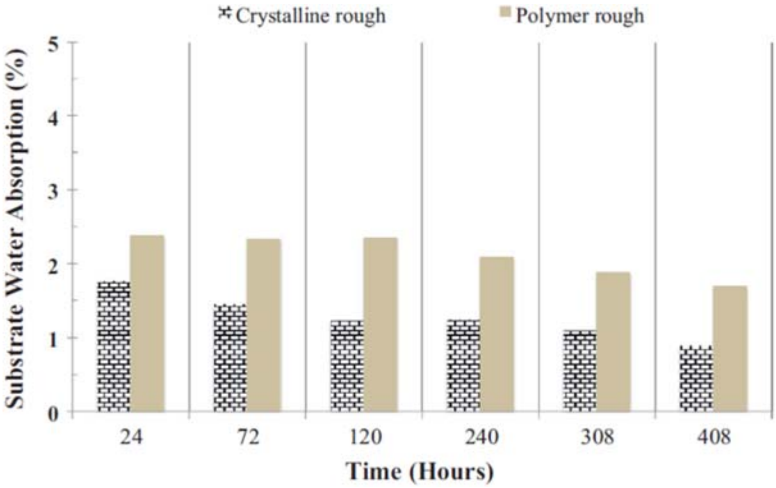


Figure 12.9 Percentage water absorption as function of curing time for hygroscopic crystalline cementitious coating and for polymer-modified cementitious coating [13].

coefficient (see Chapter 2). For example, the specifications of New York State Department of Transportation require that the water permeability coefficient for hot mix asphalt must be less than 1×10^{-5} cm/second [19]. The reported permeability results of asphalts at 30 kPa (4.35 psi) were in the range of $1.07 \times 10^{-3} - 5.85 \times 10^{-3}$ cm/s [19]. Another reported permeability coefficient for tested hot mix asphalt was 5.24×10^{-7} cm/s [19]. Wells et al. [19] highlighted that the available information on water permeability testing over a broad range of membranes is limited. The crystalline CC are efficient in reducing water permeability under pressure (according to CRD-C48-92) [58] and hence they can be used for submerged structures. According to commercial literature, permeability tests under 0.5 MPa (73 psi) of water pressure for 72 hours (according to EN 12390−8) indicated 90%−94% reduction in the water penetration depth of crystalline CC (after 28 days).

12.7.2 Effectiveness of waterproofing barriers in reducing chloride ion penetration and corrosion

Chloride ion penetration is the main mechanistic step in the corrosion of steel reinforcing bars and paste disintegration by chloride binding (see Chapter 3). Chloride ponding reduces the pull-off strength of PB [15]. The chloride ion penetration of a membrane is governed by its porosity, which is dependent on solid content, type of binder, thickness, and interactions of the chloride ions with membrane structure. Increasing the membrane porosity increases the penetration rate of chloride and increases the charge passage. Chloride ion penetration is usually determined by measuring the total charge passage according to the modified AASHTO T-277 and ASTM C1202, chloride ponding according to ASTM C1543 (Withdrawn 2019) and chloride profile testing according to ASTM C1218. ASTM C1202 allows 100 coulombs as a limit for negligible charge passage (see Chapter 7).

The performances of different commercial products (acrylic, epoxy, polyurethane, chlorinated rubber, and polymer emulsion coatings) are listed in Table 12.4. The listed total charge passages in these membranes are in the range of 6–700 coulombs, which is classified according to ASTM C1202 to be negligible or very low chloride ion penetration [55]. On the other hand, the charge passage through the control mortar specimen is 975, which is classified to be low. The obtained percentage reduction in charge passage is within a wide range of $28\% - 96\%$ Table 12.5. The listed chloride diffusion coefficients through these PB are in the range of $0.7 \times 10^{-8} - 16 \times 10^{-}$ cm^2/s, while that for the control mortar specimen is 19×10^{-8} cm^2/s. The obtained percentage reduction in diffusion coefficient is within the wide range of $17\% - 96\%$. Polyurethane, epoxy, acrylic membranes, and chlorinated rubber coating show high effectiveness for reducing chloride ion penetration (over 80%). The polyurethane and epoxy membranes usually have high resistance against the penetration of chloride ion and other aggressive ions, as they form filled films with low porosity [55]. On the other hand, coating of polymer emulsions show low performance due to higher porosity of the resulting film [55]. On the other hand, according to the survey of Xi et al. [15], the tested PB (according to ASTM C1218 and ASTM C1543) are not effective in controlling the penetration of chloride ions in bridge decks. These include epoxy, auto-catalytic polyuria, and rubberized asphalt [15]. The polyuria sheets can give the best performance among these systems.

