Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications

Mark F. Vitha, Series Editor

Handbook of Coal Analysis

SECOND EDITION

JAMES G. SPEIGHT

WILEY

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CHEMICAL ANALYSIS

A SERIES OF MONOGRAPHS ON ANALYTICAL CHEMISTRY
AND ITS APPLICATIONS

Series Editor
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Volume 182

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

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Library of Congress Cataloging-in-Publication Data:

Speight, James G.
Handbook of coal analysis / Dr. James G. Speight. – 2nd edition.
pages cm
Includes bibliographical references and index.
ISBN 978-1-118-36924-1 (cloth)
1. Coal–Analysis–Handbooks, manuals, etc. I. Title.
TP325.S7145 2015
662.6′22–dc23
2014043341

Typeset in 10/12pt TimesLTStd by Laserwords Private Limited, Chennai, India

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

2 2015

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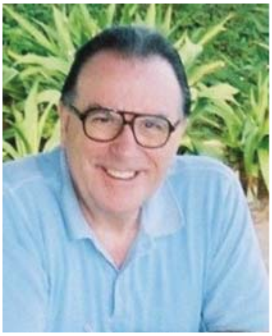

James G. Speight

Dr. James G. Speight, who has doctorate degrees in Chemistry, Geological Sciences, and Petroleum Engineering, is the author of more than 60 books in petroleum science, petroleum engineering, and environmental sciences. He has served as Adjunct Professor in the Department of Chemical and Fuels Engineering at the University of Utah and in the Departments of Chemistry and Chemical and Petroleum Engineering at the University of Wyoming. In addition he was a Visiting Professor in Chemical Engineering at the following universities: the University of Missouri-Columbia, the Technical University of Denmark, and the University of Trinidad and Tobago.

In 1996, Dr. Speight was elected to the Russian Academy of Sciences and awarded the Gold Medal of Honor that same year for outstanding contributions to the field of petroleum sciences.

In 2001, Dr. Speight received the Scientists without Borders Medal of Honor of the Russian Academy of Sciences.

In 2001, the Academy also awarded Dr. Speight the Einstein Medal for outstanding contributions and service in the field of Geological Sciences.

In 2005, the Academy awarded Dr. Speight the Gold Medal – Scientists without Frontiers, Russian Academy of Sciences, in recognition of Continuous Encouragement of Scientists to Work Together Across International Borders.

In 2007 Dr. Speight received the Methanex Distinguished Professor at the University of Trinidad and Tobago in recognition of excellence in research.

PREFACE

The success of the first edition of this text has been the primary factor in the decision to publish a second edition.

Coal analysis is an essential task in determining the use of coal. Analytical methods help determine whether or not coal meets the needs of a specific application, or to characterize the general quality of the coal for future reference. For example, if the coal has high organic sulfur content, then it may have to be mixed or blended with a coal of lower sulfur content in order to meet sulfur emissions standards, or the sulfur may have to be cleaned out of the flue gas by flue-gas desulfurization (FGD), which is an expensive procedure. Similarly, analysis may determine whether a trace element, such as arsenic or mercury, may be eliminated from a coal by washing or whether it must be removed during flue gas cleaning. Finally, in extreme cases, analysis may determine that the coal cannot be used.

Furthermore, coal is again being seriously considered as an alternate fuel source to petroleum, not so much for the production of liquids but more for the generation of power and as a source of chemicals. The reaffirmation by the United States to a clean environment through the passages of the various environmental laws as well as serious consideration to the effects of combustion products (carbon dioxide) on the atmosphere are all given consideration in this new text.

In addition, the demand for coal products, particularly liquid fuels (gasoline and diesel fuel) and chemical feedstocks (such as aromatics and olefins), is increasing throughout the world. Traditional markets such as North America and Europe are experiencing a steady increase in demand whereas emerging Asian markets, such as India and China, are witnessing a rapid surge in demand for liquid fuels. This has resulted in a tendency for existing refineries to seek fresh refining approaches to optimize efficiency and throughput. In addition, the increasing use of the heavier feedstocks by refineries is forcing technology suppliers/licensors to revamp their refining technologies in an effort to cater to the growing customer base.

As in the previous Edition, this Edition has references cited throughout the text, which will allow the reader to such citations for more detail. However, it should be noted that only selected references could be employed lest the reference lists outweigh the actual text. It would have been impossible to include all of the relevant references. Thus, where possible, references such as review articles, other books, and those technical articles with substantial introductory material have been used in order to pass on the most information to the reader.

In addition, chapters have been added to give the reader an introduction to the formation of coal, which will help understands the complexity of the organic portion of coal as well as the complex nature of the inorganic portion of coal (the mineral matter). Overall, the book will provide the reader with a detailed overview of the chemistry and technology of coal analysis as is required in the 21st century. Moreover, the text will prove useful for those scientists and engineers already engaged in the coal industry who wish to gain a general overview or update of the science of coal and the various analytical test methods.

The book will also provide the reader with the necessary information about testing and analyzing coal. Moreover, it will explain the meaning of test results and how these results can predict coal behavior and its corresponding environmental impact during use and include:

- Coverage of nomenclature, terminology, sampling, and accuracy and precision of analysis.
- Explanation of coal behavior relative to its usage alongside the corresponding environmental issues.
- Presentation of necessary standard tests and procedures.
- Step-by-step test method protocols for proximate analysis, ultimate analysis, mineral matter, physical and electrical properties, thermal properties, mechanical properties, spectroscopic properties, and solvent properties.
- Emphasis on relevant American Society for Testing and Materials (ASTM) standards and test methods

To assist readers in understanding the material, a comprehensive Glossary is provided in which each item is defined in straightforward language that will enable readers to better understand the terminology related to coal. References at the end of each chapter lead readers to more in-depth discussions of specialized topics.

This book will be an essential reference for analytical chemists, process chemists, and engineers in the coal industry as well as other professionals and researchers who are looking to coal as a means to decrease dependence on foreign oil sources and devise more efficient, cleaner methods of energy production from coal.

Dr. James G. Speight
Laramie, Wyoming

August 2014

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HISTORY AND TERMINOLOGY

1.1 INTRODUCTION

Coal is an organic sedimentary rock that contains varying amounts of carbon, hydrogen, nitrogen, oxygen, and sulfur as well as trace amounts of other elements, including mineral matter, as well as methane which is found within the pore systems of the coal (ASTM D121; Speight, 2013a). It is a solid, brittle, combustible, carbonaceous rock formed by the decomposition and alteration of vegetation by compaction, temperature, and pressure and varies in color from brown to black and is usually stratified as a *coal seam*. The source of the vegetative precursors to coal is a variety of ancient plant forms as well as ancient woody precursors. The plant precursors that eventually formed coal were deposited as dead and decaying carbonaceous materials that were compacted, hardened, chemically altered, and metamorphosed by the pressure (in some cases accompanied by heat) of overlying sediments over geologic time (Table 1.1). When the plants died, the biomass was deposited in anaerobic, aquatic environments where the low oxygen level prevented the reduction of the biomass and release of carbon dioxide.[1]

[1] The standard method (ASTM D121) forms the basis for coal standards in which the technical terms used in the standards for coal and coke are defined. In addition, the standards includes terms related to the sampling of coal and coke under conditions required for most commercial and technical purposes related to coal and coke as well as the bias and related statistical testing terms. Also included are (1) the description of coal, both visually in the field and microscopically in the laboratory, and (2) the chemical and physical analyses of coal and coke involved in the classification of coal.

Handbook of Coal Analysis, Second Edition. James G. Speight.

TABLE 1.1 The Geologic Timescale

Era	Period	Epoch	Approximate Duration (Millions of Years)	Approximate Number of Years Ago (Millions of Years)
Cenozoic	Quaternary	Holocene	10,000 years ago to the present	
		Pleistocene	2	0.01
	Tertiary	Pliocene	11	2
		Miocene	12	13
		Oligocene	11	25
		Eocene	22	36
		Paleocene	71	58
Mesozoic	Cretaceous		71	65
	Jurassic		54	136
	Triassic		35	190
Paleozoic	Permian		55	225
	Carboniferous		65	280
	Devonian		60	345
	Silurian		20	405
	Ordovician		75	425
	Cambrian		100	500
Precambrian			3380	600

Evidence of the types of plants that contributed to carboniferous deposits can occasionally be found in the coal as fossil imprints as well as in the shale and sandstone sediments that overlie coal deposits.

Coal sediments (*coal beds*, *coal seams*) can range from fractions of an inch to hundreds of feet in thickness and are found in all geologic periods from Silurian through Quaternary, but the earliest commercially important coals are found in rocks of Mississippian age (Carboniferous in Europe). Coal is generally formed in either a fluvial environment or in a basin that is open to marine incursions and consists of more than 50% w/w (typically more than 70% v/v) carbonaceous material (organic material containing carbon, hydrogen, and other elements as well as inherent moisture, which is a moisture that occurs within the coal).

1.2 DEFINITIONS AND TERMINOLOGY

Simply and by definition, coal is an organic rock. In addition, coal is also defined as a black or dark-brown combustible mineral substance consisting of carbonized vegetable matter, used as a fuel.

It is customary (especially through this text) to use the word *coal* in the singular form but the word is, in reality, applicable to materials having a rather wide range of properties – this is similar to the use of the word *petroleum* (or *crude oil*), which encompassed a variety of materials from low-boiling (light) conventional crude oil to the thicker viscous high-boiling heavy oil (Speight, 2014). In terms of coal, one sample might be a wet, easily crumbling brown material looking like partially decayed wood (Lignite) while another would be a very hard, glossy black, lustrous material (anthracite). In addition, the heating value (Chapter 8) of these samples would range from about 5000 to about 15,000 BTU/lb. Thus, the use of the word *coal* in this text implies either a single family member of a uniquely defined material as well as a family of natural-occurring family of organic rocks having both similarities and differences within the members of that family.

The name *coal* is thought to be derived from the Old English *col* that was a type of charcoal at the time. Generally, coal was not mined to any large extent during the early Middle Ages (prior to 1000 AD) but there are written records of coal being mined after 1000 AD. Moreover, coal is, in some areas, referred to as *sea-coal* as it is occasionally found washed up on beaches, especially those in the north east area of England. However, the rapidly expanding use of coal throughout the nineteenth century and the early part of the twentieth century has seen a phenomenal increase in coal use. This increased popularity has made it necessary to devise acceptable methods for coal analysis with the goal of correlating fuel composition and properties with behavior (Vorres, 1993; Speight, 2013a).

In the modern system of terminology, coal is subdivided into various types that are the result of geological processes pressure to the dead precursors over time and under suitable conditions (which are difficult to define), it is transformed successively into: (1) lignite, (2) sub-bituminous coal, (3) bituminous coal, and (4) anthracite (Speight, 2013a,b).

Lignite (sometimes referred to as *brown coal*) is the lowest rank of coal and used almost exclusively as fuel for electric power generation. *Sub-bituminous coal*, which has properties that range from similar properties of lignite to those of bituminous coal, is used primarily as fuel for steam-electric power generation (Speight, 2013b) and is an important source (through pyrolytic decomposition) of low-boiling aromatic hydrocarbons for the chemicals industry (Speight, 2013a). *Bituminous coal* is a dense black sedimentary rock that often has well-defined bands of bright and dull material; it is used primarily as fuel in steam-electric power generation, with substantial quantities used for heat and power applications in manufacturing and to make coke. *Anthracite* (black coal, hard coal, stone coal, blind coal, black diamond, and crow coal) is a hard, glossy black coal and is the most metamorphosed type of coal (the highest rank of the coal series) in which the carbon content is between 92.1% and 98%. Anthracite does not emit tar or other hydrocarbonaceous vapor when heated below the point of ignition – it ignites with difficulty and burns with a short, blue, and smokeless flame. Finally, although not an official definition in the sense of the four previous definitions, *steam coal* is the name given to a grade of coal that has properties between those of bituminous coal and anthracite and which was once widely used as a fuel for steam locomotives. With respect to this specialized use, it is sometimes known as *sea coal* in the United States.

Peat is considered by some observers/scientists/engineers to be a precursor of coal and to be a type of coal but the lack of any obvious resemblance to any other four coal types presented earlier tends to negate such inclusion into the coal sequence.

It was during the Industrial Revolution in the eighteenth and nineteenth century the demand for coal surged. The great improvement of the steam engine by James Watt, patented in 1769, was largely responsible for the growth in coal use. The history of coal mining and use is inextricably linked with that of the Industrial Revolution – iron and steel production, rail transportation, and steamships. Coal was also used to produce gas for gas lights in many cities, which was called *town gas*. This process of coal gasification witnessed the growth in gas lights across metropolitan areas at the beginning of the nineteenth century, particularly in London. The use of coal gas in street lighting was eventually replaced with the emergence of the modern electric era. With the development of electric power in the nineteenth century, the future of coal use became closely tied to electricity generation. The first practical coal-fired electric generating station, developed by Thomas Edison, went into operation in New York City in 1882, supplying electricity for household lights.

Steam coal, also known as thermal coal, is used in power stations to generate electricity (Speight, 2013a, 2013b). The earliest conventional coal-fired power stations used lump coal, which was burnt on a grate in boilers to raise steam. Currently, the coal is first milled to a fine powder, which increases the surface area and allows it to burn more quickly. In these pulverized coal (PC) combustion systems, the powdered coal is blown into the combustion chamber of a boiler where it is burnt at high temperature. The hot gases and heat energy produced converts water – in tubes lining the boiler – into steam.

As a result of the surge in coal use during the decades of the nineteenth and twentieth century, the use of coal increased and it was during this time that coal properties were not consistent and that certain types of coal were available – the adage *coal was not coal was not coal* gained wide acceptance and several types of coal existed. Thus, coal is now classified as various types and each type has distinctly different properties from the other types. In fact, each country has a varied system of nomenclature to describe the various types of coal and it is only through measurement of the analytical properties that any relationship can be made between the various names (Table 1.2). However, the terminology is not always standard and whether or not a standard terminology will ever be accepted remains to be seen. But understanding the analytical chemistry and analytical properties of coal is an essential aspect in international trade.

1.3 PRECURSORS OF COAL

Coal formation began during the Carboniferous Period, which is known as the *first coal age* and major coal deposits were formed in every geological period since the Upper Carboniferous Period, 270–350 million years ago (Table 1.1).

Layers of plant debris – such as lignin, were deposited in wet or swampy regions under conditions of limited exposure to air and complete decay as the debris accumulated, thereby resulting in the formation of peat. As the peat became buried by sediment, it was subjected to higher temperatures and pressures resulting in chemical and physical changes that, over time, formed coal. Cycles of plant debris accumulation and deposition were followed by diagenetic

TABLE 1.2 Variations in the English and German Systems of Coal Nomenclature

German Classification[a]	English (UK) Designation	Volatiles (% w/w)	Carbon (% w/w)	Hydrogen (% w/w)	Oxygen (% w/w)	Sulfur (% w/w)	Heat Content (Btu/lb)[b]
Braunkohle	Lignite (brown coal)	45–65	60–75	6.0–5.8	34–17	0.5–3.0	<12,250
Flammkohle	Flame coal	40–45	75–82	6.0–5.8	>9.8	ca. 1.0	<14,150
Gasflammkohle	Gas flame coal	35–40	82–85	5.8–5.6	9.8–7.3	ca. 1.0	<14,600
Gaskohle	Gas coal	28–35	85–87.5	5.6–5.0	7.3–4.5	ca. 1.0	<15,030
Fettkohle	Fat coal	19–28	87.5–89.5	5.0–4.5	4.5–3.2	ca. 1.0	<15,200
Esskohle	Forge coal	14–19	89.5–90.5	4.5–4.0	3.2–2.8	ca. 1.0	<15,200
Magerkohle	Non-baking coal	10–14	90.5–91.5	4.0–3.75	2.8–3.5	ca. 1.0	15,200
Anthrazit (Steinkohle)	Anthracite	7–12	>91.5	<3.75	<2.5	ca. 1.0	<15.175

[a] While Braunkohle (brown coal) has the approximate properties of US lignite, the next six grades in the table (Flammkohle, Gasflammkohle, Gaskohle, Fettkohle, Esskohle, and Magerkohle) represent a step-by-step transition from sub-bituminous coal to bituminous coal (US classification, ASTM D388) while the last class (Anthrazit) is approximately equivalent to anthracite, but more inclusive (US anthracite has < 6% volatiles).

[b] Rounded to the nearest 10 units; 1 kJ/kg = 0.4299 Btu/lb.

(i.e., biological) and tectonic (i.e., geological) actions, and, depending on the extent of temperature, time, and forces exerted, the different ranks of coal formed – this concept is not new and came into being during the latter part of the eighteenth century.

Indeed, in order to emphasize the complexity of coal and the complexity of the coal-forming processes, a note regarding some of the potential precursors is worthy of consideration. However, there is also the cautious assumption that there are little, if any, differences (natural selection notwithstanding) between the natural product chemicals known now and those in existence at the time of deposition of the coal beds. Perhaps a reasonable assumption, but it is fraught with uncertainties.

Thus, the makeup of the organic portion of plants consists of carbohydrates, lignin, and proteins, as well as other polymers (Table 1.3). Indeed, it is these higher polymers that are often considered as contributors to the organic substance of coal. But, of course, the relative amount of each of these constituents varies greatly with the particular species of plant; as well as the relative stage of growth of the plant. Furthermore, recognition of the fact that each of the aforementioned compound types is a very broad classification (and does not make any attempt to include individual molecular types) indicates the general complexity of the original plant debris. It is only this fact (probably more than any other single contribution) that determines the complexity of the final *coal molecule*.

Nevertheless, it is possible (in an attempt to simplify an already complex situation) to acknowledge some generalities; the lignin content of plants may fall within the range of 10–35% w/w while in woody material the lignin may be within the narrower range of 25–30% w/w (all of these approximations are given as percentages of the dry weight of the plant material). In fact, the protein content of grasses has been assigned to fall within the range of 15–20% w/w while woody materials contain little, if any, protein constituents; the cellulose (carbohydrate) content of grasses falls in the range of 20–55% w/w (all of these approximate ranges are given as percentages of the dry weight of the plant material).

TABLE 1.3 Examples of the Types of Macromolecules in Plants

Natural Polymer[a]	Plant Tissue	Structures Present
Carbohydrates	Cell	Mono- and polysaccharides
Cellulose	Wood, other tissues	Mono- and polysaccharides
Cutin	Leafs, stems	Hydroxy acids
Hemicellulose	Wood, other tissues	Mono- and polysaccharides
Lignin	Wood	Alkyl phenols
Lipids	Seeds	Fats, steroids, phospholipids
Phospholipids	Seeds	Glycerol, fatty acids
Proteins	Various	Amino acids, polypeptides
Sporopollenin	Spores, pollen	Polymeric carotenoids
Waxes	Cuticles, surface structure	Long-chain hydrocarbons

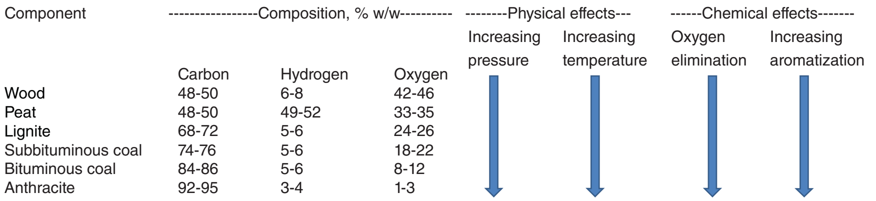
[a] Listed in alphabetical order.

Thus, from these broad generalities alone, plant debris is complex and the original plant debris that formed the precursors to coal may have been even more complex (depending on location and the circumstances leading to the deposition. Giving consideration to (1) the different chemical precursors of coal (as presented subsequently), (2) the varied geological environment, (3) the maturation conditions, and (4) the variation of coal analysis within a seam, the rationale for an average structure of coal defeats itself. The complexity of the original precursors includes: various carbohydrates and polysaccharides, a variety of proteins, vegetable oils, fats, waxes (including lower molecular weight hydrocarbons), as well as plant resins, tannins, alkaloids, porphyrins, and the inorganic mineral) constituents of plants. On this note, is necessary to point out that mineral matter in coal is often classified as inherent mineral matter or as extraneous mineral matter (Chapter 4). The inherent mineral matter is the inorganic material that originated as part of the plant material that formed the organic debris in the source bed. On the other hand, extraneous mineral matter is the inorganic material that was brought into the coal-forming deposit by various means from external sources.

1.4 COAL-FORMING PROCESSES

The *coalification process* (*coal-forming process*) is, simply defined, the progressive change in the plant debris as it becomes transformed from peat to lignite and then through the higher ranks of coal to anthracite (Francis, 1961; Speight, 2013a). In the peat swamp, as dead plant matter accumulates, aerobic bacteria rapidly oxidize cellulose and other components producing methane (CH_4), carbon dioxide and ammonia (from the nitrogen-containing components). The resulting decomposed material compacts about 50% and is largely composed of lignin, a complex, 3-dimensional polymer rich in aromatic (benzene) rings. These bacteria quickly use up the available oxygen and die ending the first stage of the process. Anaerobic bacteria take over the decomposition process and they produce acids as metabolic waste products. When the pH of the medium is sufficient ($\text{pH} = \sim 4$), these bacteria die. The product at this stage is a gel-like material called *Gytta* (sometime referred to as *proto-coal*). When the Gytta is buried to a depth of 2000–3000 ft, the temperature is approximately 100 °C (212 °F) at which water and other volatiles are driven off. Furthermore, as part of the coalification process, it is usually *assumed* that a regular (or at least a near-regular) progression exists from lignite to anthracite and that the progression is consecutive (Figure 1.1) but concurrency (i.e., simultaneous formation of different coal types) must also be considered a possibility and may even be the norm under certain conditions and in a variety of locales. In summary, *consecutiveness* is not proven, although it is often claimed.

Whereas the degree of coalification generally determines the rank of the coal, the process is not a series of regular, or straightforward, chemical changes. Indeed, complexity is the norm insofar as the metamorphosis of the plant debris relies not only on geological time but also on other physical factors, such as temperature and pressure. Thus, the occurrence of a multitude of different and complex, chemical reactions



Component	Composition, % w/w			Physical effects		Chemical effects	
	Carbon	Hydrogen	Oxygen	Increasing pressure	Increasing temperature	Oxygen elimination	Increasing aromatization
Wood	48-50	6-8	42-46	↓	↓	↓	↓
Peat	48-50	49-52	33-35				
Lignite	68-72	5-6	24-26				
Subbituminous coal	74-76	5-6	18-22				
Bituminous coal	84-86	5-6	8-12				
Anthracite	92-95	3-4	1-3				

*Some observers have raised the possibility that the process is not sequential but that each coal is a by-product of the process.

Figure 1.1 Schematic representation of the coalification process.

(no matter how simple they appear on paper or how simply they occur in laboratory simulations) is inherent in the coalification process.

Thus, the theories about the formation of coal require that the original plant debris eliminate hydrogen and oxygen either occasionally or continuously under the prevailing conditions, ultimately leading to a product containing approximately 90% carbon (i.e., anthracite). In order for this maturation to proceed, chemical principles require that oxidation reactions be completely inhibited; that is, the chemistry proceeds according to carbonaceous residue coal organic debris but not according to:

$C_nH_m+ \rightarrow$ carbonaceous residue $\rightarrow$ coal
Organic
debris

Rather than:

$C_nH_m + O_2 \rightarrow CO_2 + H_2O$
Organic
debris

The formation of coal under the slow conditions generally referred to as geological time may, nevertheless, be regarded as occurring in the absence of oxygen, thereby promoting the formation of highly carbonaceous molecules through losses of oxygen and hydrogen from the original organic molecules (Figure 1.1).

1.5 HETEROATOMS IN COAL

The type of analytical characterization that is performed in order to determine the properties of coal are used to predict its technological behavior. Typically, there are two characteristics that influence the use of coal: its composition and its rank. Coal composition is in turn represented by: (1) type (nature of the organic components) and (2) grade, which is determined by the amount of mineral matter in the coal (or, in other words, by the dilution of the organic matrix by mineral matter).

At this point, it is pertinent to discuss the heteroatom species in coal (the non-hydrocarbon species in coal, i.e., nitrogen-, oxygen-, and sulfur-containing species) insofar as these species can arise from the plant precursors as well as from external sources such as might occur during the maturation process. These species (presented subsequently in alphabetical order rather than by effects) are also influential in determining the extent of atmospheric emissions that often have an adverse effect (and draw adverse comments) on the use of coal as an energy source (Speight, 2013a,b).

1.5.1 Nitrogen

Nitrogen is typically found in coal in the 0.5–1.5% range by weight. As with oxygen, a number of different types of nitrogen-C containing compounds have been isolated from coal-derived liquids (Speight, 2013a). Examples of these include aniline derivatives, pyridine derivatives, quinoline derivatives, iso-quinoline derivatives, carbazole derivatives, and indole derivatives, which carry alkyl and aryl substituents (Schweighardt et al., 1977; Palmer et al., 1992; Baxby et al., 1994; Palmer et al., 1994).

Nitrogen has been the least studied of the principal elements in coal but, except in rare cases, the nitrogen present in coal is bound into the organic carbonaceous part. Fragmentary information is available concerning the nitrogen-containing compounds present in coal, but they do appear to be stable and are thought to be primarily heterocyclic. The original source of nitrogen in coal may have been both plant and animal protein. Plant alkaloids, chlorophyll, and other porphyrins contain nitrogen in cyclic structures stable enough to have withstood changes during the coalification process and thus to have contributed to the nitrogen content of coal. The amount of nitrogen in coal appears to be only weakly correlated with coal rank (Davidson, 1994).

A wide variety of aromatic nitrogen compounds is found in the coals; no evidence of saturated amines was found. Pyrrole derivatives, pyridine derivatives, pyridine derivatives, and aromatic amine derivatives are found in coal; of these, pyrrole structures are the most prevalent. Pyridine nitrogen is prevalent in all except low-rank coals – the low pyridine content in low-rank (high-oxygen) coals correlates with a high content of pyridone derivatives. This observation suggests that, with increasing maturation of coal, the pyridone loses its oxygen and is transformed into pyridine.

The emissions of nitrogen oxides from coal combustion may bear a relationship to the nitrogen types in the coal, although much the nitrogen may remain in the char (Hindmarsh et al., 1994; Wang et al., 1994), (analogous to nitrogen remaining in petroleum coke (Speight, 2014). However, the influence of coal properties on nitrogen oxide (NO_x) emission levels is not well defined. It is clear that several factors influence NO_x formation, the roles and interaction of such factors as nitrogen partitioning (between the volatiles and chars), nitrogen functionality, coal rank, coal nitrogen content and volatile content in the formation of NO_x. However, it has been demonstrated repeatedly that the selection of coals on the basis of coal nitrogen content is an inappropriate and ineffective means of restricting NO_x emissions. The selection of coals should be the sole preserve of the generating utility that has the best understanding of the influence of their combustion plant design and operation on the level of NO_x emissions. Furthermore, the continued use of coal nitrogen as a controlling specification for coal supplies to an expanding utility market will not only fail to limit NO_x emission levels but will also result in the limitation on the development of new coal resources.

Thus, it can be assumed that the amount of nitrogen in the coal and the way in which it is bound into the coal structure affects the amount and distribution of nitrogen oxide emissions. The proportion of the coal sulfur volatilized on partial gasification could be related to the coal substance gasified, using one equation for all the coals. For coal nitrogen, however, a single equation can describe the data from both pyrolysis and partial gasification (Middleton et al., 1997).

The suggestion that the nitrogen functionality exerts an indirect effect, possibly related to rank, is a reasonable explanation but has not been fully proven by application of analytical techniques.

1.5.2 Oxygen

The inclusion of oxygen in both the organic and inorganic portions of coal presumably arises from a variety of plant sources, although there is also the strong possibility that oxygen inclusion occurs during the maturation by contact of the precursors with aerial oxygen and with the oxygenated waters that percolate through the detrital deposits. The oxygen content of coal ranges from a high of 20–30% by weight for a lignite to a low of around 1.5–2.5% by weight for an anthracite.

In the organic portion of coal, oxygen is present in hydroxyl (–OH), usually phenol groups, carboxyl groups (CO_2H), methoxyl groups ($–OCH_3$), and carbonyl groups (=C=O). In low-rank coal, the hydroxyl oxygen averages about 6–9%, while high-rank coals contain less than one percent. The percentages of oxygen in carbonyl, methoxyl, and carboxyl groups average from a few percent in low rank and brown coal to almost no measurable value in high-rank coal. The inorganic materials in coal that contain oxygen are the various forms of moisture, silicates, carbonates, oxides, and sulfates. The silicates are primarily aluminum silicates found in the shale-like portions. Most of the carbonate is calcium carbonate ($CaCO_3$), the oxides are mainly iron oxides (FeO and Fe_2O_3), and the sulfates are calcium and iron ($CaSO_4$ and $FeSO_4$).

The oxygen content of a given coal is normally determined by difference:

$$\%\ \text{oxygen} = 100 - (\%\text{C} + \%\text{H} + \%\text{N} + \%\text{S} + \%\text{ash})\ \text{(all calculated on a dry basis)}$$

1.5.3 Sulfur

Sulfur is an important consideration in coal utilization and, hence, there is a considerable amount of published work relating to the development of methods to improve the efficiency of the techniques as well as improve the accuracy and precision of the sulfur determination. The sulfur content of coal is quite variable, typically in the range of 0.5–5.0% w/w – this includes both inorganic and organic sulfur. Inorganic sulfur is present mainly in the form of iron pyrite. Sulfur contained in the precursor proteins and amino acids may be a source of sulfur in coal but hydrogen sulfide and pyrite are quite capable of reacting with the coal precursors to produce sulfur constituents as found in coal (Baruah and Upreti, 1994; Speight, 2013a).

The inclusion of sulfur in coal is largely unknown and has been presumed to arise from the sulfur-containing plant constituents such as protein and oils although there are other means by which sulfur might be included into the coal (Casagrande, 1987; Palmer et al., 1992; 1994). The predominant mode of sulfur incorporation into coal varies with the nature of the coal.

Sulfur is present in coal in three forms, either as (1) organically bound sulfur, (2) inorganic sulfur (pyrite or marcasite, FeS_2), and (3) inorganic sulfates (ASTM D2492; ISO 157) (Wawrzynkiewicz and Sablik, 2002; Speight, 2013a,b and references cited therein). The amount of organic sulfur is usually <3% w/w of the coal, although exceptionally high amounts of sulfur (up to 11%) have been recorded. Sulfates (mainly calcium sulfate, $CaSO_4$, and iron sulfate, $FeSO_4$) rarely exceed 0.1% except in highly weathered or oxidized samples of coal. Pyrite and marcasite (the two common crystal forms of FeS_2) are difficult to distinguish from one another and are often (incorrectly) designated simply as pyrite.

Free sulfur as such does not occur in coal to any significant extent. The amount of the sulfur-containing materials in coal varies considerably, especially for coals from different seams. In addition, pyrite is not uniformly distributed in coal and can occur as layers or slabs or may be disseminated throughout the organic material as very fine crystals. The content of sulfates, mainly gypsum ($CaSO_4 \cdot 7H_2O$) and ferrous sulfate ($FeSO_4 \cdot 7H_2O$), rarely exceeds trace amounts (i.e., <0.1%) except in highly weathered or oxidized coals.

When coal is mined, fresh sulfur-bearing minerals in the coal and rocks are exposed to air and water. The resulting chemical reactions produce sulfuric acid and precipitates. The acid water flowing from coal mines, if not treated, can damage life forms in the receiving streams. The iron and sulfate precipitates often discolor stream beds with yellow and orange stains. In a similar manner, when burned, sulfur escaping in the flue gases can combine with water in the atmosphere to produce acidic precipitation (*acid rain*). For the same reasons, burning high-sulfur coal can be corrosive to the metal equipment used in a power plant.

Organic sulfur can represent >50% of the total sulfur found in some coals can arise from the interaction of peat-type precursors with hydrogen sulfide to produce organic sulfur (Casagrande, 1987). On the other hand, there are several lines of evidence (Chou, 1990), which lead to the conclusion that sulfur in plant material is the principal source of sulfur in low-sulfur coal whereas in medium- and high-sulfur coals, seawater is also a predominant source of sulfur (Chou, 1990).

The most abundant sulfur functional types found in coal are believed to be derivatives of the thiophene ring system. Other important sulfur types are aryl sulfides, alkyl sulfides, and acyclic sulfides. It should, however, be kept in mind that most of the information on sulfur compounds has been obtained by the analysis of small molecules obtained upon the decomposition of the coal matrix and the more drastic degradation techniques are very likely to alter the chemical structure of the sulfur compounds originally present in the coal matrix.

1.5.4 Other Elements

A variety of other elements also occur in coal but their presence and amounts are strictly dependent upon the coal source (Speight, 2013a).

Chlorine occurs in coal (and is believed to be a factor not only in fouling problems but also in corrosion problems. The chlorine content of coal is normally low, usually only a few tenths of a percent or less. It occurs predominantly as sodium, potassium, and calcium chlorides, with magnesium and iron chlorides present in some coals. There is evidence that chlorine may also be combined with the organic matter in coal.

Mercury has been identified as a very dangerous environmental contaminant, largely by reason of the process of concentration in the food chain. Thus, the presence of mercury in coal is an extremely sensitive issue. The possible emission of mercury that may be found in coal is an environmental concern. In addition, mercury can go through a series of chemical transformations that convert elemental mercury (itself a toxin) to a highly toxic form (Tewalt et al., 2001). The most toxic form of mercury is methyl-mercury, an organic form created by a complex bacterial conversion of inorganic mercury, which enters and accumulates within the food chain, particularly in aquatic organisms such as fish and birds, causing various diseases in animals and humans. The creation of methyl-mercury in ecosystems is a function of mercury availability, bacterial population, nutrient load, acidity and oxidizing conditions, sediment load, and sedimentation rates. Methyl-mercury in coal is known to be associated with iron (Fe), copper (Cu), and sulfur (S). In particular, it is often associated with sulfur in both pyrite and marcasite (FeS_2); where it is found in the form of a solid solution and in association with the mineral sphalerite (ZnS). In the coal combustion process, mercury is released mainly as elemental mercury, since the thermodynamic equilibrium favors this state at coal combustion temperatures. In the combustion zone, mercury is vaporized from the coal as elemental mercury (Hg). As the flue gas temperature decreases, elemental mercury is oxidized to form mercuric oxide (HgO), as well as mercuric chloride ($HgCl_2$), and mercurous chloride (Hg_2Cl_2), subject to the presence of chlorine in the system.

Most coals contain small amounts of *mineral carbonates* made up primarily of calcium carbonate and to a lesser extent ferrous and other metal carbonates. Some coals contain a comparatively large amount of the inorganic carbonates and the determination of carbon dioxide content is required in estimating the mineral matter content of these high-carbonate coals. Indeed, it is necessary to have a knowledge of the carbonate content of coal in order to correct the carbon figure and since, without resorting to very elaborate analyses, it would be impossible to express the carbonate content as definite quantities of calcium carbonate, magnesium carbonate, etc., it is customary, and sufficient for all analytical purposes, to express it simply in terms of carbon dioxide.

Arsenic and *selenium* occur in coal to the extent of several parts per million and, on combustion of the coal a varying quantity of these elements are released or retained in the ash, depending largely on the conditions under which the combustion takes place and on the nature of the coal ash.

1.6 PHYSICAL STRUCTURE

The behavior of coal during processing is determined by its physicochemical composition and structure. The examination of the physical and chemical structure of coal has been hampered by the inability to find techniques that measure any meaningful properties of such large complex structures. Most attacks on the problem have been by means of breaking down the structure into smaller, more tractable pieces, examining these and making inferences about the original structure. With many types of coal, the severity of the treatment needed to rupture the molecules raises doubts as to the validity of the method. It is claimed with some justification (but still with considerable doubt) that brown coal, which is geologically younger, may bear more resemblance to the molecules of classical organic chemistry.

Structurally, coal is a complex system in which organic material dominates, typically representing 85–95% w/w of a dry coal (Speight, 2013a). These organic materials occur in various different petrographic types (macerals), which reflect the nature of the precursor plant material. Various inorganic materials, particularly aluminosilicates and pyrites (especially in high-sulfur coals), comprise 5–15% of the coal. A third structural element, and perhaps its most distinctive feature when compared to other solid fossil fuel sources like petroleum and oil shale, is an extensive network of pores. These pores provides coal a high surface area ($>100\,m^2/g$) for bituminous coal, sub-bituminous coal, and lignite and an appreciable volume of pore space, allowing access to a significant fraction of the organic material.

Briefly, the maceral *vitrinite* is the most common component of coal and is derived from the same biogenic precursors as coals, namely land plants and humic peats. Vitrinite forms during diagenesis by the thermal alteration of lignin and cellulose in plant cell walls. It is therefore common in sedimentary rocks that are rich in organic matter, such as shale formations and marls with a terrigenous origin. In fact, vitrinite reflectance (Chapter 7) to establish rank of bituminous coals has the following advantages: (1) steady increase of vitrinite reflectance with rank, (2) independence from composition or homogeneity of the reflectance measurement, (3) independence of sample size, and (4) minimal effects of oxidation. Carbonate minerals, evaporite minerals, and sandstone minerals have very low vitrinite content.

There is a much more important aspect of coal composition that must be considered. For example, chemical constituents represent the molecular structure of coal but the form in which these chemical constituents eventually become incorporated into the coal matrix must also be given due consideration. Thus, in terms of the chemical origin of coal, certain plant tissues contain chemical constituents of markedly similar molecular structures but there must be some attempt to recognize that incorporation into the coal precursor of a particular plant tissue (or a large part of the tissue of that particular plant) can also occur. While the maturation process may cause chemical changes to the individual chemical constituents of the tissue, this same maturation process(es) may also cause physical changes to the tissue (in to) that may cause it to appear as a recognizable entity in the coal (ASTM D2793; ASTM D2796; ASTM D2797; ASTM D2799).

There has, however, been a tendency to depart from these types of investigations over the last four decades and to concentrate on the so-called molecular structure of coal in the hope that elucidation of this elusive entity will assist in the understanding of the technological behavior of coal. Fortunately, there has been a surge of interest within the last decade in the physical macrostructure of coal with special emphasis on the relation of the petrographic properties of coal to its technological behavior. Indeed, equating technological behavior of coal (or, for that matter, any feedstock) with a definite entity should warrant far more attention than the attempts to equate technological behavior with a hypothetical (albeit, unknown) molecular structure.

1.7 PETROLOGY AND PETROGRAPHY

1.7.1 Petrology

Coal petrology, which dates back to the beginning of the twentieth century, is the fundamental discipline that deals with the origin, occurrence, physical and chemical properties, and utilization of coal (Bustin et al., 1983; Taylor et al., 1998; Belkin et al., 2009). Thus, coal petrology is the study of the organic and inorganic constituents of coal and their transformation via metamorphism. Coal petrology is applied to the studies of the depositional environments of coals, correlation of coals for geological studies, and the investigation of coals for their industrial utilization. Traditionally, the latter has been dominated by the use of coal petrology in the optimization of coal blends for the production of metallurgical coke, but can also include the use of petrology in evaluating coals for beneficiation (coal preparation for downstream utilization) and combustion. Therefore, coal petrology has a strong influence on the types of analytical methods that are applied to coal.

In addition to its chemical properties, the efficient use of a coal also requires a knowledge of its physical properties, such as its density (which is dependent on a combination of rank and mineral matter content), hardness, and grindability (both related to coal composition and rank). Other properties include its abrasion index (derived mainly from coarse-grained quartz) and the particle size distribution. Float-sink testing may also be included with the analysis process. This involves separating the (crushed) coal into different density fractions as a basis for assessing its response to coal preparation processes. Float-sink techniques may also be used to provide a coal sample that represents the expected end product of a preparation plant, in order to assess the quality of the coal that will actually be sold or used rather than the in-situ or run-of-mine material represented by an untreated (raw) coal sample.

Another factor that must be taken into account in determining coal quality is the degree of coal oxidation. Oxidation may affect both the organic and inorganic components and may lead to deterioration of the coal properties. Another possible consequence of coal oxidation is the spontaneous combustion (Misra and Singh, 1994; Lyman and Volkmer, 2001; Beamish et al., 2001; Beamish, 2005). The propensity to oxidation is mainly determined by the rank of the coal in conjunction with the maceral and mineral (e.g., pyrite) content. Low-rank coals are particularly prone to spontaneous combustion. Other factors, such as the access of air to coal stockpiles, may need to be controlled in order to reduce the risk of spontaneous combustion. Petrographic examination may help to identify coals that have become oxidized.

1.7.2 Petrography

Coal petrography (a branch of coal petrology) specifically deals with the analysis of the maceral composition and rank of coal and therefore plays an essential role in predicting coal behavior and should be an essential part of any coal analysis and testing program (Esterle and Ferm, 1986; Unsworth et al., 1989; Esterle et al., 1994). The fundamentals of organic petrography, maceral nomenclature, classification of coal components, and analytical procedures, have been well established by the International Committee for Coal and Organic Petrology (ICCP, 1963, 1971a,b, 1975, 1993, 1998, 2001; Sýkorová et al., 2005).

Coal is a rock formed by geological processes and is composed of a number of distinct organic entities called macerals and lesser amounts of inorganic substances (mineral matter). The essence of the petrographic approach to the study of coal composition is the idea that coal is composed macerals, which each have a distinct set of physical and chemical properties that control the behavior of coal. The organic units, composing the coal mass (macerals), are the descriptive equivalent of the inorganic units composing rock masses (minerals) and to which pathologists are accustomed to giving distinctive names (Stopes, 1919, 1935).

One of the most important aspects of coal petrography is an understanding of the effects that the petrographic constituents have on the behavior of coal during processing, in particular the processing sequences that are designed to produce gaseous and liquid fuels. While some data are available, a considerable amount of investigative work still remains to be carried out.

In keeping with the theme of this present text, a brief discussion of the influence of the petrographic composition of coal in relation to the technological properties of coal is warranted, although more specific reference will, as the data allows, be made to the various processes throughout the text.

Petrographically and chemically, coal is a complex material and it is often convenient to describe coal in several ways. The most common way, of course, is in terms of the elemental (ultimate) composition (Chapter 6) where coal may actually be classified on the basis of the general formula: $C_nH_nN_xO_yS_z$ where n is the number of carbon atoms, y is the number of hydrogen atoms, x is the number of nitrogen atoms, y is the number of oxygen atoms, and z is the number of sulfur atoms. Indeed, one of the most important outcomes from the petrographic analysis of coal is the understanding of the effect that the petrographic composition has on the technological properties. In fact, the behavior of the petrographic constituents during coal utilization is now being documented with some regularity.

1.7.2.1 Lithotypes Coal lithotypes represent the macrostructure of coal and are, in fact, descriptive of the coal. A piece of coal will usually exhibit a definite banded appearance due to the accumulation of different types of plant debris during the formation of the organic sediment (Smith and Smoot, 1990; Muller et al., 1990). This may be due to not only the deposition of a variety of different organic compounds that are believed to be the precursors of coal (Chapter 1) but also the accumulation of different parts of the plant (as well as different plants, e.g., trees, ferns, mosses, etc.) during the formation of the sediment (Murchison, 1991; Puttmann et al., 1991; Speight, 2013a and references cited therein). Each compound type, tissue type, or plant type then progresses through the various maturation stages that eventually lead to coal.

1.7.2.2 Macerals The organic constituents in coal and non-coal organic-rich rocks are termed macerals (in the broader sense, and particularly for dispersed organic material, the term kerogen is also used). Macerals are the (optical) microscopically identifiable constituents in coal, somewhat analogous to minerals in an inorganic rock (Stopes, 1935). By convention, maceral names always have an -*inite* suffix. Thus, macerals are generally divided into the vitrinite (or *huminite* in lower rank coals), inertinite, and liptinite groups (Speight, 2013a and references cited therein).

Huminite/vitrinite macerals are derived from humic substances, the alteration products of lignin and cellulose. Huminite refers to macerals in lignite and subbituminous rank (see below) coals (Sýkorová et al., 2005), and vitrinite to maceral of bituminous and anthracitic ranks. The distinction with vitrinite is based on the division of the maceral group into three subgroups: (1) telovitrinite, (2) detrovitrinite, and (3) gelovitrinite, which are each further subdivided into two macerals. The dominant parameter for these newly ordered and in part newly defined subgroups is the degree of destruction (degradation), whereas the macerals can be further distinguished by their morphological characteristics and their degree of gelification (ICCP, 1998).

Inertinite macerals are, to a certain degree, derived from the same starting materials as the huminite/vitrinite macerals (ICCP, 2001). In contrast to the latter maceral group, the inertinites have been oxidized, with fire thought to be the primary cause of their formation. The macerals fusinite and semifusinite are the products of such oxidation and, in most coals, are the most abundant inertinite macerals. Secretinite is a product of the oxidation of plant secretions. Macrinite is problematical, in part, because it has been confused with what is now recognized as secretinite. Multiple pathways have been proposed for macrinite (ICCP, 2001). Funginite, with a fungus origin, is grouped with inertinites derived from plant cells by ICCP (2001). Fungi, however, are not plants, but encompass two distinct eukaryote kingdoms, *Fungi* and *Protoctista*-kingdom slime molds. Micrinite is thought to have originated as a secondary maceral from the breakdown of hydrogen-rich liptinite.

The method of preparation of the samples for microscopic examination may vary according to the methods favored by a particular laboratory. However, there are standard methods described for the examination of coal samples by microscopic techniques. For example, a crushed coal sample will be formed into a briquette with a cold-setting epoxy resin. When the resin is set, the surface is ground using water-resistant, adhesive-backed silicon carbide papers of grit size numbers 240, 320, 400, and 600. Then, polishing is carried out using aluminum oxide powders of specified sizes followed by treatment with a nap-free cloth of cotton and silk and chemo-textile material backed with water-resistant adhesive. There are, of course, suggested sequences for this procedure to produce a surface suitable for microscopic examination.

1.7.3 Microlithotypes

Microlithotypes are the microscopic analogs of the coal lithotypes and, hence, represent a part of the fine microstructure of coal(s). The microlithotypes are, in fact, associations of coal macerals with the proviso that the "associations" should occur within an arbitrary minimum bandwidth (50 μ, 50 × 10 mm). The composition of the microlithotypes in coal(s) appears to be limited by the types of organic matter present in the original coal precursor.

In more general terms, the microlithotype vitrite is composed predominantly of vitrinite and is a common constituent of humic coals (Table 1.4), especially vitrains. On the other hand, clarite (which also contains exinite in addition to vitrinite) is more commonly found as thick bands in clarains but does not occur in many other coals; clarite may also contain inorganic impurities such as clay, pyrite, and carbonates. Fusite consists predominantly of inertinite and also contains impurities such as kaolin (as well as other clays), pyrite, and carbonate minerals. Durite is composed predominantly of exinite and inertinite and has actually been classified as existing in two forms: durite and durite I; the former (durite E) indicates that the durite is relatively rich in exinite whereas the latter (durite I) indicates the durite to be relatively rich in inertinite.

1.7.4 Inorganic Constituents

Inorganic elements can be included in coal as minerals or as elements incorporated in the organic structure (Chapter 4). The most common example of the latter is the incorporation of sulfur into macerals as organic sulfur. Minerals can be incorporated into the peat during deposition, result from epigenetic processes, or be the consequence

TABLE 1.4 United States Bureau of Mines System and International System of Coal Nomenclature

System	Coal Type	Characteristics
Bureau of Mines	Banded coal	Anthraxylon[a] present Opaque matter present
	Bright coal	<20% w/w opaque matter
	Semi-splint coal	20–30% w/w opaque
	Splint coal	>30% w/w opaque matter
	Non-banded coal	Anthraxylon absent
	Cannel coal	Spore debris present
	Boghead coal	Algal debris present
International System		
	Humic (banded)	Low hydrogen content
	Clarain	Striated, glossy
	Durain	Nonstriated
	Fusain	Charcoal-like
	Vitrain	Black, vitreous
	Sapropelic	High hydrogen content
	Cannel	Liptobiolithic (non-banded)
	Boghead	Liptobiolithic (non-banded)

[a] The glossy jet-black constituent of banded bituminous coal.

of metamorphic changes within the coal. Clay minerals, quartz, calcite, siderite, and pyrite/marcasite are the most common minerals in coals. All naturally occurring elements have been found in coal.

Coal petrography techniques, in addition to determining maceral/microlithotype composition, also includes microscopic measurements of certain parameters that are indicators of the degree of coalification (metamorphism) termed coal rank. The coal rank series, from the lowest to the highest degree of metamorphism, is as follows: lignite, subbituminous, high volatile bituminous, medium volatile bituminous, low volatile bituminous, semi-anthracite, anthracite, and meta-anthracite (Table 1.5).

1.7.5 Petrology, Petrography, and Behavior

Although *coal rank* plays an important role in defining coal use, *coal type* and *coal grade* are also extremely important consideration (Table 1.6). These parameters are the primary factors that influence a coal's specific physical and chemical properties and these properties in turn determine the overall quality of the coal and its suitability for specific purposes.

In general terms, the behavior of coal during combustion, carbonization, pyrolysis, gasification, and direct conversion to liquids depends on the type and amount of the macerals present (Fryer et al., 1975; Falcon, 1978; Stach et al., 1982; Bend et al., 1991; Derbyshire, 1991; Kalkreuth et al., 1991; Murchison, 1991; Sen, 1992; Speight, 2008; Suárez-Ruiz and Crelling, 2008; Gagarin, 2010). Indeed, it would be

TABLE 1.5 General Description of Different Ranks of Coal Including Peat for Comparison

Rank (Excluding Peat)	Properties
Peat	A mass of recently accumulated to partially carbonized plant debris that is not classed as coal; an organic sediment that has a carbon content <60% w/w on a dry ash-free basis.
Lignite	The lowest rank of coal (also called *brown coal*), which may contain recognizable plant structures; the heating value is <8300 Btu/lb on a mineral matter free basis and a carbon content from 60% to 70% w/w on a dry ash-free basis.
Sub Bituminous	Coal with a carbon content on the order of 71–77% w/w on a dry ash-free basis) and a heating value between 8300 and 13,000 Btu/lb on a mineral matter free basis; on the basis of heating value, this coal is subdivided into sub bituminous A, sub bituminous B, and sub bituminous C coals.
Bituminous	Coal with a carbon content on the order of 77% and 87% w/w on a dry ash-free basis and a heating value that is much higher than lignite or sub bituminous coal; on the basis of volatile matter production, bituminous coal is subdivided into low volatile bituminous coal, medium volatile bituminous coal, and high volatile bituminous coal; often referred to as *soft coal* (in relation to anthracite).
Anthracite	The highest rank of coal with a carbon content greater than 87% w/w on a dry ash-free basis and the highest heating value per pound on a mineral matter free basis; often subdivided into semi-anthracite, anthracite, and meta-anthracite on the basis of carbon content and *hard coal* (in relation to bituminous coal).

most surprising if this were not the case in view of the differences in ultimate composition alone of the various macerals (Table 1.7). Furthermore, it appears that no two coals (no matter how close their relationship in the various classification systems) have exactly the same petrographic composition and, consequently, the same reactive properties.

The basic chemical parameters of a coal are determined by proximate analysis (moisture, ash, volatile matter, and fixed carbon percentages) and ultimate analysis (carbon, hydrogen, nitrogen, sulfur, and oxygen contents). Other analyses that may be carried out include determining the forms of sulfur in the coal (pyritic, sulfate, and organic) and the carbon (or CO_2) content, which is derived from the carbonate fraction. Chlorine content (Spears, 2005), which is mainly associated with inorganic salts (relatively high proportions of chlorine may give rise to corrosion in coal utilization) and phosphorous content (an undesirable element in coals destined for use in the steel industry) may also be determined. The ash content of a coal may be analyzed to determine the presence of metal oxides (these influence coal and ash behavior during

TABLE 1.6 Differentiation of Coal Rank, Coal Type, and Coal Grade

Rank

- Indicative of the degree of metamorphism (or coalification) to which the original mass of plant debris (peat) has been subjected during its burial history.
- Dependent on the maximum temperature to which the *proto-coal* has been exposed and the time it has been held at that temperature.
- Also reflects the depth of burial and the geothermal gradient prevailing at the time of coalification in the basin concerned.

Type

- Indicative of the nature of the plant debris (*proto-coal*) from which the coal was derived, including the mixture of plant components (wood, leaves, and algae) involved and the degree of degradation before burial.
- The individual plant components occurring in coal, and in some cases fragments or other materials derived from them, are referred to as *macerals*.
- The kind and distribution of the various macerals are the starting point for most coal petrology studies.

Grade

- Indicative of the extent to which the accumulation of plant debris has been kept free of contamination by inorganic material (mineral matter), before burial (i.e., during peat accumulation), after burial, and during coalification.
- A high-grade coal is coal, regardless of its rank or type, with a low overall content of mineral matter.

industrial usage) whereas the proportions of certain trace elements, some of which could be potentially hazardous to human health are worth evaluating.

The analytical procedures used to determine the petrographic, physical, and chemical properties and these tests are standardized in a number of international test methods (Peters et al., 1962; Karr, 1978a,b,c; Diessel, 1980; Stach et al., 1982; Ward, 1984; Diessel, 1992; Van Krevelen, 1993); Taylor et al., 1998; Thomas, 2002; Speight, 2008; Suárez-Ruiz and Crelling, 2008). The organic constituents of coal (liptinite, inertinite, and huminite/vitrinite) are, individually and in combination (microlithotypes), fundamental to many coal properties.

The inorganic constituents of coal are often expressed using simple parameters such as ash yield, mineral matter, and sulfur content. Knowledge of the inorganic constituents including trace elements in the coal may take on a more complex role if emissions of the so-called hazardous air pollutants (HAPs) are regulated. Hazardous air pollutants generally include antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), nickel (Ni), lead (Pb), selenium (Se), mercury (Hg), cobalt (Co), chromium (Cr), and manganese (Mn), with chlorine (Cl) and the radionuclides, thorium (Th) and uranium (U), also being included in some assessments.

TABLE 1.7 Analysis of Macerals

Property	Maceral		
	Exinite	Vitrinite	Fusinite
Carbon, % w/w	82.0 ± 1.0	82.5 ± 1.0	93.0 ± 1.0
Hydrogen, % w/w	8.5 ± 0.5	5.5 ± 0.2	2.85 ± 0.2
Nitrogen, % w/w	1.0 ± 0.5	1.6 ± 0.4	0.9 ± 0.1
Oxygen, % w/w	6.8 ± 0.5	9.5 ± 0.5	2.3 ± 0.2
Sulfur, % w/w	0.5 ± 0.1	0.5 ± 0.1	0.5 ± 0.1
Volatile matter, % w/w	45 ± 5.0	12 ± 2.0	5.0 ± 1.0

In summary, certain waxy and resinous macerals are reactive to coal conversion processes while other macerals, notably those of the inertinite group, are notoriously unreactive. Thus, as petrography facilitates the qualitative and quantitative identification of the constituents of coal, it will, no doubt, find increasing application as a method for predicting and elucidating the behavior of any coal to conversion processes designed for the production of synthetic gaseous and liquid fuels (ASTM D2793).

1.8 COAL AND COAL ANALYSIS

It has been (and often still is) presumed that coal formation invokes the concept of a *regular* progression from lignite (in a stepwise manner) to the higher-rank members of the coal series, ultimately leading to the anthracite coals. However, even using modern analytical techniques, it is difficult to assemble evidence in favor of only one or the other of these theories insofar as each theory has its own particular merits and, moreover, the chemical makeup of the starting material and end product (coal) is, at best, extremely speculative making the task that much more difficult. Indeed, there may be some merit in accepting both theories as part of the coal-forming process.

To confuse the issue of the analytical chemistry of coal even further, it has been suggested that there exists a somewhat lesser dependence of the molecular chemistry of coal on rank and the chemistry of coal is heavily influenced by its source as well as by the early formation history (Berkowitz, 1988). It is also possible that coals of similar rank may, therefore, be chemically much more diverse than is usually supposed, which may not be detectable by analytical test methods. Indeed, this concept is in agreement with similar conclusion about the formation of petroleum insofar as the chemical nature of the crude oil, with particular reference to the asphaltene constituents, is dependent not only upon the types of precursors but also on the relative mix of these precursors that formed the *protopetroleum* (Speight, 2014) as well as on regional variations in the maturation conditions due to variations resulting from climatic differences between various geological eras/periods (Bend, 1992; Speight, 2013a, 2014).

The concept of source material and formation history playing a larger role in the determination of coal chemistry and coal analysis is quite logical. In fact, the potential (and the more likely reality) that there are localized variations in precursor-type, mix of the precursors, as well as variation in maturation conditions are given little consideration as part of the coal-forming processes. The age-old concept of *high heat and pressure*, which one assumes would be a chemical equalizer insofar as all chemical and physical reactions proceed toward a graphite-type material, are given much more credence, for whatever reasons. Perhaps it is also time to cease considering coal as a graphitic material and look to coal as a natural product that is subject to local and regional variations in maturation conditions rather than as a conglomeration of large polynuclear aromatic sheets. Indeed, the perception of the chemical and physical behavior of coal has, for many years, been *guided* by the results of a series of tests that, at best, give only gross properties and afford no information whatsoever (or at the most optimistic, very little information) about the nature of coal.

Finally, although all test methods can provide important information about the suitability of coal for a particular use, in addition to data from proximate analysis (Chapter 5) and from ultimate analysis (Chapter 6), other coal quality parameters that need to be taken into account (e.g., in coal combustion, coal carbonization, and coking processes) include information from the following tests (which are listed alphabetically rather than by preference:

- *Ash fusion temperature* (Chapter 5) indicates the behavior of the ash residues from the coal at high temperatures and is mainly related to the chemical composition of the ash and the nature of the coal's mineral matter; the data are used to indicate whether the ash will remain as a fine powder within the furnace system after the coal is burned or whether some of it might melt to form a slag on the heat exchange surfaces of the boiler.
- *Free-swelling index (FSI)* (Chapter 8) is a measure of the increase in volume of the coal when it is heated in the absence of air; this test is also used to characterize coals for combustion and the data are in part rank-dependent parameter as well as dependent on the maceral composition of the coal – the vitrinite maceral group is the main contributor to the swelling properties.
- *Gieseler plastometer* (Chapter 8) monitors how the coal behaves as the different macerals melt, devolatilize, and resolidify at different temperatures during the carbonization process; the data are particularly significant when different coals are blended for coke production to ensure compatibility of the different blend components – coal-blending strategies, for example, coke production are generally decided on the basis of a combination of rheological and petrographic parameters using individual coal samples and the data are used to select coals to make up a blend with specific coking properties.
- *Gray-King assays* (Chapter 8) determine the proportions of coke or char (carbonaceous solids), tar (organic liquids), liquor (ammonia-rich solutions), and gas produced when the coal is carbonized (heated in the absence of air); the data provide a basis for estimating the yields of coke and coke byproducts obtained from the coal in an industrial coke oven or oil-shale processing plant.
- *Hardgrove grindability index (HGI)* (Chapter 9) indicates the ease with which the coal can be ground to fine powder; the data are related to the maceral and

maceral group composition but is also dependent on rank and mineralg content.

- *Heating value (calorific value)* (Chapter 8) indicates the amount of heat liberated per unit of mass of combusted coal; this is a rank-related parameter but is also dependent on the macerals in the coal and mineral composition.
- *Roga index* (Chapter 8) provides information on the caking properties of the coal; the index is derived from the strength or cohesion of the coke produced in the crucible, as evaluated by a subsequent tumbler test.

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2

IDENTIFICATION OF COAL

2.1 INTRODUCTION

The nomenclature of coal is not straightforward and requires considerable thought to elucidate the precise meaning of some of the terminology (Chapter 1). However, since coal and coal products will play an increasingly important role in fulfilling the energy needs of society, it is essential that coal types be understood before use. In fact, future applications will extend far beyond the present major uses for power generation and chemicals production (Speight, 2013a). A key feature in these extensions will be the development of means to provide analytical data that will help in understanding the conversion of coal from its native form into useful gases, liquids, and solids in ways that are energy efficient, nonpolluting, and economical.

The design of a new generation of conversion processes will require the analyst to have a deeper understanding of coal's intrinsic properties and the ways in which it is chemically transformed under process conditions. Coal properties-such as the chemical form of the organic material, the types and distribution of organics, the nature of the pore structure, and the mechanical properties must be determined for coals of different ranks (or degrees of coalification) in order to use each coal type most effectively.

First and foremost, *coal* is a sedimentary rock of biochemical origin. It forms from accumulations of organic matter, likely along the edges of shallow seas and lakes or rivers. Flat swampy areas that are episodically flooded are the best candidates for coal formation. During non-flooding periods of time, thick accumulations of dead plant

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Handbook of Coal Analysis, Second Edition. James G. Speight.

material pile up. As the water levels rise, the organic debris is covered by water, sand, and soils. The water (often salty), sand, and soils can prevent the decay and transport of the organic debris. If left alone, the buried organic debris begins to go through the coal series as more and more sand and silt accumulates above it. The compressed and/or heated organic debris begins driving off volatiles, leaving primarily carbon behind.

In addition to recognizing coal as an organic combustible sedimentary rock, another part of the challenge is to identify the chemical pathways followed during the thermal conversion of coal to liquids or gases (Speight, 2013a). This is accomplished by tracing the conversion of specific chemical functional groups in the coal and studying the effects of various inorganic compounds on the conversion process. Significant progress has been made in this area by combining test reactions with a battery of characterization techniques. The ultimate goal is to relate the structure of the native coal to the resulting conversion products.

There is also a major challenge to the coal analyst and this involved recognizing the heterogeneity of coal – even during the formation of one coal seam, conditions vary and, hence, the types of coal vary depending upon the character of the original peat swamp (Speight, 2013a). Within a swamp, some areas might be shallow and other areas deep. Some areas might have woody plants and other areas grassy. The environment might be changing over time, making the bottom (older part) of the coal seam very different from the top. Varying water level and movement changes the degree of aeration and hence the activity of aerobic bacteria in bringing about decay. The different types of chemical substance present in plants (such as cellulose, lignin, resins, waxes, and tannins) are present in different relative proportions in living woody tissue, in dead cortical tissue as well as in seed and leaf coatings, In addition, these substances show differing degrees of resistance to decay.

Thus, as conditions fluctuate during the accumulation of plant debris, the botanical nature and chemical composition of the material surviving complete breakdown will fluctuate also, not only on a regional basis but also on a local basis. This fluctuation is the origin of the familiar banded structure of coal seams, which is visible to the naked eye, and provides strong support case for the different chemical and physical behavior of coals.

Furthermore, coal seams, sandstone, shale, and limestone are often found together in sequences hundreds of feet thick. The key to large productive coal beds or seams appears to be long periods of time of organic accumulation over a large flat region, followed by a rapid inundation of sand or soil, and with this sequence repeating as often as possible. Such events happened during the Carboniferous Period – recognized in the United States as the Mississippian and Pennsylvanian time periods due to the significant sequences of these rocks found in several states (Chapter 1). Other coal-forming periods are the Cretaceous, Triassic, and Jurassic Periods (Table 2.1).

To complicate matters even further, coal is also considered (perhaps without sufficient scientific foundation) to be a metamorphic rock – the result of heat and pressure on organic sediments such as peat – but most sedimentary rocks undergo some heat and pressure and the association of coal with typical sedimentary rocks and its mode of formation usually keep low grade coal in the sedimentary classification system.

TABLE 2.1 General Description of Different Ranks of Coal Including Peat for Comparison

Rank (excluding peat)	Properties
Peat	A mass of recently accumulated partially carbonized plant debris that is not classed as coal; an organic sediment that has a carbon content <60% w/w on a dry ash-free basis.
Lignite	The lowest rank of coal (also called *brown coal*), which may contain recognizable plant structures; the heating value is <8300 Btu/lb on a mineral matter free basis and a carbon content from 60% to 70% w/w on a dry ash-free basis.
Sub Bituminous	Coal with a carbon content on the order of 71% to 77% w/w on a dry ash-free basis and a heating value between 8300 and 13000 Btu/lb on a mineral matter free basis; on the basis of heating value, this coal is subdivided into sub bituminous A, sub bituminous B, and sub bituminous C coals.
Bituminous	Coal with a carbon content on the order of 77% and 87% w/w on a dry ash-free basis and a heating value that is much higher than lignite or sub bituminous coal; on the basis of volatile matter production, bituminous coal is subdivided into low volatile bituminous coal, medium volatile bituminous coal, and high volatile bituminous coal; often referred to as *soft coal* (in relation to anthracite).
Anthracite	The highest rank of coal with a carbon content greater than 87% w/w on a dry ash-free basis and the highest heating value per pound on a mineral matter free basis; often subdivided into semi-anthracite, anthracite, and meta-anthracite on the basis of carbon content and *hard coal* (in relation to bituminous coal).

On the other hand, anthracite undergoes more heat and pressure and is associated with low grade metamorphic rocks and is justifiably considered to be an organic metamorphic rock. Thus, the degree of natural processing results in different quality of coal including such coal types (Chapter 1) as: (1) lignite, which is the least mature of the true coals and the most impure; it is often relatively moist and can be crumbled to a powdery, (2) sub-bituminous coal, which is poorly indurated and can be brownish in color, but is more closely related to bituminous coal than to lignite, (3) bituminous coal, which is the most commonly used coal; it occurs as a black, soft, shiny rock, and (4) anthracite, which is the highest rank of coal and is considered to be a metamorphic organic rock; it is much harder and blacker than other ranks of coal, has a glassy luster, and is denser with few impurities (Table 2.1).

As anticipated because of local and regional variations in the distribution of floral species (i.e., site specificity) the relative amounts can vary considerably from one site to another (Chapter 1) (Stutzer, 1940). In addition to variations in the types of flora, there is also the potential for regional variations in the physical maturation conditions (Table 2.2); these include differences such as variations in the oxygen content

TABLE 2.2 Variation in the Conditions that Influence Coal Formation and Composition

Phase	Variables
Selective destruction of carbohydrates and lignin	Water level and degree of brackishness, oxygen level, temperature
Concentration of waxes, resins, cuticles, and spores	Acidity or alkalinity of water, oxidation-reduction potential, time
Accumulation of colloidal organic and inorganic debris	Presence and type of microbes, rate of land subsidence
Burial	

of the water as well as acidity/alkalinity and the presence (or absence) of microbial life forms. Variations of the plant forms (Table 2.3) due to climatic differences between the geological eras/periods would also play a role in determining the chemical nature of the constituents of the prenatal coal (Bend et al., 1991; Bend, 1992; Speight, 2013a).

Thus, it is not surprising that coal differs markedly in composition from one locale to another. Indeed, pronounced differences in analytical properties of coal from one particular seam are not uncommon (Speight, 2013a), due to not only the wide variety of plant debris that could have formed the precursor but also the many different chemical reactions that can occur during the maturation process. Indeed, the continuation and development of analytical studies related to maturation indices may enable

TABLE 2.3 Variations of Plant Forms with Geologic Period

Period	Approximate Millions of Years Before Present	Botanical Characteristics
Late Silurian	400	First appearance of lignified land plants
Carboniferous	270–350	Large, diverse flora of spore-dispersing plants, including ferns and slender trees with varying amounts of branching and leaf development
Permian	225–270	Seed-fern flora (glossopteris) flourishes all over Gondwanaland[a]
Triassic and Jurassic	180–225	Seed-bearing plants flourish, with conifers and cycadophytes prominent
Cretaceous	70–135	Flowering plants evolve (Angiosperms)
Late Cretaceous	~80	Essentially modern flora in most respects
Tertiary	50–70	Grasses and sedges appear

[a] Gondwanaland is the name given to a once-existing supercontinent comprising what are now South America, Africa, India, Australasia, and Antarctica.

scientists to determine the precise pathways by which maturation occurred (Speight, 2013a and references cited therein).

Since the resurgence of coal science in the 1980s and the need for new and reconstituted analytical methods, there has been a pronounced resurgence in the attempts to determine the molecular structure of coal. But it is not obvious that there has been a concomitant increase in understanding and formulating the molecular makeup and molecular structure of coal. Indeed, the concept of a *coal structure* (often referred to as an *average structure for coal*) has continued for several decades and it is very questionable, in the minds of many scientists and engineers, as to whether or any progress has been made down the highways and byways of uncertainty than was the case some 40 years ago. There are those who can, and will, argue convincingly for either side of this question. Or it might be wondered if (even denied that) there is a need to define coal in terms of a distinct molecular structure (Speight, 2013a). In fact, this is a challenge for the analyst insofar as it is a challenge that may never be revolved. On the positive side, indications can be given by tracing the *possible* chemical precursors in the original *mess of pottage* that can lead to a variety of hydrocarbon and heteroatom chemical functional groups in coal and which can be determined by application of appropriate standard test methods.

2.2 ANALYTICAL TECHNIQUES

Coal analysis is the means by which the properties of coal are determined and used to project the uses to which the coal is suited. In fact, the data obtained from coal analyses (Table 2.4) establish the price of the coal by allocation of production costs as well as to control mining and cleaning operations and to determine plant efficiency. However, the limitations of the analytical methods must be recognized (Rees, 1966). In commercial operations, the price of coal reflects the quantity of coal but also invariably reflects the relationship of a desirable property or even a combination of properties to performance of coal under service conditions (Vorres, 1993).

Early analytical methods brought to light the many problems that are associated with the analysis of coal (Lowry, 1963; Karr, 1978a,b). Not the least of which is the heterogeneous nature of coal. With time, it was also recognized that the maturation and different types of coal (Chapter 1) as well as the mineral matter in coal (Chapter 4) could lead to analytical inconsistencies that could only be mitigated by selecting an appropriate method that produced a representative sample of the coal (ASTM D346; ASTM D2013) (Chapter 3). Other problems include the tendency of coal to gain or lose moisture and to undergo oxidation when exposed to the atmosphere. In addition, the large number of tests and analyses required to adequately characterize coal also raise issues. In fact, many of the test methods applied to coal analysis are empirical in nature, and strict adherence to the procedural analytical and sampling guidelines is necessary in order to obtain repeatable and reproducible results. The type of analysis normally requested by the coal industry may be a proximate analysis (moisture, ash, volatile matter, and fixed carbon) or an ultimate analysis (carbon, hydrogen, sulfur, nitrogen, oxygen, and ash) (Figure 2.1).

TABLE 2.4 Sampling and Analytical Methods Used for Coal Evaluation

Test/Property	Results/Comments
Sample information	
Sample history	Sampling date, sample type, sample origin (mine, location)
Sampling protocols	Assurance that sample represents gross consignment
Chemical properties	
Proximate analysis	Determination of the "approximate" overall composition (i.e., moisture, volatile matter, ash, and fixed carbon content)
Ultimate analysis	Absolute measurement of the elemental composition (i.e., carbon, hydrogen, sulfur, nitrogen, and oxygen content)
Sulfur forms	Chemically bonded sulfur, organic, sulfide, or sulfate
Ash properties	
Elemental analysis	Major elements
Mineralogical analysis	Analysis of the mineral content
Trace element analysis	Analysis of trace elements; some enrichment in ash
Ash fusibility	Qualitative observation of temperature at which ash passes through defined stages of fusing and flow

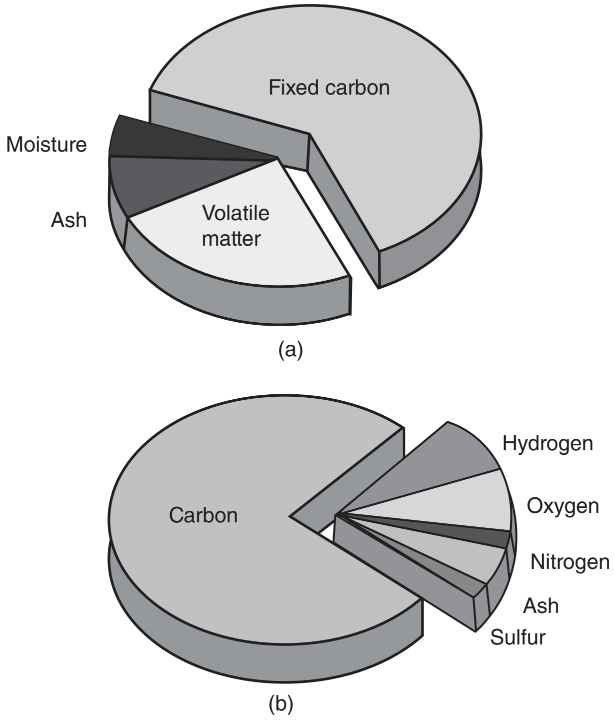

Figure 2.1 Comparison of data types from (a) proximate analysis (Chapter 5) and (b) ultimate analysis (Chapter 6). (*Source*: United States Department of energy, EIA Coal Data.)

The measurement of the desired property or properties (usually grouped together under the general title specifications) are expressed as of numerical values and, therefore, the accuracy of these measurements is thus of the utmost importance. The measurements need to be sufficiently accurate so that any are not a matter of scientific or economic consequence. In other words, the data resulting from the test methods must fall within the recognized limits of error of the experimental procedure. Thus, the numerical information can be taken as fixed absolute values and not as approximations. Indeed, the application of statistical analysis to such test methods must be treated with extreme caution. Such analysis must be based on valid assumptions and not be the result of mathematical manipulation by which the *required result* can be achieved. In other words, there is the requirement that reliable *standard* test methods be applied to coal analysis.

The data from modern coal-quality test methods data and geologic field observations are interpreted in terms of the suitability of coal for a specific use as well as to indicate the potential for environmentally deleterious effects of coal use on various ecosystems. A complete discussion of the large number of tests that are used for the evaluation of coal (and coal products) would fill several volumes (see, e.g., Ode, 1963; Gluskoter, 1975; Karr, 1978a,b; Montgomery, 1978; Karr, 1979; Gluskoter et al., 1981; Smith et al., 1994; Speight, 2013a) and such detailed treatment is not the goal of this book. The focus of the book is a description, with some degree of detail, on the test methods that are in common use as well as a critique of the methods insofar as mention is made of various procedures that are not obvious from the official description of the test method as well as any pitfalls that can occur during application of a test method to the analysis of coal.

Quite often a variation of a proximate analysis or an ultimate analysis is requested, along with one or more of the miscellaneous analysis or tests discussed in this book. Restrictions that have been placed on the coal used in coal-fired power plants and other coal-burning facilities have created a need for more coal analyses as well as a need for more accurate and faster methods of analysis. This trend will continue, and more testing will be required with the increased use of coal for electricity generation and the production of liquid products (Speight, 2013a,b).

In summary, standard test methods for coal analysis in the United States include those contained within the Annual Book of Standards of the American Society for Testing and Materials (ASTM). On occasion, other test methods, such as those recommended by the International Organization for Standardization (represented in short-hand as the International Organization of Standardization (ISO)) or those recommended by the British Standard Institute (BSI) are often employed for coal analysis (Tables 2.5 and 2.6). The former standard test methods (i.e., the ASTM methods) consist of national test methods used in the United States and Canada, while the latter (ISO, BSI test methods) have been developed for use in many countries as well as for international trade. While these methods are used throughout the coal industry and in commerce to establish coal quality, they may not be applicable in the analysis of coal samples for all aspects of coal use and the test methods must be chosen with care and diligence (Trent et al., 1982). For example, if a test method was designed for the analysis of, say, bituminous coal the applicability

TABLE 2.5 Selection of International Organization for Standardization (ISO) Standard Test Methods for the Analysis of Coal and Coke (Geneva, Switzerland)

ISO 334:1992	Solid mineral fuels – Determination of total sulfur – Eschka method
ISO 351:1996	Solid mineral fuels – Determination of total sulfur – High temperature combustion method
ISO 351:1996/Cor 1:1996	
ISO 352:1981	Solid mineral fuels – Determination of chlorine – High temperature combustion method
ISO 540:1995	Solid mineral fuels – Determination of fusibility of ash – High-temperature tube method
ISO 556:1980	Coke (greater than 20 mm in size) – Determination of mechanical strength
ISO 562:1998	Hard coal and coke – Determination of volatile matter
ISO 567:1995	Coke – Determination of bulk density in a small container
ISO 579:1999	Coke – Determination of total moisture
ISO 587:1997	Solid mineral fuels – Determination of chlorine using Eschka mixture
ISO 601:1981	Solid mineral fuels – Determination of arsenic content using the standard silver diethyldithiocarbamate photometric method of ISO 2590
ISO 609:1996	Solid mineral fuels – Determination of carbon and hydrogen – High temperature combustion method
ISO 609:1996/Cor 1:1996	
ISO 616:1995	Coke – Determination of shatter indices
ISO 622:1981	Solid mineral fuels – Determination of phosphorus content – Reduced molybdophosphate photometric method
ISO 625:1996	Solid mineral fuels – Determination of carbon and hydrogen – Liebig method
ISO 625:1996/Cor 1:1996	
ISO 687:1974	Coke – Determination of moisture in the analysis sample
ISO 728:1995	Coke (nominal top size greater than 20 mm) – Size analysis by sieving
ISO 925:1997	Solid mineral fuels – Determination of carbonate carbon content – Gravimetric method
ISO 1013:1995	Coke – Determination of bulk density in a large container
ISO 1014:1985	Coke – Determination of true relative density, apparent relative density and porosity
ISO 1014:1985/Cor 1:1994	
ISO 1170:1977	Coal and coke – Calculation of analyses to different bases
ISO 1171:1997	Solid mineral fuels – Determination of ash
ISO 1171:1997/Cor 1:1998	
ISO 1213-2:1992	Solid mineral fuels – Vocabulary – Part 2: Terms relating to sampling, testing and analysis

TABLE 2.5 (*Continued*)

ISO 1928:1995	Solid mineral fuels – Determination of gross calorific value by the bomb calorimetric method, and calculation of net calorific value
ISO 2309:1980	Coke – Sampling
ISO 2325:1986	Coke – Size analysis (Nominal top size 20 mm or less)
ISO/TR 7517:1983	Coke – Comparison of different tests used to assess the physical strength
ISO/TS 11725:2002	Solid mineral fuels – Determination of nitrogen – Semi-micro gasification method
ISO/TS 12902:2001	Solid mineral fuels – Determination of total carbon, hydrogen and nitrogen – Instrumental methods
ISO 13909-1:2001	Hard coal and coke – Mechanical sampling – Part 1: General introduction
ISO 13909-5:2001	Hard coal and coke – Mechanical sampling – Part 5: Coke – Sampling from moving streams
ISO 13909-6:2001	Hard coal and coke – Mechanical sampling – Part 6: Coke – Preparation of test samples
ISO 13909-7:2001	Hard coal and coke – Mechanical sampling – Part 7: Methods for determining the precision of sampling, sample preparation, and testing
ISO 13909-8:2001	Hard coal and coke – Mechanical sampling – Part 8: Methods of testing for bias

of the method for application to other coals such as lignite and anthracite must be assessed prior to application of the method.

2.3 STANDARD TEST METHODS

Standard test methods for routine coal analysis in the United States include those of the ASTM and those of the ISO. The former consist of national standards used widely in the United States and Canada, while the latter have been developed by ISO member nations for international trade. The test methods published by these organization are used throughout the coal industry and in commerce to establish coal quality and have become symbolic of coal analysis to determine coal use.

Coal analysis is generally divided into three categories: (1) proximate analysis, (2) ultimate analysis, and (3) miscellaneous analysis. *Proximate analysis* is the determination, by prescribed methods, of properties such as moisture content, the propensity for volatile matter production, the amount and character of the ash produced by combustion, and the Mount of fixed carbon (coke – measured by difference) (ASTM D121; ASTM D3172; ASTM D5142; ASTM D7582). Ultimate analysis involves the determination of carbon and hydrogen content as found in the gaseous products of the complete combustion of the coal, the determination of total sulfur, nitrogen, and ash content in the material as a whole, and the estimation of oxygen content by difference

TABLE 2.6 Selection of British Standard Numbers for the Analysis of Coal and Coke (British Standards Institution, London, UK)

Section	Topics
BS 1016-1	Total moisture of coal
BS 1016-6	Ultimate analysis of coal
BS 1016-7	Ultimate analysis of coke
BS 1016-8	Chlorine in coal and coke
BS 1016-9	Phosphorus in coal and coke
BS 1016-10	Arsenic in coal and coke
BS 1016-14	Analysis of coal ash and coke ash
BS 1016-21	Determination of moisture-holding capacity of hard coal
BS 1016-100	General introduction and methods for reporting results
BS 1016-102	Determination of total moisture of coke
BS 1016-104.1	Proximate analysis, determination of moisture content of the general analysis test sample
BS 1016-104.2	Proximate analysis, determination of moisture content of the general analysis sample of coke
BS 1016-104.3	Proximate analysis, determination of volatile matter content
BS 1016-104.4	Proximate analysis, determination of ash content
BS 1016-105	Determination of gross calorific value
BS 1016-106.1.1	Ultimate analysis of coal and coke, determination of carbon and hydrogen content, high temperature combustion method
BS 1016-106.1.2	Liebig method
BS 1016-106.2	Ultimate analysis of coal and coke, determination of nitrogen content
BS 1016-106.4.1	Ultimate analysis of coal and coke, determination of total sulfur content, Eschka method
BS 1016-106.4.2	Ultimate analysis of coal and coke, determination of total sulfur content, high temperature combustion method

(ASTM D3176; ASTM D5373). *Miscellaneous analysis* is a collective category for various types of physical and chemical tests for coal that are commonly requested by coal producers and buyers. Included in this category are tests such as the determination of calorific value, analysis of the forms of sulfur, analysis of the forms of carbon, chlorine analysis, major and minor elements in ash analysis, trace element analysis, carbon dioxide analysis, and determinations of free-swelling index (FSI), grindability, plastic properties of coal, and ash fusibility (Speight, 2013a,b).

However, such standards text methods were not always available for the analysis of coal and each laboratory used methods specific to that laboratory making comparison of the analytic data difficult and even suspected. Thus, as coal became a world-traded commodity, it became necessary to develop methods that could be accepted by sellers and buyers alike. By definition, a standard is defined as a document, established by consensus and approved by a recognized organization that provides, for common and repeated use, rules, guidelines, or characteristics for activities or their results. Many industry bodies and trade associations require a product (e.g., coal) to conform to a standard or a directive before it can be offered for sale. In fact, the use of standards is becoming more and more of a prerequisite to worldwide trade. Above all, any business, large or small, can benefit from the conformity and integrity that standards bring to the issues related to coal analysis.

As a result, the formation of various national standards associations has led to the development of methods for coal evaluation. For example, the ASTM has carried out uninterrupted work in this field for many decades while investigations on the development of the standardization of methods for coal evaluation has occurred in all of the major coal-producing countries (Montgomery, 1978; Patrick and Wilkinson, 1978). As a noteworthy point, there are other organizations for methods development and standardization that operate on a national level; examples are the International Organization for Standardization (ISO, 2013) and the British Standards Institution (BS, 2013), which covers the analysis of coal under one standard number (BS 1016) (Table 2.6).

Furthermore, the increased trade between various coal-producing countries that followed World War II meant that cross-referencing of the already accepted standards was a necessity and the mandate for such work fell to the ISO, located in Geneva, Switzerland; membership in this organization is allocated to participating (and observer) countries. Moreover, as a part of the multi-faceted program of coal evaluation, new methods are continually being developed and the already accepted methods may need regular modification to increase the accuracy of the technique as well as the precision of the results.

As a result of the evolution of organization that develop and promote standard test methods for coal analysis, it is appropriate that in any discussion of the particular methods used to evaluate coal for coal products, reference should be made to the relevant test. Accordingly, where possible, the necessary test numbers (ASTM) have been included as well as those, where appropriate of the British Standards Organization (BS) and the International Standards Organization (ISO) (Tables 2.5 and 2.6).

2.4 COAL CLASSIFICATION

Coal is a heterogeneous mixture of organic and inorganic materials, the properties of which may differ not only from seam to seam but also within the same seam, depending on the coal location and elevation. Coal impurities are typically classified as inherent and removable. The inherent impurities in ash-forming mineral matter are organically combined with the coal. The bulk of the coal mineral matter is interstratified material which settles into the coal deposit as a result of water penetration during and after coal formation. Some of the mineral matter can be introduced into the coal during a mechanized mining process as a result of undesirable mixing with the overburden material. As a result of coal heterogeneity, there is a wide variation in the composition and properties of coal that a classification system is needed to describe the different kinds available for a variety of uses.

The simple chemical approach to characterizing coal is to determine the amounts of the principal chemical elements (*ultimate analysis*) of coal. Using this form of characterization, carbon is the predominant element and constitutes approximately 60% w/w to approximately 95% w/w of the total. For most coals having less than of 90% w/w carbon, the hydrogen content is in the range of 5% w/w and decreases to approximately 2% w/w for coal having 95% w/w carbon. The nitrogen content of almost all coal types is on the order of 1–2% w/w while the oxygen content (2–30% w/w) is inversely related to carbon content. For example, coal having approximately 65% w/w carbon may contain 30% w/w oxygen while coal having approximately 95% w/w carbon may less than 2% w/w oxygen. The sulfur content of coal is variable with no obvious relationship to any of the other elements. Another way to characterize coal is to determine specific properties (*proximate analysis*) in which each test method (moisture, volatile matter, fixed carbon, and ash) is carried out under rigorously defined conditions so that any buyer or seller of coal should be able to reproduce the results in his or her own laboratory.

On a more detailed note, coal classification is the grouping of different coals according to certain qualities or properties, such as coal type, rank, carbon–hydrogen ratio, and volatile matter. Thus, due to the worldwide occurrence of coal deposits, the numerous varieties of coal that are available, and its many uses, many national coal classification systems have been developed. In general, these systems are based on characteristics of domestic coals without reference to coals of other countries. However, it is unfortunate that the terms used for describing similar or identical coals are not used uniformly in these various systems.

In the United States, coal is classified according to the degree of metamorphism, or progressive alteration, in the series from lignite (low rank) to anthracite (high rank) (ASTM D388) (Speight, 2013a and references cited therein). The basis for the classification is according to yield of fixed carbon and calorific value, both calculated to the mineral-matter-free basis. Higher-rank coals are classified according to fixed carbon on the dry mineral-matter-free basis. Lower-rank coals are classed according to their calorific values on the moist mineral-matter-free basis. In addition, the agglomerating character is used to differentiate certain classes of coals.

Thus, in order to classify coal, the calorific value and a proximate analysis (moisture, ash, volatile matter, and fixed carbon by difference) are needed. For lower-rank coals, the equilibrium moisture must also be determined. To calculate these values to the mineral-matter-free basis, the following Parr formulas are used (ASTM D388):

Thus (Table 2.7), coal with a fixed carbon value in excess of 69% w/w or more, as calculated on the dry, mineral-matter-free basis, are classified according to the fixed carbon value. Coal with a calorific value less than 14,000 Btu/lb, as calculated on the moist, mineral-matter-free basis, is classified according to the calorific value on a moist, mineral-matter-free basis, provided the dmmf fixed carbon is less than 69%. The agglomerating character is considered for coal with 86% w/w or more dmmf fixed carbon and for coal with a calorific value between 10,500 and 11,500 Btu/lb, as calculated on the moist, mineral-matter-free basis.

The International Classification of Hard Coals by Type System is based on the dry, ash-free volatile matter; the calorific value expressed on a moist, ash-free basis; and the coking and caking properties. A coal is given a three-figure code number from a combination of these properties (Table 2.8). Coal is first divided into classes 1.5, containing coals with volatile matter (dry, ash-free basis) up to 33%.

TABLE 2.7 Classification of Coal by Rank

		Fixed Carbon Limits (%, Dry, Mineral-Matter-Free Basic)		Volatile Matter Limits (%, Dry, Mineral-Matter-Free Basic)		Calorific Value Limits (%, Btu/lb, Moist, Mineral-Matter-Free Basic)[b]		
Class	Group	Equal to or Greater Than	Less Than	Greater Than	Equal to or Less Than	Equal to or Greater Than	Less Than	Agglomerating Character
I. Anthracite	1. Metaanthracite	98	—	—	2	—	—	Nonagglomerating
	2. Anthracite	92	98	2	8	—	—	
	3. Semianthracite[e]	86	92	8	14	—	—	
II. Bituminous	1. Low-volatile bituminous coal	78	86	14	22	—	—	Commonly agglomerating
	2. Medium-volatile bituminous coal	69	78	22	31	—	—	
	3. High-volatile A bituminous coal	—	69	31	—	14.000[a]	—	
	4. High-volatile B bituminous coal	—	—	—	—	13,000	14.000	
	5. High-volatile C bituminous coal	—	—	—	—	11,500	13,000	
						10,500	11,500	Agglomerating
III. Subbituminous	1. Subbituminous A coal	—	—	—	—	10,500	10,500	Nonagglomerating
	2. Subbituminous B coal	—	—	—	—	9,500	10,500	
	3. Subbituminous C coal	—	—	—	—	8,300	9,500	
IV. Lignite	1. Lignite A	—	—	—	—	6,300	8,300	
	2. Lignite B	—	—	—	—	—	6,300	

Source: ASTM, (2013).

[a] This classification does not include a few coals principally nonbanded varieties, that have unusual physical and chemical properties and that come within the limits of the fixed-carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48% dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free British thermal units per pound.

[b] Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

[c] If agglomerating, classify in low-volatile group in the bituminous class.

[d] Coals having 69% or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

[e] It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in the high-volatile C bituminous group.

TABLE 2.8 International Classification of Hard Coal

Groups[b]			Code Numbers[c]										Subgroups[b]		
Group Number	Alternative Group Parameters												Sub group Number	Alternative Subgroup Parameters	
	Free-Swelling Index (Crucible Swelling Number)	Roga Index												Dilatometer	Gray-King
3	>4	>45					435	535	635				5	>140	$>G_8$
						334	434	534	634				4	>50–140	G_5–G_8
						333	433	533	633	733			3	>0–50	G_1–G_4
						332 a b	432	532	632	732	832		2	≤0	E–G
2	$2\frac{1}{2}$–4	>20–45				323	423	523	623	723	823		3	>0–50	G_1–G_4
						322	422	522	622	722	822		2	≤0	E–G
						321	421	521	621	721	821		1	Contraction only	B–D
1	1–2	>5–20			212	312	412	512	612	712	812		2	≤0	E–G
					211	311	411	511	611	711	811		1	Contraction only	B–D

TABLE 2.8 (*Continued*)

0	$0\text{–}\frac{1}{2}$	0–5		100 a	100 b	200	300	400	500	600	700	800	900	0	Nonsoftening	A
			Class Numbers[d]											As an indication, the following classes have an approximate volatile matter content of: Class 6: 33–41% Class 7: 33–44% Class 8: 35–50% Class 9: 42–50%		
			0	1		2	3	4	5	6	7	8	9			
Class Parameters	Volatile Matter (Dry, Ash-Free)		0–3	>3–10		>10–14	>14–20	>20–28	>28–33	>33	>33	>33	>33			
				>3–6.5	>6.5–10											
	Calorific Parameters[e]		—	—		—	—	—	—	>13,950	>12,960–13,950	>10,980–12,960	>10,260–10,980			

Source: Adapted with permission from H. H. Lowry, ed., *Chemistry of Coal Utilization*, suppl. vol., John Wiley & Sons, Inc., 1963.

[a] (1) Where the ash content of coal is too high to allow classification according to the present systems, it must be reduced by laboratory float-and-sink methods (or any other appropriate means). The specific gravity selected for flotation should allow a maximum yield of coal with 5–10% ash. (2) 332a... > 14–16% volatile matter; 332b... > 16–20% volatile matter. (3) Classes determined by volatile matter up to $$$ volatile matter and by clalrorific parameter above 33% volatile matter.

[b] Groups and subgroups are determined by coking properties.

[c] The first figure of the code number indicates the class of the coal, determined by volatile matter content up to 33% VM and by calorific parameter above 33% VM. The second figure indicates the group of coal, determined by coking properties. The third figure indicates the subgroup, determined by coking properties.

[d] Classes are determined by volatile matter up to 33% VM and by calorific parameter above 33% VM.

[e] Gross calorific value on a moist, ash-free basis (30 ºC, 96% relative humidity, Btu/lb).

Coal with volatile matter greater than 33% w/w falls into classes 6–9 that are separated according to the gross calorific value on the moist, ash-free basis. Although the moist calorific value is the primary parameter for classes 6–9, the volatile matter does continue to increase with the rising class number.

The classes of coal are subdivided into groups according to their coking properties, as reflected in the behavior of the coals when heated rapidly. A broad correlation exists between the crucible swelling number and the Roga index (ISO Methods) and either of these may be used to determine the group number of a coal.

Coals classified by class and by group are further subdivided into subgroups, defined by reference to coking properties. The coking properties are determined by either the Gray-King coke-type assay or the Audibert–Arnu dilatometer test (International Organization for Standardization Methods). These tests express the behavior of a coal when heated slowly, as in carbonization.

In the three-figure code number that describes the properties of a coal, the first digit represents the class number, the second is the group number, and the third is the subgroup number. The international classification accommodates a wide range of coals through the use of the nine classes and various groups and subgroups.

Brown coal and lignite have been arbitrarily classified as coal having a moist, ash-free calorific value less than 10,260 Btu/lb. A code number that is a combination of a class number and a group number classifies these. The class number represents the total moisture of the coal as mined and the group number the percentage tar yield from the dry, ash-free coal (Table 2.9).

Thus, the main characteristics determine the properties of a coal: (1) composition and (2) rank (Table 2.7) and composition is, in turn, characterized by two essentially independent factors: type (nature of the organic components) and grade (presence of mineral matter) (Diessel, 1980; Stach et al., 1982; Ward, 1984; Diessel, 1992; Van Krevelen, 1993; Taylor et al., 1998; Thomas, 2002; Suárez-Ruiz and Crelling, 2008). Thus, as a means of differentiation between these terms:

- *Rank* reflects the degree of metamorphism (or coalification) to which the original mass of plant debris (peat) has been subjected during its burial history and

TABLE 2.9 International Classification of Hard Coal Using Calorific Value

Group Number	Group Parameter Tar Yield, Dry, Ash-Free (%)	Class Parameter, Total Moisture, Ash-Free[a] (%)					
		Class 10 0–20%	Class 11 20–30%	Class 12 30–40%	Class 13 40–50%	Class 14 50–60%	Class 15 60–70%
40	>25	1040	1140	1240	1340	1440	1540
30	20–25	1030	1130	1230	1330	1430	1530
20	15–20	1020	1120	1220	1320	1420	1520
10	10–15	1010	1110	1210	1310	1410	1510
00	10 and less	1000	1100	1200	1300	1400	1500

[a] The total moisture refers to freshly-mined coal. Moist, ash-free basis: 30 °C and 96% relative humidity.

this, in turn, depend on the maximum temperature and pressure parameters and the time to which the coal precursors have been exposed – for most coals rank also reflects the depth of burial and the geothermal gradient prevailing at the time of coalification in the basin concerned.

- *Type* reflects the nature of the original plant debris, including the mixture of plant components (such as wood, leaves, and algae) involved and the degree of degradation to which the debris was exposed before burial – the individual plant components occurring in coal, and in some cases fragments or other materials derived from them, are referred to as *macerals* and the kind and distribution of the various macerals are the starting point for most coal petrology studies.
- *Grade* reflects the extent to which the accumulation of plant debris has been kept free of contamination by inorganic material (mineral matter), before burial (i.e., during accumulation), after burial, and during coalification – a high-grade coal is therefore a coal (regardless of rank or type) with a low overall content of mineral matter.

These parameters are the primary factors that influence a coal's specific physical and chemical properties and these properties in turn determine the overall quality of the coal and its suitability for specific purposes. Coal petrology, which dates back to the beginning of the twentieth century, is the fundamental discipline that deals with the origin, occurrence, physical and chemical properties, and utilization of coal.

2.5 USE OF COAL

Coal is a naturally occurring combustible material with varying composition and it is not surprising that the properties of coal vary considerably from coal type to coal type and even from sample to sample within specific coal types. This can only be ascertained by application of a series of standard test methods (Speight, 2013a,b).

The constituents of coal can be divided into two groups: (1) the organic fraction, which can be further subdivided into soluble and insoluble fractions (Chapter 10) as well as microscopically identifiable macerals (Chapter 1), and (2) the inorganic fraction, which is commonly identified as ash subsequent to combustion (Chapter 4) (Speight, 2013a,b). Because of this complex heterogeneity, it might be expected that the properties of coal can vary considerably, even within a specific rank of coal.

Furthermore, depending on the rank and plastic properties, coals are divided into the following types: (1) hard coking coal, (2) semi-soft coking coal, and (3) thermal coal. *Hard coking coal*, which is used for the production of strong coke, is evaluated based on the strength, yield, and size distribution of coke produced which is dependent on rank and plastic properties of the coal. On the other hand, semi-soft coking coal (weak coking coal) is used in the coke blend, but results in a low coke quality with a possible increase in impurities. Finally, thermal coal is typically used for electricity generation (Speight, 2013a,b) and the majority of thermal coal traded internationally is fired as pulverized fuel and vary in rank from sub-bituminous coal to bituminous coal.

Evaluation of coal for any of the aforementioned uses can be achieved by the determination of several noteworthy properties (e.g., Chapters 7–9) and there are also various other properties that provide even more valuable information about the potential use for coal (Speight, 2013a,b). Indeed, there are also those properties of organic materials that offer valuable information about environmental behavior. Hence, environmental issues lead to an additional need to investigate the properties of coal.

In the broadest sense, it has been suggested that the granular nature of high rank coals is of importance in understanding the physical nature of coal if coal is modeled in terms of a granular medium, which consists of graphite-like material embedded in an insulating organic matrix. Indeed, there have been several earlier suggestions of the graphite-like nature of coal, particularly from X-ray diffraction studies (Speight, 2013a and references cited therein) and perhaps this is a means by which the behavior of coal can be modeled. But, if this be the case, the precise role of the smaller aromatic systems needs also to be defined more fully. Nevertheless, it certainly offers new lines of thinking about coal behavior.

2.5.1 PreModern Use of Coal

Coal has a very long and varied history – perhaps, the most varied history of all of the fossil fuels – and has been used for heating since the cave man. Although this type of use is undocumented, there is evidence from ancient hearths that coal was used as a fuel (Francis, 1961; Van Krevelen, 1993; Höök and Aleklett, 2009).

Coal has been the principal source of fuel and energy for many hundreds of years; perhaps even millennia, even though its use is documented somewhat less completely than the use of petroleum and its derivatives (Speight, 2014). Nevertheless, coal has been the principal source of solid and gaseous fuels gaseous fuel source during this and the last century. In fact, each town of any size had a plant for the gasification of coal (hence, the use of the term *town gas*). Most of the natural gas produced at the petroleum fields was vented to the air or burned in a flare stack but only a small amount of the natural gas from the petroleum fields was pipelined to industrial areas for commercial use. It was only in the years after World War II that natural gas became a popular fuel commodity leading to the recognition that it has at the present time. Coal has probably been known and used for an equal length of time but the records are somewhat less than complete.

There are frequent references to coal in the Christian Bible (Cruden, 1930) but, all in all, the recorded use of coal in antiquity is very sketchy. Coal appears to have been used commercially in China and there are reports that a mine in northeastern China provided coal for smelting copper and for casting coins in approximately 1000 BC. There are no records of any concern about the impact of coal on the environment and human health but they may date from the first use of coal as a fuel in China in about 1100 BC. After this time, another early known reference to the use of coal was made by the Greek philosopher and scientist Aristotle, who referred to a charcoal-like rock.

An early documented reference to the use of coal as fuel is the geological treatise *On Stones* by the Greek philosopher Theophrastus (ca. 371–287 BC). He described the certain black rocks once set on fire, burn like charcoal and are used by those who work in metals (Mattusch, 2008). Outcrop coal was used in Britain as forming part of the fuel for funeral pyres during the Bronze Age (3000–2000 BC) (Needham and Golas, 1999). Archeologists have also reported that Romans in England used coal in the second and third centuries (100–200 AD) of the present era. In Roman Britain, exploitation of coalfields occurred throughout England and Wales the end of the second century AD (Smith, 1997). Coal cinders have been found in the hearths of villas and military forts, particularly in Northumberland that were built to protect the Roman Wall as well as at other sites (Forbes, 1966; Cunliffe, 1984; Smith, 1997; Salway, 2001).

As the use of coal expanded in Britain, it became evident that there were disadvantages and side effects. For example, Eleanor, the wife and Queen of King Henry III of England, was obliged to leave the town of Nottingham where she had been staying during the absence of the King on an expedition into Wales. The Queen was unable to remain in Nottingham due to the troublesome smoke from the coal being used for heating and cooking and she removed *her royal person* from the city with haste. Over the next several decades, a variety of proclamations were issued by Henry and by his son, Edward I, which threatened the population with the loss of various liberties, perhaps even the loss of significant part(s) of the miscreant's anatomy and even loss of life, if the consumption of coal was not seriously decreased and, in some cases, halted (Galloway, 1882). There are documented examples of coal mining in Britain from the year 1200 AD which marked, perhaps, the first documented use of mined coal in England (Galloway, 1882). On another historical note, and it is worthy of repetition here, that a singular environmentally significant event occurred in England in the year 1257, which threatened the very existence of coal use and its future as a fuel.

By the late 1500s, an increasing shortage of wood in Europe resulted in the search for another form of combustible energy and coal became even more popular with the English, French, Germans, and Belgians being very willing to exploit the resource. In the mid-to-late 1700s, the use of coal increased dramatically in Britain with the successful development of coke smelters and the ensuing use of coal to produce steam power. By the 1800s, and the industrial revolution well under way, coal was supplying most of Britain's energy requirements. By this time, the use of gas from coal (*town gas*) for lighting has become established.

By contrast, in the United States, where the population density was much lower than in Europe, wood was more plentiful and many colonial fires were fueled by this resource; any coal (often in limited quantities or for specific uses such as in smelters) required for energy was imported from Britain and/or from Nova Scotia. But after the Revolutionary War, coal entered the picture as an increasingly popular source of energy. As an example, the state of Virginia supplied coal to New York City. However, attempts to open the market to accept coal as a fuel were generally ineffective in the United States and the progress was slow, if not extremely slow. It was not until the period from 1850 to 1885 that coal use in the United States increased, spurred by the emerging railroad industry as a fuel for the locomotives as well as for the manufacture of steel rails. At last, coal appeared to undergoing a transformation on as a fuel on both sides of the Atlantic Ocean.

Furthermore, in the eighteenth century, it was discovered in England (as part of the Industrial Revolution) that coal could produce a fuel that burned cleaner and hotter than wood charcoal. However, it was the overwhelming need for energy to run the new technologies invented during the Industrial Revolution that provided the real opportunity for coal to fill the first role as a dominant worldwide supplier of energy. The Industrial Revolution played a major role in expanding the use of coal. During the first half of the 1800s, the Industrial Revolution spread to the United States. However, there is evidence of coal use the fourteenth century when the Hopi Indians (in what is now the US Southwest states of New Mexico and Arizona) used coal for cooking, heating, and to bake the pottery they made from clay. Coal was later *rediscovered* in the United States by explorers in 1673 but the commercial mining of coal did not commence operation until the 1740s in Virginia. In the nineteenth century, steamships and steam-powered railroads were becoming the chief forms of transportation, and they used coal to fuel their boilers. During the Civil War (the war between the states, 1861–1865), weapons factories were beginning to use coal for energy and by 1875, coke (which is made from coal) replaced charcoal as the primary fuel for iron blast furnaces to make steel.

In 1816, the city of Baltimore, Maryland, began to light its streets with combustible gas made from coal. The first major boon for coal use occurred in 1830 when the Tom Thumb, the first commercially practical American-built locomotive, was manufactured. The Tom Thumb burned coal, and in rapid fashion, virtually every American locomotive that burned wood was converted to use coal. America's coal industry had begun taking shape. At this time, coal was being used to make glass in Fayette County, Pennsylvania. In the second half of the 1800s, more uses for coal were found. During the Civil War in the United States, weapon factories were beginning to use coal. By 1875, coke (which is made from coal) replaced charcoal as the primary fuel for iron blast furnaces to make steel.

In the 1970s, a legacy of abandoned mined areas and red-stained streams (somewhat reminiscent of the River Nile at the beginning of the ten plagues) from acid mine drainage of mines and preparation areas in the United States spurred public concern about the environmental impacts of mining (Costello, 2003). These concerns led to federal regulations to guide reclamation and limit off-site impacts to the environment. Most industrialized countries regulate modern mining practices, but in those countries with a long mining history, it will take time to mitigate the legacy of past mining. This legacy includes physical disturbances to the landscape, subsidence and settlement above abandoned underground mines, flooding and increased sedimentation, polluted ground and surface-waters, unstable slopes, long-burning fires, miners' safety, and public safety and land disturbance issues. In countries where such regulations do not exist, these issues are a continued concern. As a result of environmental concerns, various technologies have been developed that capture potentially harmful elements and compounds before they can be emitted to the atmosphere.

Coal combustion to generate electricity (Speight, 2013b) is a relative newcomer in the history of coal use – it was not until in the 1880s when coal was first used to generate electricity for homes and factories – and replaced the use of coal as a generator of coal-gas heating and lighting.

2.5.2 Modern Use of Coal

The increased use and popularity of coal is due, no doubt, to the relative ease of accessibility, which has remained virtually unchanged over the centuries. On the other hand, petroleum is now an occasional exception because of a variety of physical and political reasons.

The relatively simple means by which coal can be used is also a major factor in determining its popularity. In addition, coal can be interchanged to the three fuel types insofar as one form can be readily converted to another:

$$\text{Gas} \rightarrow \text{Liquid} \rightarrow \text{Solid}.$$

Indeed, the conversion of coal to fuel products and to chemicals as evidenced by the birth and evolution of the coal chemicals industry in the nineteenth century served to increase the popularity of coal.

More generally, here are three major pathways for coal utilization: (1) combustion, (2) carbonization, and (3) conversion all of which require analytical data to determine the suitability of the coal for any of these uses. Briefly, combustion involves burning the coal in air to liberate thermal energy (heat) which is used for domestic and industrial purposes, such as the generation of steam for use in electric power plants (Speight, 2013a,b). On the other hand, the *carbonization* process is used to produce coke in which coal is heated at high temperatures in the absence of air. Finally, the *conversion* process is used to transform coal into gaseous or liquid fuels (synthetic fuels) (Speight, 2013a). However, the primary use of coal is as a solid fuel to produce heat by burning, which produces carbon dioxide (CO_2), a greenhouse gas, along with sulfur dioxide (SO_2) which, in turn, can lead to the production of sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4) that is responsible for the formation of sulfate aerosol and acid rain:

$$[\text{Sulfur}]_{\text{coal}} \rightarrow SO_2$$

$$SO_2 + O_2 \rightarrow SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

In addition, coal contains many trace elements, including arsenic and mercury, which are dangerous if released into the environment – there are also (in certain coals) low levels of uranium, thorium, and other naturally occurring radioactive isotopes and the release of these elements into the environment can lead to radioactive contamination. Although present in *only* trace amounts, a great deal of coal is burned and the potential for releasing significant amounts of these substances is high.

When coal is used in electricity generation, the heat is used to create steam, which then is used to power turbine generators (Speight, 2013a,b). Approximately, 40% of the current electricity production is powered by coal and the total known deposits recoverable by current technologies are sufficient for at least 300 years. Modern coal power plants utilize a variety of techniques to limit the harmfulness of their waste products and improve the efficiency of burning, though these techniques are not widely implemented in some countries, as they add to the capital cost of the power plant.

In the pressurized fluid bed combustor, pressure is maintained in the boiler, often an order of magnitude greater than in the atmospheric combustor, and additional efficiency is achieved by judicious use of the hot gases in the combustion chamber (combined cycle). Both the atmospheric and pressurized fluid bed combustors burn coal with limestone or dolomite in a fluid bed which allows, with recent modifications to the system, the limestone sorbent to take up about 90% of the sulfur that would normally be emitted as sulfur dioxide. In addition, boiler reconfiguration can allow combustion to be achieved more efficiently than in a conventional combustor thereby reducing the formation of nitrogen oxide(s).

An important repowering approach attracting great interest is the integrated coal-gasification combined cycle (IGCC) system (Speight, 2013a,b). The major innovation introduced with the IGCC technology is the conversion of coal into synthesis gas, a mixture of mainly hydrogen (H_2) and carbon monoxide (CO) with lesser quantities of methane (CH_4), carbon dioxide (CO_2), and hydrogen sulfide (H_2S). Up to 99% of the hydrogen sulfide can be removed by commercially available processes before the gas is burned (Speight, 2013a, 2013b,b). The synthesis gas then powers a combined cycle in which the hot gases are burned in a combustion chamber to power a gas turbine and the exhaust gases from the turbine generate steam to drive a steam turbine.

The carbon oxides (carbon monoxide, CO, and carbon dioxide, CO_2) are also of importance insofar as coal can produce either or both of these gases during use; and both gases have the potential for harm to the environment. Reduction in the emission of these gases, particularly carbon dioxide which is the final combustion product of coal, can be achieved by trapping the carbon dioxide at the time of coal usage.

However, the production of carbon dioxide from coal needs to be decreased. In addition the production of pollutants such as sulfur dioxide (SO_2) and oxides of nitrogen (NO_x, where $x = 1$ or 2) needs attention. These gases react with the water in the atmosphere and the result is an acid:

$$SO_2 + H_2O \rightarrow H_2SO_4\text{(sulfurous acid)}$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4\text{(sulfuric acid)}$$

$$2NO + H_2O \rightarrow HNO_2 + HNO_3\text{(nitrous acid + nitric acid)}$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + H_2O \rightarrow HNO_3\text{(nitric acid)}$$

Indeed, the careless combustion of coal can account for the large majority of the sulfur oxides and nitrogen oxides released to the atmosphere. Whichever technologies succeed in reducing the amounts of these gases in the atmosphere should also succeed in reducing the amounts of urban smog, those notorious brown and grey clouds that are easily recognizable at some considerable distances from urban areas, not only by their appearance but also by their odor.

2.6 THE FUTURE

The prognosis for the continued use of coal is good. Projections that the era of fossil fuels (gas, petroleum, and coal) will be almost over when the cumulative production of the fossil resources reaches 85% of their initial total reserves may or may not have some merit. In fact, the relative scarcity (compared to a few decades ago) of petroleum is real but it appears that the remaining reserves coal, and perhaps natural gas, make it likely that there will be an adequate supply of energy for several decades (MacDonald, 1990; Speight, 2011, 2013a and references cited therein). The environmental issues are very real and must be attended to.

The use of coal in an environmentally detrimental manner is to be deplored. The use of coal in an environmentally acceptable manner is to be applauded. Technologies that ameliorate the effects of coal combustion on acid rain deposition, urban air pollution, and climate change must be pursued vigorously (Vallero, 2008). There is a challenge that must not be ignored and the effects of acid rain in soil and water leave no doubt about the need to control its causes. Indeed, recognition of the need to address these issues is the driving force behind recent energy strategies as well as a variety of research and development programs (Stigliani and Shaw, 1990; United States General Accounting Office, 1990).

As new technology is developed, emissions may be reduced by repowering in which aging equipment is replaced by more advanced and efficient substitutes. Such repowering might, for example, involve an exchange in which an aging unit is exchanged for a newer combustion chamber, such as the atmospheric fluidized-bed combustor (AFBC) or the pressurized fluidized-bed combustor (PFBC) (Speight, 2013a,b. Current awareness of these issues by a variety of levels of government has resulted, in the United States, of the institution of the Clean Coal Program to facilitate the development of pollution abatement technologies. And it has led to successful partnerships between government and industry (United States Department of Energy, 1993). In addition, there is the potential that new laws, such as the passage in 1990 of the Clean Air Act Amendments in the United States (United States Congress, 1990; Stensvaag, 1991) will be a positive factor and supportive of the controlled clean use of coal.

Indeed, recognition of the production of these atmospheric pollutants in considerable quantities every year has led to the institution of national emission standards for many pollutants. Using sulfur dioxide as the example, the various standards are not only very specific (Kyte, 1991) but will become more stringent with the passage of time. Atmospheric pollution is being taken very seriously and there is also the threat, or promise, of heavy fines and/or jail terms for any pollution-minded miscreants who seek to flaunt the laws (Vallero, 2008). Be that as it may, a trend to the increased use of coal will require more stringent approaches to environmental protection issues than we have ever known at any time in the past. The need to protect the environment is strong. One example is the passage of amendments to the Clean Air Act which attests to this fact.

Thus, as the alternatives in energy vacillate from coal to oil to gas and back again to be followed, presumably, by the eras of nuclear fuels and solar energy, there is an even greater need to ensure that emissions from coal use are clean. It is time to move away from the uncontrolled and irresponsible use of coal and to show that coal can be used in an environmentally safe manner.

Coal analysis has, by convention, involved the use of wet analysis or the use of typical laboratory bench-scale apparatus. This trend continues and may continue for another decade or two. But the introduction of microprocessors and microcomputers in recent years has led to the development of a new generation of instruments for coal analysis as well as the necessary calibration of such instruments (ASTM D5373). In particular, automated instrumentation has been introduced that can determine the moisture, ash, volatile matter, carbon, hydrogen, nitrogen, sulfur, oxygen, and ash fusion temperatures in a fraction of the time required to complete most of the standard laboratory bench procedures.

Several such instruments have been developed for the simultaneous determination of carbon, hydrogen, and nitrogen in various samples. Of course, basic requirements for the instruments are that they provide for the complete conversion of the carbon, hydrogen, and nitrogen in coal to carbon dioxide, water vapor, and elemental nitrogen, and for the quantitative determination of these gases in an appropriate gas stream.

A disadvantage of some of the instrumental methods for determining carbon, hydrogen, and nitrogen is the small sample size used in the analysis. On the best of days, a typical sample size for some of the instruments might be one-to-three milligrams but the accuracy of the system might be questioned. Other systems that use one hundred milligram samples may be preferred, provided that effluents do not flood or overpower the system and overcome the detection equipment. However, the larger sample size does increase the probability that the sample is representative of the quantity of coal being analyzed.

Most of the methods used by the new analytical all-in-one instruments are empirical and the accuracy of the results is highly dependent on the quality and suitability of the standards used to standardize the instruments.

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3

SAMPLING AND SAMPLE PREPARATION

3.1 INTRODUCTION

The mined coal contains a mixture of different size fractions, together with unwanted impurities such as rock and dirt (Speight, 2013a, b). Coal preparation (beneficiation) is the stage in coal production when the mined coal is processed into a range of clean, graded, and uniform coal products that are suitable for the commercial market. In a few cases, the mined coal is of such quality that it meets the user specification without beneficiation and it is merely crushed and screened to deliver the specified product. However, some power plants are fed from a single source of coal but many utilities buy coal from different suppliers, and some blend the coals in order to give a consistent feed to the power plant. Moreover, blending enables selective purchasing of different grades of coal. More expensive, higher-quality supplies can be mixed with lower-quality coals to produce an average blend suited to the plant needs, at optimum cost. Effective preparation of coal prior to combustion improves the homogeneity of coal supplied, reduces transport costs, improves the utilization efficiency, produces less ash for disposal at the power plant, and may reduce the emissions of oxides of sulfur (Vaysman and Lu, 2012).