The percentage reduction in chloride ion penetration is compared to the percentage reduction in water absorption in Table 12.5. A correlation between chloride ion and water penetrations through concrete is commonly reported (see Chapter 2). Table 12.5 shows that there is a reasonable correlation between the reduction in water absorption and the reduction in total charge passage through these PB. On the other hand, the reduction in the diffusion coefficient of chloride ion is not strongly correlated with the reductions in sorptivity or in the rate of water absorption. This is possibly because of different mechanisms and interactions of chloride ions with the cementitious constituents and with the polymeric systems. The PMCC was shown to have a good resistance against chloride ion penetration [41]. The chloride diffusion coefficient was found to be one to over three orders of magnitude lower than that of the untreated mortar [7]. For example, the diffusion coefficient of PMCC using acrylic was reported to be 2.3×10^{-8} cm^2/second while that of untreated concrete was reported to be 29.8×10^{-8} cm^2/second) [7].

The corrosion of reinforcing steel bars is correlated with chloride ion concentration at a depth equivalent to the depth of the bars. When such a concentration is lower than a threshold concentration no corrosion problems are expected. The time for initiating corrosion is estimated when such a threshold value is reached. Reducing chloride ion concentration increases the time required for initiating corrosion [56]. The time for initiating corrosion is commonly estimated with threshold values in the range of 0.4%–0.7% by weight of concrete [59]. However, a much lower threshold value of 0.03% was set in the analysis of the initiation of corrosion of black steel [60,61]. Xi et al. [15] considered the critical concentration of chloride ions to trigger corrosion of steel bars at about 0.05% [15]. Table 12.4 shows the estimated time for initiating corrosion of reinforcing steel bars in concrete coated with various PB. Acrylic, epoxy, and polyurethane membranes can increase the time for initiating the corrosion significantly, while chlorinated rubber and polymer emulsion membranes have minor effects on corrosion inhibition.

The corrosion retardation by coatings can be evaluated using field tests according to ASTM C876 “Standard test method for corrosion potentials of uncoated reinforcing steel in concrete.” A commercial CC containing organic active chemicals was shown to have the ability to retard the corrosion of reinforcing steel bars as confirmed by field tests according to ASTM C876 [21]. For crystalline CC, the commercial literature indicates reductions in the corrosion rate and in the corrosion potential by up to 50% and 40%, respectively, with significant enhancement of the concrete resistivity (from tests according to ASTM C876). The efficiency to prevent chloride-induced corrosion of two PMCC with acrylic polymer (with a polymer-to-cement ratios of 0.35 and 0.55) was confirmed experimentally [8]. The PMCC act as a physical barrier, reducing water and chloride content into concrete [8]. Their effectiveness increases with increasing the polymer content [8].

12.7.3 Breathability and carbonation resistance of external waterproofing barriers

Chapter 6 discusses the dualistic issue of whether a WP material shall be vapor-proofing or breathable. ACI 515.2R-13 [11] recommends that allowing moisture transmission into concrete (breathability) may assist in preventing concrete shrinkage through ensuring a moist concrete. Hence, BSI 1504-2 [6] highlights that breathability is an essential characteristic for preventing blistering of membranes and coatings. The breathability advantages of several WP systems have been highlighted in previous publications [12]. On the other hand, in the case of PB, vapor transmission below the PB decreases their adhesion strength [7]. The vapor condensation and accumulation under the barrier lead to peeling of the WP membrane [6] (see Section 12.5.1). The vapor permeability criterion for selecting WP materials is typically made based on the specific job application and requirements of WP durability. In some concrete applications, a PB may be applied on the top of integrally waterproofed concrete, which already has a reduced vapor emission and hence enhances adhesion. The transport behavior of water vapor in concrete [62] is dependent on the gradients of humidity and temperature across the WP section and within the concrete structure. It is also dependent on the types of interactions between water vapor and the WP materials (see Chapter 5). This transport mechanism is mainly achieved by diffusion and it is similar to the transport mechanism of other gases (see Chapter 2). In general, the gas permeability of PB can be measured by water absorption-desorption, dry-cup/wet-cup method, and Autoclam air permeability [7] (see also Chapter 7).