Thus, knowledge of coal character (Chapters 1 and 2) is an important aspect of coal characterization and has been used as a means of determining the suitability of coal for commercial use for decades, perhaps even centuries (Speight, 2013a, b). Therefore the techniques outlined in this chapter must always be borne in mind when consideration is being given to the suitability of a coal sample for analysis – that

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Handbook of Coal Analysis, Second Edition. James G. Speight.

is, whether or not the sample of representative of the total coal pile. It must also be borne in mind that coal which at first appears unsuitable for use by a consumer might become eminently suitable by a *simple* or convenient pretreating step almost analogous to the *conditioning* of asphalt by air blowing (2013a, b, 2014). In light of various environmental regulations and how the data might be used to predict the suitability of coal for use in an environmentally cleaner and safer manner.

For homogeneous materials, sampling protocols are relatively simple and straightforward, although caution is always advised lest overconfidence cause errors in the method of sampling as well as introduce extraneous material. On the other hand, the heterogeneous nature of coal (Speight, 2013a and references cited therein) complicates the sampling procedures. In fact, apart from variations in rank (Chapter 2), coal is often visibly heterogeneous and there is strong emphasis on need to obtain representative samples for testing and analysis (Gould and Visman, 1981).

Thus, the variable composition of coal offers many challenges to analyst to analyst who needs to ensure that the sample under investigation is representative of the coal. Indeed, the substantial variation in coal quality and composition from the top to the bottom of the seam, from side-to-side, and from one end to the other, within an un-mined bed offer challenges that are perhaps unprecedented in other fields of analytical chemistry. Hence the issues that arise during drilling programs that are designed to determine the size and extent of a coal bed or coal seam. This variability in coal composition and, hence, in coal quality is often significantly, and inadvertently, increased by mining, preparation, and handling.

Transportation (by belt, rail, or truck) can initiate (due to movement of the coal) processes that result in size and density segregation. Thus, variations from one side of a conveyor belt to the other or from between side-to-side, end-to-end, and top-to-bottom of individual cars or trucks and between one location and another in the coal pile must be anticipated (ASTM D346; ASTM D2234; ASTM D4702; ASTM D4915; ASTM D4916; ASTM D6315; ASTM D6518; ASTM D6543; ISO 1988). Therefore, the challenge in sampling coal from a source or shipment is to collect a relatively small portion of the coal that accurately represents the composition of the coal. This requires that sample increments must be collected in such a manner that no piece, regardless of position (or size) relative to the sampling position and implement, is selectively collected or rejected. Thus, the coal sample must be representative of the composition of the whole coal (i.e., coal in a pile or coal in a rail car or truck) is represented by the determined properties or quality of the sample.

Optimization of coal sampling is a function of the many variable constituents of coal. The effect of fineness on the combustion of pulverized coal is dramatic and the special problems associated with collection of an unbiased sample of pulverized coal need to be addressed (ASTM D197). So-called *operating samples* are often collected from the coal streams to power plants on a regular basis not only for determination of heat balance but also to document compliance with air pollution emission regulations.

Thus, in order to test any particular coal, there are two criteria that must be followed and these are: (1) obtain a sample of the coal and (2) ensure that the sample is a true representative of the bulk material, and (last but by no means least) (3) to ensure that the sample does not undergo any chemical or physical changes after completion of the sampling procedure and during storage prior to analysis. In short, the reliability of a sampling method is the degree of perfection with which the identical composition and properties of the entire whole coal are obtained in the sample. The reliability of the storage procedure is the degree to which the coal sample remains unchanged thereby guaranteeing the accuracy and usefulness of the analytical data.

Furthermore, proper coal sizing is one of the key measures to ensure efficient combustion. Proper coal sizing, with specific relevance to the type of firing system, helps toward even burning, reduced ash losses and better combustion efficiency. Coal is reduced in size by crushing and pulverizing. Pre-crushed coal can be economical for smaller units, especially those which are stoker fired. In a coal handling system, crushing is limited to a top size of 6 or 4 mm. The devices most commonly used for crushing are the rotary breaker, the roll crusher, and the hammer mill. It is necessary to screen the coal before crushing, so that only oversized coal is fed to the crusher. This helps to reduce power consumption in the crusher. Recommended practices in coal crushing are: (1) incorporation of a screen to separate fines and small particles to avoid extra fine generation in crushing, and (2) incorporation of a magnetic separator to separate iron pieces in coal, which may damage the crusher. In case of coal lots having excessive fines, it is advisable to blend the predominantly lumped coal with lots containing excessive fines, which will limit the amount of coal fines being fired to not more than 25%. Blending coals having different qualities will also help supply a uniform coal feedstock to, say, a combustor thereby increasing combustion efficiency.

3.2 SAMPLING

Samples submitted for chemical and physical analyses are collected for a variety of reasons, but the collection of each sample should always conform to certain guidelines (Gleit et al., 1986; Golightly and Simon, 1989). Typically, coal submitted for chemical analysis is first received and prepared by the sample preparation (grinding) laboratory. The typical sizes of individual field samples vary from 3 to 15 kg. The preparation procedure usually requires that each air-dried coal sample pass through a jaw crusher; one subsample (split) of the crushed material (2–4 mm, or 5–10 mesh) is then taken for the ultimate and proximate analyses and another split is reduced to approximately 150 mm (100 mesh) by a vertical grinder for chemical analysis. An additional split is kept for archival storage and the excess sample is returned to the submitter.

The pulverization of bulk coal samples from the field serves both to homogenize the coal, which typically is quite heterogeneous, and to reduce the material to small particles needed for analysis. The comminution of a field sample and the splitting of the resulting pulverized sample into portions to be distributed to various laboratories, while minimizing contamination from grinding surfaces, sieves, and other coals, are essential to the success of all subsequent chemical measurements (Swaine, 1985).

3.2.1 General Aspects

Sampling methods fall into various categories that can be precise or non-precise insofar as the sample does or does not represent the complete coal pile. For example, the sampling methods can be classified as: (1) random sampling, (2) systematic sampling, (3) stratified sampling, (4) convenience sampling, (5) judgment sampling, (6) quota sampling, and (7) snowball sampling. No matter which method is used, there may always be a sampling error, which is the degree to which a sample might differ from the whole population of the coal pile.

Random sampling is the purest form of probability sampling and each member of the population has an equal and known chance of being selected and bias is minimized. *Systematic sampling* is often used instead of random sampling and, depending on the material to be sampled, can be as good as the random sampling method. *Stratified sampling* is a commonly used probability method that is superior to random sampling because it reduces sampling error and is used to select a *sufficient* number of samples from, say, each level of the coal pile – *sufficient* refers to a sample size large enough for us to be reasonably confident that the stratum represents the population.

On the other hand, *convenience sampling* is typically used in exploratory research where only an approximation of the data will suffice. *Judgment sampling* is a common method of sampling and the sample is *assumed* to be repetitive without and foundation for this belief and the confidence that the chosen sample is truly representative of the coal pile is low. *Quota sampling* is similar to stratified sampling and then convenience sampling or judgment sampling is used to select the required number of samples from each stratum. *Snowball sampling* is a method used when the desired sample characteristic is rare and does introduce bias because the technique itself reduces the likelihood that the sample will represent a good cross section from the population.

For coal sampling, more is required in terms of the sampling method and there must be a high probability that the sample represents the whole coal pile. Sampling methods (such as ASTM D2013) should cover the reduction and division of gross or divided samples up to and including the individual portions used for laboratory analysis. Furthermore, the application of precise techniques in sample collection helps to ensure that data from each analysis performed on the samples will be useful. For interpretations and comparisons of elemental compositions of coal beds to be valid, the samples must be collected so that they are comparably representative of the coal bed. Such interpretations and comparisons should never be based on data from different types of samples (Swanson and Huffman, 1976; Golightly and Simon, 1989).

Thus, sampling plays a role in all aspects of coal technology. The usual example given is the determination of coal performance in a power plant. However, an equally important objective relates to exploration and sampling of coal reserves, as they exist in the ground. The issues in this case relate not only to determining the extent of the coal resource but also to the quality of the coal so that the amount may be determined. Thus, sampling in connection with exploration is subject to (1) the location, (2) the spacing of the drilled holes, (3) depth from which the sample is taken, and (4) size of core drills used. These criteria must be taken into consideration when assessing the quality and quantity of coal in the deposit being explored.

More to the current point, reliable sampling of a complex mixture such as coal is difficult, and handling and, quite often, the variations in coal handling facilities make it difficult to generate fixed rules or guidelines that apply to *every* sampling situation. The proper collection of the sample involves an understanding and consideration of the minimum number and weight of increments, the particle size distribution of the coal, the physical character and variability of the constituents of coal, and the desired precision of the method. Thus, preliminary to any laboratory testing of coal, it is imperative that a representative sample of the coal be obtained in as reproducible and repeatable manner as possible. If not, data derived from the most carefully conducted analysis are meaningless.

A *gross sample* of coal is a sample that represents a quantity, or *lot,* of coal and is composed of a number of increments on which neither reduction nor division has been performed (ASTM D2234). The recommended maximum quantity of coal to be represented by one gross sample is 10,000 tons (usually the tonnage shipped in a *unit train*, i.e., one hundred cars of which each one contains 100 tons of coal although a unit train may now contain 110 cars or more). Mineral matter content (often incorrectly designated as ash content) is the property most often used in evaluating sampling procedures. The density segregation of the mineral matter speaks to the movement of the coal particles relative to each other during transportation. Environmentally, sulfur content has also been applied in the evaluation of sampling procedures.

The sampling procedures (ASTM D346; ASTM D2234; ASTM D4702; ASTM D4915; ASTM D4916; ASTM D6315; ASTM D6518; ASTM D6543) are designed to give a precision such that if gross samples are taken repeatedly from a lot or consignment and prepared according to the standard test methods (ASTM D197; ASTM D2013) and one ash determination is made on the analysis sample from each gross sample, the majority (usually specified as 95 out of 100) of these determinations will fall within ±10% of the average of all of the determinations. When other precision limits are required or when other constituents are used to specify precision, defined special-purpose sampling procedures may need to be employed.

Thus, when a property of coal (which exists as a large volume of material) is to be measured, there usually will be differences between the analytical date derived from application of the test methods to a *gross lot* or *gross consignment* and the data from the *sample lot*. This difference (the *sampling error*) has a frequency distribution with a mean value and a variance. Variance is a statistical term defined as the mean square of errors; the square root of the variance is more generally known as the *standard deviation* or the *standard error of sampling*.

Recognition of the issues involved in obtaining representative samples of coal and minimization of the *sampling error* has resulted in the designation of methods that dictate the correct manner for coal sampling (ASTM D346; ASTM D2234; ASTM D4702; ASTM D4915; ASTM D4916; ASTM D6315; ASTM D6518; ASTM D6543; ISO 1988; ISO 2309).

Every sampling operation consists of either extracting one sample from a given quantity of material or of extracting from different parts of the lot a series of small portions or *increments* that are combined into one gross sample without prior analysis; the latter method is known as *sampling by increments*. In fact, the number of riffling stages required to prepare the final sample depends on the size of the original *gross lot*. Nevertheless, it is possible by use of these methods to reduce an extremely large consignment (that may be of the order of tons, i.e., several thousand pounds) to a representative sample (one pound or less) that can be employed as the sample for the application of laboratory test methods.

The precision of sampling is a function of the size of increments collected and the number of increments included in a gross sample, improving as both are increased, subject only to the constraint that increment size not be small enough to cause selective rejection of the largest particles present. Recognition of this was evidenced in the specification of minimum number and weight of increments in coal sampling (ASTM D2234). The manner in which sampling is performed as it relates to the precision of the sample thus depends upon the number of increments collected from all parts of the lot and the size of the increments. In fact, the number and size of the increments are operating variables that can, within certain limits, be regulated by the sampler.

Considerations pertinent to the procurement of a representative sample of coal from a gross lot include:

1. The *lot* of coal must first be defined (e.g., a single truck, about 20 tons, a barge, about 1500 tons, a unit train, about 10,000 tons, or a ship cargo, about 100,000 tons.
2. The number of increments (e.g., the number of shovels, required to constitute the gross sample, which is usually 200–500 lb) must be established. (3) For raw, dirty, or poorly cleaned coal, the minimum number of increments is 35.
3. For thoroughly cleaned coal (i.e., maximum practical reduction of ash and sulfur), the minimum increments is 15.
4. The precision (ASTM D2234) is based on one analytical determination falling within one-tenth of the true value 95 times out of 100. To reduce this error by one-half, four times as many gross samples must be used.
5. The weight per increment varies according to the top size of the coal.
6. Increments must be systematically spaced and stationary sampling employs a grid system, which may be a simple left front-middle center-right rear grid for samples from a railroad car or a surveyed grid system to take samples from a storage pile.
7. Additionally, increments taken from a coal storage pile take into account any variations in the depth of the pile.
8. Increments from a moving coal stream are often collected on a preset interval of time by a mechanical sampling device. The opening of the device must be sufficient to accommodate a full stream cut in both directions without disturbing the coal.

Stream sampling and *flow sampling* are terms usually reserved for the collection of sample increments from a free-falling stream of coal as opposed to the collection of increments from a motionless (stopped) conveyor belt. Coal that passes from one belt to another at an angle tends to become segregated because the momentum caused by density differences and by particle size differences, with a predominance of coarse particles on one side and a predominance of fine particles on the other side.

Sampling at rest is acquiring of a coal sample when there is no motion. In such instances, it may be difficult, if not impossible, to ensure that the sample is truly representative of the gross consignment. An example of coal being sampled at rest is when samples are taken from railcars (*car-top sampling*), and caution is advised both in terms of the actual procedure and in the interpretation of the data. Again, some degree of segregation can occur as the coal is loaded into hopper cars. In addition, heavy rainfall can cause the moisture content of the coal to be much higher at the top and sides of the rail car than at the bottom. Similarly, the onset of freezing conditions can also cause segregation of the moisture content.

Sampling error is the difference that occurs when the property of the representative sample compared to the true, unknown value of the gross lot or consignment. The sampling error has a frequency distribution with a mean value and a variance. *Variance* is a statistical term defined as the mean square of errors. Its square root is the more broadly known statistic called the *standard deviation*, or *standard error*, of sampling. Sampling error can thus be expressed as a function of the sampling variance or sampling standard deviation, each of which, in turn, is directly related to the material and the specifics of sample collection.

One aspect of coal sampling materials that has been employed when it is suspected the gross coal sample (the coal pile or the coal in a rail care after transportation) is non-randomly distributed is known as *stratified sampling* or *representative sampling*. The procedure consists of collecting a separate sample from each stratum of the gross material lot and determining the properties from each sample so obtained. Incremental sampling has been considered to be a form of stratified sampling in which the strata are imaginary because there is no physical boundary between the imaginary strata and any such segregation is identified with the portions from which the individual increments are collected. The *within-strata* and *between-strata* variances are a function of the size and number of increments.

Preparation plant performance testing and routine quality control in mining operations and preparation plants require sampling coal both in situ and at various stages of processing following removal from the bed. Other than channel sampling for sampling coal in situ, and the sampling of coal slurries, the sampling techniques for quality control purposes and preparation plant are necessary. However, assessing preparation plant performance may require complex sampling programs for the sampling of many coal streams with widely different sampling properties involving collection of sample increments for which the timing has to be tightly coordinated. Such sampling almost always depends upon manual sampling with a variety of sampling implements, often in locations with difficult if not inadequate access.

Storage of laboratory coal samples for subsequent analysis is also a part of proper sample handling. Long-term storage without change is achieved by placing the samples in a plastic bag containing dry ice, sealing them tightly in glass beakers, and storing them under vacuum. Normally, oxidation and deterioration of 60-mesh laboratory samples stored in air increase with decreasing panicle size and decreasing rank of coal.

In summary, the precision of sampling improves with the size of each of the increments collected and with the number of increments included in a gross sample; and manual sampling involves the principle of ideal sampling insofar as every particle in the entire mass to be sampled has an equal opportunity to be included in the sample.

3.2.2 Manual Sampling

There are two considerations involved with the principle of manual sampling (that every particle in the entire mass to be sampled has an equal opportunity to be included in the sample): (1) the dimensions of the sampling device and (2) proper use of the sampling device. The opening of the sampling device must be 2–3 times the top size of the coal to meet sampling method (ASTM D2234) requirements and design criteria have been established for several types of hand tools that can be used for manual sampling (Figure 3.1). The main considerations are that the width is not less than the specified width and the device must be able to hold the minimum specified increment weight without overflowing.

One particular method of sampling (ASTM D6883) that relates to the standard practice for manual sampling of stationary coal from railroad cars, barges, trucks, or stockpiles. These procedures described in this method are to be used to provide gross

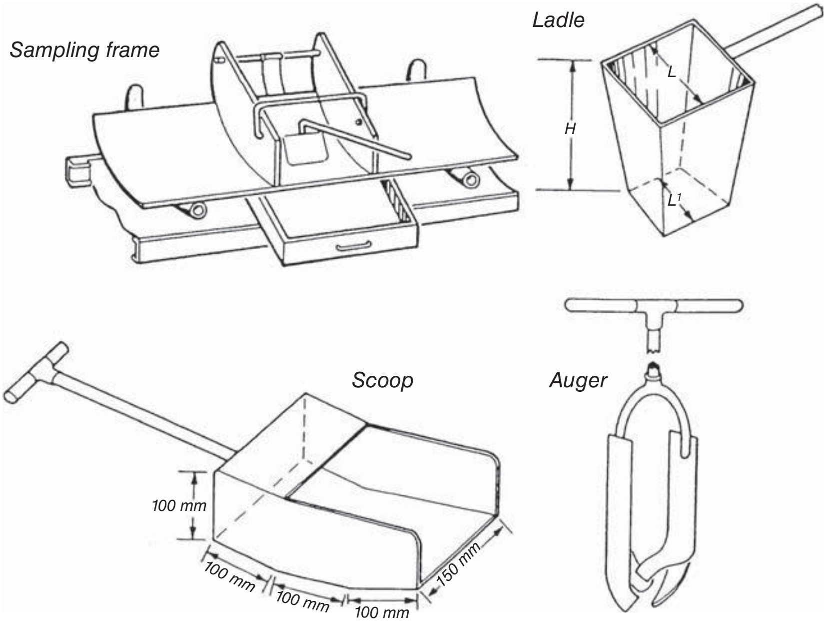

Figure 3.1 Sampling tools.

samples for estimating the quality of the coal. The gross samples are to be crushed, divided, and further prepared for analysis (ASTM D2013).

The practices described by the method provide instructions for sampling coal from beneath the exposed surface of the coal at a depth (~24 in, 61 cm) where drying and oxidation have not occurred. The purpose is to avoid collecting increments that are significantly different from the majority of the lot of coal being sampled due to environmental effects. However, samples of this type do not satisfy the minimum requirements for probability sampling and, as such, cannot be used to draw statistical inferences such as precision, standard error, or bias. Furthermore, this method is intended for use only when sampling by more reliable methods that provide a probability sample is not possible.

Systematic spacing of increments collected from a stopped belt is universally accepted as the reference method of sampling that is intrinsically bias-free. *Stationary sampling*, that is, sampling coal at rest in piles, or in transit in trucks, railcars, barges, and ships, suffers decreased reliability to an indeterminate degree.

Sampling from coal storage piles (*sampling at rest*) is not as simple as may be perceived and can have serious disadvantages. For example, coal in conical-shaped piles suffers segregation effects that result in fines predominating in the central core as well as a gradation of sizes down the sides of the pile from generally fine material at the top of the pile to coarser coal at the base of the pile. If at all possible, coal piles should be moved before sampling that, in turn, determines how the coal is sampled.

Where it is not possible to move a pile, there is no choice but to sample it *as is* and the sampling regime usually involves incremental spacing of the samples over the entire surface. Reliability of the data is still in doubt. However, without attempt at incremental spacing of the sample locations, any sample taken directly from an unmoved storage pile is a *grab sample* that suffers from the errors that are inherent in the structure of the pile as well as in the method by which the sample is obtained.

Alternatively, samples from large coal piles can be acquired by core drilling (ASTM D5192) or by use of an auger, or the coal can be obtained at various depths and locations (by means of heavy equipment such as a bulldozer) so that manual sampling can be performed (ASTM D6610). There are a wide variety of devices that are available for machine sampling (mechanical sampling) and include flow-through cutters, bucket cutters, reciprocating hoppers, augers, slotted belts, fixed-position pipes, and rotating spoons (Figures 3.2–3.4). A major advantage of these systems is that they sample coal from a moving stream.

There are numerous situations where coal must be sampled at rest despite the potential for compromising the reliability of the acquired sample(s). A major problem with sampling coal at rest is that an inevitable and unknown degree of segregation will prevail and there is no possible way to penetrate all parts of the entire mass in such a way that every particle has an equal opportunity to be included in the sample.

The commonest situation where coal must be sampled at rest arises where the coal has to be sampled from railcars. The alternatives for sampling from hopper cars are top, bottom, and a combination of the two. However, as coal is loaded into hopper cars, it suffers segregation related to the loading process that is not necessarily obvious, and the degree to which it will affect results of samples is unpredictable.

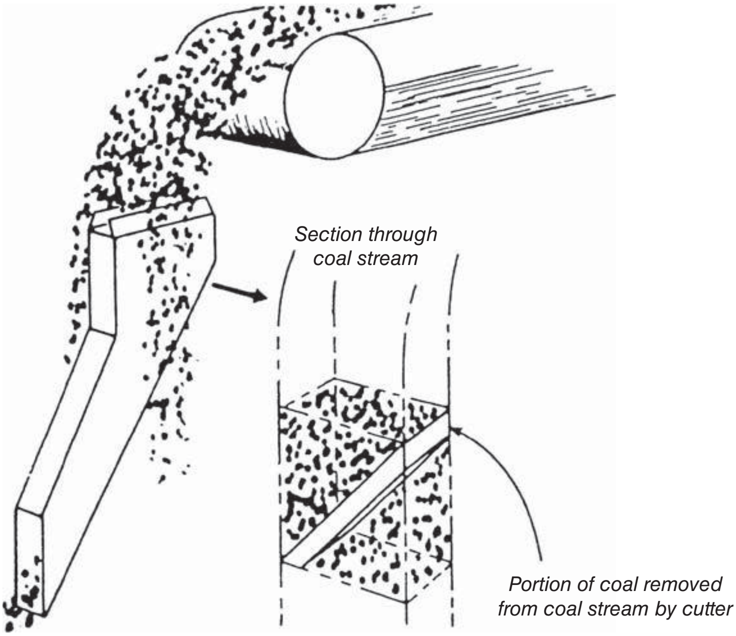

Figure 3.2 A Cross-cut primary cutter.

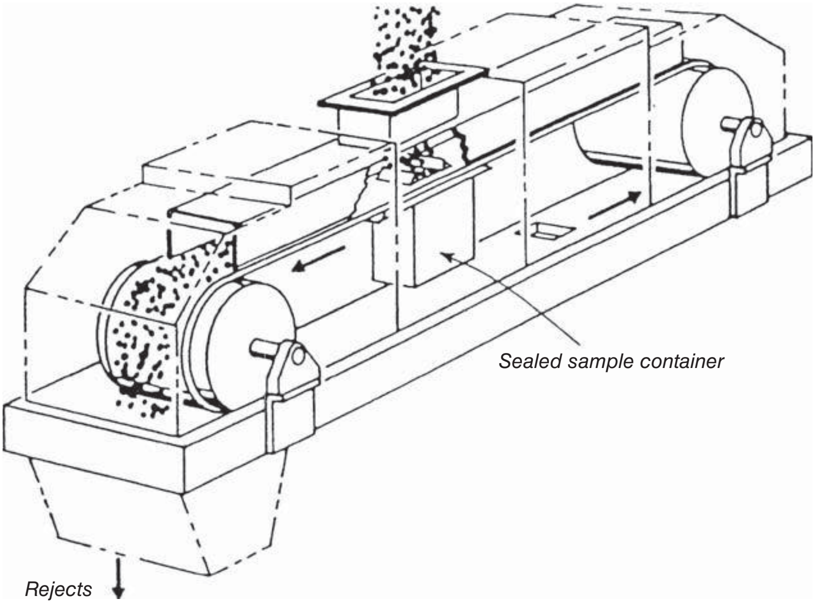

Figure 3.3 A slotted belt secondary cutter.

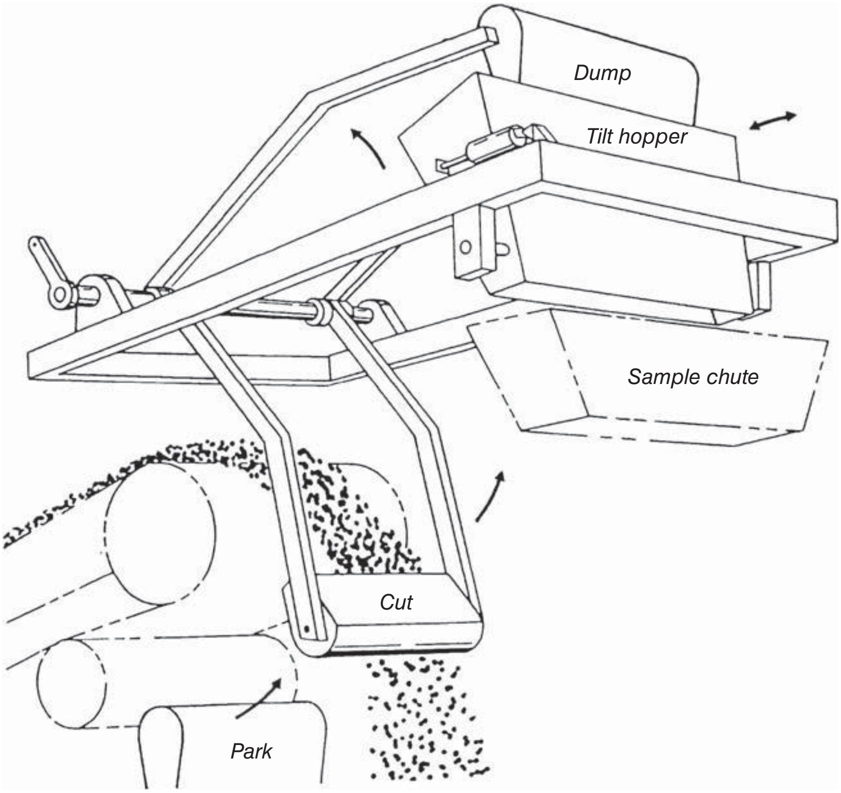

Figure 3.4 A swing-arm primary cutter.

Sometimes the segregation is clearly evident, such as when cars are loaded from a stream that enters the car from the side, causing the large pieces to be shot to the far side while fines remain at or close to the near side. Having made such a statement, segregation can also occur in a more discreet or subtle manner and any differences in texture and appearance are not always clearly visible.

In addition, when a significant amount of surface moisture present, some will begin migrating downward immediately resulting in a substantially higher moisture content at the bottom of the car than at the top. Furthermore, the difference in moisture at different levels may become more pronounced as time passes, owing to the effects of evaporation and precipitation. Heavy rainfall can cause the moisture content to be much higher at the top and sides than at the bottom and, if freezing conditions prevail (as they often do during Wyoming winters) the outcome will be even more obvious.

In *car-top sampling*, only the coal near the top surface has the potential to be included in the sample thereby violating the basic tenet of obtaining a representative sample. Thus, the uncertainties regarding the accuracy of the results are increased and any conclusions drawn from the data are highly suspect. Therefore, if car-top sampling is a necessity, the increments must not be collected predominantly from any given location relative to the dimensions of the rail car. Furthermore, if the rail cars vary substantially in size, the number of increments per car should be varied proportionately.

An alternate operation to sample the coal is to employ *bottom sampling* in which coal is sampled as it is discharged from the bottom of hopper cars. Since the coal is *sampled in motion*, bottom sampling is considered to be an improvement over car-top sampling.

Stream sampling (*flow sampling*) is the sampling of coal in motion, usually from one part of the plant to another. However, increment collection must involve cutting across the full stream. The collection of increments from the sides of a moving belt is sometimes loosely called stream sampling (ASTM D6609) or flow sampling and this terminology therefore should not be accepted as assurance that increments were collected from a free-falling stream. Such procedures are less reliable because the increments collected are subject to analytical bias caused by any segregation of the coal (including the mineral matter) that has occurred on the conveyer belt. In fact, coal larger than one inch top size, or coal heaped to a depth of more than about eight inches on a conveyor belt, exhibits a tendency to segregate. Coal that passes from one belt to another at an angle invariably becomes more segregated, with a greater predominance of coarse particles on the far side and a greater predominance of fine particles on the near side.

When the falling stream is more than one foot thick or is more than about two feet wide, the forces involved tend to be greater than the forces that can be resisted with handheld equipment and simple mechanical devices are often useful. A pivoted scoop with the needed mechanical advantage is useful and slide gates (a dropout section at the bottom of a scraper conveyor) or a flop gate in a vertical chute are other possibilities. In the event that such alternatives are not feasible, partial stream cuts are permissible, but the reliability of the sampling is reduced. To combat any reduction in the reliability, partial stream cuts need to be made systematically at different points in the stream so that all parts of the coal stream are represented proportionately.

Despite the potential advantages of the procedure, sampling coal in motion may suffer from disadvantages such as that (1) it is not always possible to penetrate the full depth of the coal cascading out of the car, (2) attempts to penetrate the stream result in sample scoop overflow, (3) increment collection is limited to the exposed surface at the sides of the car and moisture is often higher at the sides of the car than for the entire contents of the car, (5) flow rates are highly variable, and (6) disproportionate amounts of coarse coal are often collected because the coarse particles segregate and roll down the exposed surface.

3.2.3 Mechanical Sampling

A wide variety of mechanical devices are now in use and include flow-through cutters, bucket cutters, reciprocating hoppers, augers, slotted belts, fixed-position pipes, and rotating spoons. These systems typically collect the primary increments and perform at least part of the sample preparation by crushing and dividing it down to the 4-mesh or 8-mesh stage of reduction specified (ASTM D2013).

Conventional designs of most mechanical sampling systems for large tonnages of coal use some form of *cross-stream primary cutter* to divert the primary increments from the main stream of coal (Figure 3.2). A major advantage of these systems is that they sample coal from a moving stream and most of them satisfy the principle that every particle in the entire mass has an equal opportunity to be included in the primary increments.

One of the more innovative primary cutter designs that reduce the component of impact velocity perpendicular to the direction of coal flow in the plane in which the cutter is moving, is the *swing-arm* (*axial) cutter* (Figure 3.4). This design achieves this goal by passing through the stream at an obtuse angle instead of at a right angle and can be moved at higher speeds than a cross-stream cutter without causing analytical bias that is associated with disturbance to the coal flow.

The *pipe sampler* is an off-the-belt sampler that collects increments from within the stream cross section by means of one or two pipes. The sampling pipes are mounted at an obtuse angle on a horizontal axle positioned at right angles to the direction in which the coal flows and increments are collected through an orifice that is located in the bottom wall of the sampling pipe.

The *rotary car dumper system* (*tube sampler*) consists of several large-diameter tubes, each with one or two openings that are attached to a rotary car dumper. The openings are located in the path of the coal as it is discharged from the railcar. If, as has been claimed, the tubes collect coal predominantly from the top and far side of the car, the method is susceptible to bias because of the potential segregation of the coal constituents.

The *spoon sampler* consists of one or more pipes, arranged like the spokes of a wheel. Openings located at the tips collect the sample as the device is rotated through coal on a moving belt. This machine can be designed to collect very small primary increments but the spoon pipes may overflow during increment collection and the sample may be of questionable reliability.

The *auger drill* is also used as a sampling device for penetrating a stationary mass of coal and withdrawing material from its interior. At least two specialized auger-sampling machines, designed for sampling from trucks, are commercially available. One of these uses a 10-in. auger and is intended for sampling uncrushed run-of-mine coal and a truck-mounted portable version is also being used for sampling from railcars.

3.3 SAMPLE PREPARATION

Once a gross sample has been taken, it is reduced in both particle size and quantity to yield a *laboratory sample*. This aspect is known as *coal preparation*.

Sample preparation (ASTM D2013) includes drying (in air), as well as crushing, dividing, and mixing a gross sample to obtain a sample that is ready for analysis. As written, this test method covers the reduction and division of gross or divided samples up to and including the individual portions for laboratory analysis. Reduction and division procedures are prescribed for coals of the following groups: (1) Group A includes coals that have been cleaned in all sizes and allows smaller weight laboratory samples to be retained than in (2) Group B *that* includes all other coals, including unknown coals.

Two processes of sample division and reduction are covered as follows: (1) Procedure A, in which manual riffles are used for division of the sample and mechanical crushing equipment for the reduction of the sample, (2) Procedure B, in which mechanical sample dividers are used for the division of the sample and mechanical crushing equipment for the reduction of the sample. A third process, that is, in reality, a combination of procedures A and B may be used at any stage.

Other standards are used to collect the gross sample and this test method allows for one division of the gross sample before crushing. The mass and top size of the gross or divided sample collected by using these guides and practices are usually too large for chemical or physical testing. However, any bias in the gross or divided sample before adherence to this practice will remain in the final sample resulting from use of this method. Therefore, the standard to be used to collect the gross sample should be carefully selected. Often, the sample is collected, reduced, and divided (one or more times) by use of a mechanical sampling system and the remaining sample may be further divided on-site to facilitate transporting it to the laboratory where further reduction and division likely occurs before analysis. But, division and reduction of a sample may occur at more than one location. Samples are reduced and divided to an analysis sample but some test methods require a sample of different mass or top size; this method can be adapted to provide a sample of any mass and size consist from the gross or divided sample to, and including, the analysis sample.

Part of the procedure may, since moisture losses are a perpetual problem, include weighing, air-drying, and reweighing (ASTM D3302) before crushing and dividing. This provides a sample in which the moisture loss during the preparation procedure has been determined and provided a stabilized sample that is not subject to further moisture loss. Thus, sample preparation is not just simply a matter of dividing a gross sample into manageable or usable increment. Moreover, the task must be accomplished in a manner that produces an unbiased sample ready for analysis.

Sample preparation, when improperly executed, is the source of the second largest component of the overall variance of sampling and analysis. Although it is not specified as a requirement, it is generally recognized that the variance of sample division and analysis is not more than 20% of the total variance of sampling, division, and analysis (ASTM D2013). The particle size distribution (*size consist*) of the laboratory sample depends on its intended use in the laboratory and the nature of the test methods to be applied. The minimum allowable weight of the sample at any stage of reduction depends on the size consist and the degree of precision desired (ASTM D2013).

Many issues such as (1) loss or gain of moisture, (2) improper mixing of constituents, (3) improper crushing and grinding, and (4) oxidation of coal may arise during the sampling and sample preparation processes. To minimize moisture contamination, all standard methods include an air-drying stage in the preparation of the analysis sample. In this manner, all subsequent handling and analysis are made on a laboratory sample of relatively stable moisture content. Be that as it may, all collecting, handling, reducing, and division of the gross sample should be performed as rapidly as possible and in as few steps as possible to guard against further moisture loss or gain in the ambient laboratory conditions.

The distribution of mineral matter in coal presents problems for the crushing, grinding, and uniform mixing at each step of the sampling procedure. The densities of the various coal constituents cause segregation, especially if there is a wide particle size distribution. Thus, crushing and/or grinding coal from a large particle to a very small particle should involve a reasonable number of steps that are based on the starting particle size and nature of the coal. At the same time, too many handling steps increase the exposure of the coal to air and increase the chance of moisture variation and coal oxidation. On the other hand, attempting to crush, grinding, or pulverizing coal from a large particle size to a small particle size in one operation tends to produce a wide range of particle sizes and a high concentration of very fine particles.

Coal is susceptible to oxidation at room temperature and, like the potential for change in the moisture content, the adverse effects of oxidation must be considered in sampling, coal preparing, and coal storage. Moreover, where possible, the coal preparation steps should be carried out rapidly and in as few steps as possible to minimize oxidation of the coal. Sample containers used should have airtight lids to guard against moisture loss and exposure of the coal to air. In addition, the containers should be selected to hold only the desired amount of sample and to leave a minimum of air space. Even then, analysis of a sample should be carried out as soon as possible after it is received. Prolonged storage before analysis is often disadvantageous.

The effect of fines content on the combustion of pulverized coal is quite dramatic (Field et al., 1967; Essenhigh, 1981) and the problems associated with collection of an unbiased sample of pulverized coal need attention (ASTM D197). Operating samples are often collected from the feedstocks to power plant boilers on a shift or daily basks for calculation of heat balances and operating efficiencies. Another objective of operating samples is to document compliance with air pollution emission regulations based on fuel composition.

3.4 WASHABILITY

Coal washing is a process by which mineral matter is removed from coal using any one of several washing processes to leave the coal as near mineral-free as is required by the buyer or by legislation. The degree of washing require and the method of washing is determined by the mineral matter content of the coal that has been determined previously on run-of-mine coal, which is raw coal as it leaves the mine prior to any type of crushing or preparation.

Mineral matter occurs in coal as in two clearly defined forms, *intrinsic mineral matter* and *extrinsic mineral matter*. The former is present in intimate association with the pure coal substance itself and originated from inorganic material essential to the growth of the vegetable matter from which the coal was originally formed. Owing to its physical condition, such mineral matter cannot be separated from the coal substance by physical means but, since it seldom exceeds one percent, by weight, of the coal substance, it does not lead to undue difficulties with ash when the coal is burned in the normal way.

On the other hand, extrinsic mineral matter, which is purely adventitious, is derived from the roof and floor of the coal seam and from any non-coal or inorganic material that may be associated with the seam itself. It consists generally of pieces of stone, clay, and shale together with infiltrated inorganic salts that have become deposited in the natural fissures in the coal seam (e.g., pyrite, ankeritic material). Such material can be reduced very much in amount by suitable methods of coal cleaning and, indeed, may be completely separated from the coal, provided it can be broken apart from the coal particles.

In simplest terms, the gravimetric separation of light and heavy fractions is used to accomplish coal washing. This involves one or more float/sink tests, carried out on predesignated size fractions into which the coal is divided by screening. Solutions or suspensions of different specific gravities are used for the separations. This is performed repetitively with higher and higher specific gravity solutions, separating the size fraction into gravity fractions. The coal is generally of lower density than the mineral matter and these gravity fractions thus generally exhibit higher and higher ash content. Each size fraction and each gravity fraction is dried, weighed, and analyzed. The analysis is usually made for ash and sulfur content but is frequently extended to include heating value and other variables.

In the test method for determining the washability characteristics of coal (ASTM D4371), the need for a standard procedure to conduct washability analyses that will serve as an aid to technical communication to coal suppliers and purchaser is recognized. This test method standardizes procedures utilized for performing washability analyses, from the data which can be used for interpreting preparation plant efficiency, for determining preparation plant design, and for determining the potential recovery and quality of coal reserves. This test method describes procedures for determining the washability characteristics of coarse-coal fractions and fine-coal fractions. Each sample being tested can have more than one coarse-coal size fraction and more than one fine-coal size fraction (ASTM D 4749 provides a test method for the sieve analysis of coal).

In this test method (ASTM D4371), the specific gravity fractions are obtained by subjecting the material being studied to a series of solutions, each with a discrete specific gravity, that cover the range of specific gravities in question. These solutions are obtained by the mixing of various organic liquids that are relatively inert toward the coal. The distribution, as determined by the analysis, is affected by the physical condition of the sample subjected to the washability analysis, for example, the moisture content and the size content of the material. Furthermore, this method may not be the most technically correct test method to determine washability characteristics of low-rank coals because of problems relative to the loss of moisture through drying during sample preparation and analysis. Methods that are directly applicable to low-rank coal are not yet available.

The testing procedure consists of washing the coal in a hand jig or subjecting it to a series of various organic liquids of increasing specific gravity. Although certain closely sized portions of a coal sample may show washing characteristics quite different from those of other portions of the same sample, it is customary in practice to have to examine the characteristics of a sample containing all size ranges simply as a whole. A *hand jig*, consisting of a Henry tube, is suitable for moderately small graded coals (Figure 3.5). The jig, or moving portion of the washer, is a brass tube about 30 in. long and 4–6 in. diameter, fitted with handles at the top and having a gauze bottom (ca. 40 mesh), held in position by two set screws and a reinforcing disc, all of which form a loose bottom to the jig. The whole apparatus is immersed in an outer vessel containing water. When jigging is complete, the samples are set aside to air-dry in a dust-free atmosphere and then weighed. Each sample is ground, the percentage of moisture and ash are determined and, from the results, a set of washability curves can be constructed.

The determination of the washability characteristics of coal by the float and sink (float-sink) method can be applied to coal of any particle size provided suitably large vessels to hold the larger lumps are available. Air-dried coal, not dry coal, should be used since the separation depends partly on the difference in specific gravity of the clean coal and dirt particles and the specific gravity, in turn, is dependent on the moisture content of the coal. If the coal is dried before the test is carried out, the conditions will then differ from those in the commercial washers and the results will be at variance with those obtained in practice.

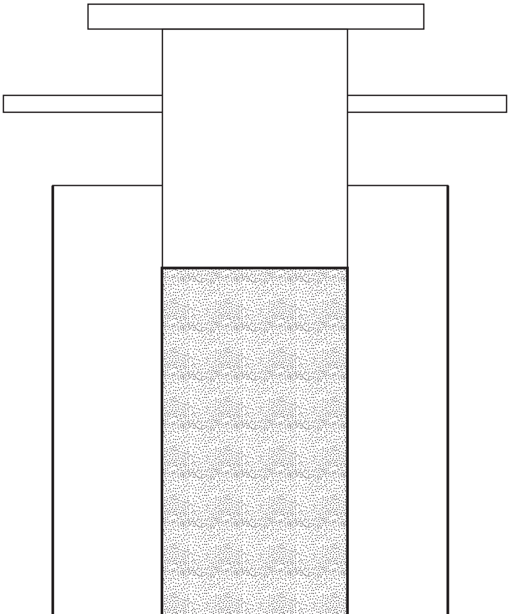

Figure 3.5 A Henry tube.

The solutions used are generally mixtures of organic liquids such as benzene (sp. gr. 0.88), toluene (0.87), carbon tetrachloride (1.60), and bromoform (2.90) and for most purposes a range of liquids from specific gravity 1.20 to 1.60 by increments of 0.05 is adequate. If the coal contains an appreciable quantity of large pieces, it is advantageous to separate the sample into two portions on a one-inch screen and wash the two fractions separately. The larger sized fraction may be suitably washed in increments in a tall glass cylinder, the floats removed as soon as separation is complete and the sinks removed from the bottom of the cylinder from time to time as the occasion demands.

It is customary to start with the lightest liquid and then to treat the sinks with the liquid of next higher specific gravity. The various fractions are then set aside to air-dry and are mixed with the corresponding fractions obtained by washing the coal of less than the one-inch or two-inch screen size. Care should be exercised when taking the original sample of coal of such wide size range for analysis that a thoroughly representative sample is obtained.

If the coal to be washed has no corresponding fraction over one inch, the sample is air-dried and a small representative portion is removed for determination of moisture and ash. Weighed portions of the coal are then treated with liquid of specific gravity 1.20 and, after the initial separation of floats and sinks, allowed to stand until separation is complete. The floats are filtered from the solution through a filter paper in a Buchner funnel and set aside to air-dry. The sinks are recovered in a similar manner and allowed to dry. The test is repeated with the other portions of the sample. All the floats are collected together as are the sinks. The air-dried sinks are subjected to a liquid of specific gravity 1.25, the floats are separated as before and the sinks are subjected to the next liquid, and so on until finally the sinks at, say, 1.60 are obtained. All samples are air-dried and weighed (combined with their corresponding samples of coal over\in. if necessary) and crush all or a portion of each sample for determination of moisture and ash.

If bromoform is used, it is best to wash the fractions after filtration with a little methyl alcohol to dissolve the bromoform since the high boiling point of bromoform (151 °C.) makes it difficult to remove completely by air-drying.

Furthermore, although it has been recommended that solutions of inorganic salts, for example, calcium chloride, zinc chloride, in water may be used to replace the more expensive organic solvents but it is almost impossible to remove these salts from the various fractions, even by much washing with water, with the result that the ash figures become less reliable.

With decreasing particle size, the practical feasibility of gravity separation diminishes because the efficiency of separation is reduced. Particularly in low-volatile coals, a substantial proportion of the coal may be lost in these fines if other means are not applied for separating them from the slime (clay) and recovering them. *Froth flotation* is one technique that is used for this purpose.

In principle, *froth flotation* consists of bubbling air through a suspension of fine coal and water to which various chemical agents have been added to improve the processes. The separation occurs by reason of a preferential physical attachment of air bubbles to the coal. The coal particles float to the top and are removed. The procedure is sometimes repeated, reprocessing the float fraction several times to simulate multistage full-scale froth flotation.

Selective flotation of one mineral in preference to another is accomplished by depositing on the grains of the first a film of a suitable reagent that will promote the flotation of that mineral. Reagents which condition the surface of a material in this manner are known as Collectors, those inducing the formation of a stable froth in which the material floated can collect are termed *frothers*, while reagents having the property of inhibiting the flotation of one or more constituents of a mixture are called Depressants.

Coal cleaning by froth flotation is applied essentially to those coals that are inherently soft and are generally obtained in a size range so small as to be difficult to treat by other methods of coal cleaning, which are based primarily on the differences in specific gravity between the clean coal particles and those of the reject material. Specially cleaned coking coals for use in the manufacture of coke for electrode carbons are usually prepared by froth flotation, the collectors employed being generally creosote oil fractions from coal tar, essential oils, pine oil, etc.

The mechanical processes involved in *jig washing* and in *float-sink* tests are those that yield a series of increments of the original coal with increasing mineral matter content. As a consequence, it is often found that the integrated ash for the whole sample differs appreciably from the value obtained by direct determination. This difference is the result of the ash being prepared under two sets of conditions. First, each separate increment is ashed (i.e., combusted so that the only residue is mineral ash) under conditions that differ from increment to increment because the mineral matter present on coal can change from one increment to the other. Second, the whole of the coal is ashed to give a certain reproducible ash yield obtainable from any average sample of the original coal. The divergence will be the greatest for those coals containing a large percentage of pyrite sulfur, especially if this is also associated with a high alkali or alkaline earth content. The divergence can be minimized, but not entirely eliminated, if the ashing processes are carried out in two stages as recommended in the proximate analysis.

The net result of the washability test methods is to subdivide coal into fractions having progressively mineral matter ash content and progressively increasing specific gravities. From the data furnished by the tests, the washability characteristics of the sample can be ascertained. These characteristics are most conveniently presented by the construction of the *washability curves* for the coal under examination.

Normally three curves are constructed for each coal: (1) the instantaneous ash curve or the coal characteristic curve, which gives the ash content of any of the individual layers into which the coal has, or can be, separated, (2) the integrated ash curve for clean coal, which gives the percentage yield of cleaned coal having an ash content of a certain amount and which gives the ash content of a mixture of any number of consecutive layers of cleaned coal from the top downward to a fixed layer, together with the corresponding yield expressed as a percentage of the original coal, (3) the integrated ash curve for dirt, which gives the percentage yield of reject material having an ash content greater than a certain amount, or gives the ash content of a mixture of any number of consecutive layers of dirty coal from the bottom layer upward to a fixed layer, together with the yield expressed as a percentage of the original coal.

If the coal contains fusain, this maceral will appear in the lightest fraction. If much is present, its relatively high mineral matter content may have such a weighted effect on the ash yield of the first fraction as to make it greater than the ash yielded by the second and indeed further fractions. As a result, the characteristic curve may develop a pronounced curvature upward and to the right at the top extremity. Fusain, and its disturbing effect, should not, however, be ignored because if the sample of coal washed is representative of the main bulk of coal to be washed, then the effect of the presence of the fusain must be acknowledged.

3.5 ACCURACY AND PRECISION

It is only through meticulous sample and sample preparation that accuracy and precision can be assured. In any form of analysis, accuracy and precision are required otherwise the analytical data are suspected and cannot be used with any degree of certainty. This is especially true of analytical data that are used for commercial operations where the material is sold on the basis of *purity*. Being a complex material, one may wonder about the purity of coal but in this sense the term purity refers to the occurrence (or lack thereof) of foreign constituents within the organic coal matrix. Such foreign constituents (impurities) are water, pyrite, and mineral matter. Therefore, at this point, it is advisable at this time to note the differences that are inherent in the terms *accuracy* and *precision*.

3.5.1 Accuracy

The word *accuracy* is used to indicate the reliability of a measurement, or an observation but it is, more specifically, a measure of the closeness of agreement between an experimental result and the true value. Thus, the accuracy of a test method is the degree of agreement of individual test results with an accepted reference value.

Accuracy is often expressed inversely in terms of the standard deviation or variance and includes any systematic error or bias. Accuracy includes both the random error of precision and any systematic error as well. The effect of systematic error on the standard deviation is to inflate it. In the measurement of coal quality for commercial purposes, accuracy expressed in this manner is generally of less interest than is systematic error itself. When systematic error is reduced to a magnitude that is not of practical importance, accuracy and precision can become meaningful parameters for defining truly representative sampling and for interpretation of the results of the various test methods.

Estimation of the limits of accuracy (deviation from a true or theoretical value) is not ordinarily attempted in coal analysis. Precision, on the other hand, is determined by means of cooperative test programs. Both repeatability, the precision with which a test can be repeated in the same laboratory, usually but not always by the same analyst using the same equipment and following the prescribed method(s), and reproducibility, the precision expected of results from different laboratories, are determined. Values quoted in test methods are the differences between two results that should be exceeded in only 5 out of 100 pairs of results, equal to $2\sqrt{2}$ times the standard deviation of a large population of results.

3.5.2 Precision

On the other hand, *precision* is a measure of the degree to which replicate data and/or measurements conform to each other, that is, it is the degree of agreement among individual test results obtained under prescribed similar conditions. Hence, it is possible that data can be very precise without necessarily being correct or accurate. These terms will be found throughout any text that is devoted to a description of standard methods of analysis and/or testing and have been (incorrectly) used interchangeably. Precision is commonly expressed inversely by the imprecision of results in terms of their standard deviation or their variance. Precision, by definition, does not include any systematic error or bias.

3.5.3 Repeatability

Repeatability is the difference between replicate determinations performed in duplicate within the same laboratory, by the same analyst, using the same equipment and the same prescribed methods. Replicate determinations are determinations performed separately and independently of each other. *Reproducibility* is the difference between results obtained by different laboratories performing their analyses by the same prescribed methods on splits of the same sample.

The specification of repeatability and reproducibility intervals, without specification of a statistical confidence level, weakens the precision and accuracy specifications to the extent that this leaves open to question the magnitude of the underlying variance. If, for example, the repeatability interval is never to be exceeded, the variance would have to be zero. From a practical standpoint, this is difficult, if not impossible. Furthermore, the variances (standard deviations) are of direct importance in regard to the details of performing sampling and testing operations because the overall variances can be partitioned into components associated with identifiable sources of variation. This permits assessment of the relative importance of specific details with regard to precision and accuracy. With regard to reproducibility, for example, there is a component of random variance that affects the degree of agreement between laboratories but does not affect the degree of agreement within laboratories (repeatability). Virtually nothing is known about this component of variance except that it exists, and the standard methods do not address this factor directly. However, recognition of it is evidenced in the standard methods by specification of reproducibility intervals that are universally larger than would be accounted for by the variances associated exclusively with the specified repeatability intervals.

In the overall accuracy of results, the sampling variance is but one component, but it is the largest single component. This is a matter of major importance that is frequently missed by the uninitiated. There are test methods (ASTM D2234; ISO 1988) that describe not only the procedure for the collection of a gross sample of coal but also the method for estimating the overall variance for increments of one fixed weight of a given coal. The precision is such that if gross samples are taken repeatedly from a lot or consignment and one ash determination is made on the analysis sample from each gross sample, 95 out of 100 of these determinations will fall within plus or minus one-tenth of the average of all the determinations. However, under some conditions, this precision may not be obtained and, in terms of performance, the statement should be held in the correct perspective.

At present, when multi-seam blended coal samples ranging from ten percent by weight mineral matter to as much as thirty percent by weight mineral matter occur, such precision could result in a corresponding difference as large as four to five percent with corresponding differences in the amount of ash that remains after combustion. The response to such concerns is the design of a sampling program that will take into consideration the potential for differences in the analytical data. Such a program should involve acquiring samples from several planned and designated points within (in this case) the coal pile so that allowance is made for changes in the character of the coal as well as for the segregation of the mineral matter during and up to that point in the coal history. This is, the sampling characteristics of the coal play an extremely important role in the application of text methods to produce data for sales.

For coal that is sampled is in accordance with standard methods (ASTM D2234; ASTM D4596; ASTM D4916; ASTM D6315; ASTM D6518) and with the standard preparation of the samples for analysis (ASTM D346; ASTM D2013), the overall variance of the final analytical data is minimized and falls within the limits of anticipated experimental difference.

3.5.4 Bias

The purpose of introducing the term bias into coal analysis is to endure the correctness of the analytical data. Understanding the terms *precision* and *bias* as used in quantitative test methods (ASTM E177; ASTM D3670; ASTM D6300; ASTM D6708) is a necessary part of ensuring the accuracy of the data produced by the analytical test methods.

The issue of testing for bias in a coal sampling system (ASTM D6518) is an essential part of coal analysis and is of significant importance (Gould and Visman, 1981). Accordingly, the term *bias* represents the occurrence of a systematic error (systematic errors) that is (are) of practical importance.

The measurement of systematic error is carried out by taking the differences of replicate results and, from a statistical standpoint, to detect a systematic error it is necessary to reduce the precision limits of the mean to a value less than some multiple of the standard deviation of the differences. Systematic error must be of a magnitude that is of practical importance in order to be classified as *bias*. Without proper experimental design, the systematic error may be of a magnitude that is of practical importance because of the various errors. These errors (errors of omission) render the data confusing or misleading and indicate the unreliability of the test method(s).

However, rather than attempt to remove all bias, the aim is to reduce the bias to acceptable levels where, in each case, it does not exceed a designated magnitude. Then the test for bias can be designed to confirm the presence of bias when the probability of a bias of that magnitude exists. Indeed, the nature of the problem is such that the absence of bias cannot be proven.

The issues of *relative bias* or *absolute bias* also need consideration. Relative bias, on the one hand is likely to involve comparisons of gross sample results while absolute bias, on the other hand, is where the measurement of bias is based on comparison with bias-free reference values and usually involves increment-by-increment comparisons.

The test for bias includes the following essential steps: (1) pretest inspection, (2) choice of test method specifications, (3) establishment of detailed procedures for conduct of the test method, (4) preliminary test method increment (sample) collection, processing, and analysis, (5) determination of number of observations required, (6) final increment (sample) collection, processing, and analysis, and (7) statistical analysis and interpretation of the data.

Each variable coal constituent or property to be examined requires assignment of a test method for that variable. As a practical matter, each constituent or property is determined by a test method that can often be viewed on a stand-alone basis. Furthermore, exclusive of moisture, all constituents should be evaluated on dry basis and using a standard size of the coal. Most constituents of coal are affected by errors in size distribution that are associated with size selectivity. Screen tests to obtain size distribution information, particularly in the tails of the size distribution (ISO 1953), can sometimes prove helpful but size is not always suitable as a test variable.

Once the data are available, certification of sampling systems as unbiased, without qualification, is insufficient and certification should also be accompanied by a statement of (1) the mean levels of each variable constituent that prevailed during conduct of the test, (2) the nominal sizing of the coal, and (3) some indication of the preparation (washing) to which the coal has been subjected, since these influence the sampling constants and may affect the magnitude of bias observed.

3.5.5 Method Validation

Finally, an important requirement in the practice of coal analysis is method validation, which is the process of defining an analytical requirement, and confirming that the method under consideration has performance capabilities consistent with what the application requires. Implicit in this is that it will be necessary to evaluate the performance capabilities of the laboratory performing the analysis. Therefore, the judgment of method suitability is not the only important aspect of coal analysis but the ability of the analytical laboratory to produce valid and correct data is just as important.

While it is implicit in the method validation process that the standards organizations (such as ASTM, ISO, and BSI) have performed the necessary studies to assure the validity of the method, it is also necessary to assure the clients that the laboratory and the laboratory personnel are equally capable of producing reliable data using the validated test method. This includes the use and reliability of the determination of the method performance parameters using equipment that is within specification, working correctly, and adequately calibrated. The operator carrying out the studies must be competent in the field of work under study and have sufficient knowledge related to the work to be able to make appropriate decisions from the observations. Furthermore, method validation is usually considered to be very closely tied to method development, indeed it is often not possible to determine exactly where method development finishes and validation begins. Many of the method performance parameters that are associated with method validation are in fact usually evaluated, at least approximately, as part of method development.

Thus, method validation is the process of proving that an analytical method is acceptable for its intended purpose. Methods for product specifications and regulatory submission must include studies on specificity, linearity, accuracy, precision, range, detection limit, and quantitation limit. The process of method development and validation covers all aspects of the analytical procedure and the best way to minimize method problems is to perform validation experiments during development. In order to perform validation studies, the approach should be viewed with the understanding that validation requirements are continually changing and vary widely, depending on the type of product under tested and compliance with any necessary regulatory group.

In the early stages of method development, it may not be necessary to perform all of the various validation studies. However, the process of validating a method cannot be separated from the actual development of the method conditions, because the developer will not know whether the method conditions are acceptable until validation studies are performed. The development and validation of a new analytical method may therefore be an iterative process. Results of validation studies may indicate that a change in the procedure is necessary, which may then require revalidation. During each validation study, key method parameters are determined and then used for all subsequent validation steps.

The first step in the method development and validation cycle should be to set minimum requirements, which are essentially acceptance specifications for the method. A complete list of criteria should be agreed on during method development and the end users before the method is developed so that expectations are clear. Once the validation studies are complete, the method developers should be confident in the ability of the method to provide good quantitation in their own laboratories. The remaining studies should provide greater assurance that the method will work well in other laboratories, where different operators, instruments, and reagents are involved and where it will be used over much longer periods of time.

The remaining precision studies comprise much of what is often referred to as *ruggedness*. *Intermediate precision* is the precision obtained when an assay is performed by multiple analysts using several instruments on different days in one laboratory. Intermediate precision results are used to identify which of the aforementioned factors contribute significant variability to the final result.

The last type of precision study is *reproducibility* that is determined by testing homogeneous samples in multiple laboratories, often as part of inter-laboratory crossover studies. The evaluation of reproducibility results often focuses more on measuring bias in results than on determining differences in precision alone. Statistical equivalence is often used as a measure of acceptable inter-laboratory results. An alternative, more practical approach is the use of *analytical equivalence* in which a range of acceptable results is chosen prior to the study and used to judge the acceptability of the results obtained from the different laboratories. Performing a thorough method validation can be a tedious process, but the reliability of the data generated with the method is directly linked to the application of quality assurance and quality control protocols, which must be followed assiduously (Quevauviller, 2002).

3.6 REPORTING COAL ANALYSES

Analyses may be reported on different bases (ASTM D3180; ISO 1170) with regard to moisture and ash content and a series of formulas are available for reporting the data (Table 3.1). Indeed, results that are *as determined* refer to the moisture condition of the sample during analyses in the laboratory; a frequent practice is to air-dry the sample, thereby bringing the moisture content to approximate equilibrium with the laboratory atmosphere in order to minimize gain or loss during sampling operations (ASTM D2013; ISO 1988). Loss of weight during air-drying is determined to enable calculation on an *as-received* basis (the moisture condition when the sample arrived in the laboratory). This is, of course, equivalent to the *as-sampled* basis if no gain or loss of moisture occurs during the transportation to the laboratory from the sampling site. Attempts to retain the moisture at the *as-sampled* level include shipping in sealed containers with sealed plastic liners or in sealed plastic bags.

Analyses reported on a *dry* basis are calculated on the basis that there is no moisture associated with the sample. The moisture value (ASTM D3173; ISO 331; ISO 589; ISO 1015; ISO 1018; ISO 11722) is used for converting the *as determined* data to the *dry* basis. Analytical data that are reported on a *dry, ash-free* basis are calculated on assumption that there is no moisture or mineral matter associated with the sample. The values obtained for moisture determination (ASTM D3173; ISO 589) and ash determination (ASTM D3174) are used for the conversion. Finally, data calculated on an *equilibrium moisture* basis are calculated to the moisture level determined (ASTM D1412) as the equilibrium (capacity) moisture.

Hydrogen and oxygen reported on the moist basis may or may not contain the hydrogen and oxygen of the associated moisture and the analytical report should stipulate which is the case because of the variation in the conversion factors. These factors apply to calorific values as well as to proximate analysis and to ultimate analysis.

When hydrogen and oxygen percentages do contain hydrogen and oxygen of the moisture, values on the dry basis may be calculated according to the formulas:

$$H_d = (H^1 - 0.1111M^1) \times 100/(100 - M^1)$$

$$O_d = (O^1 - 0.8881M^1) \times 100/(100 - M^1)$$

H_d and O_d are weight percent of hydrogen and oxygen on the dry basis, and H^1 and O^1 are the given or determined weight percent of hydrogen and oxygen, respectively,

TABLE 3.1 Formulas Used for Reporting Coal Analysis (ASTM D3180)

1. For conversion from the as-determined (ad) basis to the as-received (ar) basis (all values are expressed in weight percent). For moisture (A/),

$$M_{ar} = M_{ad} \times (100 - ADL/100) + ADL$$

ADL = air-dry loss in weight percent of as-received sample)

2. For hydrogen (H) and oxygen (O), including the hydrogen and oxygen in the moisture associated with the sample:

$$H_{ar} = (H_{ad}, - O.1119\ M_{ad}) \times (100 - ADL/100) + 0.1119\ M_{ar}$$
$$O_{ar} = (O_{ad} - 0.8881\ M_{ad}) \times (100 - ADL/100) + 0.8881\ M_{ar}$$

3. For hydrogen and oxygen not including the hydrogen and oxygen in the moisture associated with the sample,

$$H_{ar} = (H_{ad} - 01119\ M_{ad}) \times (100 - ADL/100)$$
$$O_{ar} = (O_{ad} - 0.8881\ M_{ad}) \times (100 - ADL/100)$$

4. For converting from the as-determined to the dry (d) basis, the following formulas are applied to hydrogen and oxygen:

$$H_d = (H_{fl}, - 0.1119\ M_{ad}) \times (100/100 - M_{ad})$$
$$O_d = (O_a, - 0.8881\ M_{ad}) \times (100/100 - M_{ad})$$

5. For converting all other parameters from one basis to another, the following general formula is applied when using the appropriate conversion factor:

$$P_{wanted} = P_{given} \times \text{conversion factor}$$

Note: The parameters must be expressed as a weight percentage, except gross calorific value, which is expressed as Btu/lb.

for the given or determined weight percent of moisture M^1. Rearrangement of these equations to solve for H^1 and O^1 yields equations for calculating moisture containing hydrogen and oxygen contents H^1 and O^1 at any desired moisture level M^1.

The mineral matter in coal loses weight during thermal conversion to ash because of the loss of water of constitution of clays, the loss of carbon dioxide from carbonate minerals such as calcite, and the oxidation of pyrite (FeS_2) to ferric oxide (Fe_2O_3). In addition, any chlorine in the coal is converted to hydrogen chloride but the change in weight may not be significant.

Analyses and calorific values are determined on a mineral matter-free basis by the Parr formulae (ASTM D388) with corrections for pyrite and other mineral matter.

The amount of pyrite is taken to be that equivalent to the total sulfur of the coal, which despite the potential error, has been found to correlate well in studies of mineral matter. The remaining mineral matter is taken to be 1.08 times the weight of the corresponding (iron oxide free) ash:

$$\mathrm{mm} = 1.08\mathrm{A} + 0.55\mathrm{S}$$

In this equation, mm, A, and S are weight percent of mineral matter, ash, and total sulfur, respectively.

Such data are necessary for calculation of parameters in the classification of coal by rank and which are dry, mineral matter-free volatile matter (or fixed carbon) as well as moist mineral matter-free gross calorific value. For volatile matter and fixed carbon data, it is also necessary to assume that 50% by weight of the sulfur is volatilized in the volatile matter test and therefore should not be included as part of the organic volatile matter (nor should the loss from clays and carbonate minerals):

$$\mathrm{FC}_{\mathrm{dmmf}} = 100(\mathrm{FC} - 0.15\mathrm{S})/[100 - (\mathrm{M} + 1.08\mathrm{A} + 0.55\mathrm{S})$$
$$\mathrm{VM}_{\mathrm{dmmf}} = 100 - \mathrm{FC}$$

$\mathrm{FC}_{\mathrm{dmmf}}$ and $\mathrm{VM}_{\mathrm{dmmf}}$ are the fixed carbon and volatile matter, respectively, on a dry, mineral matter-free basis; FC, M, A, and S are the determined fixed carbon, moisture, ash, and total sulfur, respectively.

In the Parr formula for moist, mineral matter-free calorific value, the moisture basis used is that of the inherent moisture of the coal in the seam (natural bed moisture, capacity moisture):

$$\text{Moist, mm} - \text{free Btu} = 100(\mathrm{Btu} - 50\mathrm{S})/[100 - (1.08\mathrm{A} + 0.55\mathrm{S})]$$

Btu is the calorific value (Btu/lb), A is the ash (% w/w), and S is sulfur (% w/w); all are on the moist (natural bed) basis. Coal analyses are generally reported in tabular form and the data can be represented graphically (Speight, 2013a).

3.7 INTERRELATIONSHIPS OF THE DATA

Just as a relationship exists between the various properties of petroleum with parameters such as depth of burial of the reservoir (Speight, 2014), similar relationships exist for the properties of coal (Speight, 2013a). Variations in hydrogen content with carbon content or oxygen content with carbon content and with each other have also been noted. However, it should be noted that many of the published reports cite the variation of analytical data or test results not with rank in the true sense of the word but with elemental carbon content that can only be approximately equated to rank.

Other relationships also exist, such as variations of natural bed moisture with depth of burial as well as the variations in volatile matter content of vitrinite macerals obtained from different depths (Speight, 2013a). This latter observation (i.e., the decrease in volatile matter with the depth of burial of the seam) is a striking contrast to parallel observations for petroleum where an increase in the depth of the reservoir is accompanied by an increase in the proportion of lower molecular weight (i.e., more volatile) materials. Similarly, the tendency to a carbon-rich material in the deeper coal seams appears to be in direct contrast to the formation of hydrogen-rich species (such as the constituents of the gasoline fraction) in the deeper petroleum reservoirs. Obviously, the varying maturation processes play an important role in determining the nature of the final product, as does the character of the source material (Speight, 2013a).

Finally, it is also possible to illustrate the relationship of the data from proximate analysis and the calorific value to coal rank.

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4

MINERAL MATTER

4.1 INTRODUCTION

Coal is a sedimentary rock composed of three categories of substances: (1) organic carbonaceous matter – macerals, (2) inorganic (mainly crystalline) minerals, and (3) fluids (Chapters 1 and 2) (Speight, 2013a). The latter occur in pores within and between the other two solid constituents. The fluids in coal prior to mining are mainly moisture and methane. Thus, in addition to organic matter, coal also contains a significant proportion of inorganic material in the form of minerals and other inorganic contaminants, collectively referred to as mineral matter. When applied to coal, the term *mineral matter* is an inclusive term that refers to the mineralogical phases as well as to all other inorganic elements in coal, that is, the elements that are bonded in various ways to the organic (C, H, O, N, S) components.

Coal preparation is aimed at reducing the quantity of mineral matter and the efficient use of the methods chosen depends on its concentration and composition. However, no matter how effective the coal preparation technique, there is always a significant amount of residual mineral matter. This residual material is of considerable importance in coal utilization and the amount of residual mineral matter (that may be site dependent) is intimately associated with the organic components and becomes involved in various ways when the coal is finally used. In fact, the mineral portion of coal has been largely ignored for too many years and it is only within the last four decades that the analysis of coal ash for environmentally hazardous trace elements has become an analytical *must do task* because of the consequences of release into the atmosphere during combustion (Grieve and Goodarzi, 1993;

Handbook of Coal Analysis, Second Edition. James G. Speight.

Forsythe et al., 1994; Bhangare et al., 2011). Mineral matter must be considered an integral part of the coal structure and so the ash (and its contents) must also be given consideration when a use is designed for coal.

The inorganic constituents of coal are often expressed in the form of ash yield – which is often incorrectly referred to as ash-in-coal instead of the more correct term: *the ash-forming propensity of coal*. Briefly, the general term mineral matter as it applies to coal science and technology is a widely used, but often misrepresented (and even misinterpreted) expression insofar as the terms mineral matter and ash are often used interchangeably. This is, of course, incorrect since ash is, in reality, the residue remaining after complete combustion of the organic portion of the coal matrix to carbon dioxide and water, etc. Thus, the constituents of ash do not occur as such in coal but are formed as a result of chemical changes that take place in the mineral matter during the combustion (*ashing*) process. These changes usually involve the breakdown of complex chemical structures (such as can occur in clays and many minerals) with the formation of the metal oxides.

Furthermore, it is often necessary to express the amount of an inorganic constituent relative to the potential to produce environmental emissions during coal use – as exemplified by the amount of sulfur dioxide produced during combustion (Speight, 2013a, b). Furthermore, many of the elements that may be of environmental concern occur in the fly ash after coal combustion and, in the case of power plants using flue-gas desulphurization (FGD) systems, in the flue gas desulfurization (or scrubber) by-products (Speight, 2013a, b). Coal beneficiation processes prior to utilization (Speight, 2013a) generally serve as a means of reducing the levels of some mineral elements. Such elements – especially those that occur at significant levels in the residue from utilization processes – can cause waste control or waste disposal problems, such as leaching into the environment following ground water or surface water infiltration.

Thus, minerals in coal have been, and continue to be, a subject of much interest (Golightly and Simon, 1989). Early studies approached the subject somewhat indirectly by means of chemical analysis of high temperature ash and back calculation to obtain estimates of the mineral matter. Others supplemented chemical studies by hand picking the coarser minerals or performing density separations for chemical tests and optical microscopic studies. With the introduction of radio frequency ashing at low temperature ($<150\,°C$), it became possible to directly investigate all of the mineral constituents (Miller, 1984).

4.2 ORIGIN AND OCCURRENCE

The term *mineral matter* refers to the inorganic constituents of coal and is all of the elements that are not part of the organic coal substance (carbon, hydrogen, nitrogen, oxygen, and sulfur) (Speight, 2013a). Furthermore, mineral matter is the principal source of the elements that make up the ash when the coal is burned in air or oxygen. Four of the five elements generally considered to be organic (carbon, hydrogen, oxygen, and sulfur) are also present in inorganic combination in coals. Carbon is present in mineral (usually calcium, magnesium, and iron) carbonates; hydrogen is present in free water and in water of hydration; oxygen is present a mineral in oxides, water, sulfates, and silicates; and sulfur is present in sulfides and sulfates.

Mineral matter in coal is usually classified as (1) *inherent mineral matter* and (2) *adventitious mineral matter*. *Inherent mineral matter* is the inorganic material that is too closely associated with the coal substance to be readily separated from it by methods available at present. *Adventitious mineral matter* is the inorganic material that is less intimately associated with the coal and can be readily separated. There are also suggestions that the minerals transported and deposited into the peat swamp by wind and water should be called *allogenic mineral matter* or *detrital mineral matter*, and that the remaining minerals, all of which formed in place (*authigenic mineral matter*), should be divided into those that formed contemporaneously with coal formation (*syngenetic mineral matter*) and those whose formation followed the initial stages of coalification (*epigenetic mineral matter*).

Mineral matter generally represents a significant proportion of coal composition and the amount of mineral mater in coal varies from seam to seam, even along the same seam. The mineral matter content of coal varies considerably and may even be as high as 35% w/w of the coal and although a reasonable value for the *average* amount of mineral matter is much lower, caution is advised when using *average* numbers. The average usually bears no relationship to reality where the range can vary from considerably below the average to considerably above the average. Coal performance on the basis of the average may be acceptable but use of coal with a much higher mineral matter content than the average value may cause considerable problems in a power plant. Generally, mineral matter in coal (whatever the content) is considered both undesirable and detrimental in coal utilization and the presence of mineral matter affects almost every aspect of mining, preparation, transportation, and utilization.

The composition of the mineral matter in the coal (or the composition of the mineral ash after combustion) is of importance for, as examples, the performance of design of post-combustion clean-up equipment, such as electrostatic precipitators and flue gas desulfurization units (Kelly and Spottiswood, 1982, 1989; Hjalmarsson, 1992). The alkali metals (sodium, potassium, and lithium) affect (decrease) the resistivity of the ash and can influence sulfur removal. Aluminum, silicon, and iron can influence the size of the electrostatic precipitator. But, moreover, the fly ash can cause degradation of any catalyst used downstream by blocking the pores as well as causing erosion. This is in addition to any possible detrimental effects of the mineral matter in a coal conversion plant. Again, catalyst poisoning as well as adverse catalytic effects of the mineral constituents on the process may occur (Jenkins and Walker, 1978). On the other hand, any potential beneficial catalytic effects of the mineral constituents of coal (especially in relation to conversion processes) also need evaluation and precise definition. Furthermore, ash fusibility can be strongly influenced by differences in calcium, magnesium, and iron content. Too high a magnesium content can cause clinkering troubles leading to magnesia swelling (Mackowsky, 1968).

While many environmental issues focus on the discharge of gaseous material such as sulfur oxides and nitrogen oxides (Speight, 2013a, b, 2014), the discharge of mineral slag to the surrounding environment is also cause for concern. The constituents of these slags and their relative toxicity to the flora and fauna, not only in the immediate vicinity of the plant but also in areas quite remote from the plant, are also cause for concern. In addition, it is quite possible that the toxic materials can be transported by surface and ground waters as well as by the prevailing winds (e.g., sulfur dioxide and fly ash).

Coal may also be recognized as a source of valuable elements and inorganic materials. For example, coal may provide a supply of uranium or other desired elements while the production of sulfur from coal (by conventional gas-cleaning methods) is also feasible. Hence, it is now recognized to be an essential aspect of coal analysis and that the nature of the mineral constituents of coal be more thoroughly understood in order to evaluate the nature of the inorganic material, for example, fly ash and discharge, produced when coal is employed as a fuel or feedstock (Babu, 1975; Braunstein et al., 1977; Given and Yarzab, 1978; Quast and Readett, 1991; Straszheim and Markuszewski, 1991).

Knowledge of the type of mineral matter and its constituents is an extremely important aspect of the analytical chemistry of coal. When coal is combusted, mineral matter undergoes major changes that lead to problems of clinker formation, fly ash, slagging, and boiler tube corrosion (Speight, 2013a, b). In fact, the efficiency of a combustion unit is related to the amount of ash produced, since it is a diluent. On the positive side, ash has been utilized as a construction material and is a possible source of refractory materials, as cement additives, or as adsorbents for gas cleaning processes. However, the composition of the ash must be known before it can be utilized in this way.

One of the principal impediments to the study of mineral matter in coal has been the difficulty of obtaining statistically valid (representative) samples of the mineral phases that are free of organic matter. At first glance, it appears that it would be simple to separate minerals from coal by specific gravity techniques. Coal, the organic portion, has a low specific gravity (in the range 1.2–1.4), whereas the minerals occurring in coal have specific gravity of 2–5 and greater. The finely disseminated nature of the minerals in coal precludes their complete separation, however. An incomplete separation based on specific gravity, which is the basis of many *coal cleaning* or *coal washing*, processes, is effective in fractionating the sample into some portions that are relatively mineral rich and some that contain relatively organic rich (Speight, 2013a, b). Specific gravity can be utilized to determine modes of occurrence of chemical elements and minerals in coal and this makes the procedure important but the procedure will most likely not provide an acceptable representative sample of minerals in coal.

4.2.1 Origin

Mineral matter originates from the inorganic constituents of the vegetation, which acted as the precursor to coal and from the mineral matter that was transported to the coal bed from a remote site. Thus, mineral matter in coal has often been classified as inherent and extraneous mineral matter (Francis, 1961; Stach et al., 1982; Spears and Zheng, 1999).

The *inherent mineral matter* is that mineral matter which had its origin in the organic constituents of the plant giving rise to the coal bed but the *extraneous mineral matter* was brought into the coal-forming deposit by mechanical means from outside, for example, as dust by air or as suspended or dissolved material carried by water. The inherent mineral matter is also sometimes defined as the inorganic material combined with the organic coal substance, but such material need not be derived from the coal-forming plants.

The inherent mineral matter is usually much smaller in quantity than the extraneous mineral matter and can be expected to differ quite markedly in composition from the inorganic residue of the major coal-forming plant types. This is due (in no small part) to re-use of the inorganic elements by succeeding vegetation and to leaching of inorganic constituents by the waters percolating and flowing through the peat bog during coalification. The percolating waters may be presumed to have an increased dissolving action on the inorganic constituents because of their content of humic acids (Stevenson and Butler, 1969), carbon dioxide, and other products of decay. Furthermore, the differences in solubility and reactions of the inorganic elements present in the plants dictate that these elements not contribute to the coal mineral matter in proportion to their presence in the plant material.

There has been considerable discussion and conjecture about the origin of the so-called inherent and extraneous mineral matter in coal. Indeed, it is in regard to this particular aspect of coal technology that many researchers find this terminology not only misleading but also difficult to apply, especially to those minerals that are contemporaneous with the peat bog in which the coal was formed; such minerals may not have been incorporated into the plant matrix prior to the formation of the coal bed. In fact, the intimate interrelationship between coal and mineral matter can only be adequately explained if it is accepted that the mineral matter became part of the coal matrix either during the early stages of coalification in the peat bog or at some early stage of the subsequent maturation process.

Mineral matter that originated within the immediate environs of the peat bog is often referred to as *authigenic mineral matter* whereas mineral matter that was transported by water or by wind is often referred to as *allogenic mineral matter*. The additional term *syngenetic mineral matter* (Speight, 2013a) is also applied to mineral matter that may have been transported into future coal deposits (i.e., this mineral matter was not a part of the plant substance that contributed to the coal precursor nor was it introduced during the coalification process) by water or wind. On the other hand, *epigenetic mineral matter* refers to that material which was deposited into the peat bog by descending (or ascending) solutions in cracks or fissures or in the bedding planes of the coal; such mineral matter may often be found as cleat fillings (Spears and Caswell, 1986).

4.2.2 Occurrence

Mineral matter is common to all types of coal and it has been recognized from the time when coal was first mined for general use that coal contained some material other than the main (organic) coal substance. The presence of the mineral matter is even more apparent when the coal is examined in-place in the seam, after being mined or finally prepared for market, and, finally, when the residue from its combustion is examined. In the bed, extraneous matter is apparent as definite horizontal layers of varying thickness and extent, as surface deposits or fillings in the vertical cleats, and more unusually as intrusions of clay-like (or other) material which occurs irregularly throughout the coal deposit. Furthermore, these horizontal layers that attain a considerable thickness may serve as a means of separating different coals or simply as separating the different phases of formation of one particular coal. However, bands of this type are always regarded as being formed during the deposition of the coal precursors.

The most common minerals in coal (e.g., illite clay, pyrite, quartz, and calcite) are made up of these most common elements (in rough order of decreasing abundance): oxygen, aluminum, silicon, iron, sulfur, and calcium. These minerals and other less common minerals usually contain the bulk of the trace elements present in coal (Abernethy and Gibson, 1963; Finkelman, 1982; Finkelman, 1993; Davidson and Clarke, 1996; Davidson, 2000). Although much is known about the minerals in coal, much remains to be learned about their occurrence, abundance, origin, and composition. For example, the type of clay mineral in a coal, whether montmorillonite or illite, determines how a coal will react when burned. Montmorillonite may or may not break down (dissociate) into its constituent parts when coal is burned; if it does dissociate, then, upon cooling, it may recombine with other elements or minerals to form mineral deposits on the inside surfaces of furnaces and boilers. This process (*slagging* or *fouling*) produces barriers to heat exchange in the affected equipment, which can substantially reduce its efficiency and require costly repairs. Illite, however, with its simpler composition, does not cause such problems under normal furnace operating conditions.

Obviously, the amount and type of minerals found in coal varies widely and depends on the coal history. The most abundant minerals are the clay minerals of which illite, kaolinite, and montmorillonite occur most frequently. Pyrite is the common sulfide mineral while sulfates are relatively rare but increase with weathering. Carbonates form readily in nonacid areas (dolomite and ankerite are encountered frequently) and quartz (which is found virtually in all coals) may occur in concentrations as high as 20% w/w of the total mineral matter. Sulfide minerals often constitute as much as 25% of the coal mineral matter.

Moreover, there may be regional variations in the mineral distribution in coal and even a cursory examination of the major minerals that occur within the coal matrix presents only a general indication of the vast number of metals that can occur in coal. Even though less than twelve elements usually constitute the major portion of coal ash (Table 4.1), there are many individual mineral elements present which (on the basis that a *trace element* is a particular element that occurs in concentrations of less than 0.1%; <1000 ppm) in the earth's crust are classified as trace elements (Finkelman, 1982, 1993).

Extensive chemical analyses on coals have shown that elements with relatively large ranges of concentrations (e.g., arsenic, As; barium, Ba; cadmium, Cd; iodine, I; lead, Pb; antimony Sb; and zinc, Zn) include those that are found in coals within

TABLE 4.1 Common Inorganic Constituents of Coal Ash[a]

Constituent[b]	% w/w
Alumina (Al_2O_3)	20–60
Calcium oxide (CaO)	1–15
Carbon	0–2 (depending on the furnace temperature)
Iron oxide (FeO)	2–15 (often inversely related to the amount of Fe_2O_3)
Iron oxide (Fe_2O_3)	2–25
Magnesium oxide (MgO)	0.5–4
Manganese oxide (MnO)	0–2
Phosphorus pentoxide (P_2O_5 as phosphate)	0–1
Potassium oxide (K_2O)	0.5–3
Silica (SiO_2)	40–90
Sodium oxide (Na_2O)	0.5–3
Sulfur trioxide (SO_3 as sulfate)	0.5–10
Titanium dioxide (TiO_2)	0–2

[a] Fly ash and bottom ash which are subcategories of coal ash have different sub-ranges for the oxides presented in the table.

[b] Listed alphabetically rather than by occurrence.

sulfate and sulfide minerals. In addition, many elements appear to be positively correlated in coals such as calcium and manganese, zinc and cadmium, the chalcophile elements (i.e., those elements which commonly form sulfides; such as cobalt, Co; nickel, Ni; lead, Pb; and antimony, Sb) and the lithophile elements (i.e., those elements that commonly occur in silicate phases, such as silicon, Si; titanium, Ti; aluminum, Al; and potassium, K).

4.3 MINERAL TYPES

A variety of minerals have been reported to be present in coals although many occur infrequently and are not regularly found in all coals or may be detectable only in trace amounts in various suites of coals (O'Gorman and Walker, 1971; Gluskoter, 1975; Gluskoter et al., 1977; Finkelman, 1982; Roscoe and Hopke, 1982; Finkelman 1993; Filippidis et al., 1996). A large number of distinct mineral phases have been reported in various coals although lists of minerals in coal may contain as many as 50–60 minerals, most fall into one of five groups: (1) aluminosilicate minerals, which are clay minerals, (2) silicate minerals, which are principally quartz minerals, (3) carbonate minerals, (4) sulfide and sulfate minerals, and (5) other minerals that include minerals that may occur in trace amounts or may be specific to a particular coal having originated because of the localized deposition and maturation conditions (Speight, 2013a).

The complex environmental conditions that occur at the time the organic detritus is laid down of and the geological upheaval that may have occurred during the

TABLE 4.2 Minerals Commonly Occurring in or Associated with Coal

Mineral-Type	Approximate Molecular Composition
Clay minerals[a]	
Illite	$KAl\cdot(AlSi_3O_{10})(OH)_2$
Kaolinite group	$A1_4Si_40_{10}(OH)_8$
Montmorillonite	$Na_2(Al\cdot Mg)(Si_4O_{10})(OH)_2$
Smectite	$A1_2Si_40_{10}(OH)_2$
Sulfides	
Marcasite	FeS_2 (orthorhombic)
Pyrite	FeS_2 (isometric)
Sphalerite	ZnS
Carbonates	
Ankerite	$CaCO_3\cdot MgCO_3\cdot FeCO_3$ $[CaCO_3\cdot Mg\cdot Fe\cdot Mn)CO_3]$
Calcite	$CaCO_3$
Dolomite	$CaCO_3\cdot MgCO_3$
Siderite	$FeCO_3$
Oxides	
Hematite	Fe_2O_3
Quartz	SiO_2
Other minerals	
Barite	$BaSO_4$
Feldspar	$(K\cdot Na_2)_2O\cdot Al_2O_3\cdot 6SiO_2$
Gypsum	$CaSO_4\cdot 2H_2O$
Halite	$NaCl$
Phosphates	$Ca_{10}(PO_4)_6(OH)_2$
	$Ca_{10}(PO_4)_6(F)_2$
	$Ca_{10}(PO_4)_6(Cl)_2$

[a] Individual minerals are listed alphabetically within each mineral group.

maturation process can play an important role in determining which minerals survive in coal (Cecil et al., 1982). Nevertheless, the large majority of minerals found in coal can be classified into several types, such as shale, kaolin compounds, sulfide derivatives, and carbonate derivatives (Table 4.2).

4.3.1 Clay Minerals

Clay minerals are the most commonly occurring inorganic constituents of coals (Gluskoter, 1975) (as well as the strata associated with coals) and, therefore, can act as the source of a wide variety of metals in substantial or trace amounts. Many different clay minerals have been reported within and associated with coal – the most common clay minerals found in coals are kaolinite and illite while montmorillonite, chlorite, and sericite have also been regularly reported to occur in various

TABLE 4.3 Various Minerals of the Clay Minerals Groups

Group	Minerals
Kaolinite	Kaolinite Dickite Nacrite Halloysite
Smectite	Bentonite Glauconite Montmorillonite Nontronite Pyrophyllite Saponite Sauconite Talc Vermiculite
Illite (Mica)	Illite Muscovite

types of coal. In addition, kaolinite-rich clay is commonly associated with coal in most of the coal basins of the world and is generally referred to as *tonstein* or *kaolin-tonstein*.

The name *clay* is often used in various contexts: (1) to indicate particle size (< 2 in.; < 0.005 mm), (2) to indicate a rock composed predominantly of clay minerals, and (3) as a name for a group of minerals, the clay minerals – the aluminosilicates minerals. In the context of this book, the last two categories are used. Furthermore, clay minerals are the most common inorganic constituents of coal and of the strata associated with coal seams.

Chemically, clay minerals are hydrated aluminosilicates, which are characterized by a sheet-like structure and can be conveniently divided into three groups: (1) the kaolinite group, (2) the montmorillonite group, and (3) the potash clay (or hydrous mica) group (Table 4.3). The kaolinite group all has the same chemical composition and differ only in individual crystal structures. The montmorillonite group can be represented by means of ion substitutions in the general chemical formula. For example, in montmorillonite itself, approximately 16% of the aluminum is substituted by magnesium and by other ions such as calcium, sodium, potassium, and hydrogen (as well as some additional magnesium).

4.3.2 Silicate Minerals

Silicate minerals (quartz, silica minerals) are a widely distributed mineral species consisting of silicon dioxide (silica, SiO_2) (Table 4.2). It is one of the most common minerals and is found in many varieties with very diverse modes of occurrence.

Quartz (SiO_2) is the dominant form in which silica is found in coals and it is ubiquitous. There is some distinction between clastic grains of quartz introduced by wind or water and authigenic quartz deposited from solutions. Quartz is also a major component of clay and siltstone partings in coal that are of detrital origin.

Quartz is a primary constituent of rocks such as granite, quartz, porphyry, and rhyolite. It is also a common constituent in many gneisses (laminate rocks) and crystalline schists (foliated rocks). It is also, in a sense, mobile since by the weathering of silicates, silica passes into solution and is redeposited in cavities, crevices, and along joints of rocks of all types. Thus, it is not surprising that quartz also occurs in all coals either by virtue of its proximity to the coal bed or by deposition at a later stage of coal formation.

4.3.3 Carbonate Minerals

Carbonate minerals are the salts of carbonic acid (H_2CO_3) and the extensive possibilities for interchanging the more common metals, such as calcium, magnesium iron, and manganese, is realized in the wide variety of carbonate minerals that occur in nature. Consequently, it is not surprising that a wide variety of carbonate minerals also occurs in coals (Table 4.2).

The major cations found in the carbonate minerals in coals are calcium, magnesium, and iron. The rather pure end member calcite ($CaCO_3$) is dominant in some coals whereas siderite ($FeCO_3$) is dominant in others. Calcite and ankerite (a mixed crystal composed of Ca, Mg, and Fe carbonates) are abundant in some coals. Calcite ($CaCO_3$) and siderite ($FeCO_3$) are commonly reported as constituents of the mineral matter in coals while the more complex carbonates dolomite ($CaCO_3 \cdot MgCO_3$) and ankerite ($2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$) are also frequently reported.

4.3.4 Sulfide and Sulfate Minerals

The *sulfide* minerals of particular importance here are the pyrite group (Table 4.4), which are essentially metal disulfides occurring in widespread locations and different crystalline forms; pyrite itself is found in large deposits in metamorphic rocks. The dimorphs pyrite (FeS_2) and marcasite (FeS_2) are the dominant sulfide minerals in

TABLE 4.4 Common Members of the Pyrite Group of Minerals

Mineral	Formula
Cattierite	CoS_2
Laurite	RuS_2
Marcasite	FeS_2
Pyrite	FeS_2
Vaesite	NiS_2
Villamaninite	$(Cu \cdot Ni \cdot Co \cdot Fe)S_2$

coal; pyrite is the more abundant. Pyrite and marcasite have different crystal forms; pyrite is isometric, and marcasite is orthorhombic. These two minerals are readily observed and, to some degree, easily removed as well as being especially interesting because they contribute significantly to the total sulfur content that causes boiler tube fouling, corrosion, and pollution by emission of sulfur dioxide when coal is burned (Beer et al., 1992).

The dominant sulfide mineral in coal is pyrite while marcasite has also been reported to be present in many types of coal. These minerals are dimorphic in that they are identical in chemical composition (FeS_2) but differ in crystalline form-pyrite is cubic whereas marcasite is orthorhombic. Other sulfide minerals that have been found (but to a lesser extent) in coals are galena (lead sulfide; PbS) and sphalerite (zinc sulfide; ZnS).

The related sulfate minerals are not as common as the sulfides and are not usually present in unweathered fresh) coals. Obviously, the anaerobic maturation of (the majority of) coals are not conducive to the formation of sulfates. For example, pyrite is markedly susceptible to oxidation and will decompose to iron sulfate minerals even under ambient conditions.

$$Fe_2S_3 + O_2 \rightarrow FeSO_4$$

The sulfate minerals identified in coal do not generally comprise a significant portion of the mineral matter in fresh, unoxidized coal samples. The iron disulfides oxidize rapidly after the coal is mined, however, and a number of hydrated sulfates ($FeSO_4 \cdot xH_2O$) have been reported in weathered coals and in coal refuse banks. The sulfates gypsum ($CaSO_4 \cdot 2H_2O$) and barite (Ba_2SO_4) are found in fresh coal. Most of the sulfates that form on weathering (oxidation) of pyrite are various hydrated states of ferrous and ferric sulfate.

4.3.5 Other Minerals

A large number of minerals, in addition to those already discussed, have been reported to occur in coal. Not all have been positively identified and often it is impossible to determine from the reports whether the mineral was intimately associated with the coal or was in the rock units making up the roof, floor, or a parting within the seam. Most of these other minerals are of limited significance in coal utilization, but a few are worth noting. Authigenic apatite [calcium fluoro-chloro-hydroxy phosphate, $Ca_5(PO4)_3 \cdot F \cdot Cl \cdot OH$] has been found in coal produced in widely separated areas of the world.

4.3.6 Effect of Mineral Matter on Coal Use

Mineral matter in coal is one of the most important sources of problems in coal combustion, including fouling, slagging, and corrosion. Mineral matter transformation and slag formation are specific properties of coal that provide more information on the suitability for coal combustion and/or gasification. For example, if the combustion products contain a significant fraction of molten ash particles, deposition on the turbine blades occurs which blocks the flow path and degrades performance and if the ash particles are solid, erosion of the blades occurs which also degrades performance. In addition, mineral matter can cause corrosion of the blades. The size distribution, concentration and composition of the ash, as well as the turbine design, determine the lifetime of the turbine blades.

When coal is burned, most of the mineral matter and trace elements generally form ash; however, some minerals break down into gaseous compounds which go out the furnace's flue. Pyrite, for example, breaks down into the individual elements such as iron and sulfur. Each element then combines with oxygen to become, respectively, iron oxide and sulfur dioxide. Iron oxide, a heavy solid, becomes part of the ash and sulfur dioxide is emitted as part of the flue gas. Some trace elements also dissociate from their organic or mineral hosts when coal is burned and follow separate paths. Most become part of the ash, but a few of the more volatile elements, such as mercury and selenium, may be emitted in the flue gas.

Furthermore, the mineral content of coal determines what kind of ash will be produced when it is burned. The fusion temperature (melting point) of the ash dictates the design of furnaces and boilers. In general, if the fusion temperature is relatively low, then the molten ash is collected at the bottom of the furnace as bottom ash, requiring one design; however, if the fusion temperature is relatively high, then the part of the ash that doesn't melt easily (*fly ash*) is blown through the furnace or boiler with the flue gas and is collected in giant filter bags, or electrostatic precipitators, at the bottom of the flue stack, requiring a different design.

Coal that is relatively rich in iron-bearing minerals (such as pyrite or siderite) has a low fusion temperature while coal relatively rich in aluminum-bearing minerals (such as kaolinite or illite) tends to have a high fusion temperature. If an electric generating or heating plant is designed to burn one type of coal, then it must continue to be supplied with a similar coal or undergo an extensive and costly redesign in order to adapt to a different type of coal. Similarly, furnaces designed to use coal that produces high amounts of heat will suffer severe losses in efficiency if they must accept coal that burns with substantially less heat.

For example, the different states of iron (Fe^{2+} or Fe^{3+}) are the dominant reason for different sintering behavior under different conditions. The iron-bearing minerals in ash, such as wustite (FeO), almandite ($3FeO{\cdot}Al_2O_3{\cdot}3SiO_2$), and fayalite ($Fe_2SiO_4$, also called iron chrysolite – chrysolite is magnesium-iron silicate, $Mg{\cdot}Fe{\cdot}SiO_4$), are the most important factors influencing ash sintering behavior because of the initial melting behavior during coal combustion.

4.4 EVALUATION

The use of coal as a fuel and the varied, often detrimental, effects of the mineral matter on the fuel properties of coal has been a source of concern for consumers (Alpern et al., 1984). Even the interactions of the mineral constituents themselves (Table 4.5) has directed interest toward the mineral constituents of coals but with the

TABLE 4.5 Reactions of Minerals at High Temperature

Mineral	Reaction
Carbonate	Loss of carbon dioxide Reaction of residual oxides with organic and pyritic sulfur Formation of sulfates
Clay	Release of water of hydration or water formed by the reaction Structural rearrangement
Oxides	Possible reaction with silicates or silica
Pyrite	In air, converted to ferric oxide (Fe_2O_3) and sulfur dioxide May also decompose to ferrous sulfide (FeS)
Sulfate	Elimination of water of hydration Elimination of sulfur trioxide Formation of metal oxide
Quartz	Typically no reaction – thermally stable Minor reaction with iron oxide

tendency to an increased use of coal for power generation as well as for gasification and conversion plants that will enable coal to act as a source of liquid and gaseous fuels. Therefore, methods by which the mineral matter can be evaluated have been a constant target for quantitative and qualitative improvement.

Furthermore, the broad definition which defines mineral matter as all elements in coal except carbon, hydrogen, nitrogen, oxygen, and sulfur needs some modification since four of these five elements occur in inorganic locations and are, therefore, part of the mineral matter. For example: (1) carbon occurs in carbonates; (2) hydrogen occurs in water of hydration, as well as in any free water in the coal; (3) oxygen occurs in carbonates, sulfates, and silicates as well as in water, in water of hydration, and free water in the coal; and (4) sulfur occurs in sulfates and sulfides, predominantly pyrite and marcasite.

There are several options available for the choice of an analytical technique, although in practice it may be necessary to use more than one technique because of the limitations of the various methods with respect to concentrations of the individual elements or the method may be determined by the amount of available sample. For example, application of any one of the conventional *wet* analytical methods (such as for the determination of silicates) may require up to 10 g of sample ash whereas a variety of spectrophotometric techniques may require only micrograms (1×10^{-6} g) of sample.

Finally, it must always be recognized that mineral matter in coal is the parent material in coal from which ash is derived. The amount of mineral matter in coal (as deduced from an *ashing technique*) is commonly calculated using data on ash and ash-forming constituents.

4.4.1 Ashing Techniques

There are many minerals in coal which will produce as ash residue and, although the ash composition varies around wide limits, the ash may appear to be composed of only a few of the more common elements but it is often the trace elements that can give ash some of its more obnoxious properties (Speight, 2013a, b).

The determination of the mineral matter content of coal (determined as mineral ash after combustion) has been an essential part of coal evaluation for many years (Rees, 1966; Given and Yarzab, 1978; Huggins et al., 1982; Nadkarni, 1982; Kishore Nadkarni 2008). For example, when coal is cleaned by various processes to reduce the sulfur and mineral content, it is an advantage to be aware of the mineral (ash) content to determine the best cleaning method insofar as the various cleaning methods have different tolerance levels for the mineral constituents of coal. Furthermore, the ash content is also a means of assessing the adequacy of the various sampling procedures (Chapter 3) and it is one of the criteria normally specified in contracts between a purchaser and a supplier of coal.

The amount of mineral matter in coking coal (Speight, 2013a) is an indication of the amount of ash that will eventually be part of the coke made from the coal. Thus, the higher the mineral matter content of the coal, the lower the proportion of usable carbon in the coke and the more the fluxing limestone that must be added to the furnace to assist in removal of the mineral matter that leads to ash formation. However, the fouling tendency of a coal is dependent upon several factors, not the least of which is the nature of the mineral matter and the resulting ash (Beer et al., 1992).

Similarly, the higher the mineral matter content, the lower the heat of combustion obtainable from a unit sample of coal. Hence the need for removal of mineral matter during cleaning and preparation operations (Speight, 2013a). A high mineral matter content also introduces additional problems such as a loss in the combustion efficiency as well as problems related to handling and disposing of larger amounts of mineral ash. Obviously, mineral matter in coal will (and often does) cause problems during utilization and measures to counteract any adverse effects that will arise from the presence of the mineral matter are necessary. On the other hand, the potential benefits that could arise from the presence of this same mineral matter should not be ignored; catalytic effects in processes designed for liquefaction and gasification of coal may be cited as examples (Speight, 2013a).

Mineral matter in coal is often determined indirectly with the ash analysis (determined by direct combustion of the sample) forming the basis of the calculation. However, determination and chemical analysis of the ash content of coal gives the average content of the inorganic elements in a particular coal but is not an indication of the nature or distribution of the mineral matter in coal. Nevertheless, ash analysis can provide valuable data which, when used with data from other sources, may give a representation of the mineral content of coal.

However, it must be emphasized that there has to be some attempt to recognize the limitations of the method before any projections relating to the mineral composition of coal is possible. For example, the high temperature required for the "ashing" may result in the loss of the volatile constituents of the minerals or the mineral constituents will undergo a chemical change. In the former case, certain of the mineral elements will escape detection while in the latter case the constituents of clays or shale (to cite an example) will lose water of hydration or the carbonate minerals will lose carbon dioxide and the oxides so produced may even undergo further reaction with sulfur oxides or with silica to produce completely different mineral species.

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SO_3 \rightarrow CaSO_4$$

$$CaO + SiO_2 \rightarrow CaSiO_3$$

At the same time, pyrite will be converted to ferric oxide and oxides of sulfur:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Any organically combined inorganic elements may be converted to the respective oxides and eliminated (e.g., nitrogen and sulfur) or may be retained in the ash (e.g., various metals that may be combined with an organic fragment). The pathways of these various reactions can be followed by differential thermal analysis which allows for the identification of the various minerals in more complex mixtures.

Unfortunately, there are limitations to the use of the analytical data derived from ashing techniques. For example, the indefinite amount of sulfur which may be retained in the ash will reduce the reliability of the experimental data values. Moreover, the ash yield as obtained by standard test methods is only an approximation of the noncombustible material in coal. The relationship of ash composition to clinkering, boiler tube slagging, and other high-temperature behavior of the mineral constituents is complex and can be difficult to interpret but these disadvantages should not detract from a method that does have some merits.

The determination of the yield of ash from coal is an essential part of coal evaluation (Rees, 1966; Given and Yarzab, 1978; Huggins et al., 1982; Nadkarni, 1982). However, ash, as stated earlier, is the residue remaining after burning the coal or coke under rigidly controlled conditions of sample weight, temperature, time, atmosphere, and equipment specifications. Thus, the mineral matter content of coal cannot be determined qualitatively or quantitatively from the ash that is formed when the coal is oxidized. High temperature ashing of coal at 750 °C (1382 °F) (ASTM D3174; ISO 1171) causes a series of reactions involving the reactions of the mineral matter (see below).

Ash, as determined by the standard test method (ASTM D3174), is the residue remaining after burning the coal and coke and differs in composition from the original inorganic constituents present in the coal. Incineration causes an expulsion of all water, the loss of carbon dioxide from carbonates, the conversion of iron pyrites into ferric oxide, and other chemical reactions. In addition, the ash, as determined by this test method, will differ in amount from ash produced in furnace operations and other firing systems because incineration conditions influence the chemistry and amount of the ash.

Approximately one gram of the sample (weight to the nearest 0.1 mg) that has been pulverized to pass through a No. 60 sieve (ASTM D2013) is placed in a cold muffle furnace and heated at such a rate that the temperature reaches 450–500 °C (842–932 °F) after 1 h. The heating is continued so that a final temperature of 700–750 °C (1292–1382 °F) is reached by the end of the second hour and heating is continued at this temperature for an additional 2 h. At the end of the heating period, the sample is removed from the furnace, covered, allowed to cool under conditions that minimize moisture pickup, and weighed. The yield of ash is determined by the formula:

$$\text{Ash, } \%\text{w/w} = [(\text{A} - \text{B/C}) \times 100$$

A is the weight of the sample container, cover, and ash residue, B is the weight of the empty sample container and cover, and C is the weight of the sample.

The 4-h incineration period is often sufficient for most coals to reach a condition of complete burn-off, certain non-reactive coals may require additional time. If unburned carbon is observed in the sample container or if duplicate results are suspected, the samples should be returned to the furnace for sufficient time to reach a constant weight. On the other hand, the 4-h time limit may be reduced if the sample reaches a constant weight in less time but caution is advised in using a reduced heating period and adherence to the 4-h time period is usually recommended.

Some coal samples contain a high amount of carbonates (calcite, $CaCO_3$) or pyrite (FeS_2) or both. In such cases, sulfur retained as sulfates may be both unduly high and non-uniform between duplicate samples. Sulfate sulfur in the ash can be determined (ASTM D1757) and the requisite correction made and the ash yield should be reported and designated both as determined and corrected.

A reliable method of measuring the mineral matter content of a coal is an acid demineralization procedure. The method depends on the loss of weight of a sample when treated with 40% hydrofluoric acid at 50–60 °C. Treatment of the sample with hydrochloric acid before and after the treatment with hydrofluoric acid helps prevent the retention of insoluble calcium fluoride (CaF_2) in the coal. Pyrite is not dissolved in the treatment, consequently, pyrite and a small amount of retained chloride must be determined separately. Since two-thirds of the mass of the pyrite (FeS_2) is accounted for by the presence of ferric oxide (Fe_2O_3) in the residual ash, the mineral matter content is then given by the formula:

$$\text{MM} = \text{weight loss} + \text{HCl} + |(\text{FeS}_2) + \text{residual ash}$$

4.4.2 Ash Analysis and/or Direct Mineral Analysis

The evaluation of coal mineral matter by the ashing technique can be taken further insofar as attempts can then be made to determine the individual metal constituents of the ash. On the occasion when the mineral matter has been successfully separated from the coal, it is then possible to apply any one (or more) of several techniques (such as X-ray diffraction, X-ray fluorescence, scanning electron microscopy, and electron probe microanalysis) not only to investigate the major metallic elements in coal but also to investigate directly the nature (and amount) of the trace elements in the coal (Jenkins and Walker, 1978; Prather et al., 1979; Raymond and Gooley, 1979; Russell and Rimmer, 1979; Jones et al., 1992).

However, when coal ash is prepared for complete analysis, it has been considered necessary to ensure that sulfur is not retained in the ash. If sulfur is retained in the ash, the analysis will most likely be inaccurate unless corrections of the data to a sulfur dioxide free basis are made. In addition, attempts must be made to ensure that important elements are not lost during the ashing procedure by virtue of the higher temperatures (ca. 850 °C, 1560 °F) that are used. In fact, a low-temperature ash sample can be of the order of 150% w/w of the high-temperature ash sample. In order to alleviate the issue of element loss by the use of high temperatures, various low-temperature ashing techniques have been developed. One method involves passage of *activated* oxygen (i.e., oxygen generated by passing commercial grade oxygen through a high-energy electromagnetic field produced by a radio-frequency oscillator) over a dry, finely ground coal sample. Throughout this whole procedure, the temperature typically remains below 200 °C (390 °F) and is usually in the range of 150–160 °C (300–320 °F).

The analysis of coal ash for major and minor elements is important for determining the ash chemistry – the current method (ASTM D3682) requires fusion of the sample with lithium tetraborate followed by analysis by atomic absorption spectrophotometry (AAS). Presently the list of routinely determined ash elements includes Si, Al, Fe, Ti, Ca, Mg, Na, K, P, and S. For our research samples, a more complete ash characterization is necessary so that elements such as Sr, Ba, Mn, and Zn are also determined. In addition, methods utilizing mixed-flux fusions are being evaluated to eliminate the need to use one flux (lithium metaborate) for highly siliceous ashes and another flux (lithium tetraborate) for ashes containing high contents of iron oxides. The variability in the ash chemistry is encountered when analyzing lignite ash versus bituminous coal ash. The determination of additional elements, coupled with the need to reduce analysis turnaround time, has prompted the evaluation of multi-element sequential and/or simultaneous determination systems such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) for coal ash analysis.

Thus, the determination of trace elements in coal ash is relatively straightforward and will be indicative of the trace element content of the coal if the particular trace element is not volatilized during ashing. The current method (ASTM D3683) utilizes ash generated at 500 °C (930 °F) the determinations of Be, Cu, Cr, Mn, Ni, Pb, V, and Zn by flame AAS. While flame AAS is satisfactory for most of the trace elements mentioned, many coal ashes contain levels of Pb and V that are just above the flame method detection limits; hence, quantification for those elements may contain some inaccuracies.

One other technique for the investigation of trace elements in coal applies the float-sink principle in which comminuted coal can be separated into several specific gravity fractions by flotation in mixtures of liquids such as perchloroethylene and naphtha; a liquid such as bromoform ($CHBr_3$) can also be employed for further subfractionation. In the methods, the crushed material is placed in a liquid with a density of 1.75 g/cc – the organic (coal) fraction floats and the non-coal (mineral matter) sinks and is removed. This procedure can be employed as a fractionation technique to remove significant proportions of the mineral matter from coal without resorting to the use of heat.

On the occasion when the mineral matter has been successfully separated from the coal, it is then possible to apply any one of several techniques (such as X-ray diffraction, X-ray fluorescence, scanning electron microscopy, and electron probe microanalysis) not only to investigate the major metallic elements in coal but also to investigate directly the nature (and amount) of the trace elements in the coal (Jenkins and Walker, 1978; Prather et al., 1979; Raymond and Gooley, 1979; Russell and Rimmer, 1979; Jones et al., 1992). Generally, no single method yields a complete analysis of the mineral matter in coal and it is often necessary to employ a combination of methods.

The wet chemical or *classical* procedures, including many colorimetric and some electrochemical procedures can be time-consuming. They are generally very accurate, however; they can be precise, and they do not require any special expensive equipment or facilities. However, these methods are less sensitive than some instrumental methods.

One issue that has already been mentioned is the amount of sulfur in the ash that is due to a high amount of carbonates (calcite, $CaCO_3$), or pyrite (FeS_2), or both, in the coal. Sulfur retained as sulfates may be both unduly high and non-uniform between duplicate samples. The reasons vary from inconsistencies in the furnace temperature and furnace ventilation that have an influence on sulfur trioxide retention in the ash. Consequently, sulfur in ash as determined in the laboratory cannot be assumed to be equivalent to sulfur present in the mineral matter in coal or to the retention of sulfur in ash produced under the conditions of commercial utilization.

Sulfate sulfur in the ash is determined (ASTM D1757) and the requisite correction made and the ash yield should be reported and designated both as determined and corrected. The sulfate sulfur so determined can be used to calculate the sulfur trioxide portion of ash so that the ash content or ash composition can be reported on a sulfur trioxide free basis.

In this method (ASTM D1757), a specified quantity of ash is digested in boiling dilute hydrochloric acid solution to which bromine water is added to convert sulfite that may be present to the sulfate form. After neutralization and precipitation of iron with ammonium hydroxide, the mixture is filtered and sulfate in the filtrate is determined gravimetrically as barium sulfate ($BaSO_4$). Alternatively, a specified quantity of ash and Eschka mixture are ignited together in air. The sulfates are dissolved in hot water and separated from undissolved ash residue and magnesium oxide by filtration. Sulfate in the filtrate is determined gravimetrically as barium sulfate ($BaSO_4$). However, barium in coal ashes can result in incomplete recovery of sulfate sulfur. High iron content in coal can introduce error if, during the sulfate precipitation, the iron is either partially adsorbed by the barium sulfate precipitate or is co-precipitated as iron sulfate.

A compositional analysis of the ash in coal is often useful in the total description of the quality of the coal. Knowledge of ash composition is also useful in predicting the behavior of ashes and slags in combustion chambers. Utilization of the ash by-products of coal combustion sometimes depends on the chemical composition of the ash. In addition, concern over release of certain trace elements to the environment as a result of coal utilization has made the determination of these elements an increasingly important aspect of coal analysis.

Major and minor elements in coal, having concentrations easily detectable by most modern analytical techniques, can be determined by a number of acceptable procedures. Various approaches, combining a number of specific procedures, are frequently referenced in the literature. For example, the presently accepted procedure (ASTM D2795) determines silicon, aluminum, iron, titanium, and phosphorus colorimetrically, calcium and magnesium chelatometrically, and sodium and potassium by flame photometry. This standard test method was withdrawn in 2001 but it still used in some laboratories.

Another test method (ASTM D3682) covers the analysis of the commonly determined major and minor elements (such as silicon, aluminum, iron, calcium, magnesium, sodium, potassium, and titanium) in laboratory coal ash and in combustion residues from coal utilization processes by atomic absorption/emission spectroscopy. In the test method, the ash sample or combustion residue to be analyzed is standardized by ignition in air at 750 °C (1382 °F) to a constant weight. The ash is fused within lithium tetraborate ($Li_2B_4O_7$) followed by a final dissolution of the melt in either dilute hydrochloric acid (HCl) or dilute nitric acid (HNO_3). The solution is analyzed by atomic absorption/emission spectroscopy for applicable elements. As always, the chemical composition of laboratory-prepared ash does not represent the composition of mineral matter in the coal or the composition of fly ash and slag resulting from commercial-scale burning of the coal but it is recommended that sulfur be determined by other test methods (ASTM D1757; ASTM D5016).

The less common elements in coal ash (e.g., beryllium, chromium, copper, manganese, nickel, lead, vanadium, zinc, and cadmium) can also be determined using atomic absorption (ASTM D3683). In the test method, the ash is dissolved by mineral acids and the individual elements determined by atomic absorption spectrometry.

For certain analytical purposes, it may be desirable to separate the minerals from the coal in an unaltered form. In early studies, density separation methods were used, which were unsatisfactory because of the enrichment of certain minerals in the process. A low-temperature ashing, or plasma ashing, technique has been developed that is more reliable and faster than density separations. In this method, low-pressure oxygen is activated by a radio-frequency discharge. The excited oxygen atoms and other oxygen-containing species oxidize the carbonaceous material at low temperatures ($\sim$150 °C, 302 °F). The effects of low-temperature ashing and of the oxidizing gas stream on the minerals in coal are minimal. Some pyrite can be oxidized and to some extent organic sulfur can be fixed as sulfates. The rates of these reactions are functions of operating conditions, such as radio-frequency power level and oxygen flow rate.

Factors that affect the rate of low-temperature ashing other than radio-frequency power and oxygen flow rate, mentioned earlier, are the coal particle size and depth of sample bed. Typical conditions for ashing are a particle size of less than 80 mesh, a sample layer density of 30 mg/cm^2, oxygen flow rate of 100 cm^3/min, chamber pressure of about 2 torr, and a 50-W net radio-frequency power. The total time required is 36–72 h and specified conditions must be met during the procedure in order to obtain reproducible results.

X-ray fluorescence analysis (ASTM D4326) is a rapid, simple, and reasonably accurate method of determining the concentration of many minor and trace elements in whole coal. The method is dependent on the availability of suitable standards. Although the major elements in coal (carbon, hydrogen, oxygen, and nitrogen) cannot be analyzed by X-ray fluorescence, most other elements at levels greater than a few parts per million (ppm) are readily determined. Sulfur should be determined by an alternate method (ASTM D1757).

In the test method, (ASTM D4326), the coal to be analyzed is ashed under standard conditions and ignited to constant weight. Previously ashed materials are ignited to constant weight under standard conditions. The ash is fused with lithium tetraborate ($Li_2B_4O_7$) or other suitable flux and either ground and pressed into a pellet or cast into a glass disk. The pellet or disk is then irradiated by an X-ray beam of short wavelength (high energy). The characteristic X-rays of the atom that are emitted or fluoresced upon absorption of the primary or incident X-rays are dispersed and intensities at selected wavelengths are measured by sensitive detectors. Detector output is related to concentration by calibration curves or by computerized data-handling equipment. All of the elements are determined as the element and reported as the oxide and include silicon, aluminum, iron, calcium, magnesium, sodium, potassium, phosphorus, titanium, manganese, strontium, and barium.