The crystalline CC are breathable. On the other hand, the air permeability of many PB, such as epoxy and polyurethane, is almost zero [7]. This prevents concrete breathability and causes the accumulation and condensation of vapor at the interface between the barrier and the concrete leading to damages. In fact, such a durability problem (for the membrane and the concrete) is considered as one of the main disadvantages of many polymer coatings [7]. The reported diffusion coefficient of carbon dioxide in various membrane systems was reported to be in the following order: PVC < polyurethane < epoxy < acrylic < integral surface penetrating WP treatments [9,63].

Air permeability governs the carbonation process in concrete (see Chapter 3): increasing air permeability increases the carbonation rate and hence increases the corrosion of reinforcing steel bars [7]. Increasing the thickness of the membrane increases the diffusion path and hence decreases the diffusion rate. The PB are effective against carbonation-related deterioration when the thickness of the coatings is above 200 μm [9]. The carbonation resistances of various PB were investigated by Park [63]. He found that all the tested coatings reduced the decline of calcium hydroxide (reduced the consumption by carbonation reaction) and decreased the carbonation depth slightly [63]. The protection performance was reported to be according to the following order: acrylic > epoxy > polyurethane (one-component moisture cured) > PVC [63]. Based on the findings of Park [63] and others, Pan et al. [9] ranked the performance of the polymeric WP barriers against carbonation-related deterioration according to the following order: PVC > polyurethane > epoxy > acrylic > other integral surface penetrating WP treatments. This is the opposite trend of the aforementioned trend of the diffusion coefficient of carbon dioxide. Gas diffusion is also associated with durability problems of other harmful gases such as sulfur dioxide that causes sulfate attack. Polyurethane membranes were reported to be more effective than epoxy in chemical resistance under the exposure to harmful gases such as sulfur dioxide [9]. On the other hand, epoxy membranes were reported to be more effective than bitumen and water-based solid acrylic [9]. In general, the PB have higher chemical resistance than hydrophobic and hydrophilic penetrating surface treatments [9]. According to the commercial literature, crystalline CC can enhance the carbonation resistance of coated concrete. Tests according to RILEM CPC-18 lead to a percentage reduction in the range 35%–40% in the depth of carbonation. The PMCC are characterized with low permeability and good breathability [7]. A good water vapor permeability was also confirmed experimentally for two PMCC with acrylic polymer (with a polymer-to-cement ratios of 0.35 and 0.55) [8].

12.7.4 Enhancing concrete resistance against freezing and thawing and scaling

Concrete deterioration by the cycles of freezing and thawing from water phase change in concrete pores is related to water transport and the thermal properties of the coatings (see Chapters 2 and 3). The freezing and thawing action increases with the accumulation of water beneath the WP barriers [7]. Hence, the freezing and thawing resistance of polymeric membranes can be correlated to their above-mentioned WP performance (see Tables 12.4 and 12.5). The resistance of membranes against the cycles of freezing and thawing is usually measured according to ASTM C666 (see Chapter 7). The survey of Xi et al. [15] indicated high resistance against freezing and thawing action for epoxy, auto-catalytic polyuria, cold-applied, self-adhering sheets of rubberized asphalt [15]. The polyuria sheets showed the best performance against the cycles of freezing and thawing among the investigated systems. The CC lead to redistricted chloride ion penetration with a marked reduction in the surface deterioration when compared to uncoated concrete. The commercial literature indicates that crystalline CC enhances the concrete resistance against cycles of freezing and thawing in the presence of salts as per tests according to ASTM C 672.

References

[1] Jianxia, S. (2012). 6.14-Durability design of concrete hydropower structures. In A. Sayigh (Ed.), *Comprehensive renewable energy* (pp. 377−403). Oxford: Elsevier.

[2] Mehta, P. K. (1991). *Concrete in the marine environment*. Boca Raton, FL, USA: CRC Press.

[3] ACI. (1999). *Committee 212, ACI 212.3R-91 Chemical admixtures for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[4] ASTM. (2014). *D449/D449M Standard specification for asphalt used in dampproofing and waterproofing*. West Conshohocken, PA, USA: Annual Book of ASTM Standards.