If the sample to be analyzed has been stored and the absorption of moisture or carbon dioxide, or both, is in question, the ash should be re-ignited using the 500–750 °C (932–1382 °F) staged combustion procedure before analysis. Alternatively, the ignition loss can be determined using the 500–750 °C (932–1382 °F) staged combustion procedure on a separate sample weighed out at the same time as the test portion and the necessary corrections made. Materials previously ashed, fly ash, or bottom ash must be ignited to constant weight at 750 °C (1382 °F) and cooled in a desiccator before analysis sample preparation, or alternatively, weight loss or gain must be determined on a second sample at 750 °C (1382 °F) taken at the same time as the analysis sample so that analysis determined on an as-received basis can be reported on an ignited ash basis.

Infrared absorption bands from 650 to 200 cm^{-1} have been used extensively to analyze, both qualitatively and quantitatively, minerals in coal ash. One such test method (ASTM D5016) is a procedure using a high temperature tube furnace and infrared detection for the rapid determination of sulfur in ash from coal and coke and is an alternative test method for a previously described test method (ASTM D1757). The purpose of this test method is to determine the percent sulfur trioxide (SO_3) portion of the major and minor elements in coal ash. This test method may be used to determine the percent sulfur trioxide (SO_3) portion of ash (ASTM D3174; ASTM

D5142) for coal containing high amounts of calcium. The ash may then be reported on a sulfur trioxide free basis.

In the test method, a weighed test portion is mixed with a promoting agent (that aids in the quantitative release of all sulfur present in the test portion as sulfur dioxide) and ignited in a tube furnace at a minimum operating temperature of 1350 °C in a stream of oxygen. Some promoters may contain sulfur and the sulfur content should be determined by analyzing the promoter as a sample and appropriate corrections made based on the mass of the promoter and its sulfur content.

The combustible sulfur contained in the test portion is oxidized to gaseous oxides of sulfur. Moisture and particulates are removed by traps filled with anhydrous magnesium perchlorate. The gas stream is passed through a cell in which sulfur dioxide is measured by an infrared absorption detector. Sulfur dioxide absorbs infrared energy at a precise wavelength within the infrared spectrum. Energy is absorbed as the gas passes through the cell body in which the infrared energy is being transmitted; thus, at the detector, less energy is received. All other infrared energy is eliminated from reaching the detector by a precise wavelength filter. The absorption of infrared energy can be attributed only to sulfur dioxide whose concentration is proportional to the change in energy at the detector. One cell is used as both a reference and a measurement chamber. Total sulfur as sulfur dioxide is detected on a continuous basis.

Ashing temperature, heating rate, and furnace ventilation have an important influence on sulfur trioxide retention; thus, observance of the prescribed ashing conditions can be critical. Sulfur in ash as determined by these methods cannot be strictly related to the sulfur oxides retained in ash produced under the conditions of combustion in boiler furnaces, or other commercial combustion processes.

There is also a standard test method for determination of major and minor elements in coal ash by ICP-AES (ASTM D6349). In the test method, the sample to be analyzed is ashed under standard conditions and ignited to constant weight – residues from coal combustion processes (such as fly ash and bottom ash) are normally digested on an as received moisture basis. The ash is fused with a fluxing agent followed by dissolution of the melt in dilute acid solution.

Alternatively, the ash is digested in a mixture of hydrofluoric, nitric, and hydrochloric acids. The solution is analyzed by ICP-AES for the elements. The basis of the method is the measurement of atomic emissions. Aqueous solutions of the samples are nebulized and a portion of the aerosol that is produced is transported to the plasma torch where excitation and emission occurs. Characteristic line emission spectra are produced by a radio frequency ICP. A grating monochromator system is used to separate the emission lines and the intensities of the lines are monitored by photomultiplier tube or photodiode array detection. The photocurrents from the detector are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of elements. Background must be measured adjacent to analyte lines of samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured.

Coal contains several elements whose individual concentrations are generally less than 0.01%. These elements are commonly and collectively referred to as trace elements. These elements primarily occur as part of the mineral matter in coal. Hence, there is another standard test method for determination of major and minor elements in coal ash by ICP-AES, inductively coupled plasma mass spectrometry (ICPMS), and graphite furnace atomic absorption (GFAA) spectrometry (ASTM D6357). The test methods pertain to the determination of antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, vanadium, and zinc (as well as other trace elements) in coal ash.

In the test method, the coal or coke to be analyzed is ashed under controlled conditions, digested by a mixture of *aqua regia* and hydrofluoric acid, and finally dissolved in 1% nitric acid. The concentration of individual trace elements is determined by either ICPAES or ICPMS. Selected elements that occur at concentrations below the detection limits of ICPAES can be quantitatively analyzed by GFAA spectrometry.

In some cases, the use of a high-speed pulverizer for size reduction should be avoided. The use of jaw crushers followed by final preparation in an agate mortar and pestle is recommended to prevent contamination of the sample. Separate test portions should be analyzed for moisture content (ASTM D3174; ASTM D5142) so that calculations to other bases can be made.

An internal standard is needed to compensate for differences in physical properties (such as viscosity) between the calibration standard and the test samples and drift caused by thermal changes in the laboratory that will affect the instrument optics. An appropriate internal standard element should not be naturally present in the test samples in appreciable concentrations and should not present spectral interferences with any analyte. In addition, the internal standard should be a strong emitter so that its relative concentration can be kept low and be as chemically similar to the analyte as possible.

In summary, if the inorganic components present in the coal are not volatilized during ashing of the coal, and the ash content is known, these elements can be determined in the ash and calculated to a coal basis. Unfortunately, there are test conditions were selected elements in coal, such as sodium, lead, and cadmium, are volatilized during the ashing procedure and such occurrence can cast doubt on the universal applicability of elemental analysis methods for coal that require muffle furnace ashing. Furthermore, it must be recognized that some standard test methods require modification or they are not applicable and lead to inaccuracies in the produced test data.

Wet ashing techniques include the use of mixtures of perchloric and other acids for the dissolution of coal. While wet ashing minimizes the risk of volatilization of the major, minor, and trace elements, most coal analysis laboratories avoid the use of perchloric acid. Other approaches of coal sample preparation for analysis such as microwave oven digestion and slurry techniques exhibit contamination problems and/or low recovery for many elements.

4.4.3 Non-Ashing Techniques

Spectrophotometric techniques have been the basis of many coal analysis methods. One of the most widely used techniques for analysis of trace elements is atomic absorption spectrometry, in which the standards and samples are aspirated into a flame. A hollow cathode lamp provides a source of radiation that is characteristic of the element of interest and the absorption of characteristic energy by the atoms of a particular element. X-ray fluorescence is also employed as a quantitative technique for trace element determination and depends on election of orbital electrons from atoms of the element when the sample is irradiated by an X-ray source.

Another method for trace element determination is neutron activation analysis (NNA) (Weaver, 1978), which is a highly sensitive, nondestructive method for the analysis of many elements. Briefly, the samples are irradiated in a nuclear reactor, which produces radioisotopes of the elements and appropriate measurements of the activities of the generated (daughter) species affords a means of calculating the concentrations of the parent isotopes (elements).

Although these three spectrophotometric methods are mentioned here as a means of examining the variety of trace elements that occur in coals, they are by no means the only applicable methods but are used as examples. Each method has various detection limits for the different elements and it is also essential to recognize the limitations of the individual methods before any attempt is made to interpret the data. Nevertheless, the methods have found considerable use as means by which trace elements in coal can be identified as well as giving indications of the concentrations of the various elements.

Three methods for determining mineral carbon dioxide in coal were investigated using bituminous coal. The titrimetric method is claimed to be superior to either of the then-used British standard gravimetric or manometric methods (BS 1016). The procedure involves the decomposition of carbonate minerals with hydrochloric acid and absorption of the evolved carbon dioxide in a mixture of benzylamine, ethanol, and dioxane. This mixture forms a stable salt of benzylcarbamic acid, which is then titrated with sodium methoxide. The method was said to be suitable for all concentrations of carbon dioxide. It is especially accurate for low concentrations and it is much more rapid than other methods tested.

Several other methods have been used to determine the trace elements in the mineral matter of coal, as well as in whole coal and coal-derived materials. These methods include (1) spark-source mass spectrometry (SSMS), (2) NNA, (3) optical emission spectroscopy, and (4) atomic absorption spectroscopy.

SSMS has been used extensively in the determination of trace elements in coal. Whole coal samples as well as ash residues, fly ash, and coal dust have been analyzed using this technique.

NNA techniques are frequently used for trace element analyses of coal and coal-related materials (Weaver, 1978). Precision of the method is 25%, based on all elements reported in coal and other sample matrices. Overall accuracy is estimated at 50%. NNA utilizing radio-chemical (RC) separations is employed by investigators when the sensitivity for a particular element or group of elements is inherently low or when spectral interference for a given element in a specific matrix is too great to be adequately detected. This situation was more prevalent before the advent of Ge(Li) spectrometry when only low-resolution NaI(TI) detectors were available.

Although thermal (slow) neutrons derived from nuclear reactors are the most practical source of particles for nuclear excitation and generally provide the more useful reaction, other excitation sources such as 14-MeV (fast) neutrons from commercially available accelerators or generators have also been applied to coal analysis.

Optical emission spectroscopy has been extensively applied to the quantitative and semi-quantitative determination of multiple trace elements in coal ash with a variety of excitation and optical parameters, internal standards, calibration standards, and procedures.

X-Ray diffraction analysis is probably the best developed and most widely used method for identifying mineral phases in coal and is the most promising method for the identification of minerals in coals (Rao and Gluskoter, 1973). These techniques may be applied to minerals from coal after the mineral matter has been separated from organic matter in the coal. However, its application can be limited because of orientation effects, and a reliable method of sample preparation is necessary to prevent these from occurring. X-ray diffraction profiles are determined by using a conventional diffractometer system with monochromatic x-radiation. For qualitative analysis, the specimen is scanned over a wide angular range to ensure that all the major diffraction peaks of the component minerals are recorded. Diffraction spacings are then calculated from the peak positions and the elements present in the sample are determined by using standard tables of diffraction spacing.

Scanning electron microscopy with an energy-dispersive X-ray system accessory has been used to identify the composition and nature of minerals in coals and to determine the associations of minerals with each other. Examinations can be made on samples resulting from ashing techniques or whole coal. With this technique, it is possible to identify the elemental components and deduce the mineral types present in coal samples. Computerized systems to evaluate scanning electron microscopy images have been developed and are useful in characterizing the minerals in coal mine dusts and in coal.

Recent studies on iron sulfide minerals in coals, minerals in coals, and *in situ* investigation of minerals in coal all used the scanning electron microscope (SEM) as the primary analytical tool. The ion microprobe mass analyzer (IMMA) is more sensitive than either the energy dispersive X-ray spectrometer or the wavelength dispersive X-ray spectrometer, both of which are used as accessories to an electron microscope.

Optical microscopy is another method that has been used to determine the distribution of minerals in coal. This method is based on the detailed microscopic examination of polished or thin sections of coal in transmitted and/or reflected light. In principal, observing several of its optical properties, such as morphology, reflectance, refractive index, and anisotropy, makes identification of a mineral type possible.

Finally, a semi-quantitative, direct-current arc spectrographic method is available and has been used to determine 64 elements in coal ash. The automated method is rapid and economical for evaluating both major and trace-element concentrations. The automated data acquisition and analysis system used in conjunction with this approach is an extension of a scanning microphotometer concept (Helz, 1965; Helz et al., 1969). The method provides a rapid, economical method for evaluating both major and trace-element concentrations in coal ash and the data within the limits of precision and accuracy for which the method was designed.

4.4.4 Data Handling and Interpretation

First and foremost, it is incorrect to refer to the *ash content* of coal and it is only correct to refer to the *mineral matter content* of coal. Coal does not contain ash and contrary to popular belief and nomenclature, mineral matter and ash are not the same. Ash is produced by combustion of coal in oxygen and the ash constituents, usually metal oxides, are formed from the mineral matter by routes involving some of the chemistry outlined subsequently.

Determination of a good value for the percent of mineral matter content (%MM) is a very important component of coal analysis. If this quantity cannot be determined directly by the acid demineralization or low-temperature ashing procedure discussed previously, or by other suitable methods, then it is possible to calculate a reasonable value for the mineral matter in coal, provided the necessary data are available.

Because of the changes that occur in MM occur during the ashing procedure, a number of formulas have been devised to allow calculation of the MM content from various parameters determined during the analyses of the coal. Minimally, this involves a calculation based on total content of ash and sulfur. The two formulas most commonly used are (1) the Parr formula and (2) the King–Maries–Crossley formula.

The Parr formula is the one that is most often used in the United States and requires only ash and sulfur values as determined in routine analysis:

$$\%\mathrm{MM} = 1.08\mathrm{A} + 0.55\mathrm{S}$$

A is the percentage of ash and S is the percentage of sulfur. The first term in this formula, 1.08A, is a correction for the loss in weight due to the elimination of water in the decomposition of clay minerals at high temperatures. Water of hydration of mineral matter has been estimated to be 8% of the ash value. The second term in the formula is a correction for the loss in weight when pyrite burns to ferric oxide (Fe_2O_3). The Parr formula treats all sulfur as pyritic and makes no allowance for the decomposition of carbonates or fixation of sulfur in the ash.

On the other hand, the King–Maries–Crossley formula is a more elaborate formula that allows for a number of effects. The original formula is:

$$\%\mathrm{MM} = 1.09\mathrm{A} + 0.5\mathrm{S}_{\mathrm{pyr}} + 0.8\mathrm{CO}_2 - 1.1\mathrm{SO}_{3\mathrm{ash}} + \mathrm{SO}_{3\mathrm{coal}} + 0.5\mathrm{Cl}$$

A is percentage of ash, S_{pyr} is the percentage of pyritic sulfur, CO_2 is the percentage of mineral carbon dioxide, SO_{3ash} is the percentage of SO_3 in ash, SO_{3coal} is the total sulfur appearing as sulfates in coal, and Cl is percentage of chlorine, which is known to occur in some coals (Spears, 2005). In this formula, the various numbers represent correction factors for the loss in weight due to the elimination of water in the decomposition of clay minerals (1.09), for the oxidation of pyrite to ferric oxide and sulfur dioxide (0.5), for the loss of carbon dioxide from mineral carbonates (0.8), and for the fixation of sulfur in the ash (1.1). The addition of the value representing the sulfate content of the coal sample and one-half the chlorine (assuming one-half the chlorine in coal is found in the mineral matter) completes the formula. The revised King–Maries–Crossley formula is:

$$\%\mathrm{MM} = 1.13\mathrm{A} + 0.5\mathrm{S}_{\mathrm{pyr}} + 0.8\mathrm{CO}_2 - 2.8\mathrm{S}_{\mathrm{ash}} + 2.8\mathrm{S}_{\mathrm{coal}} + 0.5\mathrm{Cl}$$

With this formula, a reasonably accurate value of the mineral matter can be calculated, but many parameters need to be determined in order to perform the computation.

An ultimate analysis that can claim to represent the composition of the organic substance of a coal is said to be on the *dry, mineral-matter-free* (dmmf) basis. The dmmf basis is a hypothetical condition corresponding to the concept of a pure coal substance. Since the dry, ash-free basis for coal neglects the changes in mineral matter when coal is burned, the dry, mineral-matter-free basis is preferred whenever the mineral matter can be determined or calculated. In fact, the classification of coal (ASTM D388) depends on the calculation of the volatile matter yield and fixed carbon values on the dry, mineral-matter-free basis. Calorific values are calculated on the moist, *mineral-matter-free basis.* The Parr formula is used in the classification system to calculate the mineral matter from ash and sulfur data.

Finally, several types of interference effects may contribute to inaccuracies in the determination of major and minor elements. The interferences can be classified as (1) spectral interferences, (2) physical interferences, and (3) chemical interferences.

Spectral interferences involve an overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line.

Physical interferences are generally considered to be effects associated with the such properties as change in viscosity and surface tension can cause significant inaccuracies, especially in samples that may contain high dissolved solids or acid concentrations, or both. If these types of interferences are operative, they must be reduced by dilution of the sample or utilization of standard addition techniques, or both.

Chemical interferences, which can be highly dependent on matrix type and the specific analyte element, are characterized by molecular compound formation, ionization effects, and solute vaporization effects. If such effects are observed, they can be minimized by careful selection of operating conditions, by buffering the sample, matrix matching, and standard addition procedures.

4.5 CHEMISTRY OF ASH FORMATION

The thermal and oxidation changes in which the mineral matter takes part during the combustion of coal are very complex but, fortunately, the majority of the reactions are fairly clearly understood (Table 4.5) (Falcone and Schobert, 1984; Speight, 2013a) and it has been possible to derive a formula that enables the mineral matter content of the original coal to be calculated from a knowledge of the quantity of ash produced on combustion, together with the quantities of pyrite sulfur, chlorine, carbonate present in the coal. The formula has been deduced from a consideration of the stoichiometric relationships existing between the reactants and products in reactions of the following types, all of which take place during combustion of coal and which together account for practically all the inorganic reactions involved in the process:

When coal burns in air, as in the determination of ash in proximate analysis, all the organic material is oxidized or decomposed to give volatile products and the inorganic material associated with the coal is subjected to the combined effects of thermal decomposition and oxidation. As a result, the quantity and the composition of the resulting ash differ considerably from those of the inorganic materials originally associated with the pure coal substance.

For example, two samples of Pliocene lignite coals from the Ptolemais basin of Greece, one from the upper and one from the lower lignite seams, which contained the same minerals, namely calcite, dolomite, quartz, kaolinite, illite, pyrite and gypsum, but in different proportions, showed differences in ash composition when heated and dried in air at 50 °C (90 °F) intervals from 50 to 1200 °C (122–2190 °F) (Filippidis et al., 1996), which is indicative of the need for a consistency in the temperature of the ashing prior to ash analysis.

It is, therefore, impossible to determine accurately the composition of the pure coal substance from the usual ultimate analysis simply by making allowance for the quantity of ash left behind as a residue when the coal is burned. Results obtained in this fashion are, as a consequence, quoted as being on the *dry, ash-free basis* and no claim is therefore made that these results do in fact represent the composition of the pure coal substance. If, however, it were possible to calculate accurately the quantity of mineral matter originally present in the coal sample, then by making due allowance for this material, the composition of the pure coal material could be deduced with reasonable precision and certainly with a greater accuracy than could be obtained by adopting the analytical figures calculated to a dry, ash-free basis.

It is difficult to determine, either qualitatively or quantitatively, the mineral matter content of a coal from the high-temperature ash. During high-temperature ashing, as designated by various standards (usually 750 °C, 1382 °F), a series of reactions takes place involving the minerals in the coals. Of the major mineral groups, only quartz is not significantly altered during high-temperature ashing.

The clay minerals in coal contain water that is bound within the mineral lattice – kaolinite contains 13% w/w bound water, illite contains 4.5% w/w bound water, and montmorillonite contains 5% w/w bound water. In addition, montmorillonite that occurs in mixed-layer clay also contains interlayer or adsorbed water. All the water is lost during the high-temperature ashing, for example,

$$A1_2O_3 \cdot 2SiO_2 \cdot xH_2O \rightarrow A1_2O_3 \cdot 2SiO_2 + xH_2O$$

During high-temperature ashing, pyrite and marcasite (FeS_2) are oxidized to ferric sulfate [$Fe_2(SO_4)_3$] and sulfur dioxide (SO_2). Some of the sulfur dioxide may remain in the ash in combination with calcium, but much is lost. If all of the possible sulfur dioxide is emitted during ashing, there would be a 33% loss in weight with respect to the weight of pyrite or of marcasite in the original sample.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Calcium carbonate (calcite, $CaCO_3$) is calcined to lime (CaO) during high-temperature ashing and carbon dioxide is evolved, resulting in a 44% reduction in weight from the original calcite, for example

$$CaCO_3 \rightarrow CaO + CO_2$$

Other metal carbonates behave similarly, that is, the oxides are formed during the ashing procedure.

The stable mineral quartz (silicon dioxide, silica, SiO_2) is the only major mineral found in coal that is inert during high-temperature ashing.

Sulfates in coal ash are derived from two sources, (1) sulfates (generally of calcium or magnesium) present as such in the coal sample, and (2) sulfates formed by the absorption of sulfur oxides by the basic constituents of the ash during incineration of the coal and occurring mainly as calcium sulfate but also, to some extent, as alkali sulfates. The quantity of sulfates from the first source is usually very small and, in normal cases, can usually be neglected in comparison with those derived by absorption. Consequently a determination of the sulfate in the ash enables a measure of the quantity formed during incineration to be established.

During combustion of the coal, organic chlorides are decomposed and liberate the chlorine atom as hydrochloric acid, while inorganic chlorides decompose with evolution of hydrochloric acid and ultimately leave a residue of the metallic oxide. Since approximately half the chlorine in coal occurs as inorganic chloride and the remainder as inorganic chloride, a correction for the chlorine present originally as inorganic material is easily applied when the total chlorine is known.

Except for oxygen and sulfur, elements that normally constitute the ash residues derived from coal combustion can arbitrarily be grouped as follows: (1) *major elements,* that is, elements in concentrations greater than 0.5% in the whole coal and these normally include aluminum, calcium, iron, and silicon; (2) *minor elements,* that is, those in the range of concentration of about 0.02 to in the whole coal and these usually include potassium, magnesium, sodium, and titanium, and sometimes phosphorus, barium, strontium, boron, and others, depending on the geologic area; and (3) *trace elements,* that is, all other inorganic elements usually detected in coal at less than 0.02% (200 ppm) down to parts per billion and below. Most nonmetallic elements, even though they are more volatile than metals, leave a detectable residue in coal ash.

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5

PROXIMATE ANALYSIS

5.1 INTRODUCTION

The proximate analysis of coal is *an assay of the moisture, ash, volatile matter, and fixed carbon* (Table 5.1) as determined by series of prescribed or standard test methods (ASTM D3172) (Earnest 1982; Earnest and Culmo 1983; Earnest 1984; Riley, 2007). The procedure was developed as a simple means of determining the distribution of products obtained when the coal sample is heated under specified conditions. Moreover, by definition, the proximate analysis of coal separates the products into four groups: (1) moisture, (2) volatile matter, consisting of gases and vapors driven off during pyrolysis, (3) fixed carbon, the nonvolatile fraction of coal, and (4) ash, the inorganic residue remaining after combustion. On occasion, proximate analysis may also include ash fusion temperature and the free-swelling index of coal or the swelling properties of coal (ASTM D720; ISO 8264) (Chapter 8).

The proximate analysis of coal is presented as a group of test methods (ASTM D3172; ASTM D3173; ASTM D3174; ASTM D3175; ASTM D5142; ISO 1171) that has been used widely as the basis for coal characterization in connection with coal utilization. These analyses are in contrast to the ultimate analysis of coal that provides information about the elemental composition.

The standard test method for proximate analysis (ASTM D3172) covers the methods of analysis associated with the proximate analysis of coal and coke and it is, in fact, a combination of the determination of each of three of the properties

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Handbook of Coal Analysis, Second Edition. James G. Speight.

TABLE 5.1 Examples of the Proximate Analysis of US Coals

Coal	Moisture (% Fuel)	Ash (% Dry Fuel)	Volatile Matter (% Dry Fuel)	Fixed Carbon (% Dry Fuel)
Antelope	23	5.51	43.3	51.2
Belle Ayr	25	6.84	48.2	45.8
Beulah Lignite	26.89	13.86	42.78	43.36
Black Thunder	21.3	6.46	54.26	39.28
Blind Canyon	3.3	10.4	43.58	46.03
Decker	17.99	5.11	44.03	50.87
Eagle Butte	23.74	6.4	45.55	48.05
Eastern Kentucky	1.17	10.154	36.82	53.03
Hanna Basin	11	11.05	38.4	50.6
Illinois #6	11.83	10.13	40.95	48.91
Kentucky #11	3.97	22.21	34.97	42.82
Kentucky #9	8.3	14.64	37.88	47.47
Pittsburgh #8	1.02	10.68	40.16	49.16
Pocahontas #3	0.62	4.51	18.49	77
Roland	9.89	6.29	44.52	49.2
San Miguel Lignite	18.5	52.178	30.62	17.42
Upper Freeport	0.74	21.66	24.09	54.25

and calculation of a fourth. Moisture, volatile matter, and ash are all determined by subjecting the coal to prescribed temperature levels for prescribed time intervals. The losses of weight are, by stipulation, due to loss of moisture and, at the higher temperature, loss of volatile matter. The residue remaining after ignition at the final temperature is called ash. Fixed carbon is the difference of these three values summed and subtracted from 100. In low-volatile materials such as coke and anthracite coal, the fixed carbon value equates approximately to the elemental carbon content of the sample.

The term *volatile matter content* (of coal) is actually a misnomer insofar as the majority of the volatile matter is the volatile product of the thermal decomposition of coal through the application of high temperatures. The extent to which the more volatile smaller molecules of coal add to this is dependent on the coal and should be determined by other nondestructive methods such as extraction by solvent(s). Relative yields and boiling point profiles provide the extent to which natural molecules contribute to the volatile matter without any influence from high temperature cracking.

The final results of the proximate analysis of coal (ASTM D3172; ASTM D3173; ASTM D3174; ASTM D3175; ASTM D5142; ISO 562) are usually reported to the first decimal place; any subsequent figures have little or no significance. The final report of the analysis should always contain the results on a basis of air-dried coal (i.e., coal in its most stable condition and in which it was analyzed), but for purposes of classification or comparison it is often necessary to convert to another basis such as *dry coal*, *dry-ash-free coal*, or *as received* coal.

5.2 MOISTURE CONTENT

There are several sources of the water that occurs in coal and all coals are mined with some water, such as: (1) adventitious moisture, which consists of groundwater and other extraneous moisture and can be evaporated, (2) inherent moisture, which occurs within the pore systems of the coal and is analyzed quantitatively, and (3) adventitious moisture, which is removed by evaporation in air. Furthermore, moisture in coal may also be classified into four possible forms within coal: (1) surface moisture, which is water that is held on the surface of coal particles or macerals, (2) hydroscopic moisture, which is water held by capillary action within the micro-structure of the coal, (3) moisture which is produced by thermal decomposition of the organic matrix of the coal and was part of the original organic precursors, and (4) mineral moisture, which comprises part of the crystal structure of hydrous silicates such as clay minerals.

The vegetation from which coal was formed had a high percentage of water that was both physically and chemically bound and varying amounts of this water were still present at different stages of the coalification process. But the overall result of the continuation of the coalification process was to eliminate much of the water, particularly in the later stages of the process, as is evident from a comparison of the moisture contents of different ranks of coal from lignite to anthracite (Table 5.2). Water is present in most mines and circulates through most coal seams. After mining, many coals are washed with water during preparation for market and are then subject to rain and snow during transportation and storage. All of these sources contribute to the moisture in coal and to the problems associated with the measurement of this moisture.

The total moisture in coal is the determination of the moisture (in all forms except water of crystallization of the mineral matter) that resides within the coal matrix. In fact, moisture (or water) is the most elusive constituent of coal to be measured in the laboratory is moisture. The moisture in coal ranges from 2% to 15% by weight in bituminous coal to nearly 45% by weight in lignite.

TABLE 5.2 Composition and Property Ranges for Different Ranks of Coal

	Anthracite	Bituminous	Subbituminous	Lignite
Moisture (%)	3–6	2–15	10–25	25–45
Volatile matter (%)	2–12	15–45	28–45	24–32
Fixed carbon (%)	75–85	50–70	30–57	25–30
Ash (%)	4–15	4–15	3–10	3–15
Sulfur (%)	0.5–2.5	0.5–6	0.3–1.5	0.3–2.5
Hydrogen (%)	1.5–3.5	4.5–6	5.5–6.5	6–7.5
Carbon (%)	75–85	65–80	55–70	35–45
Nitrogen (%)	0.5–1	0.5–2.5	0.8–1.5	0.6–1.0
Oxygen (%)	5.5–9	4.5–10	15–30	38–48
Btu/lb	12,000–13,500	12,000–14,500	7500–10,000	6000–7500
Density (g/ml)	1.35–1.70	1.28–1.35	1.35–1.40	1.40–1.45

The total moisture is analyzed by loss of mass between an air-dried sample and the sample after driving off the inherent moisture with heat and can be measured by (1) heating the coal with toluene, (2) drying the coal in a minimum free-space oven at 150 °C (302 °F) within a nitrogen atmosphere, or (3) air-drying the coal at 100–105 °C (212–220 °F). The first two methods are suitable for use with low-rank coal but the third method is only suitable for high-rank coal since air drying low-rank coal under such conditions can promote oxidation of the coal.

The standard methods of determining the amount of moisture in coal include a variety of test methods that are designed to differentiate between the various types of moisture in the coal: (1) ASTM D1412 (ISO 1018), standard test method for determination of the equilibrium moisture of coal at 96–97% relative humidity and 30 °C, (2) ASTM D2961, standard test method for determination of the total moisture of coal reduced to number 8 (2.38-mm) top sieve size (limited-purpose method), (3) ASTM D3173, standard test method for determination of the moisture in the analysis sample of coal and coke, and (4) Method D3302, standard test method for determination of the total moisture in coal. In addition to these test methods, the method of preparing coal samples for analysis (ASTM D2013, standard test method for preparing coal; samples for analysis) gives directions for air-drying coal samples. It has been suggested that the best technique is to determine loss during drying in air (ASTM D3302; ISO 11722) followed by co-distillation of moisture with xylene. Alternatively, moisture can be determined in an oven (at a fixed temperature) that is swept with dry nitrogen or another inert gas (ISO 589).

Determining of the moisture in the analysis coal by weight loss at 104–110 °C (220–230 °F) may not be as straightforward as it may seem and caution is advised (as it is in application of any test methods). The method (ASTM D3173) is not always suitable for low-rank coal because it does not use an inert gas as the purge gas and recommends too short a drying period. Oxidation – which results in a weight increase during oxidation of the sample – can occur and incomplete removal of the moisture under the conditions of temperature is not always achieved during the recommended one-hour drying time. In addition, as may be the case with some low-rank coals, decarboxylation (removal of carbon dioxide) during the drying period can also incur weight loss. To circumvent this potential deficiency, a modified test method has been recommenced (ISO 331) in which the oven is purged with dry, purified, and preheated nitrogen.

No absolute method for determining the true moisture content of coal by heating has been devised because of the wide variance in the temperatures at which different forms of moisture (including surface, inherent, chemically combined moisture in the coal) and water of hydration in clay minerals are liberated. There are, however, several test methods of an empirical nature of methods for determining the amount of moisture in coal. In one method, weight loss of coal was measured after heating to 106 °C (222 °F) in a flow of dry oxygen-free nitrogen. Although two other methods (weight loss in air and direct measurement of moisture released in a nitrogen atmosphere), also at 106 °C (222 °F), yielded results within acceptable tolerances, those performed in a nitrogen atmosphere gave consistently higher results because heating in air sometimes oxidizes coal and offsets the moisture loss through addition of oxygen. Measuring indirect weight loss after heating in nitrogen at 130 °C (266 °F) for thirty minutes with a flow rate of ninety oven-volume changes per hour is, perhaps, a more convenient method.

Moisture loss can (and often does) occur during grinding and/or pulverization and is believed to be related to the types and amounts of banded (maceral) ingredients in the coal. Losses are least for vitrain and increase in order of vapor pressures for moisture (e.g., vitrain < clarain < durain < fusain).

The role of water in coal and the quantitative measurement of water are complicated because the water is present within the coal matrix in more than one form (Allardice and Evans, 1978). Thus, the total moisture includes both the surface moisture and the residual moisture remaining in the sample after determining the air-dry loss (ASTM D3302). Thus:

$$M = [R(100-ADL)/100] + ADL$$

M is the total moisture, % by weight, R is the residual moisture, % by weight, and ADL is the air-drying loss, % by weight.

To determine the total moisture, either an analysis sample can be prepared from the moisture sample, or the regular analysis sample can be used for this purpose, provided that the moisture analysis is performed on the analysis sample within a prescribed time after the air-dry sample is prepared. When separate analysis samples are used for moisture and for the other determinations that are made, moisture determinations must be made on both. The moisture obtained on the regular analysis sample is then used only for the purpose of calculating results to the dry basis. The moisture determined on the analysis sample prepared from the separate moisture sample is combined with the air-dry loss to determine the total moisture and the total moisture is then used for calculation of as-received basis results.

The methods for the determination of the total moisture in coal have been placed into the following categories: (1) thermal methods that often include distillation methods, (2) a desiccator method, (3) distillation method that often include extraction and/or solution methods, (5) chemical methods, and (6) electrical methods.

Most common tests for moisture involve a thermal drying procedure, usually at a temperature a few degrees above the boiling point of water; the moisture released upon heating is measured either directly or indirectly. Another thermal method that is often used involves moisture determination by measuring the weight loss of a coal sample upon heating in various atmospheres. If the coal is susceptible to oxidation, as most low-rank coals with high moisture content are, the heating should be done in an inert atmosphere.

The desiccator method involves weight loss (of the coal) or the gain in weight of a desiccant in a weighing tube that adsorbs the moisture from the atmosphere above the coal. This test method is probably the more accurate method, since the tube absorbs only water, although other gases, such as methane, may be evolved. Moisture may also be determined as the loss in weight when coal is heated to various temperatures (with the atmosphere and pressure variable) or by the determination of the weight gain of a vessel containing a desiccant through which passes the volatile materials evolved when the coal is heated.

The distillation method of moisture determination requires the collection and determination of the water evolved from the coal when the sample is heated in a boiling solvent which is itself immiscible with water. The solution and extraction methods require either solvent extraction of the water from the coal (followed by subsequent determination of the water content of the solvent) or use of a standard reagent that will exhibit differences in concentration by virtue of the water in the coal. A nonthermal solvent method of determining moisture involves the use of an extraction procedure in which the coal is shaken with a solvent that extracts the water from the coal. The degree of change in some physical property of the solvent, such as density, is then used as a measure of the water extracted.

The chemical methods of water determination invoke the concepts of direct titration of the water or chemical reaction between the water and specific reagents that causes the evolution of gases and the water is determined by measurement of the volume produced. In addition, chemical methods used for determining moisture include (1) application of the Karl Fischer method of determining water content and 20 reaction of quicklime with water in coal and the subsequent measurement of the heat generated by the reaction.

Electrical methods of measuring coal moisture involve the determination of the capacitances or the resistances or the dielectric constant of coal from which the water content can be determined. These methods have been used by industry, particularly for moving streams of coal.

Each method has advantages or disadvantages that must be considered prior to the application or acceptance of the method. Furthermore, the applicability of any one method is not only dependent on accuracy (as well as the reproducibility of that accuracy) but also on the applicability of that method to the whole range of coal types.

After thermal drying methods, distillation methods are the next most commonly used. In these procedures, coal is heated in a liquid that has a boiling point higher than that of water and is immiscible with it. Xylene, toluene, or a petroleum fraction of a selected boiling range is the liquids normally used. The distilled vapors are condensed in a graduated tube and the volume of water is measured after the two liquids separate (ISO 1928; ISO 348; ISO 1015). This type of method is considered particularly advantageous for use with low-rank coal, since air is excluded from the coal and any error due to oxidation is minimized. This is also a direct method of measuring moisture and consequently there is no error due to the loss of other gases.

Thus, the procedure is particularly applicable for use with high-moisture, low-rank coal that may also be sensitive to aerial oxygen. For example, with lignite (and other low-rank coals), oxidation during the one-hour heating period can, conceivably, cause a weight increase, albeit sufficiently small, but that is significant enough to reduce the amount of moisture found in the coal. In addition, although the moisture as determined will, indeed, be mostly moisture, it may, however, include some adsorbed gases while some strongly adsorbed moisture will not be included. Caution is also necessary to ensure that the coal sample is not liable to thermal decomposition at the temperature of the moisture determination.

In all of the methods for total moisture determination, the total moisture may be determined by means of a single-stage method or by means of a two-stage method in which the as-received sample is air-dried at approximately room temperature and the residual moisture is determined in the sample (ASTM D3302; ISO 589). The air-drying step reduces the water in the sample to an equilibrium condition depending on the laboratory humidity and, as a result, minimizes any potential changes in the moisture content that might occur when the sample is prepared for further analysis. As a result, the single-stage method does not involve the intermediate stage and is classified as a limited-purpose method, recognizing that certain coals will give results that reflect varying levels of oxidation. High-rank coal may be affected somewhat less by this treatment than lower-rank coal.

Determination of the residual moisture (ASTM D3173) involves another determination and the data are used for calculating other analytical results to the dry basis. It is also used in conjunction with the air-dry loss, when it is determined, to calculate results to the as-received basis.

On those occasions when *very wet coal* that is in comparatively large pieces of coal are in hand, one unique method is available for determination of the moisture content. In the test method, the sample (in a container) is transferred to a clean, weighed metal tray and reweighed immediately. The coal is then spread evenly over the surface of the tray, by means of a spatula (or other instrument) and should be left on the tray until the coal can be dislodged from the spatula blade by tapping, and allow to air-dry in a well-ventilated room free from dust. Reweighing is performed periodically until two successive weightings differ by less than 0.1% by weight of the weight of the original sample. At that time, the final weight of the air-dried coal is determined by weighing the sample, the container, and tray together; the cleaned container is weighed and the loss in weight (due to moisture lost by air-drying) is expressed as a percentage of the original sample. The entire sample can then be crushed and ground (with reduction in bulk if necessary) to give a sample possessing the necessary size qualities that, without further drying, can be subjected to a determination of moisture content as specified in the test for proximate analysis.

Another test method is applicable determination of the moisture content of *moderately dry coal* and can, in fact, be used for all coal samples that can be handled without appreciable loss of moisture. The principle of the method is that the coal is heated with an inert liquid that does not mix with water and which has a boiling point greater than that of water so that on distillation the water is carried over with the vapor from the liquid and, on condensation, separates from it in a graduated receiver. The Dean and Stark apparatus (Figure 5.1) or one of its many modifications can be used for this purpose.

In the procedure (ISO 331), coal (with the weight depending on moisture content) is weighed into a flask and dry toluene is added. The apparatus is assembled and, after bringing the toluene to the boil, boiling is continued until no more water separates out in the receiver. When no change in the volume of the water takes place over a specified time interval (usually 15 min), any moisture adhering to the inner tube of the condenser is transferred to the receiver by washing down with dry toluene and the receiver is allowed to cool until it reaches room temperature. Once all of the

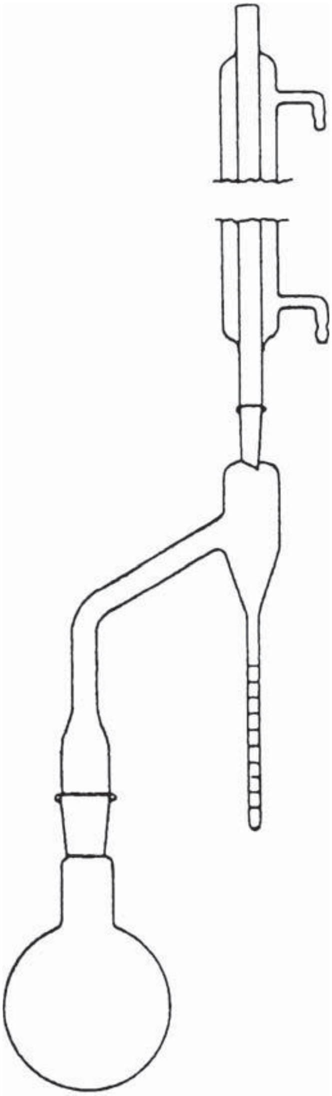

Figure 5.1 Dean and Stark equipment.

water has been collected in the bottom of the receiver, read the lowest level of the water–toluene meniscus, apply any calibration correction necessary, and express the quantity of water obtained as a weight percent of the coal. A well-defined cutoff point for moisture release is achieved without significant oxidation of the coal and, for this reason, the use of toluene or xylene distillation methods for brown coal is recommended.

This test method is applicable to coal of any size but it is limited by the diameter of the neck of the flask. The apparatus must be scrupulously clean (usually by a mixture of sulfuric acid and potassium dichromate after which the apparatus is washed with distilled water and dried in an oven at ca. 110 °C, 230 °F). The condenser should be cleaned periodically in the same manner and the receiver should be capable of collecting up to 10 ml water with graduations in 0.1 ml or 0.05 ml with a calibration for the water–toluene meniscus.

Other methods that have been applied to the determination of the amount of moisture in coke have been investigated: (1) extraction of coke using anhydrous methanol and addition of calcium hydride with coal constituents (CaH_2) from which the amount of released heat is measured; and (2) extraction of coke using anhydrous dioxan and measurement of the refractive index of the solution to determine its water content. The application of these methods to coal may be subject to error because of (1) interaction of the coal in contrast to coke) with the calcium hydride leading to chemical errors and (2) the influence of extractable constituents on the refractive index of the dioxan.

It is often difficult to apply indirect weight loss procedures to the determination of moisture content in low-rank coal that has high moisture content and that are susceptible to oxidation. Some ovens may be inadequate for determining the amount of moisture in brown coal but it must be ascertained that moisture does not continue to be released from the coal after prolonged periods of heating leaving no sharp moisture-release cutoff point. On this basis, water is perhaps best removed from low-rank coal by distillation with toluene in which a well-defined moisture cutoff is reached (ISO 1015).

The continuous measurement of moisture in coal has been accomplished by (1) electrical conductivity, (2) dielectric constant, (3) microwave attenuation, (4) neutron scattering, (5) nuclear magnetic resonance, (6) infrared, and (7) thermal conductivity.

5.2.1 Test Methods

Generally, the moisture content of coal is determined by measuring the weight loss of a sample (expressed as a percentage of the sample) that has been comminuted to pass through a 250-μ (60-mesh) sieve (ASTM D3173; ISO 331; ISO 687). The sample (ca. 1 g) is maintained under controlled conditions (107 ± 3 °C; 225 ± 5 °F) in an inert atmosphere for 1 h.

Moisture determination (ASTM D3173; ASTM D3302) is dependent on the extent of sample preparation and the condition of the coal sample. The entire procedure for determining the total moisture in coal, after collecting the gross sample, begins with preparing the sample for analysis (ASTM D2013). If the gross sample is sufficiently dry, it may be sieved immediately and air-dried. If the sample is too wet to reduce in size, it should be weighed before size reduction and air-dried using an oven that is set at 10–15 °C (18–27 °F) above room temperature with a maximum oven temperature of 40 °C (106 °F); if ambient temperature is 40 °C (106 °F), ambient temperature shall be used. In this manner, the moisture in the sample is reduced to an equilibrium condition with the air in the laboratory and changes in moisture content are minimized during the crushing and grinding operations and even during analysis. After reduction of the gross sample to number 4 or number 8 top size, it is divided and a laboratory sample taken. The laboratory sample is then air-dried and reduced to number 8 top size if necessary. If the total moisture is to be determined (ASTM D3302), residual moisture is determined by heating at 104–110 °C (219–230 °F) for approximately 1 h.

Air-drying removes most of the surface moisture of coal, while a temperature of approximately 107 °C (225 °F) is needed to remove inherent moisture. At temperatures of approximately 200–300 °C (392–572 °F), moisture from the decomposition of organic materials is driven off, but water of hydration requires a considerable amount of energy for expulsion. For example, the water of hydration in clay minerals may require a temperature in excess of 500 °C (932 °F). However, the issues of decomposition moisture and water of hydration of mineral matter are not usually commonly dealt with in conventional analysis because the temperatures specified in the test methods for moisture determination are well below those needed to remove such moisture.

Usually the first moisture value to be obtained on a coal sample is the *air-dry loss moisture*. This moisture loss occurs during an attempt to bring the coal sample into equilibrium with the atmosphere in the sample preparation room. The practice of using temperatures above room temperature may accelerate oxidation but shortens the time needed for air-drying, hence temperature above 40–50 °C (104–122 °F) are not recommended for air-drying.

In the test method for determination of the equilibrium moisture in coal (ASTM D1412; ISO 1018), a sample is brought into equilibrium in a partially evacuated desiccator with an atmosphere of 96–97% relative humidity at 30 °C (86 °F). However, as in all methods of determining moisture, precautions must be taken to obtain reliable results from this test method. Over-dried and/or oxidized coal results in low moisture values. To prevent over-drying, the sample should be kept wet before this test is run and using a dry nitrogen atmosphere can prevent oxidation of the coal during the test. During the test itself, it is important to observe the temperature and time limits for equilibration (as specified in the test method). Furthermore, sudden lowering of the temperature or a sudden surge of air into the desiccator after equilibration may cause condensation of moisture on the coal. In addition, loss of part of the coal sample when a sudden surge of air is allowed into the evacuated desiccator voids the results of the test.

Sample handling should be kept at a minimum during moisture determination thereby eliminating the potential for loss or gain of moisture during prolonged handling. Heat generated by the crushing and grinding operations used during reduction of the gross sample may be sufficient to cause moisture loss. Alternatively, or in addition, the relative humidity of the sample during preparation and the relative humidity in the testing laboratory may also change during the time that is required for a complete analysis. Air-drying steps in the analysis and efficient sample handling help minimize the effects of relative humidity changes.

Exposure of the coal sample to the atmosphere for extended periods of time increase the chances of oxidation, which result in a weight gain by the coal sample that offsets part of the loss of moisture and give moisture results that are incorrect. In the determination of moisture by a weight loss method, it is necessary to attain a constant weight, which requires alternate heating and cooling of samples. Prolonged heating or an excessive number of alternate heating and cooling should be avoided to minimize the chances of oxidation.

The natural bed moisture of coal is determined (ASTM D1412; ISO 1018) by wetting the coal, removing the excess water by filtration, and then allowing moisture equilibration to occur by standing the coal over a saturated solution of potassium sulfate in a closed vessel, thereby maintaining the relative humidity at 96–97%. The vessel must be evacuated to about 30 mm mercury and the whole maintained at 30 ± 0.2 °C (86 0 ± 0.4 °F) for 48 h for coals of higher rank than lignite while lignite will require 72 h to reach equilibrium. The method can also be employed to estimate the surface or extraneous moisture of wet coal; such moisture is the difference between the total moisture of the coal and the natural bed moisture.

5.2.2 Data Handling and Interpretation

Moisture values are very important due to the influence they have on other measured and calculated values used in coal analysis and, ultimately, to the part they play in the buying and selling of coal. The moisture values obtained from the various drying procedures are expressed as a percentage, by weight, of the sample used in the particular test. Consequently, a correction factor must be used to make the various moisture values additive so that total moisture values can be obtained.

The various forms of moisture in coal are described according to the manner in which they are measured by some prescribed standard method. These forms are (1) inherent moisture, (2) surface or free moisture, (3) total moisture, (4) air-dry loss moisture, (5) residual moisture, (6) as-received moisture, (7) decomposition moisture, and (8) water of hydration of mineral matter.

Inherent moisture (*bed moisture*, *equilibrium moisture*, *capacity moisture*) is assumed to be the water held within the pore system and capillaries of coal and is not to be identified with *residual moisture*. *Surface moisture* (*free moisture*) is, as the term implies, water held on the surface of the coal. *Total moisture* is the moisture determined as the loss in weight in an air atmosphere under rigidly controlled conditions of temperature, time, and air flow (ASTM D3302) and is the sum of the *inherent moisture* and *free moisture* and is the sum of the *air-dry loss* and *residual moisture*. *Air-dry loss moisture* is the loss in weight resulting from the partial drying of coal, and *residual moisture* is that remaining in the sample after determining the air-dry loss moisture. *As-received moisture* also is equal to the total moisture or is the sum of the inherent and free moisture present in the coal at the time of the analysis. *Decomposition moisture* is produced from the thermal decomposition of organic constituents of coal. *Water of hydration of mineral matter* is the water that is incorporated into the crystal lattices of the clay and inorganic minerals in coal.

The total moisture is used for calculating other measured quantities to the as-received basis. The total moisture is important in assessing and controlling the commercial processing of coals. It is used to determine the amount of drying that is needed to reach a given moisture requirement and to determine the amount of dust-proofing and freeze-proofing agents to add. In coking processes, coals with high moisture content require more heat for vaporization of the moisture, which leads to longer coking cycles and decreased production. The total moisture of the coal used must be accurately known to allow for proper charging of the coke ovens and overall control of the coking process.

Inherent or equilibrium moisture is used for calculating moist mineral-matter-free calorific values for the rank classification of high-volatile bituminous coals. It is also used for estimating free or surface moisture, since total moisture is equal to the sum of the inherent moisture and the free moisture and is considered the inherent moisture of the coal as it occurs in the unexposed seam, where the relative humidity is probably near 100%. However, due to physical limitations, equilibrium moisture determinations are made at 96–97% relative humidity and used as inherent moisture values.

Surface moisture is obtained by subtracting equilibrium moisture from total moisture. However, there is no sharp dividing line between inherent moisture and surface moisture. The measurement of inherent moisture depends on the fact that its vapor pressure is less than that of surface moisture. Drying, pulverizing, dust proofing, and the general handling of coal all depend on surface moisture data since wet coal is very difficult, and in some instances almost impossible, to pulverize.

There is no simple and reliable method of determining the water of hydration of mineral matter. The average value of 8% of the ash is used as the value for water of hydration of mineral matter in coals in the United States. This value is acceptable, although it is an average of values that range from 2% to 3% and up to 15% to 20%. Water of hydration values are used to correct ash to the form of hydrated minerals in mineral matter calculations.

5.3 ASH

Ash is the noncombustible residue left after coal is burned and represents the bulk mineral matter after carbon, oxygen, sulfur, and water (including from clay minerals) has been driven off during combustion. The test method is reasonable straightforward, with the coal thoroughly burned under specified conditions and the ash yield is expressed as a percentage of the original weight (ASTM D3174; ISO 1171).

The ash is composed primarily of oxides and sulfates and it should not be confused with mineral matter, which is composed of the unaltered inorganic minerals in coal (Chapter 4) (Given and Yarzab, 1978; Speight, 2013). Thus, ash is formed as the result of chemical changes that take place in the mineral matter during the *ashing* process. The quantity of ash can be more than, equal to, or less than the quantity of mineral matter in coal, depending on the nature of the mineral matter and the chemical changes that take place in ashing. The various changes that occur include (1) loss of water from silicate minerals, (2) loss of carbon dioxide from carbonate minerals, (3) oxidation of iron pyrite to iron oxide, and (4) fixation of oxides of sulfur by bases such as calcium and magnesium. In fact, incineration conditions determine the extent to which the weight changes take place and it is essential that standardized procedures be closely followed to ensure reproducibility.

There are two types of minerals in coal: (1) extraneous mineral matter and (2) inherent mineral matter. The *extraneous mineral matter* consists of materials such as calcium, magnesium, and ferrous carbonates pyrite; marcasite; clay; shale, sand; and gypsum. *Inherent mineral matter* represents the inorganic elements combined with organic components of coal that originated from the plant materials from which the coal was formed.

The use of coal with mineral matter that gives a high alkali oxide ash often results in the occurrence of slagging and fouling problems. As oxides, most ash elements have high melting points, but they tend to form complex compounds (often called eutectic mixtures) that have relatively low melting points. On the other hand, high-calcium-low-iron ash coals tend to exhibit a tendency to produce low-melting range slag, especially if the sodium content of the slag exceeds about 4% w/w.

The chemical composition of coal ash is an important factor in fouling and slagging problems and in the viscosity of coal ash in wet bottom and cyclone furnaces. The potential for the mineral constituents to react with each other (Table 5.3) (Given and Yarzab, 1978) as well as undergo significant mineralogical changes is high. In addition, coal with a high iron content (usually >20% w/w ferric oxide) ash typically exhibits ash-softening temperatures under 1205 °C (2200 °F).

In some test methods, it is recommended that the color of the ash should be noted as it gives an approximate indication of the fusion point. Generally, highly colored ash has a low fusion point while white ash, provided they are relatively no basic oxides, has a high fusion point.

5.3.1 Test Methods

Slagging, fouling, and clinkering difficulties have been found to correlate not only with the composition of coal ash but also with the *fusibility* of the coal ash (ASTM D1857; ISO 540) insofar as ash fusibility related to composition. The critical temperature most commonly referenced in the evaluation of the properties of coal ash is the softening temperature. The test method used for determining the ash content of coal (ASTM D3174) for the proximate analysis and the ultimate analysis is not always applicable to the preparation of ash for identification of the ash constituents because of the loss of ash constituents during the ashing procedure.

The determination of mineral ash in coal is usually by heating (burning) an accurately weighed sample of the coal in an adequately ventilated muffle furnace at temperatures in the range 700–750 °C (1290–1382 °F) for 4 h (ASTM D3174). In this test method, the coal sample is placed in a cold furnace and heated gradually so the temperature reaches 450–500 °C (840–930 °F) in 1 h and 700–750 °C (1290–1380 °F) at the end of the 2 h – the ISO method (ISO 1171) recommends a final temperature of 815 °C (1500 °F). In both methods, the sample is ignited at

TABLE 5.3 Behavior of Minerals at High Temperature

Inorganic Species	Behavior on Heating	Consequences for Analysis
Clays	Lose structural OH groups with rearrangements of structure and release of H_2O	Ash weighs less than MM[a]; yield of water increases apparent organic hydrogen, oxygen, and VM[a]
Carbonates	Decompose with loss of CO_2; residual oxides fix some organic and pyritic S as sulfate	Ash weighs less than MM, but this effect partly neutralized by fixation of S as sulfate; CO_2 from carbonates increases apparent VM, organic carbon, and organic oxygen
Quartz	Possible reaction with iron oxides from pyrite and organically held Ca in lignites; otherwise, no reaction	None, unless reactions indicated take place
Pyrite	In air, burns to Fe_2O_3 and SO_2; in VM test, decomposes to FeS	Increases heat of combustion; ash weighs less than MM; S from FeS_2 contributes to VM
Metal oxides	May react with silicates	None (?)
Metal carboxylates (lignites and subbituminous only)	Decompose, carbon in carboxylate may be retained in residue	Uncertainty about significance of ash; most of organic sulfur in coal fixed as sulfate in ash

[a] MM, mineral matter; VM, volatile matter.

the appropriate final temperature to constant weight. Typically, the experimental data should be reproducible within ±0.2% of the end result. There are also other methods, predominantly thermal, which can be used for the analysis of coal ash.

The important weights in this determination are those with the coal in the dish before and after drying, the difference between them giving the weight of moisture expelled. These must be determined, therefore, as accurately as possible and, to enable this to be accomplished, the weight of the dish alone should be as small as possible. Suitable petri dishes of thin glass and measuring 5 cm in diameter and 1 cm in height meet all the requirements of weight and area.

If the coal under investigation oxidizes appreciably at 100 °C (212 °F), it is often be necessary to carry out the determination in an inert atmosphere either by passing a current of oxygen-free nitrogen through the oven or by using an oven that can be evacuated. In either case, it is an advantage to keep the free space in the oven down to a minimum so as to render more effective the displacement action of the nitrogen or the attainment of a suitable vacuum.

Variations in the amount of ash arise from the retention of sulfur that originates from the pyrite. Sulfur in ash is usually determined as sulfate (ASTM D1757; ASTM D5016) and the method may give abnormally high amounts of sulfur. This is due to the sulfur retention from pyrite (and marcasite). If the forms of sulfur in coal are known (ASTM D2492), the amount of pyrite retention can be estimated (see also ASTM D3174, Note 2). Nevertheless sulfur retention will give rise to anomalous results.

For high-rank coal, if the amount of pyrite and carbonate minerals is low, sulfur retention is not a major issue and ashing may be carried out rapidly. For coal that has substantial amounts of pyrite and calcite, the preferred procedure involves burning the coal at low temperatures to decompose the pyrite before the decomposition point of the carbonate minerals is reached and less sulfur remains in the coal to react with the oxides that are formed at higher temperatures. Another method to combat sulfur retention consists of (1) ashing the coal, (2) treating the ash residue with sulfuric acid, and (3) igniting to constant yield of ash. The amount of ash is calculated back to the calcium carbonate basis by subtracting three times the equivalent of carbon present as mineral carbonate from the ash as weighed.

In light of the fact that coal ash is measured by removal (combustion) of the organic part of the coal, there are methods for measuring the mineral matter content of coal. Such a method involves demineralization of the coal that depends upon the loss of weight of a sample when it is treated with aqueous hydrofluoric acid at 55–60 °C (130–140 °F) (Given and Yarzab, 1978; ISO 602). However, pyrite is not dissolved by this treatment and must be determined separately. Other methods include the use of physical techniques such as scanning electron microscopy and X-ray diffraction.

A compositional analysis of the ash in coal is often useful in the total description of the quality of the coal. Knowledge of the composition of ash is useful in predicting the behavior of ashes and slags in combustion chambers. The amount and composition of ash are important in determining the best cleaning methods for coals, in selecting coals to be used in the production of coke, and in selecting pulverizing equipment to be used in commercial pulverizing operations. Utilization of the ash by-products of coal combustion sometimes depends on the chemical composition of the ash.

A wide range of trace elements occurs in coal, primarily as a part of the mineral matter. The release of certain trace elements into the environment as combustion products or in the disposal of ash is a concern for coal-burning facilities. The determination of certain trace elements in coal and coal ash is becoming an increasingly important part of coal analysis.

In the preparation of ash samples for analysis, slow burning of the coal samples is necessary to prevent the retention of sulfur as sulfate in the ash. The retention of sulfur as calcium sulfate ($CaSO_4$) in coal ash (900 °C, 1650 °F) is related to the amounts of calcium and sulfur in whole coal and the ashing temperature to which it is subjected. Iron oxides formed during oxidation of pyrite contributed to the catalytic oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) that reacts with calcium to form calcium sulfate ($CaSO_4$) during the ashing process. The amount of sulfur retained in power plant ash formed at temperatures exceeding 1000 °C (1832 °F) is directly related to the concentration of unburned carbon. If the rate of burning is too rapid, some of the sulfur oxides produced from burning pyrite may react with metal oxides to form stable sulfates. The result is that indefinite amounts of sulfur are retained, which introduces an error into all the analytical results unless all other items are corrected to the sulfur trioxide-free basis.

In selected test methods (ASTM D3682; ASTM D4326), the ash is prepared by placing a weighed amount (usually 3–5 g) of coal (sieved to the specified size) in a cold muffle furnace. The temperature is gradually raised to 500 °C (932 °F) in 1 h and to 750 °C (1382 °F) in 2 h. The analysis of coal ash involves a combination of methods to determine the amounts of silica (SiO_2), alumina ($A1_2O_3$), ferric oxide (Fe_2O_3), titanium oxide (TiO_2), phosphorus pentoxide (P_2O_5), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O), and potassium oxide (K_2O).

A variety of methods have been recommended for the analysis of coal ash and these include: (1) atomic absorption (ASTM D3682; ASTM D3683; ASTM D4606; ASTM D6414), (2) inductively coupled plasma-atomic emission spectroscopy (ASTM D6349; ASTM D6357), and (3) X-ray fluorescence (ASTM D4326).

In the test for the fusibility of coal ash (ASTM D1857; ISO 540), the temperatures are observed at which triangular cones prepared from the ash begin to deform and then pass through specified stages of fusion when heated at a specified rate. The test procedure provides for performance of the test in a controlled atmosphere. It is first performed in a mildly reducing atmosphere and is then repeated with a second set of cones in an oxidizing atmosphere. The critical temperature most commonly referenced in the evaluation of the properties of coal is the softening temperature, that is, the temperature at which the cone has fused down to a spherical lump in which the height is equal to the width at the base. The significance of performing the test in reducing and oxidizing atmospheres is that most oxides of metals exhibit higher fusion temperatures in their highest state of oxidation. In practical combustion, there invariably are zones where the supply of oxygen is depleted or carbon dioxide is reversibly reduced to carbon monoxide in the presence of excess hot carbon. This can produce a reducing atmosphere in a hot zone where ash particles in an incipient state of fusion begin to melt. Slagging, fouling, and clinkering difficulties have been found to correlate with the fusibility of the ash.

5.3.2 Data Handling and Interpretation

Several formulae have been proposed for calculating the amount of mineral matter originally in the coal using the data from ashing techniques as the basis of the calculations. Of these formulae, two have survived and have been used regularly to assess the proportion of mineral matter in coal and these are the Parr formula and the King–Mavies–Crossley formula.

In the Parr formula, the mineral matter content of coal is derived from the expression:

$$\text{Mineral matter, } \%\ \text{w/w} = 1.08\text{A} + 0.55\text{S}$$

where A is the percentage of ash in the coal and S is the total sulfur in coal.

On the other hand, the King–Mavies–Crossley formula is a little more complex and attempts to take into account all of the chemical possibilities that can arise when minerals are present:

$$\begin{aligned}\text{Mineral matter, } \%\,\text{w/w} &= 1.09\text{A} + 0.5\text{S}_{\text{pyr}} + 0.8\text{CO}_2 - 1.1\text{SO}_3(\text{ash}) \\ &\quad + \text{SO3(coal)} + 0.5\text{Cl}\end{aligned}$$

where A, again, is the percentage of ash in the coal, S_{pyr} is the percentage of pyrite sulfur in the coal, CO_2 is the percentage of carbon dioxide that originates from the mineral matter in the coal, SO_3 (ash) is the percentage of sulfur trioxide in the ash; SO_3 (coal) is the percentage of sulfur trioxide in the coal, and Cl is the percentage of chlorine in the coal.

The ash value is the analytical value most commonly used for evaluating sampling procedures and is one of the values normally specified in coal contracts. In combustion, high ash content reduces the amount of heat obtainable from a given quantity of coal. High ash content also leads to the problem of handling and disposing of larger amounts of ash produced during combustion. The composition of coal ash is considered in the amount of clinkering and boiler tube slagging that may occur in a boiler. The design of most boilers is such that only coals with a specified range of ash content may be used in the efficient operation of the boiler. The amount of ash in coal used in a coking process is an indication of the amount of ash that will remain in the coke that is made. Coke with a high ash content that is used in a blast furnace requires more fluxing limestone to compensate for the ash and a greater volume of coke to obtain the required amount of usable carbon.

Various processes that result in a reduction of the mineral matter content and the sulfur content can be employed to clean coal. The ash content of raw coal is often used to select the best cleaning method and the ash content of the cleaned coal is used to measure the effectiveness of the cleaning process. In the commercial pulverization of coals, the amount and nature of ash is carefully considered before selecting pulverizing equipment or setting up the process.

5.4 VOLATILE MATTER

Volatile matter in coal refers to the components of coal, except for moisture, which are liberated at high temperature in the absence of air. Briefly, volatile matter consists of a variety of paraffin-type hydrocarbons, aromatic hydrocarbons, as well as sulfur-containing (and other heteroatom-containing) compounds. The test methods require the use of high temperature (on the order of 900 ± 5 °C, 1650 ± 10 °F) in some (Australian and United Kingdom) laboratories, which involves heating the coal sample to for 7 min in a cylindrical silica crucible in a muffle furnace. In other laboratories, the (ASTM) procedure that are preferred involve heating the sample to a slightly higher temperature (950 ± 25 °C, 1740 ± 45 °F) in a vertical platinum crucible. The use of different temperatures will give different results and for clarification, the test method employed for the determination must be indicated.

Volatile matter, as determined by the standard test methods (i.e., ASTM D3175; ISO 562), is the percentage of volatile products, exclusive of moisture vapor, released during the heating of coal or coke under rigidly controlled conditions. The measured weight loss of the sample corrected for moisture establishes the amount of material (volatile matter) evolved from the coal under the conditions of the test. However, the method, being empirical, requires close adherence to detailed specifications and since the test is essentially an assay of the sample of coal on a small scale rather than a purely chemical test, it is necessary, in order that results may be comparable between different laboratories that the conditions prescribed must be followed rigidly.

The type of heating equipment and the size and shape of the sample holders as well as the material from which they are made (platinum crucibles specified) all have some influence on the rate of heating of the sample and the range of temperatures to which it is exposed. The crucibles used are 10–20 ml capacity of specified size with deep-fitting lids. And there are two procedures for determination of volatile matter.

5.4.1 Test Methods

The determination of the volatile matter content of coal (ASTM D3175; ISO 562) is an important determination because volatile matter data are an integral part of coal classification systems (Chapter 2) and also form the basis of evaluating coals for their suitability for combustion and carbonization. The methods for determining volatile matter content are based on the same principle and consist of heating a weighed sample of coal (usually ca. 1 g) in a covered crucible to a predetermined temperature; the loss in weight (excluding losses due to water) is the volatile matter content (expressed as a weight percent).

In the test method (ASTM D3175), one gram of coal is weighed and placed in a pre-weighed platinum crucible (10–20 ml capacity, 25–35 mm in diameter, and 30–35 mm in height) with a close-fitting cover. The crucible is then suspended at a specified height in the furnace chamber. The temperature of the region in the furnace where the crucible is suspended must be maintained at $950 \pm 20\,^{\circ}\mathrm{C}$ ($1740 \pm 36\,^{\circ}\mathrm{F}$). After the more rapid discharge of volatile matter, as evidenced by the disappearance of the luminous flame, the cover of the crucible should be tapped to ensure that the lid is still properly seated to guard against the admission of air. After heating for exactly seven minutes, the crucible is removed from the furnace and cooled. The crucible should be weighed as soon as it is cold. The percentage loss of weight minus the percentage moisture equals the volatile matter. The residue in the crucible is coke and it is often advantageous to indicate the nature of the coke button obtained, since it provides a useful guide to the caking properties of the coal. It is usually described under the following headings: color, luster, swelling, fissuring, structure, both internal and surface, and hardness.

If decrepitation or entrainment takes place, the coal sample may be either heated more slowly or blended with a coking coal (the total volatile matter of which is known) in the ratio of 4 to 1 and the test carried out with the blend.

A modified procedure is used for coal that does not yield a coherent cake as residue in the determination and that evolve gaseous products at a rate sufficient to carry solid particles out of the crucible when heated at the standard rate. Such coal is referred to as sparking coal and normally include all low-rank noncaking coal and lignite, but may include other coal as well (ASTM D121; ASTM D3175). In this procedure (ASTM D3175, Section 7.3), the sample is suspended and heated in a cooler zone of the furnace such that the temperature inside the crucible reaches 600 ± 50 °C (1112 ± 90 °F) in 6 min. After the preliminary heating, the crucible is lowered into the hot zone (950 ± 20 °C, 1742 ± 36 °F) of the furnace and held there for 6 min. The crucible is then removed from the furnace and set on a metal block to cool before weighing. The cooling period should be kept constant and should not exceed 15 min to ensure uniformity of results. The volatile matter is calculated in the same manner as in the regular method.

The rate of heating of the sample influences volatile matter values and makes it necessary to calibrate equipment to achieve a satisfactory and reproducible heating rate. This calibration can be accomplished by using either a manual or an automatic mechanical device that lowers the sample crucible at a reproducible rate into the electrically heated furnace.

The crucibles and covers must be properly shaped to ensure a proper fit. A loose-fitting cover allows air to come in contact with the hot coal sample, with subsequent formation of volatile carbon oxides. Such an occurrence would result in a volatile matter value that is too high. Oxidation is not a serious problem in volatile matter determinations, since the rapid release of large amounts of gases during the test does prevent the entry of air into the crucible, thereby reducing the chance of oxidation. Addition of a few drops of a volatile material, such as toluene, may also help prevent oxidation.

The standard crucible method used for coal may be unsuitable for coke because coke often requires a higher temperature for the removal of the last remnants of the volatile matter. A thermogravimetric procedure in nitrogen at 1000 °C (1830 °F), or higher if necessary, for a specified period (30 min or more) that can be sued for coal (Beamish, 1994) may be desirable for coke. However, the precise conditions must be formally acknowledged when the yield of volatile matter is declared.

The specification giving a maximum clearance between the crucible and the lid is to standardize the amount of oxygen admitted to the heated sample. Unlimited oxygen results in complete conversion of the organic material to carbon dioxide and water. Limited oxygen provides for the formation of coke. This is analogous to the carbon residue tests so often used in petroleum technology (Speight, 2001, 2015).

The composition of the volatile matter evolved from coal is, of course, substantially different for the different ranks of coal and the proportion of incombustible gases increases as the coal rank decreases. Furthermore, in macerals isolated from any one particular coal, the volatile matter content decreases in a specific order; thus, exinite produces more volatile matter than vitrinite that, in turn, yields more volatile matter than inertinite.

The arbitrary nature of the test for volatile matter content precludes a detailed discussion of the various national standards. However, in general terms, the temperature is in the range of 875–1050 °C (1605–1920 °F), the duration of heating is 3.20 min. and the crucibles may be platinum, silica, or ceramic material. The German standard specifies a temperature of 875 °C (1605 °F) to be in accord with the industrial coking practice while other standards specify temperatures of 1000 °C (1830 °F) to 1050 °C

(1920 °F) to ensure maximum evolution of volatile matter under the test conditions: a temperature of 950 ± 20 °C (1740 ± 35 °F) is specified (ASTM D3175).

The various standards usually specify that a single crucible be employed although there has been a tendency in France and Belgium to advocate the use of two crucibles. In this method, the coal is heated in a crucible that is enclosed in a larger crucible with the space between the two crucibles filled with carbon (charcoal).

The chief differences in the methods for the determination of volatile matter emanating from the thermal decomposition of coal are: (1) variations in the size, weight, and materials of the crucibles used, (2) the rate of temperature rise, (3) the final temperature, (4) the duration of heating, and (5) any modifications that are required for coals which are known to decrepitate or which may lose particles as a result of the sudden release of moisture or other volatile materials. In essence, all of these variables are capable of markedly affecting the result of the tests and it is, therefore, very necessary that the standard procedures be followed closely.

The advantage of using two crucibles in methods of this type is believed to arise because of the need to prevent partial oxidation and, hence, the reduction of accrued errors due to loss of material as carbon oxides. Indeed, the very nature of the test for volatile matter content (which is not a determination of low molecular weight volatile matter in the coal but is more a test for volatile matter formed as a result of a wide variety of decomposition reactions during the test) dictates that partial oxidation reactions be excluded.

Furthermore, the lower rate of heating (resulting from the insulating effect of the charcoal) assists in preventing the election of solid particles that can occur when lower rank coals (in 10–20-ml platinum crucibles) are heated at the higher rate by direct insertion into the hot furnace. There is, therefore, no need for a modification of the method when it is applied to the lower rank coals (an advantage) since, in borderline cases, the result may be up to 2% lower (i.e., 32% volatile matter instead of 34% volatile matter) when the modification (the lower heating rate) is employed.

Mineral matter may also contribute to the volatile matter by virtue of the loss of water from the clays, the loss of carbon dioxide from carbonate minerals, the loss of sulfur from pyrite (FeS_2), and the generation of hydrogen chloride from chloride minerals as well as various reactions that occur within the minerals thereby influencing the analytical data (Given and Yarzab, 1978).

The characterization of coal either as agglomerating or as non-agglomerating for the purposes of rank classification is carried out in conjunction with the determination of the volatile matter content. Thus, if the residue remaining from the determination is in the form of an agglomerate button that is capable of supporting a 500-g weight without pulverization of the button or if the button shows swelling or cell structure, the coal is classified as agglomerating.

5.4.2 Data Handling and Interpretation

It is actually inaccurate to describe a coal as *containing 35% volatile matter* or as a coal *with 35% volatile matter* since the volatile matter is not present as such in the coal. The volatile matter is simply those products of the thermal decomposition of the coal substance that are expelled from the standard crucible under the standard conditions of the test and consequently a coal should be described accurately as *yielding 35% volatile matter*. While the first two statements are those most widely used and generally accepted in fuel technology literature, it should always be remembered that the suggestions they imply are incorrect.

Determination of volatile matter content using a slower heating rate is applicable to a wider variety of coals. However, the values obtained are sometimes lower (1–3% absolute) than those obtained from the regular method. This illustrates the empirical nature of this test and the importance of strict adherence to detailed specifications. The complexity of the constituents of coal that undergo decomposition during this test makes it necessary to have wide tolerances for reproducibility and repeatability.

Volatile matter values are important in choosing the best match between a specific type of coal burning equipment and the coal to use with the equipment. Such values are valuable to fuel engineers in setting up and maintaining proper burning rates. Volatile matter values are used as an indication of the amount of smoke that may be emitted from furnaces or other types of coal burning equipment. Limits may be set on the volatile matter content of the coal used in certain coal burning facilities in order to control smoke emissions.

In addition, the quantity of volatile matter released by coal during slow heating (beginning at room temperature) differed from the amounts released by rapid heating (i.e., the instant application of final temperature). When the coal is heated slowly, the volatile matter yield decreases and fixed carbon increases. In addition, there is also a relationship between the yield of volatile matter released by coal during rapid pyrolysis and the temperature to which the coal is subjected as well as to the atomic hydrogen to carbon ratio of the coal. Over the range of 200 °C (390 °F) to 1000 °C (1830 °F), the relationship is linear and partially treated coal, in which only part of the volatile matter is driven off, yields the calculated additional amount of volatile matter when heated to a higher temperature.

5.5 FIXED CARBON

Fixed carbon is the material remaining after the determination of moisture, volatile matter, and ash. The data produced should not be confused with the carbon content of coal as determined by ultimate analysis (Chapter 6) since some carbon is lost in hydrocarbons with the volatile matter. The fixed carbon value is used as an estimate of the approximate yield of thermal coke yield from a sample of coal – in a manner similar to the carbon residue produced from petroleum fractions (Speight, 2014a, b). Fixed carbon is determined by subtracting the mass of volatiles, determined earlier, from the original mass of the coal sample.

The fixed carbon value is one of the values used in determining the efficiency of coal burning equipment. It is a measure of the solid combustible material that remains after the volatile matter in coal has been removed. For this reason, it is also used as an indication of the yield of coke in a coking process. Fixed carbon plus ash essentially represents the yield of coke. Fixed carbon values, corrected to a dry, mineral-matter-free basis, are used as parameters in the coal classification system (ASTM D388).

Thus, an interesting comparison, the test for determining the carbon residue (Conradson), that is, the coke-forming propensity of petroleum fractions and petroleum products (ASTM D189; ASTM D2416) advocates the use of more than one crucible. A porcelain crucible is used to contain the sample and this is contained within two outer iron crucibles. This corresponds to the thermal decomposition of the sample in a limited supply of air (oxygen) and the measurement of the carbonaceous residue left at the termination of the test.

5.6 COAL ASSAY

In some instances, the information gained from the proximate analysis coal sample requires being supplemented by data that provides a more detailed examination of the behavior of the coal during carbonization. Such a test provides data relating to the yields and qualities of coke, tar, liquor, and gas that can be correlated with those obtained in large-scale practice. Two types of assay have been developed, one for use at 600 °C (1112 °F) that can be related to low temperature carbonization processes and the other at 900 °C (1650 °F) that gives results allied to those obtained in high temperature carbonization practice such as gas and coke manufacture.

5.6.1 Gray–King Assay at 600 °C (1112 °F)

In the test method, the charge of coal is heated in a silica retort by means of an electric furnace that is arranged so that it can be pushed over the retort after having been heated to the necessary temperature. The volatile products pass from the retort to a condenser that can be cooled, if necessary, in a vessel containing a cooling medium, and in which the tar and liquor collect. The remaining gases are freed from ammonia by passage through a glass scrubber containing glass beads drenched with dilute sulfuric acid and then pass into the gas holder, a three-to-four liter vessel containing water saturated with gas from previous assays, where they are collected at constant pressure by means of the arrangement; any evolved water is collected in a glass or metal jar.

During the first period of heating observe the temperatures at which the following events occur: (1) appearance of oil vapor, (2) evolution of gas as distinct from displacement due to expansion, and (3) further evolution of gas, at the onset of which the rate of discharge of water from increases suddenly. These three temperatures are usually clearly defined and are characteristic of the sample being assayed.

Correlation of the data with industrial practice is easily accomplished and the behavior of any coal on carbonization on the large scale is fairly accurately predictable. For example: (1) the coke yield and the volatile matter remaining in the coke are approximately equal to those furnished on the large scale, (2) the gas yield is usually slightly greater than the large-scale yield, mainly because of the necessity for reducing as much as possible the period of carbonization in industrial practice, (3) the tar yield is much greater than that given by large-scale technique. Normally the commercial yield varies from 50% to 80%, of the assay yield of tar, (4) the yields of ammonia are comparable, and (5) if an analysis of the gas is required it is advisable to carry out two assays and use the gas from the first to sweep the air out of the assembled apparatus before the second test is commenced. The gas obtained from the second experiment will then be practically free from contamination with air.

5.6.2 Gray–King Assay at 900 °C (1652 °F)

In this assay, the tar vapors are cracked over crushed silica brick and the increased yield of gas is accommodated in a larger receiver of some ten liters capacity. Owing to the possibility of tar fog remaining uncondensed, the condenser in this case is followed by a U-tube packed with absorbent cotton wool and both are immersed in a mixture of crushed ice and salt. The cracking material is contained in the retort that is heated by two electric furnaces, one carbonizing the 6-in. coal layer at a final temperature of 900 °C (1650 °F) and the other maintaining the cracking zone at 800 °C (1470 °F).

Since the high-temperature assay is used mainly for the examination of gas-making coals, the range of coke types normally encountered is considerably smaller than that met with in low-temperature assays and, as a consequence, no standard classification of coke types has been drawn up, nor is such a classification so necessary in this case. Nevertheless a full description of the coke should always be made.

During the performance of the test, the temperature of the cracking furnace is fairly critical, especially during the early stages of the carbonization. With the carbonization furnace increasing in temperature at the prescribed rate, the influence of this on the temperature of the cracking furnace is appreciable when it is remembered that the cracking furnace current has been originally adjusted to maintain 800 °C (1470 °F) against room temperature.

Strongly swelling coals should be carbonized either in admixture with electrode carbon or, preferably, without dilution, in a special retort in which the section containing the coal has been enlarged in diameter to 30 mm, the remaining part of the tube being unaltered. This permits a 20 g. charge of a highly swelling coal to be carbonized without the necessity of adding electrode carbon.

5.6.3 Other Carbonization Tests

In those circumstances in which the detailed information furnished by the Gray–King assay is not essential, one or other of two simpler tests that, in practice, are frequently carried out in addition to the assay may be used to assess the caking characteristics of coal. These are the *agglutinating value test* and the *free swelling index test*. The former gives a measure of the caking properties of a coal while the latter indicates the degree of swelling which a sample of coal will undergo during carbonization, both factors of importance in the carbonization industries.

In the *agglutinating value test*, the caking properties of the coal are progressively destroyed by the addition of sand of specified characteristics until the coal-sand mixture, on carbonization under controlled conditions, just fails to satisfy one or both of two conditions.

The *agglutinating value* (sometimes referred to as the *caking index*) of coal is the maximum whole number ratio of sand to coal in a 25 g. mixture which, on carbonization at 900 ± 15 °C (1650 ± 27 °F) for 7 min in a standard silica crucible, produces a carbonized mass capable of supporting a 500 g weight and yielding less than 5%, of loose, unbound material. It is essential for this test that not only are the experimental conditions rigidly observed but the coal must always be ground to the same degree of fineness to ensure strictly comparable figures (different size distributions may lead to widely different agglutinating values) and the sand used must be of uniform quality in respect to sharpness and purity as well as particle size.

An approximate idea of the degree of swelling (the *swelling index*) experienced by a coal on carbonization may be obtained from the coke button left after the determination of volatile matter, but in many cases this measure of the swelling power is not sufficiently discriminating, principally because this is not the main function of the test.

For this reason, a standard crucible test has been devised in which the chief features, compared with other tests, are the use of a leveled coal surface, a crucible of special shape and unidirectional heating by a gas flame. As a result, regularly shaped coke buttons are obtained and the degree of swelling is assessed by comparison with profiles of standard buttons.

The conditions for obtaining the correct heating should be checked by means of a fine wire thermocouple inserted through a pierced lid and having its unprotected junction in contact with the center of the base of the empty crucible. The end of the couple should be formed into a flattened loop so that the junction and a portion of each wire rests on the bottom of the crucible during a temperature measurement. The couple should be made of wires not heavier than 34-gauge platinum or 26-gauge base metal.

As an extension of the proximate analysis or coal assay, it is worthy of note that new methods continued to be developed. For example, thermogravimetric analysis has been extended to cover determinations of volatile matter (as well as determination of moisture and ash) in coal and coke. These constituents can be measured by pyrolyzing the samples in oxygen and air and the weight loss at prescribed temperatures was measured by using a thermobalance.

Fixed carbon and percentages of moisture, volatile matter, and ash were measured in coal in less than fifteen minutes using a thermogravimetric analyzer. For coal analysis, the sample is purged with nitrogen at 100 °C (212 °F) to dry the sample and remove oxygen. The percentage of moisture (weight loss) is read at this point. The loss of volatile matter can be measured by heating the sample to 600 °C (1112 °F) at 160 °C/min (288 °F/min) and heating at 600 °C (1112 °F) for 2 min; switching the purge gas to oxygen while heating to 900 °C (1652 °F) yields a residual weight equivalent to the ash content. Results from tests using this method have not yet been compared with results from tests using standard coal procedures.

5.7 OTHER METHODS

Although, in many laboratories the aforementioned methods remain the methods of choice for determining the proximate analysis of coal, there is also a test method for the proximate analysis of coal by instrumental procedures, assuming that calibration is an integral part of the procedure (ASTM D5142). This method covers the determination of moisture, volatile matter, and ash and the calculation of fixed carbon in the analysis of coal and coke samples prepared in accordance with standard protocols (ASTM D2013) and which are determined sequentially in a single instrumental procedure by establishing the loss in mass of the analysis specimen when heated under rigidly controlled conditions of temperature, time, atmosphere, and specimen mass.

The results may require a correction for bias or be corrected for instrument calibration using samples of known proximate analysis. However, the standard test methods (ASTM D3173; ASTM D3174; ASTM D3175) are considered to be the referee test methods. The instrumental test methods are not applicable to thermogravimetric analyzers using microgram size samples. The moisture value determined can be used for calculating other analytical results to a dry basis and, when used in conjunction with the air-dry moisture loss (ASTM D2013; ASTM D3302), the calculated total moisture can be used to convert dry basis analytical results to the as-received basis. In addition, the result of the ash determination can be applied in ultimate analysis (ASTM D3176) for converting the analytical data to an ash-free basis or for application in the equations related to mineral matter content.

Briefly, and as expected, moisture is determined by establishing the loss in mass of the analysis specimen of coal or coke when heated under rigidly controlled conditions of temperature, time, atmosphere, sample mass, and equipment specifications. Volatile matter is determined by measuring the loss in mass of the moist or dried analysis specimen of coal or coke when heated under rigidly controlled conditions. The measured weight loss is the yield of volatile matter, after correcting for the moisture content. Ash is determined by amount of residue after burning the coal under rigidly controlled conditions of sample weight, temperature, time, atmosphere, and equipment specifications. In these instrumental methods, moisture, volatile matter, and ash may be determined sequentially in a single instrumental procedure.

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6

ULTIMATE ANALYSIS

6.1 INTRODUCTION

The ultimate analysis of coal involves determination of the weight percent carbon as well as sulfur, nitrogen, and oxygen (usually estimated by difference). Trace elements that occur in coal (Vesper et al., 2008; Diehl et al., 2012) are typically included as a part of the ultimate analysis.

The carbon determination includes carbon present as organic carbon occurring in the coal substance and any carbon present as mineral carbonate. The hydrogen determination includes hydrogen present in the organic materials as well as hydrogen in all of the water associated with the coal (Chapter 5). In the absence of evidence to the contrary, all of the nitrogen is assumed to occur within the organic matrix of coal. On the other hand, sulfur occurs in three forms in coal: as (1) organic sulfur compounds, (2) inorganic sulfides that are, for the most past, mostly the iron sulfides pyrite and marcasite (FeS_2), and (4) inorganic sulfates (e.g., Na_2SO_4, $CaSO_4$). The sulfur value presented for ultimate analysis may include, depending on the coal and any prior methods of coal cleaning, inorganic sulfur and organic sulfur.

Moisture and ash yield (Chapter 5) are not determined as a part of the data presented for ultimate analysis but must be determined so that the analytical values obtained can be converted to comparable bases other than that of the analysis sample. In other words, analytical values may need to be converted to an *as received* basis, a *dry basis*, or a *dry, ash-free basis*. When suitable corrections are made for any carbon, hydrogen, and sulfur derived from the inorganic material, and for conversion of ash

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Handbook of Coal Analysis, Second Edition. James G. Speight.

to mineral matter, the ultimate analysis represents the elemental composition of the organic material in coal in terms of carbon, hydrogen, nitrogen, sulfur, and oxygen.

The standard method for the ultimate analysis of coal and coke (ASTM D3176) includes the determination of elemental carbon, hydrogen, sulfur, and nitrogen, together with the ash in the material as a whole. Oxygen is usually calculated by difference. The recommended test methods for elemental analysis include the determination of carbon and hydrogen (ASTM D3178), nitrogen (ASTM D3179), sulfur (ASTM D3177; ISO 334; ISO 351) with associated determination of moisture (ASTM D3173), and ash (ASTM D3174) to convert the data to a moisture-ash-free basis.

6.2 CARBON AND HYDROGEN

Carbon and hydrogen that, respectively, account for 70–95% by weight and 2–6% by weight (dry-ash-free) of the organic substance of coal are often thought to be the most important constituents of coal. Almost all of the carbon and hydrogen in coal occurs in the combined form in the complex organic compounds that make up coal. But carbon also occurs in the mineral carbonates, with calcite being the principal component and hydrogen is also present in the various forms of moisture found in coal.

6.2.1 Test Methods

All methods of determining the carbon and hydrogen content of coal are very similar insofar as the determination of elemental carbon and hydrogen is performed by combustion in a closed system (combustion train) and the products of combustion are collected in an absorption train. The percentages by weight of carbon and hydrogen are calculated from the gain in weight of the relevant segments of the absorption train. This method gives the total percentages of carbon and hydrogen in the coal, including any carbon in the carbonates and any hydrogen in free moisture and in water of hydration of silicates. Reporting hydrogen and oxygen in the free water (moisture) associated with the sample may optionally be included or excluded from the hydrogen and oxygen values. The test method recommends making a notation of the option (*as received*, or *dry*, or *dry, ash-free*) used as the basis for reporting results. Hydrogen in the water of hydration of silicates is generally ignored but can introduce errors in the cases of coals containing high amounts of mineral matter. Overall, it is preferable, therefore, that the hydrogen and oxygen associated with the free moisture not be included in the hydrogen and oxygen values and that moisture be reported as a separate item.

Several automated elemental analysis systems that are suitable for coal analyses are allowing the simultaneous determination of carbon, hydrogen, and nitrogen for multiple samples. In fact, rather than by difference (which also accumulates all of the errors of other determinations), oxygen can be determined using a separate combustion system. The systems convert coal (catalytically) to N_2, CO_2, and H_2O, which are separated with a gas chromatographic column and detected through a sensor, such as a dual thermal conductivity cell. Sulfur can be determined using a similar system that excludes the oxygen determination.

In practice, the older well-used methods (ASTM D3178; ISO 609; ISO 625) for determining carbon and hydrogen involve combustion of an exact amount of the coal in a closed system and the products of the combustion (carbon dioxide and water) determined by absorption. The combustion is usually accomplished by placing the ground coal (to pass through, for example, a 60-mesh/250-micron sieve) in a stream of dry oxygen at temperatures of the order of 850–900 °C (1560–1650 °F) (ASTM D3178). Complete conversion of the combustion gases to carbon dioxide and water can be achieved by passing the gases through heated cupric oxide.

As noted earlier, the equipment used for the determination of the carbon and hydrogen content of coals basically consists of two parts: the combustion unit and the absorption train (ASTM D3178). The combustion unit is made up of three separate electrically heated furnaces and the combustion tube. The first furnace, at the inlet end of the tube, is approximately 130 mm long and can be moved along the tube. The second and third furnaces are 330 and 230 mm in length, respectively, and are mounted in a fixed position around the combustion tube. The required operating temperatures are 850–900 °C (1562–1652 °F), 850 ± 20 °C (1562 ± 36 °F), and 500 ± 20 °C (932 ± 36 °F) for the first, second, and third furnaces, respectively. The combustion tube can be constructed from fused quartz or high-silica glass. The combustion tube is packed with lead chromate ($PbCrO_3$) or silver (Ag) gauze under the third furnace and cupric oxide (CuO) under the second furnace. Oxidized copper gauze plugs are used to contain these components in the tube.

The absorption train is composed of a tube packed with water absorbent, a second tube packed with a carbon dioxide absorbent, and a guard tube packed with equal volumes of the water and carbon dioxide absorbents. Anhydrous magnesium perchlorate ($MgClO_4$) is commonly used for the water absorbent, while sodium hydroxide (NaOH) or potassium hydroxide (KOH) impregnated in an inert carrier is used as the carbon dioxide absorber.

In the analytical procedure, a weighed amount of coal is placed in either a boat (glazed porcelain, fused silica, or platinum) and inserted into the combustion tube under the first furnace where the sample is burned in oxygen. The combustion products are allowed to flow over the heated copper oxide and lead chromate or silver and into the absorption train. The copper oxide ensures complete combustion of the carbon and hydrogen in the coal, whereas the lead chromate absorbs the oxides of sulfur. If silver gauze is used, both the sulfur oxides and chlorine will be absorbed. The pre-weighed absorbers in the absorption train absorb water and carbon dioxide and the percent of carbon and hydrogen in the sample are calculated from the gain in weight of absorbers.

This particular method of combustion analysis for carbon and hydrogen (Liebig method) is used internationally although some modifications may have been made by the various national standards organizations. The sample size can vary from as little as 1–3 mg (microanalysis) to 100–500 mg (macroanalysis) with combustion temperatures as high as 1300 °C (2370 °F). However, the method must ensure complete conversion of all of the carbon in the coal to carbon dioxide and all of the hydrogen to water. Oxides of sulfur and chlorine are removed by passing the products of combustion over heated lead chromate and silver gauze. The carbon (as carbon dioxide) and hydrogen (as water) are calculated from the increase in weight of the absorbents used to collect the water and carbon dioxide. Oxides of sulfur (and chlorine, which may be released in significant amounts) are usually removed from the combustion gases by passage over silver at circa 600 °C (1110 °F) while nitrogen dioxide is removed by lead chromate or manganese dioxide. The preliminary and final procedure involves the passage of dry air (also free of carbon dioxide) through the system in order that the absorption train may be weighed full of air before and after the determination.

It is essential that both air and oxygen are pure. If not purification can be assured by passage through a purification train consisting of (1) 30% aqueous solution of potassium hydroxide, (2) concentrated sulfuric acid, and (3) two U-tubes charged with soda lime (or other dry absorbent for carbon dioxide) and calcium chloride. It may be advisable to use two purification trains (one for each gas) leading to a common tube for delivery to the combustion train.

Usually, the coal burns smoothly in the stream of oxygen. However, if the combustion unit used for burning the sample is heated too rapidly, volatile matter may be released at such a rate that some of it may pass through the entire system and not be completely burned or absorbed. To prevent this from happening, the temperature of the combustion unit must be at the proper level and enough time must be allowed for complete combustion. In addition, a proper flow of oxygen must be maintained through the system.

The formation of oxides of nitrogen during the combustion process may lead to slightly high results for carbon and hydrogen, since the oxides are acidic in nature and would be absorbed in the absorption train. There are indications that the hydrogen value would not be greatly influenced but that the carbon value would be higher by an amount depending upon the nitrogen content and the nitrogen oxides formed during the combustion. For more precise results, the oxides of nitrogen can be removed by absorption on manganese dioxide, or in some cases lead dioxide, before absorption of the water and carbon dioxide. However, caution is advised in treating any potential error lightly.

Since inorganic carbonates and nitrogen oxides contribute to the carbon value in coal, as it is normally determined, consideration of this issue is necessary. Hydrogen values also are usually high, due to the inclusion of the various forms of moisture that are present in coal. All of these factors limit the reliability of carbon and hydrogen data for predicting the amount of combustible carbon and hydrogen in coal.

Finally, and most important, blank determinations should be carried out at regular intervals.

6.2.2 Data Handling and Interpretation

If the coal is not dried, the water collected in the adsorption train also contains water present originally as moisture in the coal (Chapter 5). The hydrogen equivalent to the percentage of moisture in the coal is deducted from the percentage of hydrogen given by the aforementioned method to arrive at the corrected figure or, alternatively, the quantity of moisture present in the weight of coal used is subtracted from the weight collected in the calcium chloride tube before calculating the equivalent weight of hydrogen burned.

Subtracting one-ninth of the determined moisture from the determined hydrogen can make a reasonable correction to the hydrogen value for the moisture in coal. A correction to the hydrogen value for the water of hydration of mineral matter is more difficult. The water of hydration of mineral matter for some (United States) coals has been estimated to be 8% of the ash value. A correction to the hydrogen value for the water of hydration can thus be estimated by multiplying the ash value by 0.08 and one-ninth of this figure will give the correction to be subtracted from the determined hydrogen. Upon making these corrections for the forms of moisture, the value for the hydrogen can be calculated:

$$H = H_{\text{as-determined}} - 2.02/18.02\,[M_{\text{as-determined}} + 8/100 \times A_{\text{as-determined}}]$$

H is hydrogen, M is moisture, and A is ash.

The results of the carbon and hydrogen analysis may be reported on any number of bases, differing from each other in the manner by which moisture values are treated. Inclusion of the hydrogen of moisture and water of hydration of mineral matter in the hydrogen value is common practice for the as-determined and as-received bases. Hydrogen values on the dry coal basis, however, are commonly corrected for the hydrogen of moisture. No corrections are normally made to the determined hydrogen value for the water of hydration of mineral matter, due to the uncertainty of the estimate of its value.

6.3 NITROGEN

Nitrogen occurs almost exclusively in the organic matter of coal. Very little information is available concerning the nitrogen-containing compounds present in coal, but they do appear to be stable and are thought to be primarily heterocyclic. The original source of nitrogen in coal may have been both plant and animal protein. Plant alkaloids, chlorophyll, and other porphyrins contain nitrogen in cyclic structures stable enough to have withstood changes during the coalification process and thus to have contributed to the nitrogen content of coal.

6.3.1 Test Methods

The standard procedure of nitrogen determination by many laboratories is the Kjeldahl method (ASTM D3179; ISO 333), although there are standard methods that involve the Dumas technique (DIN 51722) and the gasification procedure (DIN 15722). Neutron activation analysis has also been proposed for the determination of nitrogen in coal, coal ash, and related products (Volborth, 1979a).

In the Kjeldahl method, pulverized coal is boiled coal with concentrated sulfuric acid containing potassium sulfate and a suitable catalyst to reduce the time for digestion. The catalyst is usually a mercury salt, selenium itself, or a selenium compound, or a mixture of the two. Selenium is regarded as being particularly advantageous.

The Kjeldahl–Gunning macro-method is the one most widely used for determining nitrogen (ASTM D3179). By this method, any nitrogen present in the sample is converted into ammonium salts by the destructive digestion of the sample by a hot mixture of concentrated sulfuric acid and potassium sulfate. After the digestion mixture has been made alkaline with sodium or potassium hydroxide, ammonia is expelled by distillation, condensed, and absorbed into a sulfuric acid solution and the excess acid is titrated with sodium hydroxide solution. The alternative method is similar except that, after the complete digestion, the ammonia is distilled into a boric acid solution and titrated with a standard acid solution. Proper precautions should be taken in carrying out this procedure, especially the digesting and distillation steps. In addition to the possibility of losing nitrogen-containing species if the proper heating rate is not observed, there is the problem of working with hot concentrated sulfuric acid and caustic solutions.

A catalyst is used in the Kjeldahl–Gunning method to increase the rate of digestion of the coal and, hence, shorten the digestion period. For most bituminous and low-rank coals, the digestion period is on the order of three to 6 h, even with the aid of a catalyst, and anthracite may require as much as 12–16 h. A variety of catalysts, such as mercuric sulfate ($HgSO_4$) and selenium, mercuric selenite ($HgSeO_3$), or cupric selenite dihydrate ($CuSeO_4.2H_2O$), can be used. However, when a mercury-containing catalyst is used, the addition of potassium or sodium sulfide (Na_2S) to the digestion mixture is necessary. The sulfide ions precipitate any mercuric ions as mercuric sulfide (HgS) and prevent formation of a stable mercury-ammonia complex ion (ammonia is produced in the reaction).

The most serious issue associated with the use of the Kjeldahl–Gunning method is whether or not complete conversion of nitrogen in the nitrogenous compounds to ammonia occurs. The main reason is that complete conversion may not be accomplished for several reasons. The chemistry is more complex and is not always straightforward and nitrogen can, in the presence of various oxidizing agents, be oxidized to nitrogen oxides that may be lost from the analysis. In addition, pyridine carboxylic acids may be formed and these compounds are resistant to further decomposition. Thus, the somewhat limited oxidation and digestion conditions and the possible formation of unwanted but stable by-products usually require a lengthy digestion period. In many cases, to ensure complete conversion of the nitrogen to ammonia, the addition of chromic oxide (Cr_2O_3) to the digestion mixture increases the rate of digestion of coke.

The semi-micro Kjeldahl–Gunning method (ASTM D3179; ISO 333) has become a widely used method for determining nitrogen in coal but there is some doubt about whether or not nitrogen recovery is complete by this procedure. In fact, the fate of nitrogen in the Kjeldahl method depends on its chemical form in the coal, the inorganic compounds added to catalyze the hydrolysis and the amounts and types of compounds used to raise the boiling point of the mixture.

The Dumas method of nitrogen determination consists of an oxidation method in which a mixture of coal and copper oxide (CuO) is heated in an inert atmosphere to produce carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2). The carbon dioxide is absorbed, the water condensed, and the nitrogen determined volumetrically. Although the Dumas method has been employed for many years, various modifications have been made to increase accuracy and precision.

The gasification method consists of mixing coal with a mixture of two parts of the Eschka mixture (i.e., 67% w/w light calcined magnesium oxide and 33% w/w anhydrous sodium carbonate), six parts of soda lime, and one part of molybdenum oxide. The sample is then placed in a porcelain boat, covered with platinum gauze, and heated (in a quartz tube) to 200–250 °C (392–482 °F). The sample is then heated in steam at 850–950 °C (1562–1742 °F). The gases pass into 0.1N sulfuric acid where ammonia is chemically absorbed as ammonium sulfate and then determined by one of the usual techniques.

Nitrogen determination by perchloric acid digestion of coal without catalysts is reportedly safe and much more rapid than the conventional Kjeldahl procedure. Nitrogen is determined in the digest by the usual ammonia evolution and titration. However, extreme care should be taken whenever perchloric acid is used. Nuclear reactions have been successfully applied to the determination of nitrogen in coal. Coal has been irradiated with fast neutrons from a 14-MeV generator to produce ^{13}N, which decays via positron emission and has a 10-min half-life. Standard deviation for the nitrogen determinations was 0.07%. The instrumental neutron activation values were 6.8% higher (0.1% N) on the average than those obtained using the standard Kjeldahl procedure. In the Kjeldahl procedure, loss of elemental nitrogen or nitrogen oxides or resistant heterocyclic nitrogen compounds can sometimes cause data errors, although most of these have been eliminated by application of modern laboratory procedures. Because results from instrumental neutron activation for nitrogen are independent of these factors, it has been suggested that the activation method is the more accurate of the two.

6.3.2 Data Handling and Interpretation

Nitrogen data are primarily used in research and for the comparison of coals. These values are needed so that the oxygen content of a coal can be estimated by difference. During combustion, the nitrogen in coal can be converted to ammonia, elemental nitrogen, or nitrogen oxides, depending on the conditions of burning and the nature of the coal used. Nitrogen values could possibly be used to estimate the amount of nitrogen oxides that would be emitted upon burning of certain coals. Coal nitrogen values are also useful in predicting the amount of nitrogen in the products of coal liquefaction and gasification processes.

6.4 OXYGEN

Oxygen occurs in both the organic and inorganic portions of coal. In the organic portion, oxygen is present in hydroxyl (–OH), usually phenol groups, carboxyl groups

(CO_2H), methoxyl groups ($-OCH_3$), and carbonyl groups ($=C=O$). In low-rank coal, the hydroxyl oxygen averages about 6–9%, while high-rank coals contain less than 1%. The percentages of oxygen in carbonyl, methoxyl, and carboxyl groups average from a few percent in low rank and brown coal to almost no measurable value in high-rank coal. The inorganic materials in coal that contain oxygen are the various forms of moisture, silicates, carbonates, oxides, and sulfates. The silicates are primarily aluminum silicates found in the shale-like portions. Most of the carbonate is calcium carbonate ($CaCO_3$), the oxides are mainly iron oxides (FeO and Fe_2O_3), and the sulfates are calcium and iron ($CaSO_4$ and $FeSO_4$).

6.4.1 Test Methods

For many years, no satisfactory method existed for the direct determination of oxygen in coal. In practice, in the expression of the ultimate analysis it is customary to deduct from 100.0 the sum of the percentages of moisture, ash, carbon, hydrogen, nitrogen, and sulfur (ASTM D3176).

$$\%\ \text{oxygen} = 100 - (\%\text{C} + \%\text{H} + \%\text{N} + \%\text{S}_{\text{organic}})$$

The resulting figure for oxygen is, therefore, burdened with the accumulation of all the experimental errors involved in the determinations of the other constituents that form part of the equation. Consequently, the oxygen content was, and still is, of a low order of accuracy. For this reason, oxygen determined by difference should not be designated *percent oxygen* but *percent oxygen by difference*.

The most widely used procedure for oxygen determination consists of pyrolyzing coal in the presence of nitrogen and subsequent passage of the products over hot (1100 °C, 2012 °F) carbon or platinized carbon. The oxygen in the volatile products is thereby converted to carbon monoxide, which can be determined by a variety of techniques (Gluskoter et al., 1981). For example, the carbon monoxide can be oxidized to carbon dioxide, usually with iodine pentoxide, which releases free iodine. The iodine released can be determined titrimetrically or the carbon dioxide produced can be absorbed and determined gravimetrically to calculate the amount of oxygen in the original samples.

However, the various sources of oxygen in coal, such as the oxygen in the moisture and water of hydration of mineral matter, the oxygen in carbonates, and the oxygen in silicates and other inorganic compounds, in addition to the oxygen in the organic matter, all offer hurdles in producing data that are beyond question. The original procedure has been modified in several ways to reduce the contribution made by some of these oxygen sources to the determined oxygen value. Thorough drying in a nitrogen atmosphere before the pyrolysis of the sample minimizes the effect of moisture and much of the mineral matter is removed by a specific gravity separation or chemical treatment with hydrochloric and hydrofluoric acid. The reduction of mineral matter minimizes the contribution that the water of hydration and the inorganic compounds, such as carbonates, silicates, oxides, and sulfates, make to the determined oxygen value. The oxygen value obtained by this method, after all the pretreatment steps are taken to remove moisture and mineral matter, is essentially a measure of the oxygen contained in the organic matter in coal.

There are several other methods for the direct determination of oxygen that have met with some success when applied to coal and, therefore, deserve some mention here because it is conceivable that at some future date one of these methods (or a modification thereof) could find approval as a recognized standard method for the direct determination of oxygen in coal.

An oxidation method that has been applied to coal involves the combustion of a weighed amount of coal with a specific quantity of oxygen. The oxygen in the coal is determined by deducting the added quantity of oxygen from the sum of the residual oxygen and the oxygen of the oxidation products. The disadvantages of the method arise because of the difficulties associated with the accurate measurement of the substantial volume of oxygen used and the quantity and quality (i.e., composition) of the combustion products.

Another method for the determination of oxygen in coal involves reduction of the coal by pyrolysis in the presence of hydrogen whereupon the oxygen is converted catalytically to water. However, the procedure is relatively complex and, furthermore, the catalyst may be poisoned by sulfur and by chlorine.

In the neutron activation method (Volborth, 1979a,b), as illustrated by the reaction:

$$16\mathrm{O} + \text{neutron} = 16\mathrm{N} + \text{proton}$$

the concentration of oxygen being determined by measuring the radiation from the sample. The method is nondestructive and rapid, but if only the organic oxygen is to be determined, then the sample must first be demineralized.

As oxygen in coal includes both oxygen in organic matter and inorganic oxygen from mineral matter and moisture, demineralization or float-sink cleaning of coal is usually employed to remove inorganic oxygen. Using a modified method (ISO 602), the results of the direct determination of oxygen in untreated coals showed significant variations from oxygen values obtained by the difference method. The differences were primarily caused by sulfur trioxide being retained in the ash, sulfur in the pyrite form in the whole coal, and small quantities of inorganic oxygen. Much closer agreement was obtained when ash values used for calculation of oxygen by difference were corrected to a better approximation of mineral matter:

$$\text{Corrected ash} = \text{ash}_{\text{determlned}} - \mathrm{SO}_{3\text{ash}}$$

Pyrite sulfur in whole coal is added to the ash value, organic sulfur is added in the ultimate analysis as part of the coal substance, and CO, from carbonates is added to total carbon and oxygen values. Demineralized coals gave the best results for organic oxygen; values from untreated coals were usually higher because they included inorganic oxygen.

The use of gas chromatography to determine oxygen in coal is considerably faster than the methods just described. The oxygen produced from coal pyrolysis in a vacuum was catalytically converted to carbon monoxide and the total quantity of gas was measured. Gas chromatography was then used to measure the concentration of carbon monoxide in the gas.

A method employing reduction fusion using radio frequency heating of coal has been reported for the determination of oxygen in coal. An induction furnace was used to heat an iron-tin bath in a graphite crucible supported in a bed of carbon black powder that was contained in a silica thimble. All were enclosed in a reaction tube through which argon carrier gas flowed. Pyrolysis products from a sealed coal sample (10 mg) dropped into the bath were purified and oxygen was converted to carbon dioxide that was absorbed and weighed. Satisfactory results were obtained for organic oxygen in demineralized coal. For untreated coal, satisfactory results were obtained when a range of correction techniques for oxygen was applied to coals containing more than 5% ash.

6.4.2 Data Handling and Interpretation

When the oxygen value is estimated by subtracting the determined percentages of all other constituents from 100, the errors in the determined values are reflected in the estimated oxygen value. These errors may be partially compensating or they may be additive. It is important that accurate determinations are made and appropriate corrections for overlapping values, especially hydrogen, be calculated. Thus:

$$\mathrm{O} = 100 - [\mathrm{C} + \mathrm{H} + \mathrm{N} + \mathrm{S} + \text{ash}]$$

All values are expressed as percentages and C is the as-determined carbon (ASTM D3178), H is the as-determined hydrogen (ASTM D3178), N is the as-determined nitrogen (ASTM D3179), S is the as-determined sulfur (ASTM D3177, ASTM D4239), and ash is the as-determined ash (ASTM D3174). All these aforementioned values pertain to those obtained from the analysis sample. The as-determined value for carbon represents both the organic and the carbonate carbon. The as-determined value for hydrogen represents the organic hydrogen, the hydrogen in the residual moisture, and the hydrogen in the water of hydration of mineral matter. The sulfur value is the total sulfur in coal and represents that that is contained in the organic matter, pyrites, and sulfates. Ash is mostly metal oxides and silicon oxide. The estimated value of the oxygen therefore includes the oxygen contained in the organic matter, in the moisture, and in the mineral matter, except that that is combined with metals in coal ash.

A rough estimate of the oxygen contained in the organic matter in coal can be obtained by correcting the oxygen value obtained by calculation for the oxygen in residual moisture and water of hydration of mineral matter. Adding this correction to the sum subtracted from 100 gives the following expression:

$$\mathrm{O}_x = 100 - [\mathrm{C} + \mathrm{H} + \mathrm{N} + \mathrm{S} + \text{ash} + 8/9(\mathrm{H_2O} + \mathrm{H_2O}\text{ of hydration})]$$

where H_2O is the as-determined residual moisture (ASTM D3173) and H_2O of hydration is 8.0% of ash.

Several improvements in the estimation of organic oxygen can be made when the analytical data are available. Values for chlorine, carbon dioxide, pyrite sulfur, and sulfur in coal ash are helpful in improving the estimation. Failure to include the chlorine value in the sum subtracted from 100 leads to a high value for the organic oxygen. Moreover this oxygen value should be reduced for the oxygen present in the carbon dioxide that is associated with the mineral matter.

The inclusion of both total sulfur and ash in the sum that is subtracted from 100% in estimating the oxygen content of coal lowers the oxygen value, since part of the sulfur may be retained in the ash. The sulfur that is retained is therefore counted twice in the sum for subtraction. Correcting the coal ash for the sulfur trioxide (SO_3) present compensates for this error. Likewise, the coal ash should be corrected for any ferric oxide (Fe_2O_3) that results from the heating of pyrite (FeS_2) in air, as is done in the ashing process. In the ashing process, 3 oxygen atoms replace 4 sulfur atoms:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

On a weight basis, 48 parts of oxygen replace 128 parts of sulfur. This oxygen is from an external source and not from the coal itself. Since this oxygen contributes to the weight of the ash, a correction of the pyrite sulfur value is necessary. The pyrite sulfur that is replaced is accounted for in the total sulfur value. When the values are available to make these corrections, a good estimate of the percentage of oxygen in the organic or combustible portion of coal can be made, according to the following formula:

$$\begin{aligned} O, = 100 - [C + H + N + S + Cl + (\text{ash} - \%S_P - SO_{3\text{ash}}) \\ +8/9(H_2O + H_2O_{\text{hydration}} + 32/44CO_2] \end{aligned}$$

Chlorine is the as-determined chlorine (ASTM D2361, ASTM D4208), S_p is the as-determined pyrite sulfur (ASTM D2492), $SO_{3\text{ash}}$ is the as-determined sulfate (sulfur trioxide, SO_3) in ash (ASTM D1757), and CO_2 is the as-determined carbon dioxide in coal (ASTM D1756). All other terms are as given in the previous formulas and all values are expressed as percentages.

If the oxygen is determined directly, using the method previously discussed in which the moisture and mineral matter are removed from the sample before the actual oxygen determination, the oxygen value in this case represents that that contained in the organic matter. In calculating heat balances for boiler efficiency studies, it is important that an accurate value of the combustible material in coal be obtained. Thus, a correction for the oxygen content of the organic matter of coal should be made. Of course, corrections to the carbon and hydrogen values for the amount of these elements found in the moisture and inorganic constituents of coal should also be made. Oxygen data are used for determining the suitability of coals for coking, liquefaction, or gasification processes. In general, coals with high oxygen content are unsuitable for coking but may be more reactive and thus easier to gasify or liquefy.

6.5 SULFUR

Sulfur is an important consideration in coal utilization and, hence, there is a considerable amount of published work relating to the development of methods to improve the efficiency of the techniques as well as improve the accuracy and precision of the sulfur determination (Ahmed and Whalley, 1978; Chakrabarti, 1978; Attar, 1979; Raymond, 1982; Gorbaty et al., 1992).

Total sulfur data (ASTM D3177; ASTM D4239) are necessary for the effective control of the emissions of oxides of sulfur whenever coal is used as a fuel. The emission of sulfur oxides leads to the corrosion of equipment and slagging of combustion or boiler equipment, as well as contributing to atmospheric pollution and environmental damage. Sulfur data are therefore necessary for the evaluation of coals to be used for combustion purposes. In the method (ASTM D4239), the test specimen is heated in a tube furnace in a stream of oxygen to oxidize the sulfur to sulfur dioxide. The gas stream containing the sulfur dioxide is passed through a cell where it is measured at a precise wavelength by an infrared (IR) absorption detector.

Most coal conversion and cleaning processes require two sets of sulfur values: the sulfur content of the coal before it is used and the sulfur content of the products formed. In the coking of coal, some of the sulfur is removed in the coking process, which makes it necessary to obtain the before and after values. The commercial uses of coke, as in metallurgical processes, require a low sulfur content and necessitate an accurate sulfur value for the coke. In coal gasification and liquefaction processes, the sulfur in the coal is sometimes carried through to the products. It is therefore necessary to determine the amount of sulfur in each of the products before it is used. One of the primary reasons for cleaning coal is to reduce the sulfur content. It is necessary to know the sulfur content before and after cleaning in order to evaluate the cleaning process.

Total sulfur values alone are not adequate in accessing a cleaning process for reducing the sulfur content of coal. Pyrite sulfur alone can be removed by specific gravity separations and its removal depends on the way the pyrite is distributed throughout the coal. If it occurs as very small crystals widely dispersed in the coal, it is almost impossible to remove by these methods. When pyrite occurs in large pieces, it can be successfully removed by specific gravity methods. Organic sulfur cannot be reduced appreciably, since it is usually uniformly dispersed throughout the organic material in coal.

Sulfur is present in coal in three forms, either as (1) organically bound sulfur, (2) inorganic sulfur (pyrite or marcasite, FeS_2), and (3) inorganic sulfates (ASTM D2492; ISO 157); (Kuhn, 1977). The amount of organic sulfur is usually <3% w/w of the coal, although exceptionally high amounts of sulfur (up to 11%) have been recorded. Sulfates (mainly calcium sulfate, $CaSO_4$, and iron sulfate, $FeSO_4$) rarely exceed 0.1% except in highly weathered or oxidized samples of coal. Pyrite and marcasite (the two common crystal forms of FeS_2) are difficult to distinguish from one another and are often (incorrectly) designated simply as pyrite. Free sulfur as such does not occur in coal to any significant extent. The amount of the sulfur-containing materials in coal varies considerably, especially for coals from different seams. In addition, pyrite is not uniformly distributed in coal and can occur as layers or slabs or may be disseminated throughout the organic material as very fine crystals. The content of sulfates, mainly gypsum ($CaSO_4.7H_2O$) and ferrous sulfate ($FeSO_4.7H_2O$), rarely exceeds a few hundredths of a percent, except in highly weathered or oxidized coals.

6.5.1 Test Methods

The three most widely used test methods for sulfur determination are (1) the Eschka method, (2) the bomb-combustion method, and (3) the high-temperature combustion method, and all are based on the combustion of the sulfur-containing material to produce sulfate, which can be measured either gravimetrically or volumetrically.

The Eschka method has distinct advantages in that the equipment is relatively simple and only the more convenient analytical techniques are employed. However, methods involving combustion of the organic material in a *bomb* have distinct advantages insofar as sulfur is not *lost* during the process and such methods are particularly favored when the calorific value of the coal is also required. The method of decomposition involves the Parr fusion procedure in the presence of sodium peroxide and oxygen at high pressures (300–450 psi; 2.1–3.1 MPa).

In the Eschka method (ASTM D3177; ISO 334, ISO 351), 1 g of the analysis sample is thoroughly mixed with 3 g of Eschka mixture, which is a combination of two parts by weight of light calcined magnesium oxide with one part of anhydrous sodium carbonate. The combination of sample and Eschka mixture is placed in a porcelain crucible (30 ml) and covered with another gram of Eschka mixture. The crucible is placed in a muffle furnace, heated to a temperature of $800 \pm 25\,°C$ ($1472 \pm 45\,°F$), and held at this temperature until oxidation of the sample is complete. The sulfur compounds evolved during combustion react with the magnesium oxide (MgO) and sodium carbonate (Na_2CO_3) and under oxidizing conditions are retained as magnesium sulfate ($MgSO_4$) and sodium sulfate (Na_2SO_4). The sulfate in the residue is extracted and determined gravimetrically.