[5] ACI. (1986). *Committee 515, ACI 515.1R-79 A guide to the use of waterproofing, dampproofing. Protective, and decorative barrier systems for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[6] BS. (1998). *BS 1504-2, Products and systems for the protection and repair of concrete structures—Definitions, requirements, quality control and evaluation of conformity*. British Standards Institution.

[7] Pan, X., et al. (2017). A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578−590.

[8] Diamanti, M. V., et al. (2013). Effect of polymer modified cementitious coatings on water and chloride permeability in concrete. *Construction and Building Materials*, *49*, 720−728.

[9] Pan, X., et al. (2017). A review on surface treatment for concrete − Part 2: Performance. *Construction and Building Materials*, *133*, 81−90.

[10] ACI. (2018). *CT-18 Concrete Terminology*. Farmington Hills, MI, USA: American Concrete Institute.

[11] ACI. (2013). *Committee 515, ACI 515.2R-13 Guide to selecting protective treatments for concrete*. Farmington Hills, MI, USA: American Concrete Institute.

[12] Nair, P. S., & Gettu, R. (2016). Commercially available waterproofing agents in India: A review. *Indian Concrete Journal*, *90*, 36−53.

[13] Al-Kheetan, M. J., Rahman, M. M., & Chamberlain, D. A. (2017). Influence of early water exposure on modified cementitious coating. *Construction and Building Materials*, *141*, 64−71.

[14] Pavlić, I., Lebo, Ž., & Mandić, A. (2019). Application of bentonite in waterproofing of underground structures. *Polytechnic and Design*, *7*(4), 254−261.

[15] Xi, Y., Li L., & Railsback, R. (2018). *Evaluation of different types of waterproofing membranes (asphaltic and non-asphaltic) as cost effective bridge deck barriers in reducing corrosive chloride effects*. Colorado. Dept. of Transportation. Applied Research and Innovation Branch.

[16] Manning, D. G. (1995). *Waterproofing membranes for concrete bridge decks* (Vol. 220). Transportation Research Board.

[17] Russell, H. G. (2012). *Waterproofing membranes for concrete bridge decks* (Vol. 425). Transportation Research Board.

[18] ASTM. (2000). *D 4071-84 Standard practice for use of Portland cement concrete bridge deck water barrier membrane systems*. West Conshohocken, PA, USA: Annual Book of ASTM Standards.

[19] Wells, D., Palle, S., & Hopwood, I. (2018). *Waterproofing options for bridge decks*. University of Kentucky Transportation Center.

[20] Li, G., et al. (2019). Activated chemicals of cementitious capillary crystalline waterproofing materials and their self-healing behaviour. *Construction and Building Materials*, *200*, 36−45.

[21] Saricimen, H., et al. (1996). Evaluation of a surface coating in retarding reinforcement corrosion. *Construction and Building Materials*, *10*(7), 507−513.

[22] Lu, G., Zhao, W. & Dai, D. (2015). Study on preparation of cementitious capillary crystalline waterproofing coating. In 3rd international conference on mechatronics, robotics and automation. *Atlantis Press*.

[23] Cappellesso, V. G., et al. (2016). Use of crystalline waterproofing to reduce capillary porosity in concrete. *Journal of Building Pathology and Rehabilitation*, *1*(1), 9.

[24] Drochytka, R., et al. (2019). Use of secondary crystallization and fly ash in waterproofing materials to increase concrete resistance to aggressive gases and liquids. *Advances in Civil Engineering*.

[25] Bohus, S., & Drochytka, R. (2012). Cement based material with crystal-growth ability under long term aggressive medium impact. *Applied Mechanics and Materials*, Trans Tech Publ.

[26] Bohus, S., Drochytka, R., & Taranza, L. (2012). Fly-ash usage in new cement-based material for concrete waterproofing. *Advanced Materials Research*, Trans Tech Publ.

[27] Li, F., et al. (2020). Investigation on waterproof mechanism and micro-structure of cement mortar incorporated with silicane. *Construction and Building Materials*, *239*, 117865.

[28] Li, H., et al. (2020). Enhanced performances of cement and powder silane based waterproof mortar modified by nucleation C−S−H seed. *Construction and Building Materials*, *246*, 118511.

[29] Li, Y., et al. (2019). The water impermeability and self-repairing performance of the rapid setting polymer-modified waterproof mortar. *Journal of Physics: Conference Series*, *1213*, 052022.