In the bomb washing method, sulfur is determined in the washings from the oxygen bomb calorimeter following the calorimetric determination (ASTM D2015, ASTM D3286, these standards have been discontinued but are still used in many laboratories). After opening, the inside of the bomb is washed carefully and the washings are collected. After titration with standard base solution to determine the acid correction for the heating value, the solution is heated and treated with ammonium hydroxide (NH_4OH) to precipitate iron ions as ferric oxide [$Fe(OH)_3$]. After filtering and heating, the sulfate is precipitated with barium chloride ($BaCl_2$) and determined gravimetrically.

In the high-temperature combustion test method (ASTM D4239, sub-methods A, B, and C), a weighed sample is burned in a tube furnace at a minimum operating temperature of 1350 °C (2462 °F) in a stream of oxygen to ensure the complete oxidation of sulfur-containing components in the sample. Using these conditions, all sulfur-containing materials in the coal or coke are converted predominantly to sulfur dioxide in a reproducible way. The amount of sulfur dioxide produced by burning the sample can be determined by the three alternative methods mentioned earlier.

In the acid–base titration method, the combustion gases are bubbled through a hydrogen peroxide solution in a gas absorption bulb. Sulfuric acid is produced by the reaction of sulfur dioxide with the hydrogen peroxide and is determined by titration with a standard base solution. Chlorine-containing species in the sample yield hydrochloric acid in the hydrogen peroxide solution, which contributes to its total acidity. For accurate results, a correction must be made for the chlorine present in the sample (ASTM D2361; ASTM D4208; ISO 352; ISO 587). Appropriate standard reference materials should be used to calibrate commercially available sulfur analyzers to establish recovery factors or a calibration curve based on the range of sulfur in the coal or coke samples being analyzed.

In the iodimetric titration procedure, the combustion gases are bubbled through a diluent solution containing pyridine, methanol, and water. This solution is titrated with a titrant containing iodine in a pyridine, methanol, and water solution. In automated systems, the titrant is delivered automatically from a calibrated burette syringe and the end point detected amperometrically. The method is empirical and standard reference materials with sulfur percentages in the range of the samples to be analyzed should be used to calibrate the instrument before use. Alternative formulations for the diluent and titrant may be used in this method to the extent that they can be demonstrated to yield equivalent results.

The third method of measuring the sulfur dioxide in the combustion gases is by the absorption of IR radiation. Moisture and particulates are first removed from the gas stream by traps filled with anhydrous magnesium perchlorate. The gas stream is then passed through an IR absorption cell tuned to a frequency of radiation absorbed by sulfur dioxide. The IR radiation absorbed during combustion of the sample is proportional to the sulfur dioxide in the combustion gases and therefore to the sulfur in the sample. The method is empirical and standard reference materials with sulfur percentages in the range of the samples to be analyzed should be used to calibrate the instrument before use.

Some general problems associated with the determination of sulfur in coal are nonuniform distribution of pyrite particles, failure to convert all the sulfur to sulfate, and loss of sulfur as sulfur dioxide during the analysis. The nonuniform distribution of pyrite necessitates the collection of many sample increments to ensure that the gross sample is representative of the lot of coal in question. Pyrite particles are both hard and heavy and have a tendency to segregate during the preparation and handling of samples. Because the particles are harder, they are more difficult to crush and pulverize and tend to concentrate in the last portion of material that remains from these processes.

In each of the methods discussed, sulfur is oxidized to sulfur dioxide during the analysis. Some sulfur dioxide may be lost unless the necessary precautions are taken. In the Eschka method, a generous layer of Eschka mixture covering the fusion mixture helps prevent the loss of sulfur as sulfur dioxide. The mixture must be heated gradually to guard against the production of sulfur dioxide at a rate that is too high for it to be absorbed by the Eschka mixture. In the bomb washing method, the pressure of the bomb should be released slowly after the sample is burned in oxygen so that sulfur oxides will not be carried out of the bomb. In the high-temperature combustion methods, it is essential that the flow of oxygen is sufficient and that the rate of heating is not too high. A high rate of heating will lead to the evolution of combustion products, including sulfur dioxide, at a rate that is too rapid for complete absorption in the solutions or for detection by the IR cell.

The gravimetric determination of sulfate can be and is most often used to finish the Eschka and bomb-washing methods. The most serious concern is that the precipitated barium sulfate may be extremely fine and difficult to filter. This can be overcome by adding the barium chloride ($BaCl_2$) rapidly to the hot solution and stirring the mixture vigorously to obtain a barium sulfate ($BaSO_4$) precipitate that is easily filtered is to add. In addition, heating and digestion for a lengthy period improve the filterability of the precipitate. After filtering, the precipitate must be washed several times with hot water to remove adsorbed materials that will cause the results to be too high.

6.5.2 Determination of the Forms of Sulfur

As noted earlier, sulfur occurs in coal in the three forms (ASTM D2492; ISO 157): (1) inorganic sulfur or sulfate sulfur, that is, as sulfates of metals such as calcium sulfate ($CaSO_4$); (2) pyrite sulfur, that is, as pyrite or marcasite (FeS_2); and (3) organic sulfur, that is, as sulfur combined organically in the coal. Organic sulfur and pyrites account for almost all the sulfur in coal. Sulfate sulfur is usually less than 0.1%, except for in weathered coal containing an appreciable amount of pyrites. The pyrite sulfur content varies considerably more than the organic sulfur content and is of more interest because it is the form that can be most easily removed from coal by current preparation practices.

The methods used for the determination of the various forms of sulfur in coal are based on the fact that sulfate sulfur is soluble in dilute hydrochloric acid solution while pyrite and organic sulfur are not attacked. In addition, dilute nitric acid dissolves sulfate and pyrite sulfur quantitatively and attacks organic sulfur only slightly. Pyrite sulfur, however, is accurately determined by noting the quantity of iron extracted by dilute hydrochloric acid and subtracting this from the iron extracted by nitric acid, the difference being the iron present as pyrite iron (FeS_2) from which the equivalent quantity of pyrite sulfur can be calculated. Sulfate sulfur and pyrite sulfur may therefore be determined on the one sample of coal, but since the sulfate sulfur determination is rather tedious, it is customary to use separate samples for each determination. Organic sulfur is then obtained by subtracting the combined percentages of sulfate sulfur and pyrite sulfur from the total sulfur determined by the Eschka method.

In the method for determining the forms of sulfur in coal (ASTM D2492; ISO 157), the sulfate and pyrite sulfur are determined directly, and the organic sulfur is taken as the difference between the total sulfur and the sum of the sulfate and pyrite sulfur.

In the determination of sulfate, 2–5 g of the analysis sample are mixed with HCl (2 volumes concentrated HCl + 3 volumes of water), and the mixture is gently boiled for 30 min. After filtering and washing, the undissolved coal may be retained for the determination of pyrite sulfur or it may be discarded and a fresh sample used for pyrite sulfur. Saturated bromine water is added to the filtrate to oxidize all sulfur forms to sulfate ions and ferrous ions to ferric ions. After boiling to remove excess bromine, the iron is precipitated with excess ammonia and filtered. This precipitate must be retained for the determination of non-pyrite iron if a fresh sample of coal was used for the determination of the pyrite iron. The sulfate is then precipitated with $BaCl_2$ and the $BaSO_4$ is determined gravimetrically.

Either the residue from the sulfate determination or a fresh 1-g sample is used for the determination of pyrite sulfur content. The sample is added to dilute nitric acid and the mixture boiled gently for 30 min or allowed to stand overnight. This treatment oxidizes iron species to iron(III) and inorganic sulfur compounds to sulfate. The mixture is then filtered and the filtrate is saved for the determination of iron by atomic absorption spectrophotometry or by a titration procedure. If iron is to be determined by the atomic absorption method, no further work is carried out on the filtrate other than to dilute it to an appropriate volume before the determination. If a titration method is to be used for the determination of iron, the filtrate is treated with 30% H_2O_2 to destroy any coloration arising from the coal. The iron is then precipitated, filtered, and washed. The precipitate is then dissolved in HCl and the iron determined by titration with either potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).

If a new sample is used for the determination of pyrite iron, the iron determined by these procedures represents the combination of the pyrite and non-pyrite iron. The amount of non-pyrite iron must then be determined separately and subtracted from the amount determined. If the residue from the sulfate determination was used, the iron determined by the aforementioned procedures represents the pyrite iron. Once the correct value for the pyrite iron is determined, the pyrite sulfur is calculated using the following expression:

$$\%\ \text{Pyrite sulfur} = \%\ \text{pyrite iron} \times 2 \times 32.06/55.85$$

In this equation, 2 × 32.06/55.85 is the ratio of sulfur to iron in pyrite.

Some difficulties encountered in determining the amounts of the various forms of sulfur in coal are adsorption of other materials on barium sulfate ($BaSO_4$) when it is precipitated, inability to extract all the pyrite sulfur from the coal during the extraction process, and possible oxidation of pyrite sulfur to sulfate in the pulverization and storage of the coal sample. Both the adsorption of other materials on barium sulfate and oxidation of pyrite sulfur lead to high values for the sulfate sulfur. Iron ions (Fe^{2+}) are readily adsorbed on barium sulfate, which could be particularly objectionable for coals containing large amounts of non-pyrite iron. Removal of the iron by precipitation and filtration, before the precipitation of barium sulfate, minimizes the adsorption of the iron. Inadequate pulverization and mixing of the sample appear to be the major causes of the incomplete extraction of pyrite sulfur from coal. A very small amount of organic sulfur may also be extracted with the pyrite sulfur. For this reason, the amount of pyrite iron extracted is used as a measure of the pyrite sulfur. To control the oxidation of pyrite sulfur to sulfates, exposure of the coal sample to the atmosphere at elevated temperatures should be avoided, and the sample should be analyzed as soon as possible.

X-Ray fluorescence has been used extensively for determining total sulfur in coal. The economy and speed of such X-ray fluorescence methods when used for multiple determinations (e.g., Al, Si, Ca, Mg, Fie, K, Ti, P, and S) in the same prepared coal sample are probably unsurpassed by any other method.

A neutron sulfur meter was developed for continuous monitoring of the sulfur content of coal from a preparation plant. Neutrons from a radioactive source produced thermal neutrons within the sample, which produced prompt gamma-ray emissions when captured by atoms in the coal. The gamma-ray energies characteristic of sulfur were measured by a sodium iodide crystal and associated electronic equipment. Several methods to eliminate interferences from other elements, moisture, and bulk density were evaluated. Results from the neutron sulfur meter for total sulfur in coal agreed closely with chemical analyses and the method is precise ($\pm 0.05\%$ absolute), rapid, and suitable for online sulfur determination.

High-resolution X-ray spectroscopy was successfully employed to determine the chemical state of sulfur in coal. Fluorescent X-rays from pressed coal powders, excited with X-rays from a chromium target tube, were analyzed using a germanium crystal. The sulfur K_a radiation increased with increasing oxidation number, allowing quantitative determinations of the sulfur types.

Another method of directly determining organic sulfur is to subject a small (20–30 mg) sample of <200-mesh coal to low temperature ashing 1–3 h and to collect the sulfur oxides evolved in a cold trap. They are then absorbed in hydrogen peroxide (H_2O_2) and determined chromatographically.

Mossbauer spectrometry is also useful to identify multiple-iron species in coal and charred residues without using a concentration step. The results indicate that heat treatment of any kind, even at temperatures as low as 175 °C, changes the nature of the iron species in coal. Furthermore, some kind of an association between the pyrite (FeS_2) in whole coal and the organic matrix was indicated. The pyrite also appeared to be altered when the coal was heated to 175 °C.

6.5.3 Data Handling and Interpretation

The principal use of forms of sulfur data is in connection with the cleaning of coal. Within certain limits, pyrite sulfur can be removed from coal by gravity separation methods, whereas organic sulfur cannot. Pyrite sulfur content can therefore be used to predict how much sulfur can be removed from the coal and to evaluate cleaning processes. If the pyrite sulfur occurs in layers, it usually can be removed efficiently. If it occurs as fine crystals dispersed throughout the coal, its removal is very difficult.

Other uses of forms of sulfur data are the inclusion of the pyrite sulfur value in the formula for the estimation of oxygen by difference and as a possible means of predicting the extent of weathering of coal. The sulfate concentration increases upon weathering, so the sulfate sulfur value could be used as an indication of the extent of weathering of coal.

6.6 CHLORINE

Chlorine as well as other halogens occur in coal and are believed to be a factor not only in fouling problems but also in corrosion problems (Canfield et al., 1979; Slack, 1981; Chakrabarti, 1982; Hower et al., 1992; Davidson, 1996; Spears, 2005; Greta et al., 2013). The chlorine content of coal is normally low, usually only a few tenths of a percent or less. It occurs predominantly as sodium, potassium, and calcium chlorides, with magnesium and iron chlorides present in some coals. There is evidence that chlorine may also be combined with the organic matter in coal.

6.6.1 Test Methods

Methods of converting the chlorine in coal into a form suitable for its analytical determination include combusting the sample, with or without Eschka mixture, in an oxygen bomb, and heating with Eschka mixture in an oxidizing atmosphere. Eschka mixture is a combination of two parts by weight of magnesium oxide and one part of anhydrous sodium carbonate. There are two standard methods of determining chlorine in coal (ASTM D2361; ASTM D4208).

The first method (ASTM D2361) offers a choice of two procedures for combusting the coal sample. In the bomb combustion procedure, the oxygen bomb used is the same as, or very similar to, that used in the determination of the calorific value (ASTM D2015; ASTM D3286).

In the first procedure (ASTM D2361), a weighed sample (~1 g) is mixed with a weight amount (~1 g) of the Eschka mixture and placed in a crucible inside an oxygen bomb. An ammonium carbonate solution is added to the bomb to trap the chloride containing species produced in the combustion. After charging with oxygen to 25 atmospheres, the bomb is fired and allowed to stand in the calorimeter water for at least 10 min. The pressure on the bomb is then released slowly, the bomb is disassembled, and all parts of the bomb interior are washed with hot water. The washings are collected in a beaker and acidified with nitric acid. The amount of chloride in the solution is then determined by either a modified Volhard or by a potentiometric titration with silver nitrate solution. In the second procedure (ASTM D2361), 1 g of the coal analysis sample is mixed with 3 g of Eschka mixture in a suitable crucible. This mixture is covered with an additional 2 g of Eschka mixture to ensure that no chlorine is lost during combustion. The mixture is then ignited gradually in a muffle furnace by raising the temperature to 675 ± 25 °C within 1 h. This temperature is maintained for 1 h before the cooling and washing of the incinerated mixture with hot water into a beaker. The contents of the beaker are acidified with nitric acid and the chloride is determined as in the previously described procedure.

In second test method (ASTM D4208), 1 g of the analysis sample of coal is placed in a crucible inside an oxygen bomb. A sodium carbonate solution is added to the bomb to trap the chloride containing species produced. After charging with oxygen to 25 atmospheres, the bomb is fired and allowed to stand in the calorimeter water for at least 15 min. After the pressure is released very slowly, the bomb is disassembled and all parts of the bomb interior are washed with water. The washings are collected, an ionic strength adjuster (sodium nitrate, $NaNO_3$) is added, and the chloride is determined with an ion-selective electrode by the standard addition method.

In both methods, it is possible to lose some of the chlorine during combustion unless necessary precautions are taken. Thoroughly mixing the coal sample with Eschka mixture and carefully covering this with additional Eschka mixture minimize the loss of chlorine. In the bomb combustion methods, the ammonium and sodium carbonate solutions in the bomb are used to absorb the chlorine as it is released in the combustion. The 10- and 15-min waiting periods and the slow release of the pressure on the bomb help to prevent the loss of chlorine as well.

A modification of the oxygen bomb combustion method (ASTM D2361) for the determination of chlorine consisted of acidifying a solution of the adsorbed combustion products and titrating the chlorine potentiometrically. A potentiometric titration was also tried for the determination of chlorine by the oxygen flask method. Combustion products, including chlorine, were absorbed in sodium hydroxide (NaOH), and the chloride was measured using silver-silver chloride electrodes. Although there was no statistical difference in results obtained from potentiometric titration and the Eschka procedure, the latter was more precise.

There is also a test method (ASTM E256) for the determination of chlorine in organic compounds by sodium peroxide bomb ignition that is also worthy of reference. The method is intended for application to samples of organic materials containing more than 0.5% chlorine and the assumption is that halogens other than chlorine will not be present.

In a later method (ASTM D6721), a weighed sample is combusted with tungsten accelerator in a humidified oxygen gas flow, at 900 °C (1650 °F). Halogens are oxidized and converted to hydrogenated halides, which are flushed into a titration cell where they accumulate. Chlorine is converted to hydrochloric acid and once the chloride is captured in the electrolyte of the titration cell, it can be quantitatively determined by microcoulometry, where chloride ions react with silver ions present in the electrolyte. The silver ion thus consumed is coulometrically replaced and the total electrical work needed to replace it is proportional to the chloride in the test sample.

6.6.2 Data Handling and Interpretation

The chlorine in coal and in the products derived from coal is known to contribute significantly to the corrosion of the coal handling and processing equipment. Since the corrosion of this equipment is the result of several causes, one being the chlorine content of coal, it is difficult to predict the degree of corrosion within a given time frame. It is equally as difficult to predict the degree to which the chlorine content contributes to the corrosion, other than the general prediction that the higher the chlorine content, the greater the chances for corrosion of the equipment. As a general rule, coal with high chlorine content is not desirable.

Chlorine data are used in ultimate analysis to improve the estimate of oxygen by difference. The chlorine value is included in the sum of the items determined, which, when subtracted from 100, gives an estimate of the oxygen content of coal.

Although the validity of the analytical data is uncertain, generally accepted fouling classification of coal, according to total chlorine content (ASTM D2361; ISO 352; ISO 587) is as follows:

Total percent chlorine	Fouling type
in coal	
<0.2	low
0.2–0.3	medium
0.3–0.5	high
>0.5	severe

In terms of corrosion, the occurrence of chlorine in coal leads to the formation of hydrogen chloride and the condensation of water containing hydrogen chloride (hydrochloric acid) on the cooler parts of combustions equipment can lead to severe corrosion of the metal surfaces.

6.7 MERCURY

Mercury has been identified as a very dangerous environmental contaminant, largely by reason of the process of concentration in the food chain. Thus, the presence of mercury in coal (Feng and Hong, 1999; Diehl et al., 2004) is an extremely sensitive issue. The possible emission of mercury that may be found in coal is an environmental concern.

6.7.1 Test Methods

The test for total mercury (ASTM D3684; ISO 15237) involves combusting a weighed sample in an oxygen bomb with dilute nitric acid absorbing the mercury vapors. The bomb is rinsed into a reduction vessel with dilute nitric acid and the mercury is determined by the flameless cold vapor atomic absorption technique. Mercury and mercury salts can be volatilized at low temperatures. Precautions against inadvertent mercury loss should be taken when using this method. When coal samples are burned according to this procedure, provided that samples preparation in is accord with the standard procedure (ASTM D2013), the total mercury is quantitatively retained and is representative of concentrations in the whole coal. Caution is also advised in the use of the bomb, considering the chemicals required for the test method.

Another test method for the determination of mercury in coal (ASTM D6414) involves (Method A) solubilizing of the mercury in the sample by heating the sample at a specified temperature in a mixture of nitric and hydrochloric acids. The acid solutions produced are transferred into a vessel in which the mercury is reduced to elemental mercury. The mercury vapor is determined by flameless cold-vapor atomic absorption spectroscopy. An alternate method (Method B) involved solubilization of the mercury by heating the sample in a mixture of nitric acid and sulfuric acid with vanadium pentoxide. The acid solution is then transferred into a vessel in which the mercury is reduced to elemental mercury. The mercury content is determined by flameless cold-vapor atomic absorption spectroscopy. However, mercury and mercury salts can be volatilized at low temperatures and precautions against inadvertent mercury loss should be taken when using this method.

The determination of mercury of coal, and in coal combustion residues, can also be accomplished by controlled heating of the sample in oxygen (ASTM D6722). In the method, the test specimen is heated in a tube furnace in a stream of oxygen. The gas stream containing the mercury vapor passes through a pre-packed portion of the combustion train where ash, moisture, halogens, and minerals are removed. The purified gas stream containing the mercury vapor then passes through an amalgamator tube containing gold-plated ceramic beads, which collect the mercury. When all of the mercury has been collected, the amalgamator is heated releasing the mercury in the vapor form, which is then transported through a cuvette positioned in the path length of an atomic absorption spectrometer.

6.7.2 Data Handling and Interpretation

The absorbance peak height or peak area, as a function of mercury concentration, is measured at 253.7 nm. Whenever mercury is handled in any test method, precautions must be taken against loss of mercury and mercury salts that are volatile at low temperatures.

6.8 OTHER CONSTITUENTS

Several of the minor components of coal are of importance, both on account of the quantity present on occasion but more so in some cases by virtue of the special properties they possess and which are undesirable when the coal is used for certain purposes. For example, in order to arrive at a correct figure for the combustible carbon in coal it is necessary to apply a correction for the quantity of carbonate associated with the sample. Combustion analyses determine only the total carbon. Moreover, coking coals should have low phosphorus content and anthracites used for malting should contain only very small quantities of arsenic, so that the determination of these elements becomes necessary in certain cases. Since both are found normally in small amount, they are not included in the general statement of the ultimate analysis but are reported separately.

6.8.1 Carbon Dioxide

Most coals contain small amounts of mineral carbonates made up primarily of calcium carbonate and to a lesser extent ferrous and other metal carbonates. Some coals contain a comparatively large amount of the inorganic carbonates and the determination of carbon dioxide content is required in estimating the mineral matter content of these high-carbonate coals. Indeed, it is necessary to have a knowledge of the carbonate content of coal in order to correct the carbon figure and since, without resorting to very elaborate analyses, it would be impossible to express the carbonate content as definite quantities of calcium carbonate, magnesium carbonate, and so on, it is customary, and sufficient for all analytical purposes, to express it simply in terms of carbon dioxide.

One particular test method (ASTM D1756) covers the determination of carbon dioxide in coal in any form, such as mineral carbonate, from which carbon dioxide is released by action of mineral acids (e.g., hydrochloric acid). The method can be applied to high-carbonate and low-carbonate coals. The determination of carbon dioxide is made by decomposing with acid a weighed quantity of the sample in a closed system and absorbing the carbon dioxide in an absorbent (e.g., such as sodium hydroxide, NaOH, or potassium hydroxide, KOH). The increase in weight of the absorbent is a measure of the carbon dioxide in the sample, which can be used to calculate the amount of mineral carbonates in the coal.

Due to the small amount of carbon dioxide in coal and the difficulty of accurately measuring the carbon dioxide that is liberated, some strict requirements have been set for the construction and design of the apparatus to be used (ASTM D1756). The apparatus must contain an air flow meter and purifying train, a reaction unit fitted with a separator funnel and water-cooled condenser, a unit for removing interfering gases, and an absorber. The air-purifying train removes all carbon dioxide, and the water-cooled condenser removes moisture before it can enter the absorption train. Acid-forming gases, such as sulfur dioxide and hydrogen sulfide, and halogen acids are produced in the reaction and must be removed before entering the CO_2 absorber. Otherwise, they will be weighed as absorbed and measured as carbon dioxide. Anhydrous copper sulfate on pumice or granular silver sulfate is positioned in the absorption train to remove these interfering gases from the air stream before it enters the CO_2 absorber. The entire system must be gas-tight in order to prevent error, and a time schedule is specified to ensure repeatability and reproducibility.

Another option (ASTM D6316) involved determination of the total, combustible, and carbonate carbon remaining in the solid byproducts of combustion from boiler furnaces and similar reactors, including ash, fly ash, char, slag, and similar materials. The determination of total carbon is made by the oxidative thermal decomposition of a weighed quantity of sample in a closed system and, after complete oxidation and purification of the resulting gaseous products, measurement of the carbon dioxide produced by one of several methods. The evolved carbon dioxide is fixed on an absorption train and is measured quantitatively by weighing the absorbent (ASTM D3178). The carbon dioxide is measured quantitatively by an electronic detection system calibrated against an appropriate reference standard (ASTM D5373).

In this method (ASTM D5373), carbon, hydrogen, and nitrogen are determined concurrently in a single instrumental procedure and the method provides for the conversion of the subject elements in an oxygen stream in their entirety to carbon dioxide, water vapor, and nitrogen oxides. Carbon dioxide and water vapor are determined by IR detection at precise wavelengths on an aliquot of the combustion gases from which halides and sulfur oxides have been removed. Nitrogen is determined by thermal conductivity on a second aliquot additionally treated to reduce all nitrogen oxides to nitrogen and to remove residual oxygen, carbon dioxide, and water vapor.

This test method is intended for the use of industry to determine the performance of boiler furnaces and similar combustion reactors and aid in determining the quality of the solid residue from combustion. Any of several methods can be used to determine total carbon content combined with any of several methods to determine carbonate carbon, and the calculation, by difference, of the combustible carbon remaining in the sample. Alternatively, this test method applies to the determination of total carbon remaining in a material after acidification with strong acid to evolve carbonate carbon.

6.8.2 Arsenic and Selenium

Arsenic and selenium occurs in coal to the extent of several parts per million and, on combustion of the coal a varying quantity of these elements are released or retained in the ash, depending largely on the conditions under which the combustion takes place and on the nature of the coal ash.

Arsenic and selenium are determined (ASTM D4606) by mixing a weighed sample with Eschka mixture and igniting at 750 °C (1382 °F). The mixture is dissolved in hydrochloric acid and the gaseous hydride of each element is generated from the appropriate oxidation state and determined by atomic absorption spectrophotometry. The method permits measurement of the total arsenic and selenium content of coal for the purpose of evaluating these elements where they can be of concern, for example, in coal combustion. When coal samples are prepared for analysis in accordance with standard procedure (ASTM D2013), the arsenic and selenium are quantitatively retained and are representative of the total amounts in the coal.

Selenium is also determined (ASTM D4606) by treating a weighed portion of the test specimen to pyro-hydrolytic extraction which quantitatively extracts selenium. The selenium content in the absorbing solution is determined by inductively coupled plasma-mass spectrometry (ICPMS).

Fluorine is also determined (ASTM D4606) by treatment of a weighed portion of the test specimen is heated under controlled conditions of time and temperature in a tube furnace. Oxygen saturated with steam is passed over the heated test specimen and the fluorine extracted from the coal and is collected in an absorbing solution. The fluorine content in the absorbing solution is determined by ion chromatography (IC).

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7

PHYSICAL PROPERTIES

7.1 INTRODUCTION

The physical properties and the behavior of coal play an important part in dictating the methods by which coal should be handled and utilized (Table 7.1). This section considers those properties such as, for example, density and hardness, which are definitely physical in nature, in contrast to the properties (e.g., spectroscopic properties) which arise by virtue of the molecular structural types that occur within the coal (Chapter 10).

At first consideration, there may appear to be little, if any, relationship between the physical and chemical behavior of coal but in fact the converse is very true. For example, the pore size of coal (which is truly a physical property) is a major factor in determining the chemical reactivity of coal. And chemical effects that result in the swelling and caking of coal(s) have a substantial effect on the means by which coal should be "handled" either prior to or during a coal conversion operation.

Just as coal evaluation can be achieved by the determination of several noteworthy properties (Chapter 7, Chapter 8, Chapter 9), there are also various electrical properties that provide even more valuable information about the potential use for coal (van Krevelen, 1993; Evans and Allardice, 1978). Indeed, there are also those properties of organic materials that offer valuable information about environmental behavior (Lyman et al., 1990). Hence, an additional reason to study the properties of coal. In fact, knowledge of the electrical properties of coal is also an important aspect of coal characterization and behavior. Electrical properties are useful for cleaning,

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TABLE 7.1 Physical Properties Often used for Determining Coal Suitability for Use

Test/Property	Results/Comments
Physical properties	
Density	True density as measured by helium displacement
Specific gravity	Apparent density
Pore structure	Specification of the porosity or ultrafine structure of coals and nature of pore structure between macro, micro, and transitional pores
Surface area	Determination of total surface area by heat of absorption
Reflectivity	Useful in petrographic analyses
Mechanical properties	
Strength	Specification of compressibility strength
Hardness/abrasiveness	Specification of scratch and indentation hardness; also abrasive action of coal
Friability	Ability to withstand degradation in size on handling, tendency toward breakage
Grindability	Relative amount of work needed to pulverize coal
Dustiness index	Amount of dust produced when coal is handled
Thermal properties	
Claroific value	Indication of energy content
Heat capacity	Measurement of the heat required to raise the temperature of a unit amount of coal 1°
Thermal conductivity	Time rate of heat transfer through unit area, unit thickness, unit temperature difference
Plastic/agglutinating	Changes in a coal upon heating; caking properties of coal
Agglomerating index	Grading on nature of residue from 1-g sample when heated at 950 °C (1550 °F)
Free swelling index	Measure of the increase in volume when a coal is heated without restriction
Electrical properties	
Electrical resistivity	Electrical resistivity of coal measured in ohm-centimeters
Dielectric constant	Measure of electrostatic polarizability

mining, pyrolysis, and carbonizing processes. Moreover, they are of special interest in the electro linking process for permeability enhancement and as a means to locate regions with different physical properties during *in situ* coal gasification.

However, the effect of volatile matter content on electrical properties is not fully understood. Some data indicate that there is no particular correlation whereas other data indicate a slight decrease of resistivity with decreasing volatile matter content. Both the type and quantity of volatile matter may affect electrical properties. However, it should be noted that even samples with equal volatile matter may show different properties due to different origins. Both mineral matter and ash content affect electrical properties, the influence of the former being more pronounced.

These properties and the behavior of coal play an important part in dictating the methods by which coal should be handled and utilized. It must always be borne in mind when consideration is being given to the suitability of coal for a particular use. It must also be borne in mind that coal which at first appears unsuitable for use by a consumer might become eminently suitable by a simple or convenient pretreating step, almost analogous to the *conditioning* of asphalt by air blowing (Speight, 2014).

In the broadest sense, it has been suggested that the granular nature of high rank coals is of importance in understanding the physical nature of coal if coal is modeled in terms of a granular medium that consists of graphite-like material embedded in an insulating organic matrix. Indeed, there have been several earlier suggestions of the graphite-like nature of coal, particularly from X-ray diffraction studies (Speight, 1978, and references cited therein) and perhaps this is a means by which the behavior of coal can be modeled. But, if this is the case, the precise role of the smaller aromatic systems needs also to be defined more fully. Nevertheless, it certainly offers new lines of thinking about coal behavior.

At first consideration, there may appear to be little, if any, relationship between the physical and chemical behavior of coal but in fact the converse is very true. For example, the pore size of coal (which is truly a physical property) is a major factor in determining the chemical reactivity of coal. And chemical effects that result in the swelling and caking of coal(s) have a substantial effect on the means by which coal should be handled either prior to or during conversion operations.

In addition, the electrical properties of coal are also described. Knowledge of the electrical properties of coal is also an important aspect of coal characterization and behavior for use (Table 7.1). Electrical properties are useful for cleaning, mining, pyrolysis, and carbonizing processes. They are also of special interest in the electro linking process for permeability enhancement and as a means to locate regions with different physical properties during *in situ* coal gasification. Hence, this is the reason for the study and measurement of these very important properties of coal and their inclusion in this chapter.

When determining the physical properties of coal, there is often considerable debate about the *correctness* of the results obtained from measurements by two or more different analytical techniques. Provided that the methods and/or equipment used was capable of producing high-quality data, the pertinent issues relate to whether or not the sample properly prepared and properly measured and whether or not the analytical parameters applied correctly in the data handling step(s). Thus, the concept of *different techniques yielding different, albeit, correct results* can apply to the measurement of physical properties such as density, porosity, particle size, and surface area.

7.2 DENSITY AND SPECIFIC GRAVITY

For porous solids, such as coal, there are three different density measurements, viz: *true density*, *apparent density*, *particle density*, *bulk density*, and *in-place density*.

The *true density* of coal is the mass divided by the volume occupied by the actual, pore-free solid in coal. However, determining mass of coal may be deemed as being rather straightforward but determining volume presents some difficulties. *Volume*, as the word pertains to a solid, cannot be expressed universally in a simple definition. Indeed, the method used to experimentally determine volume and, subsequently, the density, must be one that applies measurement rules consistent with the adopted definition.

The true density of coal is usually determined by helium displacement and, therefore, is often referred to as the *helium density*. Helium is used because it has the ability to penetrate all of the pores of a given sample of coal without (presumably) any chemical interaction. Thus, in the direct-pressure method, a known quantity of helium and a weighed sample of coal are introduced into an apparatus of known volume whereupon the pressure of the helium at a given temperature allows calculation of the volume of the coal. In the indirect method, mercury is used to compensate for the helium displaced by the introduction of the coal (Debelak and Schrodt, 1979).

It is generally believed that use of helium gives a more accurate determination of coal density but there is evidence (Kotlensky and Walker, 1960) that part of the pore system may be inaccessible to the helium. Thus, when helium is used as the agent for determining coal density, the density (helium density) may differ from the true density and may actually be lower than the true density.

The precise determination of true density requires complete filling of the pore structure with a fluid that has no interaction with the solid. No fluid completely meets these requirements. Helium has traditionally been considered as the best choice since it is not significantly adsorbed by coal at room temperature and that the use of helium gives a more accurate determination of coal density but there is evidence (Berkowitz, 1979, 1985 and references cited therein) that part of the pore system may be inaccessible to the helium. Thus, when helium is used as the agent for determining coal density, the density (helium density) may differ from the true density and may actually be lower than the true density.

Thus, it is not surprising that coal density is variable and dependent upon the coal type. For example, the density of anthracite if on the order of 1.55 whereas bituminous coal has a density on the order of 1.35 and lignite has a density on the order of 1.25. However, such generalizations are to be treated with caution since coal density is usually determined by displacement of a fluid, but because of the porous nature of coal and also because of physicochemical interactions, the observed density data vary with the particular fluids employed and different fluids may have to be employed for different coal types (Walker and Mahajan, 1978).

A standard test method is available for determining the true density (i.e., true specific gravity) of coke (ASTM D167) that, with careful application, can be applied to coal. The method actually describes the determination of apparent specific gravity and true specific gravity of lump coke larger than 25-mm (1-in.) size and calculating porosity from the specific gravity data. Apparent and true specific gravity, as determined by this test method, are influenced by the type of coals carbonized and the operating and preparational conditions of that carbonization, that is, charge bulk density, heating rate, and pulverization level.

The test method involves the use of a cage or basket is of 13-mm (1½ 2-in.) square-mesh screen wire cloth, it is necessary to have pieces that will remain in the cage when it is removed from the water. And, since it is very difficult to collect a representative sample, care must be taken to select pieces representing the entire exposed area, if sampling must be performed in this manner. In addition, it may be necessary to dry the sample before crushing or pulverizing during the sample preparation (ASTM D346). In all cases, care must be taken to select equipment that will not abrade and add unwanted impurities to the sample during the size-reduction steps.

The *true density* of coal is usually determined by helium displacement and, therefore, is often referred to as the *helium density*. Helium is used because it has the ability to penetrate all of the pores of a given sample of coal without (presumably) any chemical interaction. In the direct-pressure method, a known quantity of helium and a weighed sample of coal are introduced into an apparatus of known volume whereupon the pressure of the helium at a given temperature allows calculation of the volume of the coal. In the indirect method, mercury is used to compensate for the helium displaced by the introduction of the coal.

A method using the gas-comparison pycnometer with helium gas as the penetrating medium is claimed to measure precisely the true volume of a pulverized coal sample. From this, the true density of coal can be calculated as the true unit volume of the solid exclusive of the pore space which is divided into the weight of the sample. The method is similar to that used to determine the density of refractory materials but the procedure is modified to yield precise density determinations of coal samples. These modifications diminish effects of trapped moisture and gases on the volume measurement (Stanton, 1982).

The true density (in fact, the helium density) has been correlated with the elemental composition of coal. Thus,

$$\text{Density}_{\text{He}} = 1.534 - 0.05196\text{H} + 0.007375\text{O} - 0.02472\text{N} + 0.003853\text{S}$$

$\text{Density}_{\text{He}}$ is the helium density (g/cm^3) and H, O, N, and S are the respective weight percent of the different elements (dmmf basis).

Coal density is a useful parameter not only for deducing the spatial structure of coal molecules but the relationship between the density and porosity suggests that emphasis must be given to density and its determination. Porosity measurement in turn provides useful information on the technical behavior of coal toward its end use. Particle density is required for calculating porosity of individual coal particles.

Methods of measurement of coal density include use of a gas pycnometer and particle density by mercury porosimetry. However, the difference in density values using different gases must be recognized since, for example, density values measured by nitrogen may be greater than those obtained when helium is used. Density measurement depends on adsorption of gas molecules and differences (between nitrogen and helium) may be due to nitrogen adsorption on the coal surface.

The particle density is the weight of a unit volume of solid including the pores and cracks (Walker and Mahajan, 1978). The particle density can be determined by any one of three methods, viz: (1) mercury displacement; (2) gas flow Ergun, 1951); and (3) silanization (Ettinger and Zhupakhina, 1960).

A gas pycnometer operates by detecting the pressure change resulting from displacement of gas by a solid object. Expanding a quantity of gas at known pressure into an empty chamber and measuring the pressure establishes a baseline. Then, a sample is placed in the chamber and the chamber is resealed. The same quantity of gas at the same pressure is again expanded into the sample chamber and the pressure is measured. The difference in the two pressures combined with the known volume of the empty sample chamber allows the volume of the sample to be determined by way of the gas law. The accuracy and precision of the gas pycnometer in determining density are good but the method relies greatly on the cleanliness of the sample material and purity of the analysis gas. The accessibility to small open pores is quite high. The volume measured by this method will be less (density greater) than that determined by mercury porosimetry or other liquid displacement methods when small, open pores are in the sample.

Mercury is a non-wetting liquid that must be forced to enter a pore by application of external pressure. The surface tension of mercury causes mercury to bridge the openings of pores, cracks, and crevices until sufficient pressure is applied to force entry. For example, at atmospheric pressure, mercury will resist entering pores smaller than about 6μm in diameter. When an object is surrounded by mercury, the mercury forms a closely fitting liquid envelope around the object. How closely the mercury conforms to the surface features of the object depends on the pressure applied. As pressure increases, mercury enters smaller and smaller voids in the sample. At a pressure of 60,000 psi, mercury has been forced to enter pores of diameters down to 0.003 µm. This fills essentially all pore volume in most materials. Typically, the volume of mercury displaced at minimum pressure and that displaced at maximum pressure are used to determine bulk (or envelope) density and skeletal density, respectively. For powders, the total volume of the grains can be determined by subtracting the inter-particle void volume from the bulk volume. A mercury porosimeter is more often used for determination of pore volume distribution by pore size determination of density is often a byproduct of a data set from porosimetry measurements.

The *apparent density* of coal is determined by immersing a weighed sample of coal in a liquid followed by accurate measurement of the liquid that is displaced (pycnometer method). For this procedure, the liquid should (1) wet the surface of the coal, (2) not absorb strongly to the coal surface, not cause swelling, and (3) penetrate the pores of the coal.

It is difficult (if not impossible) to satisfy all of these conditions as evidenced by the differing experimental data obtained with solvents such as water, methanol, carbon tetrachloride, benzene, and other fluids. Thus, there is the need to always specify the liquid employed for the determination of density by means of this (pycnometer) method. Furthermore, a period of 24 h may be necessary for the determination because of the need for the liquid to penetrate the pore system of the coal to the maximum extent.

The *particle density* is the weight of a unit volume of solid including the pores and cracks (Walker and Mahajan, 1978). The particle density can be determined by any

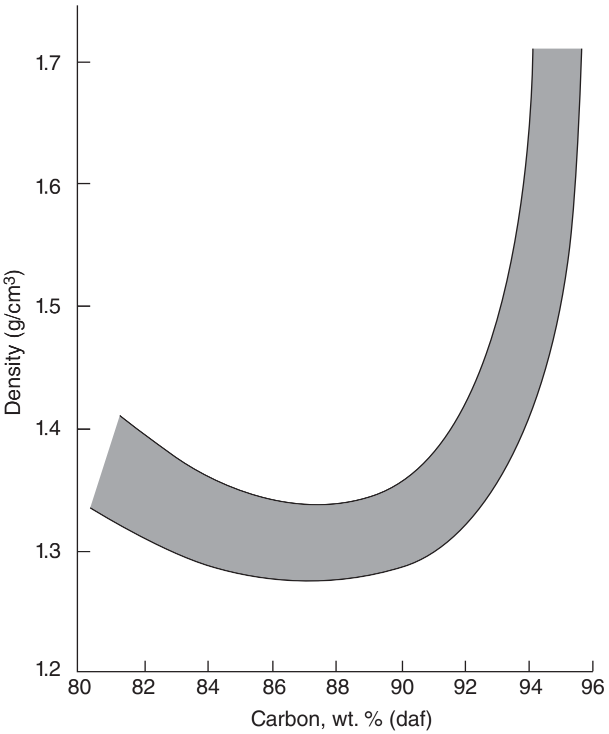

Figure 7.1 Variation of density with carbon content. *Source*: Adapted from Berkowitz, 1979.

one of three methods, viz: (1) mercury displacement (Gan et al., 1972), (2) gas flow (Ergun, 1951), and (3) silanization (Ettinger and Zhupakhina, 1960).

The density of coal shows a notable variation with rank for carbon content (Figure 7.1) and, in addition, the methanol density is generally higher than the helium density because of the contraction of adsorbed helium in the coal pores as well as by virtue of interactions between the coal and the methanol which result in a combined volume that is notably less than the sum of the separate volumes. Similar behavior has been observed for the water density of coals having 80–84% w/w carbon. Coal with more than 85% w/w carbon have usually been shown to exhibit a greater degree of hydrophobic character than the lower rank coals with the additional note that the water density may be substantially lower than the helium density; for the 80–84% carbon coals, there is generally little, if any, difference between the helium and water densities.

However, the hydrophobicity of coal correlates better with the moisture content than with the carbon content and better with the moisture/carbon molar ratio than with the hydrogen/carbon or oxygen/carbon atomic ratios. Thus, it appears that there is a relationship between the hydrophobicity of coal and the moisture content (Labuschagne, 1987; Labuschagne et al., 1988).

An additional noteworthy trend is the tendency for the density of coal to exhibit a minimum value at approximately 85% w/w carbon. For example, a 50–55% w/w carbon coal will have a density of approximately 1.5 g/cm^3 and this will decrease to, say, 1.3 g/cm^3 for an 85% carbon coal followed by an increase in density to circa 1.8 g/cm^3 for a 97% carbon coal. On a comparative note, the density of graphite (2.25 g/cm^3) also falls into this trend.

Determinations of the density of various coal macerals have also been reported (Table 7.2) and, although the variations are not great, the general order of density for macerals (having the same approximate carbon content) is:

$$\text{Exinite} < \text{vitrinite} < \text{micrinite}$$

However, it should also be noted that the density of a particular maceral does vary somewhat with the carbon content (Figure 7.2) (van Krevelen, 1993; Berkowitz, 1979, 1985).

The *bulk density* is the mass of an assembly of coal particles in a container divided by the volume of the container – that is, the mass of the solid particles per unit of volume they occupy (Table 7.3). It depends on true density, particle size and size distribution, particle shape, surface moisture, and degree of compaction. Major factors influencing the bulk density of coal are moisture content, particle surface properties, particle shape, particle size distribution, and particle density (Leonard et al., 1992). The parameter is often used in the design of coal handling, transportation, and storage systems.

The test method (ASTM D291) concerns the compaction of crushed coal to determine either its compacted or its uncompacted weight, for purposes such as charging coke ovens. In addition to the character of the coal itself, moisture content and size distribution of the coal are the two main factors that affect the cubic foot weight.

TABLE 7.2 Alcohol and Helium Density of Macerals

Macerals	% C	$D_{CH3}OH$	$d_{He(calc)}$
Exinites	85.49	1.201	1.187
	87.41	1.213	1.193
	89.10	1.288	1.267
	89.29	1.347	1.325
	83.5	1.345	1.304
	85.74	1.334	1.304
Vitrinites	88.36	1.317	1.295
	88.84	1.368	1.338
	86.77	1.463	1.435
	87.98	1.415	1.386
Micrinites	89.59	1.414	1.389
	89.78	1.413	1.385

Source: Adapted from Braunstein et al., 1977; Kroger and Badenecker, 1957.

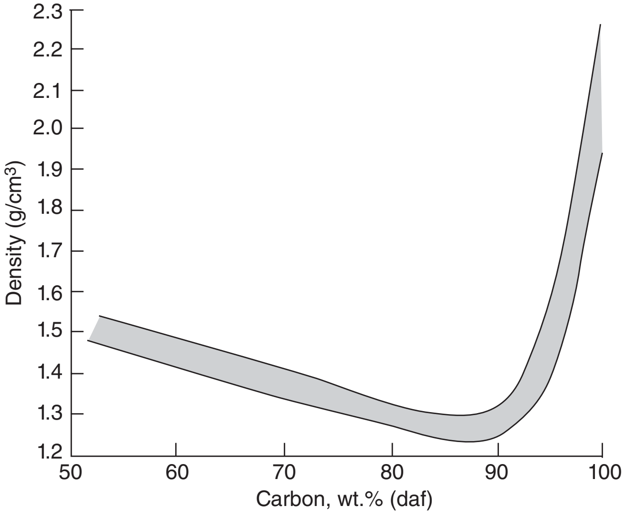

Figure 7.2 Variation of vitrinite density with carbon content. *Source*: Adapted from Berkowitz, 1979.

TABLE 7.3 Variations of the Bulk Density of Coal for Different Size Fractions

Particle Size of Coal Sample	Bulk Density (lb/ft^3)	Percent Voids
Mine run	55	37
Lump (plus 6 in.)	50	43
6 × 3 in.	48	45
3 × 2 in.	46	47
2-in. screenings	49	44
$2 \times 1\frac{1}{2}$ in.	45	48
$\frac{3}{4} \times \frac{7}{16}$ in.	42	52
$\frac{7}{16}$ in. × 0	47	46
$\frac{5}{16}$ in. × No. 0	45	48
$\frac{1}{16}$ in. × 48 M	42	52
No. 48 × 0	35	60

Source: Specific gravity of coal: 1.4.
Adapted from Baughman, 1978, page 166.

A moisture determination and sieve analysis of the coal should be reported along with the cubic foot weight for proper interpretation of the cubic foot weight. During the period of collecting the gross sample, the increments of the sample shall be stored in a waterproof container with a tightly fitting cover in order to prevent the loss of moisture.

The *in-place density* (*bank density*) of coal is the means by which coal in the seam can be expressed as tons per acre per foot of seam thickness and/or tons per square mile per foot of seam thickness. The *in-place density* of coal is the means by which coal in the seam can be expressed as tons per acre per foot of seam thickness and/or tons per square mile per foot of seam thickness (Table 7.4) and must be determined on water-saturated samples to accommodate the equilibrium moisture (Chapter 5) (Berkowitz, 1979, 1985; Speight, 2013a).

However, on the issue of the hydrophobicity of coal, recent work on the prediction of this characteristic indicates that the hydrophobicity of coal correlates better with the moisture content than with the carbon content and better with the moisture/carbon molar ratio than with the hydrogen/carbon or oxygen/carbon atomic ratios. Thus, it appears that there is a relationship between the hydrophobicity of coal and the moisture content (Labuschagne, 1987; Labuschagne et al., 1988). An additional noteworthy trend is the tendency for the density of coal to exhibit a minimum value at approximately 85% carbon. For example, a 50–55% carbon coal will have a density of approximately 1.5 g/cm and this will decrease to, say, 1.3 g/cm for an 85% carbon coal followed by an increase in density to circa 1.8 g/cm for a 97% carbon coal. On a comparative note, the density of graphite (2.25 g/cm) also falls into this trend.

Generally, the manner the bulk sample packs into a confined space is reflected by its bulk density and is related to the size distribution as well as the effects of moisture on the packing ability of the particles. There will always be such a mixture of fine and coarse particles at which the bulk density will assume the highest value, higher than assumed by any of these fractions when packed separately. As the range of particle size is increased, the bulk density is also increased (Wakeman, 1975).

The *bulk density* is not an intrinsic property of coal and varies depending on how the coal is handled. Bulk density is the mass of many particles of coal divided by the

TABLE 7.4 In-place Density of Coal

	Weight of In-Place Coal	
Rank	Tons per Acre per Foot of Thickness	Tons per Square Mile per Foot of Thickness
Anthracite	2310	1479×10^6
Semianthracite	2039	1305×10^6
Bituminous	1903	1218×10^6
Subbituminous	1767	1131×10^6
Lignite	1631	1044×10^6

Source: Adapted from Baughman, 1978, Page 166.

total volume occupied by the particles – the total volume includes particle volume, inter-particle void volume, and internal pore volume. This allows the density of coal to be expressed in terms of the cubic foot weight of crushed coal (ASTM D291), which varies with particle size of the coal and packing in a container (Table 7.3). In addition, the bulk density of coal varies with rank: (1) anthracite: 50–58 lb/ft^3, (2) bituminous coal: 42–57 lb/ft^3, and (3) lignite: 40–54 lb/ft^3.

The general formula used for soil samples (Tisdall, 1951; Birkeland, 1984; Blake and Hartge, 1986) may also be applied to coal. Thus:

$$\text{Bulk density} = \left(\frac{\text{Weight}}{\text{Volume}}\right) = \left(\frac{63}{35}\right)$$

$$\text{Porosity}(\%) = \left(1 - \frac{\text{Bulk Density}}{\text{Particle Density}}\right) * 100$$

$$\text{Porosity}(\%) = \left(1 - \frac{1.8}{2.65}\right) * 100$$

The bulk density of coal decreases with increasing moisture content until a minimum is reached (at ~6–8% moisture) but then increases with moisture content. With the use of aqueous solutions of wetting additives, the coal bulk density can be increased by up to 15% (Leonard et al., 1993).

Due to the hydrophobic nature of higher rank coals, their bulk density rapidly decreases with increasing moisture, as the water stays on the surface of the coal in between the particles, increasing the volume of the bulk solid (decreasing bulk density). Further increase in moisture leads to the minimum bulk density attained at about 6 to 8% moisture content (Leonard et al., 1992). Beyond this level of moisture, more water penetrates the spaces in between the particles and forms a water layer around them allowing for aggregation which leads to tighter packing configuration. As a result particles are packed into smaller volume which further leads to an increase in bulk density of the sample. Furthermore, small additions of chemical reagents reducing surface tension of water resulted in an increased bulk density. These experiments showed that the bulk density could be increased by 13–15% with the use of such additives (Leonard et al., 1992).

The aggregation of fines, leading to tight packing of particles, affects the bulk density of coal samples. Wettability appears to be a controlling factor in the aggregation of fine coal particles. As a result, different patterns of bulk density can be anticipated with moisture increase for hydrophilic coal samples and also for hydrophobic coal samples (Holuszko and Laskowski, 2010).

7.3 POROSITY AND SURFACE AREA

Porosity is the fraction (or percentage) of the volume of coal that is occupied by pores and can be calculated from the equilibrium moisture content (Chapter 5)

(Berkowitz, 1979, 1985). For porous solids, such as coal, there are three different density measurements: true density, particle density, and apparent density. Moreover, since coal is a porous material, porosity can have a large influence on coal behavior during mining, preparation, and utilization operations. In fact, the porosity and surface area of coal (Walker and Mahajan, 1978) have a large influence on coal behavior during mining, preparation, and utilization.

Although porosity dictates the rate at which methane can diffuse out of the coal (in the seam) and there may also be some influence during preparation operations in terms of mineral matter removal, the major influence of the porous nature of coal is noticed during the utilization of coal. For example, during conversion chemical reactions occur between gas (and/or liquid) products and surface features, much of which exist within the pore systems.

The pore systems of coal have generally been considered to consist of micropores having sizes up to approximately 100 and macropores having sizes greater than 300 Å and the total open pore volume in coal varies from 0.03 to 0.25 cm^3/gm but there is no assurance that the pore volume is related to rank (Gan et al., 1972; Walker and Mahajan, 1978). Other work (Kalliat et al., 1981), involving a small-angle X-ray investigation of porosity in coals, has thrown some doubt upon this hypothesis by bringing forward the suggestion that the data are not consistent with the suggestion that many pores have dimensions some hundreds of angstrom units in diameter but have restricted access due to small openings which exclude nitrogen (and other species) at low temperatures. Rather, the favourable interpretation is that the high values of surface area obtained by adsorption studies are the result of a large number of pores with minimum pore dimensions which are not greater than circa 30.

Moreover, there are indications that the adsorption of small molecules on coal, such as methanol, occurs by a site specific mechanism (Ramesh et al., 1992). In such cases, it appears that the adsorption occurs first at high-energy sites but with increasing adsorption the (methanol) adsorbate continues to bind to the surface rather than to other (polar) methanol molecules and there is evidence for both physical and chemical adsorption. In addition, at coverages below a monolayer, there appears to be an activation barrier to the adsorption process. Whether or not such findings have consequences for surface area, pore distribution studies remains to be seen. However, there is the very interesting phenomenon of the activation barrier which may also have consequences for the interpretation of surface effects during coal combustion (Speight, 2013a, b).

As already noted with respect to coal density, the porosity of coal decreases with carbon content (Figure 7.3) (King and Wilkins, 1944) and has a minimum at approximately the 89% carbon coals followed by a marked increase in porosity. The nature of the porosity also appears to vary with carbon content (rank); for example, the macropores are usually predominant in the lower carbon (rank) coals while higher carbon (rank) coals contain predominantly micropores. Thus, pore volume, which can be calculated from the relationship:

$$V_{\mathrm{p}} = 1/\rho_{\mathrm{Hg}} - 1\rho_{\mathrm{He}}$$

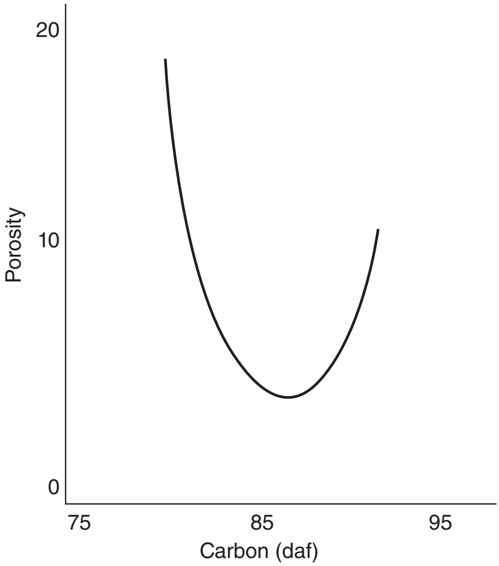

Figure 7.3 Variation of porosity with carbon content. *Source*: Adapted from Berkowitz, 1979.

In this equation, ρ_{Hg} is the mercury density and ρ_{He} is the helium density, decreases with carbon content (Figure 7.4). In addition, the surface area of coal varies over the range of 10–200 m^2/g and also tends to decrease with the carbon content of the coal.

Porosity and surface area are two very important properties with respect to the gasification of coal since the reactivity of coal increases as the porosity and surface area of the coal increases. Thus, the gasification rate of coal is greater for the lower rank coals than for the higher rank coals. The porosity of coal is calculated from the relationship:

$$\rho = 100\rho_{\mathrm{Hg}}(1/\rho_{\mathrm{Hg}} - 1\rho_{\mathrm{He}})$$

By determining the apparent density of coal in fluids of different, but known, dimensions, it is possible to calculate the pore size (pore volume) distribution. The open pore volume (*V*), that is, the pore volume accessible to a particular fluid, can be calculated from the relationship:

$$V = (1\rho_{\mathrm{Hg}} - 1\rho_{\mathrm{a}})$$

ρ_{a} is the apparent density in the fluid.

The size distribution of the pores within a coal can be determined by immersing the coal in mercury and progressively increasing the pressure. Surface tension effects prevent the mercury from entering the pores having a diameter smaller than a given

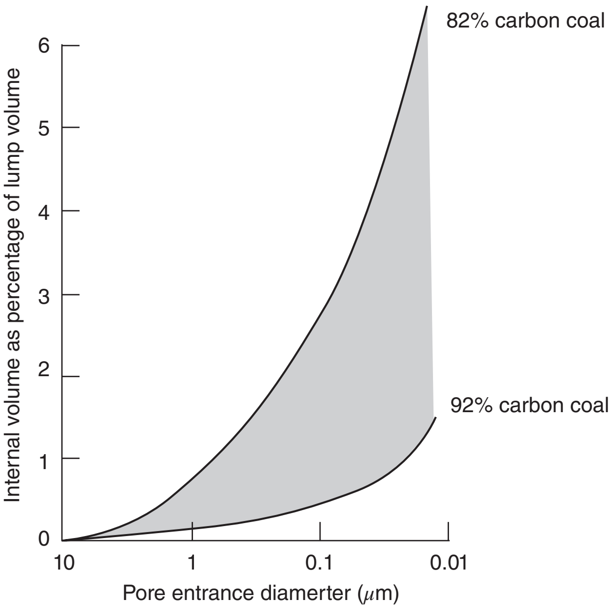

Figure 7.4 Variation of pore distribution with carbon content.

value d for any particular pressure p such that

$$p = 4\sigma \cdot \cos\theta/d$$

σ is the surface tension and θ is the angle of contact.