[30] Qin, F., Yang, F., & Liu, H. (2017). Waterproof measures for swimming pools: Use of cement-based permeable crystalline waterproof composite coatings. *Chemical Engineering Transactions*, *59*, 535−540.

[31] Zhang, X. J., & Zheng, D. M. (2012). Uniform design for preparation of cementitious capillary crystalline waterproofing coating. *Advanced Materials Research*, Trans Tech Publ.

[32] Yang, H., et al. (2019). Effects of bentonite on pore structure and permeability of cement mortar. *Construction and Building Materials*, *224*, 276–283.

[33] Liu, J., et al. (2019). Properties and hardening mechanism of alkali activated slag based hydrophobic coating at ambient curing condition. *Materials Research Express*, *6*(5), 055505.

[34] Zhang, W., et al. (2019). Study on unsaturated transport of cement-based silane sol coating materials. *Coatings*, *9*(7), 427.

[35] Jalal, P. S., et al. (2018). Effect of waterproofing systems and materials on environment. *Journal of Environmental Nanotechnology*, *7*(4), 40–45.

[36] Jappie, L. (2019). *Literature review of the use of common protective coatings for concrete structures with experiences in the South African context*. Engineering and the Built Environment, University of Cape Town. Rondebosch, Cape Town, South Africa.

[37] Drochytka, R. & Bohuš, Š. (2011). Microstructural analysis of crystalline technology by NANOSEM-FEI NOVA 200. In *18th international conference on composite materials*.

[38] Reiterman, P., & Pazderka, J. (2016). Crystalline coating and its influence on the water transport in concrete. *Advances in Civil Engineering*, *2016*.

[39] Pei, X., et al. (2017). Cementitious coatings for improved corrosion resistance of steel reinforcement. *Surface and Coatings Technology*, *315*, 188–195.

[40] Wang, F., et al. (2020). Cement based superhydrophobic coating with excellent robustness and solar reflective ability. *Journal of Alloys and Compounds*, *823*, 153702.

[41] Muhammad, N. Z., et al. (2015). Waterproof performance of concrete: A critical review on implemented approaches. *Construction and Building Materials*, *101*, 80–90.

[42] Kalibatas, D., & Kovaitis, V. (2017). Selecting the most effective alternative of waterproofing membranes for multifunctional inverted flat roofs. *Journal of Civil Engineering and Management*, *23*(5), 650–660.

[43] Rupal, A., Sharma, S. K., & Tyagi, G. (2020). Characterization and optimization of polyurethane based bituminous waterproofing membrane. In International conference on innovative technologies for clean and sustainable development. Springer.

[44] Sriravindrarajah, R. & Tran, E. (2018). Waterproofing practices in Australia for building construction. In 4th International *c*onference on *r*ehabilitation and *m*aintenance in *c*ivil *e*ngineering. EDP Sciences.

[45] Anderson, I. A. (2019). Assessment of the BDM waterproofing membrane system. Vermont. Agency of Transportation.

[46] Jalali, U. H., & Afgan, S. (2018). Analysis of integral crystalline waterproofing technology for concrete. *International Research Journal of Engineering and Technology (IRJET)*, *5*(10).

[47] Shell, B. S. (2008). *An analysis of waterproofing systems and materials*. Virginia Polytechnic Institute and State University.

[48] Berndt, M. L. (2011). Evaluation of coatings, mortars and mix design for protection of concrete against sulphur oxidising bacteria. *Construction and Building Materials*, *25* (10), 3893–3902.

[49] Guo-Zhong, L., et al. (2014). The analysis on mechanism and application of cementitious capillary crystalline waterproofing coating. In *2014 i*nternational *c*onference on *m*echanics and *c*ivil *e*ngineering (icmce-14). Atlantis Press.

[50] Zolin, B. (1986). *A guide to the use of waterproofing, damp-proofing*. *Protective, and decorative barrier systems for concrete*. Detroit, MI: American Concrete Institute.

[51] Mundo, R. D., et al. (2020). Recent advances in hydrophobic and icephobic surface treatments of concrete. *Coatings*, *10*(5), 449.

[52] Pazderka, J., & Hájková, E. (2017). The speed of the crystalline admixture's waterproofing effect in concrete. *Key Engineering Materials*, Trans Tech Publ.

[53] Pattanaik, S. C. (2011). *Self-sealing crystalline coating and self-cleaning nanocoating for the concrete substrate for a sustainable development*. In *the conference proceedings of international conference* (ICTACE 2011). Hyderabad.

[54] Braun, J. A., Maranhão, F. L., &Monte, R. (2020). Behavior of waterproofing systems exposed to environmental aAgents. In *XV international conference on durability of building materials and components (DBMC 2020).*

[55] Almusallam, A. A., et al. (2003). Effectiveness of surface coatings in improving concrete durability. *Cement and Concrete Composites*, *25*(4), 473−481.

[56] Basheer, P. A. M., et al. (1997). Surface treatments for concrete: Assessmentmethods and reported performance. *Construction and Building Materials*, *11*(7), 413−429.

[57] Gupta, R., & Biparva, A. (2017). Do crystalline water proofing admixtures affect restrained plastic shrinkage behavior of concrete? *Revista ALCONPAT*, *7*(1), 15−24.

[58] CRD. (1992). *C48-92 Standard test method for water permeability of concrete*. U.S. Army Corps of Engineers.

[59] Schueremans, L. & Van Gemert, D. (1997). *Service life prediction model for reinforced concrete constructions treated with water repellent compounds*. Conchem Proceedings (pp. 103−113). Dusseldorf.

[60] Wells, D., et al. (2014). *Sealants, treatments and deicing salt practices to limit bridge deck corrosion and experimental deck sealants and pier cap coating on interstate 471*. University of Kentucky Transportation Center. Available from http://dx.doi.org/10.13023/KTC.RR.2014.04.

[61] Wells, D., Palle S., & Hopwood II T. (2019). *Developing material specification and application criteria for sealing concrete bridge decks*. University of Kentucky Transportation Center. Available from https://doi.org/10.13023/ktc.rr.2019.09.

[62] Gretton, J. C., et al. (1998). Moisture vapor transport through waterproof breathable fabrics and clothing systems under a temperature gradient. *Textile Research Journal*, *68*(12), 936−941.

[63] Park, D. (2008). *Carbonation of concrete in relation to CO_2 permeability and degradation of coatings*. *Construction and Building Materials*, *22*(11), 2260−2268.

Index

Note: Page numbers followed by "*f*" and "*t*" refer to figures and tables, respectively.

WOODHEAD PUBLISHING SERIES IN CIVIL AND STRUCTURAL ENGINEERING

Integral Waterproofing of Concrete Structures demonstrates how integral waterproofing technologies can solve concrete durability problems based on performance and characterization experimental results.

This book first establishes a background about concrete structures and porosity linked with concrete hydration, then goes on to consider concrete durability problems from the perspective of water penetration including damages from freeze-thaw cycles, alkali silica reactions, and chloride ion penetration. The mechanisms, applications, performances, and limitations of waterproofing technologies including coatings and integral systems are compared. The book also showcases all application methods of crystallization waterproofing materials, including material spray on cured concrete and on fresh concrete, and their addition to concrete mix designs as enhancers or admixtures. Pore-blocking and lining waterproofing systems including silicate-based and hygroscopic kinds, and other waterproofing materials are also discussed.

Key features

- Includes various advanced recent technologies in the field of waterproofing;
- Presents and describes enhanced concrete characteristics and modified structures within the context of material engineering;
- Summarizes the characteristics of waterproofing systems obtained from experimental results.

This book will be of special interest to civil engineers working on both design and construction, as well as graduate students and researchers for concrete waterproofing materials and systems. It is suitable for a course in the field of concrete waterproofing.

About the author

Maher Al-Jabari is a full professor of chemical and environmental engineering at Palestine Polytechnic University, Palestine, and an international expert in the fields of waterproofing of construction materials, hazardous waste, and wastewater treatment. As well as achieving breakthroughs in protecting cementitious materials from environmental attacks and providing industrial durability solutions for concrete, Prof. Al-Jabari has been involved in international R&D projects in these fields, with a distinguished industrial record. Prof. Al-Jabari accomplished his industrial experience in International Chem-Crete Co., Richardson TX, USA; starting as a director of manufacturing and then directing Chem-Crete R&D activities that led to patented crystallization waterproofing technology.

ELSEVIER
WP
WOODHEAD
PUBLISHING
An imprint of Elsevier
elsevier.com/books-and-journals

ISBN 978-0-12-824354-1
9 780128 243541