By recording the amount of mercury entering the coal for small increments of pressure, it is possible to build up a picture of the distribution of sizes of pores (Figure 7.5) (van Krevelen, 1993). However, the total pore volume accounted for by this method is substantially less than that derived from the helium density, thereby giving rise to the concept that coal contains two pore systems: (1) a macropore system accessible to mercury under pressure and (2) a micropore system that is inaccessible to mercury but accessible to helium. By using liquids of various molecular sizes, it is possible to investigate the distribution of micropore sizes. However, the precise role or function of these micropores as part of the structural model of coal is not fully understood, although it has been suggested that coal may behave in some respects like a molecular sieve.

Although porosity dictates the rate at which methane can diffuse out of the coal (in the seam) and there may also be some influence during preparation operations in terms of mineral matter removal, the major influence of the porous nature of coal is seen during the utilization of coal. For example, during conversion chemical reactions occur between gas (and/or liquid) products and surface features, much of which exists within the pore systems.

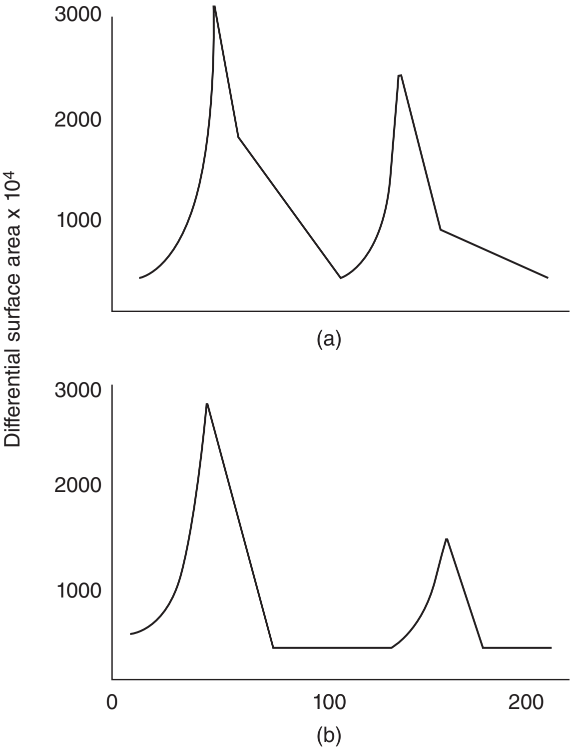

Figure 7.5 (a, b) Variation with surface area with pore size. *Source*: Adapted from Berkowitz, 1979.

The *true density* is usually determined by displacement of a fluid, but because of the porous nature of coal and also because of physicochemical interactions, the observed density data vary with the particular fluids employed (Walker and Mahajan, 1978). The apparent density of coal is determined by immersing a weighed sample of coal in a liquid followed by accurate measurement of the liquid that is displaced. For this procedure, the liquid should (1) wet the surface of the coal, (2) not absorb strongly to the coal surface, (3) not cause swelling, and (4) penetrate the pores of the coal.

The calculation of porosity is derived from the determination of the true specific gravity (ASTM D167) and is derived from the relationship:

$$\text{Porosity} = 100 - 100(\text{apparent specific gravity}/\text{true specific gravity})$$

Another method of determining porosity involves measuring the density of coal by helium displacement and by mercury displacement (please see Section 1.0, above). Thus, the porosity of coal is calculated from the relationship:

$$P = 100 \times \text{density}_{\text{Hg}}(1/\text{density}_{\text{Hg}} - 1/\text{density}_{\text{He}})$$

P indicates the porosity, density$_{\mathrm{Hg}}$ denotes the mercury density, and density$_{\mathrm{He}}$ denotes the helium density.

By determining the apparent density of coal in fluids of different, but known, dimensions, it is possible to calculate the pore size (pore volume) distribution. The open pore volume (V), that is, the pore volume accessible to a particular fluid, can be calculated from the relationship:

$$V = 1/\mathrm{density}_{\mathrm{Hg}} - 1/\mathrm{density}_{\mathrm{a}}$$

Density$_{\mathrm{Hg}}$ denotes the mercury density and density$_{\mathrm{a}}$ denotes the apparent density in the fluid under consideration.

Pore volume can be calculated from the relationship:

$$V_{\mathrm{p}} = 1/\mathrm{density}_{\mathrm{Hg}} - 1/\mathrm{density}_{\mathrm{He}}$$

Density$_{\mathrm{Hg}}$ denotes the mercury density and density$_{\mathrm{He}}$ denotes the helium density.

The pore systems of coal have generally been considered to consist of micropores having sizes up to approximately 100 A and macropores having sizes greater than 300 A (Gan et al., 1972; Walker and Mahajan, 1978). Other work (Kalliat et al., 1981), involving a small-angle X-ray investigation of porosity in coals, has thrown some doubt upon this hypothesis by bringing forward the suggestion that the data are not consistent with the suggestion that many pores have dimensions some hundreds of angstrom units in diameter but have restricted access due to small openings which exclude nitrogen (and other species) at low temperatures. Rather, the interpretation that is favored is that the high values of surface area obtained by adsorption studies are the result of a large number of pores which minimum pore dimensions which are not greater than circa 30 Å.

As already noted with respect to coal density, the porosity of coal decreases with carbon content (Figure 7.3) (King and Wilkins, 1944; Berkowitz, 1979, 1985) and has a minimum at approximately the 89% w/w carbon coals followed by a marked increase in porosity. The nature of the porosity also appears to vary with carbon content (rank); for example, the macropores are usually predominant in the lower carbon (rank) coals while higher carbon (rank) coals contain predominantly micropores. Thus, pore volume decreases with carbon content (Figure 7.4) and, in addition, the surface area of coal varies over the range 10–200 m^2/g and also tends to decrease with the carbon content of the coal.

Immersing the coal in mercury and progressively increasing the pressure can determine the size distribution of the pores within a coal. Surface tension effects prevent the mercury from entering the pores having a diameter smaller than a given value d for any particular pressure p such that:

$$p = 4\sigma \cos \Theta / d$$

In this equation, σ is the surface tension and Θ the angle of contact.

By recording the amount of mercury entering the coal for small increments of pressure, it is possible to build up a picture of the variation of surface area with pore size (Figure 7.5) (van Krevelen, 1993; Berkowitz, 1979, 1985). However, the total pore volume accounted for by this method is substantially less than that derived from the helium density, thereby giving rise to the concept that coal contains two pore systems: (1) a macropore system accessible to mercury under pressure and (2) a micropore system that is inaccessible to mercury but accessible to helium. By using liquids of various molecular sizes, it is possible to investigate the distribution of micropore sizes. However, the precise role or function of these micropores as part of the structural model of coal is not fully understood, although it has been suggested that coal may behave in some respects like a molecular sieve.

It is difficult (if not impossible) to satisfy all of these conditions as evidenced by the differing experimental data obtained with solvents such as water, methanol, carbon tetrachloride, benzene, and other fluids. Thus, there is the need to always specify the liquid employed for the determination of density by means of this (pycnometer) method. Furthermore, a period of 24 h may be necessary for the determination because of the need for the liquid to penetrate the pore system of the coal to the maximum extent.

Finally, although sorption processes can be used to study different characteristics of coal properties, such as gas content (coalbed methane potential of a deposit), gas diffusion, porosity, internal surface area, coal microstructure (porosity system) is relevant for gas flow behavior in coal and, consequently, directly influences gas recovery from the coalbed. In the direct-method determination of the *void volume* of samples using different gases (helium, nitrogen, carbon dioxide, and methane) and since gas behavior depends on pressure and temperature conditions, it is critical, in each case, to know the gas characteristics, especially the compressibility factor (Rodrigues and Lemos de Sousa, 2002).

7.4 REFLECTANCE

Coal, a black solid that *appears* to be impervious to light, does exhibit optical properties. However, in order to exhibit these properties, some preparation or conditioning of the coal is necessary.

Thus, coal may be examined in visible light by either transmission or reflectance. The former is a measure of light absorbance at various wavelengths and may be determined for thin sections of coal or finely divided coal pressed into a potassium bromide disk or solutions of coal extracts in solvents such as pyridine or films of coal that have been deposited by evaporation of a dispersing liquid.

It is often a surprise to many workers that coal, being often regarded as a black solid which appears to be impervious to light, should be recognized as having optical properties. That some preparation or conditioning of the coal is necessary is also of importance. Thus, coal may be examined in visible light by either transmission or reflectance (Tschamler and de Ruiter, 1963) The former is a measure of light absorbance at various wavelengths and may be determined for thin sections of coal or finely divided coal pressed into a potassium bromide disk or solutions of coal extracts in solvents such as pyridine or films of coal that have been deposited by evaporation of a dispersing liquid.

The reflectance of the vitrinite maceral (Chapter 1) was first studied by coal geologists attempting to determine the thermal maturity, or rank, of coal beds. More recently, it is used to study sedimentary organic matter from kerogen. It is sensitive to temperature ranges that correspond to hydrocarbon generation (60–120 °C, 140–250 °F). Thus, vitrinite reflectance can be used as an indicator of maturity in hydrocarbon source rocks. Generally, the onset of oil generation is correlated with a reflectance of 0.5–0.6% and the termination of oil generation with reflectance of 0.85–1.1%.

Coal reflectance (ASTM D2798) is very useful because it indicates several important properties of coal (Davis, 1978). Among these are the content of several macerals (ASTM D2799) and carbonization temperature. Coal reflectance is determined by the relative degree to which a beam of polarized light is reflected from a polished coal surface. The coal is crushed to pass a number 20 screen (850 μm screen) with minimal fines production and the particles are formed into a briquette held together with a binder. One side of the briquette is polished using successively finer abrasives until a smooth surface that is scratch-free, smear-free, and char-free is obtained. A metallurgical, or opaque-ore, microscope is employed to determine the reflectance with vertical illumination using polarized light.

Prior to measurement of reflectance, the sample face is covered with cedar oil or a commercial immersion oil and then multiple readings are taken of the maximum reflectance of the coal component (e.g., vitrinite) of interest. These values are compared with readings of high-index glass standards (of known reflectance) which are available with reflectance values typically ranging from 0.302% to 1.815%.

Thus, although coal always appears as a black mass, thin layers and polished faces exhibit a variety of colors. For example, in incident light, fusinite, and micrinite are white whereas exinite is a translucent yellow color; on the other hand, exinite is orange in transmitted light. Obviously, these color differences are employed for differentiating maceral types. In addition, the reflectance of coal varies with rank (Figure 7.6) and the reflectance data for air are considerably higher than those obtained using an oil medium (Table 7.5).

Coal reflectance (Chapter 7) is important in aiding the determination of the maceral composition of coal which, in turn, is helpful for the prediction of behavior in processing (Davis et al., 1991). For example, the basic use for which determination of vitrinite reflectance is applied is the measurement of the degree of metamorphism or rank of coals and the organic components of sediments. It is possible to relate the reflectance of a coal to parameters such as carbon content, volatile matter, and calorific value.

Petrographic analysis of coal provides information concerning its ingredient composition in terms of vitrain, clarain, durain, fusain, and mineral matter. Lumps and columns of coal are analyzed by making profile or vertical measurements normal to the banding of polished surfaces. The results of analysis, by particle count can be used to predict coke properties (such as strength) which would be produced from the coal

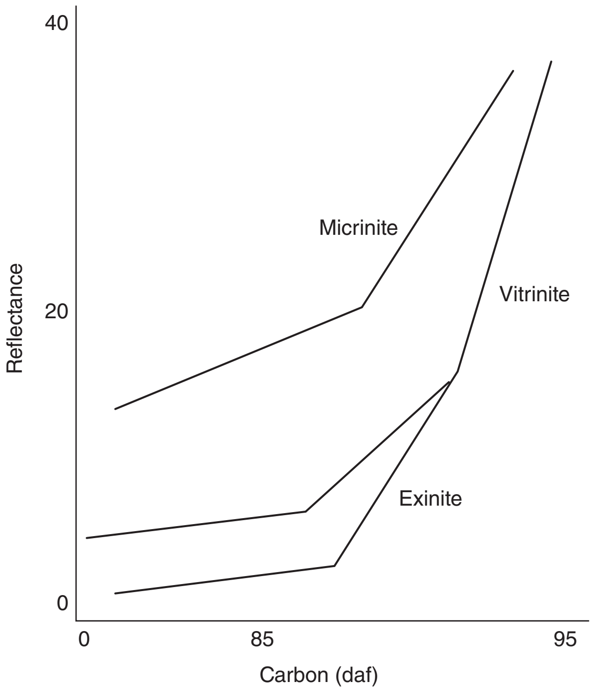

Figure 7.6 Variation of reflectance with carbon content. *Source*: Adapted from Dormans et al., 1957.

TABLE 7.5 Reflectance Data Obtained in Air and In Oil

	Maximum Reflectance, Approximate (%)	
Carbon Content of Coal (%)	Air	Oil
60	0.4	6
90	1.0	8
96	6.5	17

(Parks, 1949, 1963). Other uses include the estimation of the chemical properties of fresh coals from the reflectance of weathered specimens. The technique uses reflected light microscopy and polished sections, which are prepared by embedding coal fragments or crushed coal in mounting media. The samples are processed through several stages of grinding and polishing to obtain a surface of adequate quality for microscopic analysis. The results of the petrographic analyses that are of special interest in connection with the combustion tests concerned the effect of coal cleaning processes upon the proportion of banded ingredients.

Coal reflectance (ASTM D2798) is very useful because it indicates several important properties of coal, including the determination of the maceral composition of coal that, in turn, is helpful for the prediction of behavior in processing (Davis, 1978; Davis et al., 1991). Coal reflectance is determined by the relative degree to which a beam of polarized light is reflected from a polished coal surface that has been prepared according to a standard procedure (ASTM D2797). Samples prepared by this practice are used for microscopical determination of the reflectance of the organic components in a polished specimen of coal (ASTM D2798) as well as the volume percent of physical components of coal (ASTM D2799).

The coal is crushed to pass a number 20 (850 μm) screen (with minimal fines production) and the particles are formed into a briquette held together with a binder. One side of the briquette is polished using successively finer abrasives until a smooth surface that is scratch-free, smear-free, and char-free is obtained. A metallurgical, or opaque-ore, microscope is employed to determine the reflectance with vertical illumination using polarized light.

The standard test method for the measurement of vitrinite reflectance (ASTM D2798) covers the microscopic determination of both the mean maximum reflectance and the mean random reflectance measured in oil of polished surfaces of vitrinite and other macerals present in coals ranging in rank from lignite to anthracite. This test method can be used to determine the reflectance of other macerals. The reflectance of the maceral vitrinite or other macerals is determined in this test method by illuminating a polished surface of a section of coal in immersion oil using a microscopic system that photometrically measures the amount of light reflected from the surface. The reflected light is recorded in percent reflectance after calibration of photometric equipment by measuring the reflected light from standards of reflectance as calculated from their refractive indices. The mean maximum reflectance of the vitrinite component in coal as determined by this test method is often used as an indicator of rank (ASTM D388), independent of petrographic composition, and in the characterization of coal as feedstock for carbonization, gasification, liquefaction, and combustion processes. If mean maximum reflectance is used as a rank indicator, the types of vitrinite measured shall be specified.

Prior to measurement of reflectance, the sample face is covered with cedar oil or commercial immersion oil and then multiple readings are taken of the maximum reflectance of the coal component (e.g., vitrinite) of interest. These values are compared with readings of high-index glass standards (of known reflectance) that are available with reflectance values typically ranging from 0.302% to 1.815%.

Thus, although coal always appears as a black mass, thin layers and polished faces exhibit a variety of colors. For example, in incident light, fusinite, and micrinite are white whereas exinite is a translucent yellow color; on the other hand, exinite is orange in transmitted light. Obviously, these color differences are employed for differentiating maceral types. In addition, the reflectance of coal varies with carbon content (Figure 7.6) and the reflectance data for air are considerably higher than those obtained using an oil medium (Table 7.5).

The volume percent of physical components of coal is used as an aid in the characterization of coal for use in carbonization, gasification, and combustion processes. To determine the volume percent of the physical components of coal (ASTM D2799), the components in a representative crushed coal sample (ASTM D2797) are identified under a microscope according to their reflectance, other optical properties, and morphology. The proportion of each component in the sample is determined by observation of a statistically adequate number of points and summing those representative of each component. Only area proportions of components are determined on a surface section of a sample. However, the area and volume proportions are the same when the components are randomly distributed throughout the sample.

7.5 REFRACTIVE INDEX

The refractive index of coal can be determined by comparing the reflectance in air with that in cedar oil (Cannon and George, 1943). For vitrinite, the refractive index usually falls within the range 1.68 (58% carbon coal) to 2.02 (96% carbon coal).

The refractive index of coal can be determined by comparing the reflectance in air with that in cedar oil. A standard test method (ASTM D2798) covers the microscopic determination of both the mean maximum reflectance and the mean random reflectance measured in oil of polished surfaces of vitrinite and other macerals in coal ranging in rank from lignite to anthracite. This test method can be used to determine the reflectance of other macerals. For vitrinite (various coals), the refractive index usually falls within the range 1.68 (58% carbon coal) to 2.02 (96% carbon coal).

7.6 ELECTRICAL CONDUCTIVITY

Electrical conductivity is the inverse of resistivity. Induction logging systems were originally designed to facilitate resistivity measurements in oil-based drilling mud, where there is no conductive medium occurred between the tool and the formation. It is also often used in dry holes or when the borehole fluid is very fresh. The purpose is, as usual, to measure resistivity or conductivity in order to calculate porosity and to interpret lithology. Induction is useful in several types of ground investigation.

Coal usually has high resistivity (Verma et al., 1983; Krishnamurthy et al., 2009). This may be reduced according to its porosity, clay, and water content. The porosity of coal varies with rank and so its resistivity increases from lignite to semi-anthracite and then decreases slightly with anthracite. Clay inclusions reduce the resistivity of coal. Clay-rich formations, such as shale formations, have low resistivity. Clean, relatively dry sandstone has high resistivity, which may be reduced according to porosity, salinity, and clay content. Resistivity (or conductivity) logs may also indicate oxidation of a coal seam or alteration by an intrusion.

Electrical conductivity depends on several factors, such as temperature, pressure, and moisture content of the coal. The electrical conductivity of coal is quite pronounced at high temperatures (especially above 600 °C; 1112 °F), where coal structure begins to break down. Moisture affects electrical conductivity to a marked extent, resulting in a greatly increased conductivity. To prevent any anomalies from the conductance due to water, the coal is usually maintained in a dry, oxygen-free atmosphere and, to minimize the problems that can arise particularly because of the presence of water, initial measurements are usually taken at approximately 200 °C (392 °F) and then continued to lower temperatures.

Coal is a semiconductor (van Krevelen 1993; Speight, 2013a and references cited therein). Anthracite is a semiconductor with specific resistance ranging from 1 to 104 Ω-cm while the range is 105–1012 Ω-cm for bituminous coal. Sub-bituminous coal also behaves as a semiconductor. The highest resistances are observed with coals having 80–92% carbon; they can be considered virtual insulators. Hence, electrical conductivity, a measure of electricity transportation, is generally handled in terms of electrical resistivity for coal. To eliminate quantities not characteristic for the material, the specific electrical resistance (resistivity) and the specific conductance are utilized. The former is the resistance that a cube with unit dimensions offers to current flow and is expressed in ohm-unit length, and the latter is reciprocal of the former. Taking the expected order of magnitude of resistivity or conductivity into account, measurements can be made with a fluxmeter, an ammeter–voltmeter system, a Wheatstone bridge, and electrometers (ASTM D257) *for* the determination *of* direct current insulation resistance are strongly recommended for transient resistivity measurements. The test method covers the direct-current procedures for the determination of dc insulation resistance, volume resistance, volume resistivity, surface resistance, and surface resistivity of electrical insulating materials, or the corresponding conductance and conductivities. The method is not suitable for use in measuring the electrical resistivity/conductivity of moderately conductive materials; an alternate method (ASTM D4496) is recommended.

This alternate method (ASTM D4496) covers the determination of the measurement of electrical resistance or conductance of materials that are generally categorized as moderately conductive and that are neither good electrical insulators nor good conductors. This method applies to all materials that exhibit volume resistivity in the range of 1–10 Ω-cm or surface resistivity in the range of 10–10 Ω (per square). The method is designed for measurements at standard conditions of 23 °C and 50% relative humidity, but its principles of operation can be applied to specimens measured at lower or higher temperatures and relative humidity.

All electrical property values are strongly dependent on water content; for water, the dielectric constant is approximately 81 and resistivity is about 106 Ω-cm. The dielectric constant has been used as a measure of moisture in coal (Speight, 2013a and references cited therein). However, it should be noted that the effect is not considered to be additive due to the different electrical properties of physically and chemically bound water. With an increase in moisture content, electrical conductivity and dielectric constant increase, whereas resistivity and dielectric strength decrease. Hence, except for special purposes, for example, dielectric strength measurements of underground coal blocks; electrical measurements require the meticulous drying of coal prior to experiments.

The conductivity of coal is explained in part by the partial mobility of electrons in the coal structure lattice which occurs because of unpaired electrons or “free radicals" Mineral matter in coal may have some influence on electrical conductivity. The conductivities of coal macerals show distinct differences; fusains conduct electricity much better than clarain, durain, and vitrain.

The electrical conductivity of coal can be used to model conditions during *in situ* gasification (Duba, 1977). For example, from an initial value (at 24 °C, 75 °F) when the coal is saturated with formation water, the conductivity decreases to markedly when the coal is heated to 110 °C (230 °F) in vacuum. This low value, presumably due to dehydration of the coal, prevails for samples heated as high as 500 °C (930 °F) in dry argon. Samples of char recovered after pyrolysis to 800 °C (1470 °F) or more have a much higher conductivity. This contrast allows electrical probing to be sufficiently sensitive for monitoring the progress of the burn-front progress during *in situ* coal gasification.

The electrical conductivity of coal is generally discussed in terms of specific resistance, p (units of p are ohm-centimeters), and is the resistance of a block of coal 1 cm long and having a l-cm^2 cross-section and may vary from thousands of ohm-centimeters to millions of ohm-centimeters depending on the direction of measurement (Table 7.6). Substances having a specific resistance greater than approximately 1×10^{15} Ω-cm are classified as insulators while those with a specific resistance less than 1 Ω-cm are conductors; materials between these limits are semiconductors.

Finally, the *specific resistance* (*resistivity*) of coal is the electrical resistance of a body of a unit cross-section and of unit length, (and is expressed in ohm-centimeters:

$$p = RA/L$$

In this equation, p is the specific resistance, R is the resistance of the substance, A is the cross-sectional area, and L is the length.

TABLE 7.6 Specific Resistance of Coal

Material	Specific Resistance (Ω·cm)
Graphite	$(0.8–1.0) \times 10^{-3}$
Graphite	4×10^{-3}
Anthracite[a]	
Parallel to bedding	$(7–90) \times 10^{3}$
Perpendicular to bedding	$(17–34) \times 10^{3}$
Bituminous[a]	
Parallel to bedding	$(0.004–360) \times 10^{8}$
Perpendicular to bedding	$(3.1–530) \times 10^{9}$
Brown coal	
20–25% H_2O	10^{4}
Dry	$10^{10}–10^{13}$
Copper	1.7×10^{-6}
Water (distilled)	$8.5–25 \times 10^{6}$

Source: [a]Dry.
Adapted from Baughman, 1978, Page 170.

When wet coal is exposed to higher temperatures (0–200 °C, 32–392 °F), an increase of electrical resistivity (with a concurrent decrease of dielectric constant) is observed. This is due to moisture loss. After moisture removal, a temperature increase results in lower resistivity (and higher dielectric constant). The dependency of conductive properties on temperature is mainly exponential as in any semiconductor. At lower temperatures, the effect of temperature on electrical properties is reversible. The onset of irreversible effects is rank dependent and starts at 200–400 °C (392–752 °F) for bituminous coal and at 500–700 °C (932–1292 °F) for anthracite.

7.7 DIELECTRIC CONSTANT

The dielectric constant is more useful than electrical conductivity in characterizing coal and is a measure of the electrostatic polarizability of the dielectric coal (Chatterjee and Misra, 1989). The dielectric constant of coal is believed to be related to the polarizability of the pi-electrons (π-electrons) in the clusters of aromatic rings within the chemical structure of coal (Speight, 2013a).

The dielectric constant (specific inductive capacity) is a measure of electrostatic polarizability and of the amount of electricity that can be stored in coal. Dielectric constant is more useful than electrical conductivity in characterizing coal and is a measure of the electrostatic polarizability of the dielectric coal. The dielectric constant of coal is believed to be related to the polarizability of the Π-electrons in the clusters of aromatic rings in the coal chemical structure.

Experimental methods are applicable for a wide range of frequencies. High-frequency measurements employ commercially available dielectric constant meters, Q-meters, and so on; the impedance bridge method is widely employed at low frequencies. The levels of the frequencies experimentally applied are very important for data interpretation and comparison.

The dielectric constant of coal is strongly dependent on coal rank (Van Krevelen, 1993; Speight, 2013a and references cited therein). For dry coals, the minimum dielectric constant value is 3.5 and is observed at about 88% w/w carbon content in the bituminous coal range. The dielectric constant increases sharply and approaches 5.0 both for anthracite (92% carbon) and for lignite (70% carbon). The Maxwell Relation which equates the dielectric constant to the square of the refractive index for apolar insulators generally shows a large disparity even for strongly dried coal.

Like conductivity, dielectric constant is strongly dependent on water content. Indeed, the dielectric constant can even be used as a measure of moisture in coal (Chapter 5). Meaningful dielectric constant measurements of coal require drying to a constant dielectric constant and several forms of coal are used for dielectric constant measurements. These include precisely shaped blocks of coal, mulls of coal in solvents of low dielectric constant, or blocks of powdered coal in a paraffin matrix.

The dielectric constant varies with coal rank (Chatterjee and Misra, 1989). The theorem that the dielectric constant is equal to the square of the refractive index (which is valid for nonconducting, nonpolar substances) holds only for coal at the minimum dielectric constant. The decreasing value of dielectric constant with rank may be due to the loss of polar functional groups (such as hydroxyl or carboxylic acid functions) but the role of the presence of polarizable electrons (associated with condensed aromatic systems) is not fully known. It also appears that the presence of intrinsic water in coal has a strong influence on the dielectric properties (Chatterjee and Misra, 1989).

7.8 DIELECTRIC STRENGTH

Dielectric strength indicates the voltage gradient at which dielectric failure occurs and it is generally measured (ASTM D149) at commercial power frequencies and is expressed in volts per sample thickness. This test method covers procedures for the determination of dielectric strength of solid insulating materials at commercial power frequencies, under specified conditions. Unless otherwise specified, the tests are conducted at 60 Hz. However, this test method may be used at any frequency from 25 to 800 Hz but at frequencies above 800 Hz dielectric heating may occur. The test method is not intended for determining intrinsic dielectric strength, direct-voltage dielectric strength, or thermal failure under electrical stress (ASTM D3151). The test method is most commonly used to determine the dielectric breakdown voltage through the thickness of a test specimen (puncture). It may also be used to determine dielectric breakdown voltage along the interface between a solid specimen and a gaseous or liquid surrounding medium (flashover).

Experimental data strongly indicates that anthracite and bituminous coal are electrically anisotropic. Higher resistivity/lower conductivity is observed for specimens oriented perpendicular to the bedding plane relative to those with parallel orientation.

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8

THERMAL PROPERTIES

8.1 INTRODUCTION

The thermal properties of coal are important in determining the applicability of coal to a variety of conversion processes. For example, the heat content (also called the *heating value* or *calorific value*) is often considered to be the most important thermal property. However, there are other thermal properties that are of importance insofar as they are required for the design of equipment that is to be employed for the utilization (conversion, thermal treatment) of coal in processes such as combustion, carbonization, gasification, and liquefaction. Plastic and agglutinating properties as well as phenomena such as the agglomerating index give indications of how coal will behave in a reactor during a variety of thermal processes.

8.2 CALORIFIC VALUE

The calorific or heating value of a coal is a direct indication of the energy content and therefore is probably the most important property for determining the usefulness of coal (Figure 8.1). It is the amount of energy that a given quantity of coal will produce when burned. Heating value is used in determining the rank of coals. It is also used to determine the maximum theoretical fuel energy available for the production of steam. It is used to determine the quantity of fuel that must be handled, pulverized, and fired in the boiler.

Handbook of Coal Analysis, Second Edition. James G. Speight.

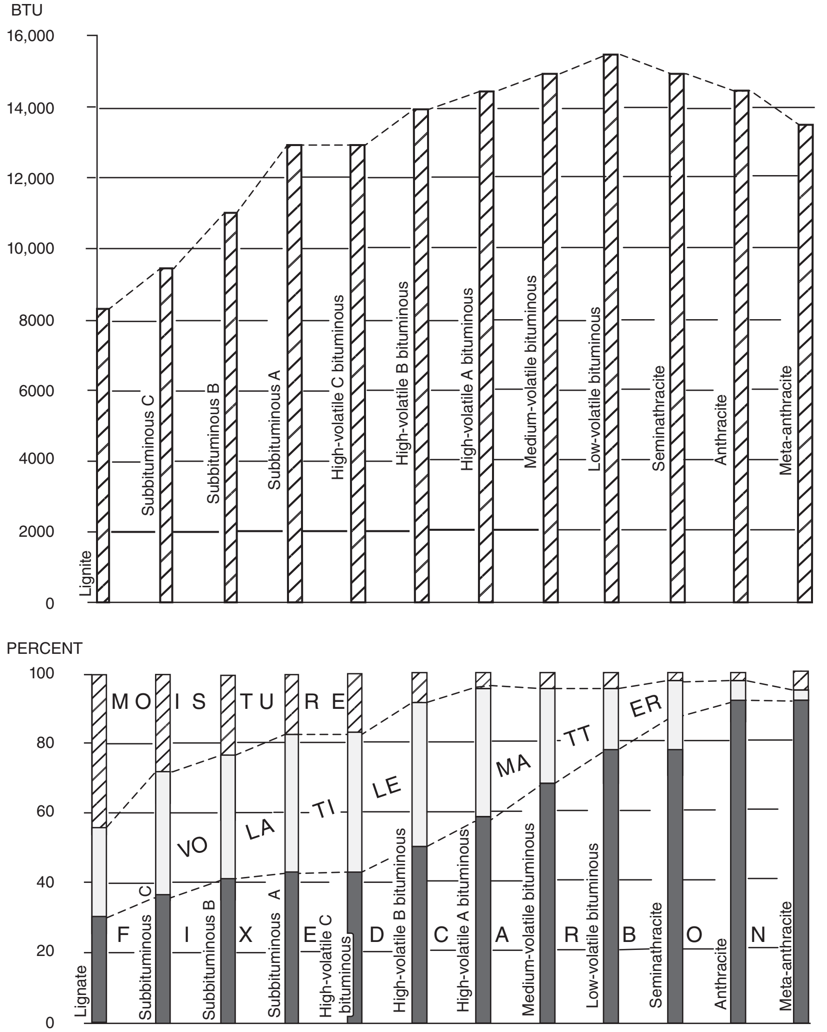

Figure 8.1 Variation of calorific value with rank. *Source*: Adapted from Baughman, 1978.

The calorific value is reported as gross calorific value (GCV), with a correction made if net calorific value (NCV) is of interest (ASTM D121; ASTM D2015; ASTM D3286; ASTM D5865; ISO 1928). For solid fuels such as coal, the gross heat of combustion is the heat produced by the combustion of a unit quantity of the coal in a bomb calorimeter with oxygen and under a specified set of conditions. The unit is calories per gram, which may be converted to the alternate units (1.0 kcal/kg = 1.8 Btu/lb = 4.187 kJ/kg).

The calorific value is the heat produced by the combustion of a unit quantity of the coal in a bomb calorimeter with oxygen and under a specified set of conditions (ASTM D121; ASTM D2015; ASTM D3286; ISO 1928). For the analysis of coal, the calorific value is determined in a bomb calorimeter either by a static (isothermal) method or by an adiabatic method with a correction made if NCV is of interest. The unit is calories per gram, which may be converted to the alternate units (1.0 kcal/kg = 1.8 Btu/lb = 4.187 kJ/kg).

The experimental conditions require an initial oxygen pressure of 300–600 psi and a final temperature in the range of 20–35 °C (68–95 °F) with the products in the form of ash, water, carbon dioxide, sulfur dioxide, and nitrogen. Thus, once the GCV has been determined, the NCV (i.e., the net heat of combustion) is calculated from the GCV (at 20 °C; 68 °F by deducting 1030 Btu/lb (2.4 × 103 kJ/kg) to allow for the heat of vaporization of the water. The deduction is not actually equal to the heat of vaporization of water (1055 Btu/lb; 2.45 × 103 kJ/kg) because the calculation is to reduce the data from a gross value at constant volume to a net value at constant pressure. Thus, the differences between the GCV and the NCV are given by:

$$\mathrm{NCV(Btu/lb)} = \mathrm{GCV} - (1030 \times \text{total hydrogen} \times 9)/100.$$

The enthalpy, or heat content, of various coals has also been reported (Table 8.1) (Baughman, 1978) but has actually received somewhat less attention than the calorific value. There are also reports of the use of differential thermal analysis (DTA) for the determination of the calorific value of coal (Muñoz-Guillena et al., 1992).

The calorific value is a direct indication of the heat content (energy value) of the coal and represents the combined heats of combustion of the carbon, hydrogen, nitrogen, and sulfur in the organic matter and of the sulfur in pyrite and is as the GCV with a correction applied if the NCV is of interest.

TABLE 8.1 Variation of Heat Content of Coal with Temperature

Temperature		Heat Content		
		As Tested		Ash-Free Basis
°C	°F	cal/g	Btu/lb	cal/g
Lignite (Texas)				
32.7	90.9	11.8	21.2	13.5
69.3	156.7	20.2	36.4	22.5
95.3	203.5	25.4	45.7	27.7
34.4	273.9	39.2	70.6	42.5
Subbituminous B (Wyoming)				
42.3	108.1	14.1	25.4	14.5
65.0	149.0	19.4	34.9	19.8
89.7	193.5	26.4	47.5	26.9
112.6	234.7	34.0	61.2	34.6

Source: Adapted from Baughman, 1978, page 173.

The calorific value is usually expressed as the GCV or the *higher heating value* (HHV) and the NCV or *lower calorific value* (LHV). The difference between the GCV and the NCV is the latent heat of condensation of the water vapor produced during the combustion process. The GCV indicates that all of the vapor produced during the combustion process is fully condensed. The NCV indicates that the water is removed with the combustion products without fully being condensed. To equalize all effects, the calorific value of coal should be compared based on the NCV basis. The calorific value of coal varies considerably depending on the ash, moisture content, and the type of coal while calorific values of fuel oils are much more consistent.

The calorific value of coal is an important property. For example, the GCV can be used to compute the total calorific content of the quantity of coal or coke represented by the sample for payment purposes. In addition, it can be used for computing the calorific value versus sulfur content to determine whether the coal meets regulatory requirements for industrial fuels. The GCV can be used to evaluate the effectiveness of beneficiation processes. Finally, the GCV can be required to classify coal (ASTM D388).

The energy content of the coal can be expressed as the *useful heating value* (UHV) that is an expression derived from ash and moisture contents for noncoking coal through the formula:

$$\text{UHV kcal/kg} = (8900 - 138 \times [\text{ash content, wt\%} + \text{moisture content, wt\%}])$$

The calorific value is neither part of the proximate analysis nor part of the ultimate analysis; it is, in fact, one of the many physical properties of coal and, as such, is often found in the various sections that deal with the physical properties of coal. In the present context, the importance of the calorific value as one of the means by which coal can be evaluated dictates that it be included in this particular section as well as in the section describing the general thermal properties of coal.

Calorimeters used for the determination of the calorific value of coal can be classified into three general types: (1) calorimeters using solid oxidizing agents in either open or closed systems; (2) calorimeters using gaseous oxygen at approximately atmospheric pressure in an open system; and (3) calorimeters using gaseous oxygen under pressure in a closed system. All three types of calorimeters are commonly used but only those belonging to the third class can be relied on for a reasonable degree of accuracy.

The bomb calorimeter provides the most suitable and accurate apparatus for the determination of the calorific values of solid and liquid fuels. Since the combustion takes place in a closed system, heat transfer from the calorimeter to the water is complete and since the reaction is one between the fuel and gaseous oxygen, no corrections are necessary for the heat absorbed during the reduction of the oxidizing agent. In addition, the losses due to radiation can be reduced to comparatively small quantities and, what is more important, can be determined with a considerable degree of accuracy, while corrections due to the heat evolved in the formation of nitric and sulfuric acids under the conditions existing in the bomb can be accurately determined.

When coal is burned on an open grate under normal air pressures, only minute traces of oxides of nitrogen are formed by the combination of the nitrogen in the fuel or in the air with the atmospheric oxygen, but under the conditions of local high temperature and pressure existing within the bomb more oxides of nitrogen are formed and these give rise ultimately to a solution containing nitric acid by dissolving in the water. This oxidation of nitrogen and solution of the products in water are exothermic reactions so that an allowance has to be made for the heat liberated by the formation of nitric acid.

In a similar way, when sulfur or pyrites burns in air, only about 5% of the sulfur is oxidized to sulfur trioxide, the remainder yielding only sulfur dioxide, but in the bomb practically all the sulfur is burned to the trioxide, which dissolves in the water to give sulfuric acid. A correction is therefore necessary for the heat liberated by the combustion of sulfur dioxide to trioxide, by the solution of this trioxide in water to give sulfuric acid and by the heat of dilution of this acid in water.

Applying a correction to the observed temperature rise makes an allowance for losses of heat by radiation from the calorimeter. This correction is expressed by a formula which appears to be complicated, but if the various temperature figures are methodically set out on the laboratory sheet besides it is easy to apply, the liability of introducing arithmetic errors is also reduced.

The Beckmann thermometer used with the bomb calorimeter should be calibrated for the normal depth of immersion with which it is used. In order to cover the normal range of laboratory temperatures, this calibration should be obtained for three settings of the zero on the scale, convenient values being 10, 15, and 20 °C. Such a series of calibrations automatically allows for emergent stem corrections and variations in the value of the degree on the thermometer scale with different quantities of mercury in the bulb, in addition to those arising from the inherent variations in the diameter of the capillary bore.

Anthracite may be difficult to burn completely, but combustion is assisted by the addition of a small known amount of liquid paraffin of known calorific value. It is also advantageous to increase the pressure of oxygen to 30 atm.

If the coal ash has a low fusion point the fused residue may enclose unburned material. In such cases, the provision of a thin layer of coarsely powdered quart/or even a calcined asbestos paper disc placed on the bottom of the crucible prevents the formation of large globules of fused ash and therefore reduces the possibility of carbon remaining unburned. By using these modifications, the residue is more easily removed from the crucible (especially if this be made of silica) for examination for unburned carbon.

If the determination of calorific value is carried out with a bomb calorimeter, the figure reported is usually corrected for the heat of formation of sulfuric acid and its dilution by water, but if the calorific value has to be reported on a dry mineral matter-free basis, the air-dried figure requires to be further adjusted to allow for the heat of formation of ferric oxide from the pyrites originally in the coal. The heat developed in the combustion of pyrite (FeS_2) is approximately 3000 calories per gram of pyrite sulfur so that the correction to be applied is dependent upon whether the calorific value is expressed as the heating power per gram or per pound.

8.2.1 Test Methods

The common method of determining the GCV of coal is with either an adiabatic (ASTM D2015; this test method was discontinued without replacement in 2000 but is still in use in many laboratories) or an isothermal bomb calorimeter (ASTM D3286). In these methods, a weighed sample is burned in an oxygen bomb covered with water in a container surrounded by a jacket.

An adiabatic calorimeter is a calorimeter that has a jacket temperature adjusted to follow the calorimeter temperature so as to maintain zero thermal head and the test method (ASTM D2015; 1SO 1928) consists of burning the coal sample in the calorimeter and the jacket temperature is adjusted during the burning so that it is essentially the same as the calorimeter water temperature. The calorific value is calculated from observations made before and after the combustion. In the isothermal method (ASTM D3286; ISO 1928), the calorific value is determined by burning a weighed sample of coal in oxygen under controlled conditions and the calorific value is computed from temperature observations made before, during, and after combustion with appropriate allowances made for the heat contributed by other processes. The computed value for the calorific value of coal is usually expressed in British thermal units per pound, kilocalories per kilogram, or in kilojoules per kilogram (1.8 Btu/lb = 1.0 kcal/kg = 4.187 kJ/kg).

In the isothermal calorimeter system (ASTM D3286), the temperature rise of the calorimeter water is corrected for the heat lost to or gained from the surrounding jacket during the burning of the sample. In both systems, the corrected temperature rise times the energy equivalent of the calorimeter gives the total amount of heat produced during the burning of the sample. The energy equivalent (also called the *water equivalent* or *heat capacity*) of the calorimeter is determined by burning standard samples of benzoic acid.

After firing, the contents of the bomb are washed into a beaker and titrated with standard sodium carbonate solution to determine the amount of acid (nitric acid, HNO_3 and sulfuric acid, H_2SO_4) produced in the combustion. Corrections for the amount of acid, the amount of fuse wire used in firing, and the sulfur content of the sample are then made to the total heat produced in the calorimeter (energy equivalent times corrected temperature rise) to determine the GCV of the solid fuel.

One source of error in this method (ASTM D3286) is in temperature measurement. If a mercury-in-glass thermometer is used, it must be calibrated accurately and consistent readings must be made. Many calorimeters are equipped with digital thermometers with thermistor probes and microprocessors to control the firing and record the temperatures at prescribed intervals. This alleviates most of the human error in recording the temperature changes.

Igniting the coal sample in the oxygen bomb can be difficult. The sample may be blown out of the crucible by introducing the oxygen too quickly. Pressing the coal sample into a pellet may prevent the sample from blowing out. Coal with a high mineral content is hard to ignite and mixing the sample with a measured amount of a standard aromatic acid and pelletizing may be helpful. After firing, restoring the bomb pressure to atmospheric pressure too rapidly may result in the loss of oxides of sulfur and nitrogen. A correction must be made to the GCV for the amounts of these acid-forming oxides produced in the bomb. Their loss results in a high calorific value. The pressure of the bomb must be restored very slowly to prevent this.

The equipment used must be checked periodically for any changes in the energy equivalent of the calorimeter, any corrosion or damage to the calorimeter bucket, any damage (however slight it may be) to the oxygen bomb, and any malfunction of the stirrers, electrical system, or other parts of the calorimeter. Any of these changes or malfunctions may change the energy equivalent of the calorimeter or introduce extra heat, which would lead to errors in the measured calorific value.

The experimental conditions require an initial oxygen pressure of 300–600 psi and a final temperature in the range of 20–35 °C (68–95 °F) with the products in the form of ash, water, carbon dioxide, sulfur dioxide, and nitrogen. Thus, once the GCV has been determined, the NCV (i.e., the net heat of combustion) is calculated from the GCV (at 20 °C; 68 °F) by deducting 1030 Btu/lb (2.4×10^3 kJ/kg) to allow for the heat of vaporization of the water. The deduction is not actually equal to the heat of vaporization of water (1055 Btu/lb; 2.45×10^3 kJ/kg) because the calculation is to reduce the data from a gross value at constant volume to a net value at constant pressure. Thus, the differences between the GCV and the NCV are given by:

$$\text{NCV (Btu/lb)} = \text{GCV} - (1030 \times \%\ \text{total hydrogen} \times 9)/100$$

In either form of measurement (ASTM D2015; ASTM D3286), the recorded calorific value is the GCV whereas the NCV is calculated from the GCV (at 20 °C; 68 °F) by making a suitable subtraction (=1030 Btu/lb = 572 cal/g = 2.395 MJ/g) to allow for the water originally present as moisture as well as that moisture formed from the coal during the combustion. The deduction, however, is not equal to the latent heat of vaporization of water (1055 Btu/lb, 2.4 MJ/g, at 20 °C, 68 °F) because the calculation is made to reduce from the gross value at constant volume to a net value at constant pressure for which the appropriate factor under these conditions is 1030 Btu/lb (2.395 MJ/g).

A more recent test method (ASTM D5865) pertains to determination of the calorific value of coal by either an isoperibol (a calorimeter that has a jacket of uniform and constant temperature) or adiabatic bomb calorimeter. In the method, a weighed sample of coal is burned under controlled conditions in an oxygen bomb calorimeter. The HHV is calculated from the temperature rise of the water in the calorimeter vessel and the effective heat capacity of the system. Corrections are made for the heat released by the ignition of the fuse and the thermo chemical reactions forming nitric and sulfuric acids.

For the adiabatic calorimeter, the jacket temperature must be adjusted to match that of the calorimeter vessel temperature during the period of the rise. The two temperatures must be maintained as close to equal as possible during the period of rapid rise. For the isoperibol calorimeter, the temperature rise may require a radiation correction. In either case, an individual test should be rejected if there is evidence of incomplete combustion. Furthermore, although it is only required to check the heat capacity once a month, this may be inadequate. A more frequent check of heat capacity values is recommended for laboratories making a large number of tests on a daily basis. The frequency of the heat capacity check should be determined to minimize the number of tests that would be affected by an undetected shift in the heat capacity values.

8.2.2 Data Handling and Interpretation

For all measurements of calorific value, caution is necessary during the sample preparation since oxidation of coal after sampling can result in a reduction of calorific value. In particular, lignite and sub-bituminous rank coal samples may experience greater oxidation effects than samples of higher rank coals. Unnecessary exposure of the samples to the air for the time of sampling or delay in analysis should be avoided. Because of the nature of the test method, the calorimeter parts should be inspected carefully after each use and any calorimeter that has been dropped should not be used without a compete inspection. Finally, the repeatability intervals of both the methods of measurement are close, but there may be a human factor that can be overcome using a calorimeter with a programmer and digital thermometer.

If a coal does not have a measured calorific value, it is possible to make a close estimation of the calorific value (CV) by means of various formulae, the most popular of which are:

1. The Dulong formula

$$\mathrm{CV} = 144.4(\%\mathrm{C}) + 610.2(\%\mathrm{H}) - 65.9(\%\mathrm{O}) - 0.39(\%\mathrm{O})2$$

2. The Dulong–Berthelot formula:

$$\mathrm{CV} = 81370 + 345\ [\%\mathrm{H} - (\%\mathrm{O} + \%\mathrm{N} - 1)/8] + 22.2(\%\mathrm{S})$$

In this equation, %C, %H, %N, %O, and %S are the respective carbon, hydrogen, nitrogen, oxygen, and organic sulfur contents of the coal (all of which are calculated to a dry, ash-free basis). In both cases, the calculated values are in close agreement with the experimental calorific values.

In some instances, an adiabatic bomb calorimeter may not be available or the sample may even be too small accurate use. To combat such problems, there is evidence that DTA is applicable to the determination of calorific value of coal. Data obtained by use of the DTA method are in good agreement with those data obtained by use of the bomb calorimeter (Muñoz-Guillena et al., 1992).

The heating value of coal is a function of rank and the standard classification of coals by rank according to their degree of coalification in ascending order from lignite to anthracite uses the heating value component (ASTM D388). This classification takes into account fixed carbon and calorific value on a mineral-matter-free basis and agglomerating character determined by examination of the residue from the volatile determination. In high volatile, medium-volatile, and low-volatile bituminous coals, the moisture and ash-free Btu (MAP Btu) commonly reported by commercial laboratories tends to increase with decreasing volatile from approximately 14,700 Btu/lb to approximately 15,600 Btu/lb. In the lower-rank coals, the MAF Btu decreases with decreasing rank, approaching roughly that of wood in the range of 6000–8000 Btu/lb for lignite.

The calorific value is normally the basic item specified in contracts for coal to be used in steam plants. It is the most important value determined for coal that is to be used for heating purposes. In coal contracts, the calorific value is usually specified on the as-received basis. Any error in the moisture value is reflected in the as-received calorific value.

The laboratory-determined calorific value is called the *GCV*. It is the heat produced by combustion of a unit quantity of coal at constant volume in an oxygen bomb calorimeter under specified conditions such that the end products of the combustion are in the form of ash, gaseous carbon dioxide, sulfur dioxide, nitrogen, and liquid water. Burning coal as a fuel does not produce as much heat per unit quantity. Corrections are made to the GCVs for this difference between the laboratory and coal-burning facility. The corrected value is referred to as the *NCV*. This is defined as the heat produced by combustion of a unit quantity of coal at constant atmospheric pressure under conditions such that all water in the products remains in the form of vapor. The NCV is lower than the GCV.

8.3 HEAT CAPACITY

The heat capacity of a material is the heat required to raise the temperature of one unit weight of a substance 1° and the ratio of the heat capacity of one substance to the heat capacity of water at 15 °C (60 °F) in the specific heat.

8.3.1 Test Methods

The heat capacity of coal can be measured by standard calorimetric methods that have been developed for other materials (e.g., ASTM C351). The units for heat capacity are Btu per pound per degree Fahrenheit (Btu/lb °F) or calories per gram per degree centigrade cal/g °C), but the specific heat is the ratio of two heat capacities and is therefore dimensionless.

The heat capacity of water is 1.0 Btu/lb °F (=4.2×10^3 J/kg °K) and, thus, the heat capacity of any material will always be numerically equal to the specific heat. Consequently, there has been the tendency to use the terms heat capacity and specific heat almost equivocally.

8.3.2 Data Handling and Interpretation

The specific heat of coal (Table 8.2) usually increases with its moisture content (Figure 8.2), decreases with carbon content (Figure 8.3), and increases with volatile matter content (Figure 8.4), with mineral matter content exerting a somewhat lesser influence. The values for the specific heats of various coals fall into the general range

TABLE 8.2 Specific Heat of Air-Dried Coal

Source	Proximate Analysis (% w/w)				Mean Specific Heat			
	Moisture	Volatile Matter	Fixed Carbon	Ash	28–65 °C	25–130 °C	25–177 °C	25–227 °C
West Virginia	1.8	20.4	72.4	5.4	0.261	0.288	0.301	0.317
Pennsylvania (bituminous)	1.2	34.5	58.4	5.9	0.286	0.308	0.320	0.323
Illinois	8.4	35.0	48.2	8.4	0.334			
Wyoming	11.0	38.6	40.2	10.2	0.350			
Pennsylvania (anthracite)	0.0	16.0	79.3	4.7	0.269			

Source: Baughman, 1978, page 172.

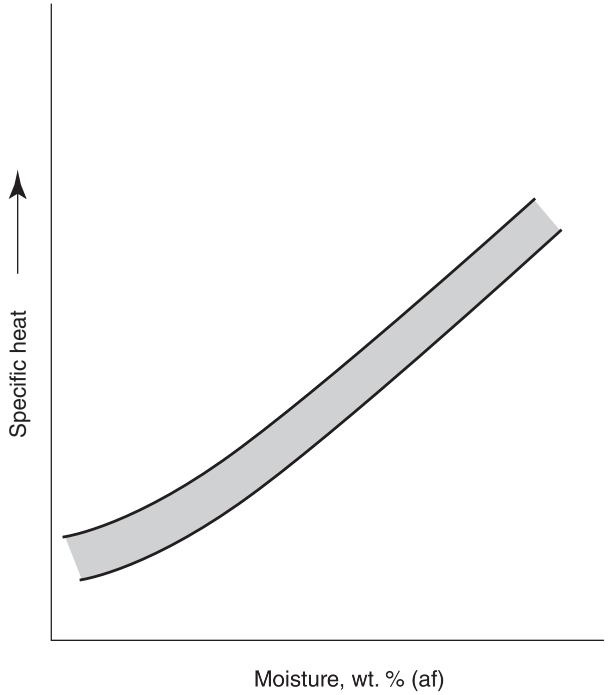

Figure 8.2 Variation of specific heat with moisture content. *Source*: Adapted from Baughman, 1978, page 172.

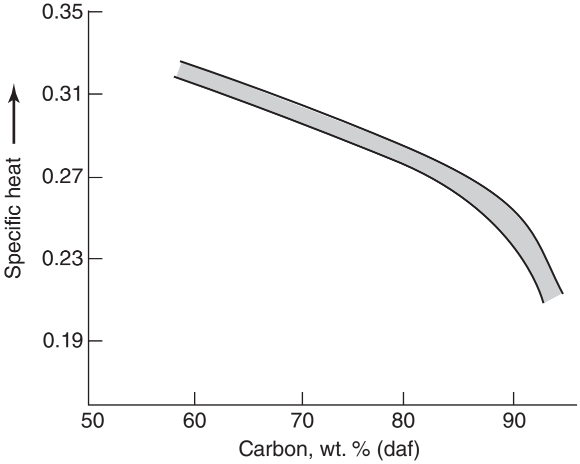

Figure 8.3 Variation of specific heat with carbon content. *Source*: Adapted from Baughman, 1978, page 172.

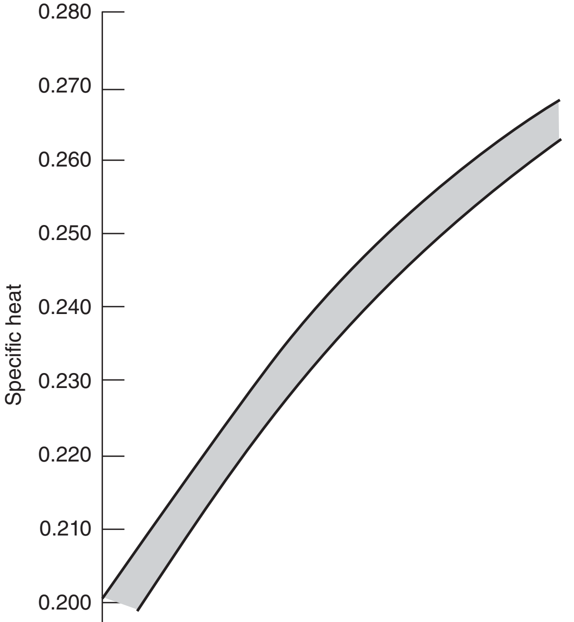

Figure 8.4 Variation of specific heat with volatile matter content. *Source*: Adapted from Baughman, 1978, page 172.

0.25–0.37 but, as with other physical data, comparisons should only be made on an equal basis (e.g., moisture content, mineral matter content, etc.) basis.

Estimates of the specific heat of coal have also been made on the assumption that the molecular heat of a solid material is equal to the sum of the atomic heats of the constituents (Kopp's law); the atomic heat so derived is divided by the atomic weight to give the (approximate) specific heat. Thus, from the data for various coals, it has been possible to derive a formula that indicates the relationship between the specific heat and the elemental analysis of coal (mmf basis):

$$C_p = 0.189\mathrm{C} + 0.874\mathrm{H} + 0.491\mathrm{N} + 0.360\mathrm{O} + 0.215\mathrm{S}$$

C, H, N, O, and S are the respective amounts (% w/w) of the elements in the coal.

8.4 THERMAL CONDUCTIVITY

Coal is a low-to-medium conductor of heat with thermal conductivity (diffusivity and expansion) values ranging from about 3×10^{-4} to 9×10^{-4} cal s^{-1} cm^{-1} °C^{-1} (Speight, 2013a, 2013b and references cited therein). The thermal conductivity A of coal is related to thermal diffusivity (α) and the heat capacity (C_p) by:

$$\alpha = \lambda/\rho C_p$$

In this equation, ρ is the density. Thermal conductivity is the time rate of heat transfer by conduction across a unit area of unit thickness for a unit temperature gradient. Thermal diffusivity is a measure of the rate at which a temperature wave travels.

8.4.1 Test Methods

Thermal conductivity is the rate of transfer of heat by conduction through a unit area across a unit thickness for a unit difference in temperature:

$$TQ = k \times A(t_2 - t_1)/d$$

Q is the heat, expressed as kcal/s cm °C or as Btu/ft h °F (1 Btu/ft h °F = 1.7 J/s m °K), A is the area, $t_2 - t_1$ is the temperature differential for the distance (d), and k is the thermal conductivity (Carslaw and Jaeger, 1959).

8.4.2 Test Methods

Steady state periodic heating and unsteady state methods can be applied to measure the thermal conductivity and diffusivity of coal. Methods such as the compound bar method and calorimetry have been replaced by transient hot-wire/line heat source and transient hot plate methods that allow very rapid and independent measurements of α and λ. In fact, such methods offer the additional advantage of measuring these properties not only for monolithic samples but also for coal aggregates and powders under conditions similar to those encountered in coal utilization systems.

No overall model applicable to the prediction of thermal conductivity/diffusivity values is available but, assuming the presence of additive contributions from the elements in coal, the following correlation has been proposed:

$$\lambda^{-1}(\mathrm{mK/W}) = \mathrm{C}/1.47\ +\ \mathrm{H}/0.0118)(273/T)^{0.5}$$

In the equation, C and H are the mass fractions of carbon and hydrogen and T is the absolute temperature in degrees Kelvin (°K); this equation yields acceptable predictions for monolithic bituminous coal.

8.4.3 Data Handling and Interpretation

However, the banding and bedding planes in coal (Speight, 2013a, 2013b and references cited therein) can complicate the matter to such an extent that it is difficult, if not almost impossible, to determine a single value for the thermal conductivity of a particular coal. Nevertheless, it has been possible to draw certain conclusions from the data available.

Monolithic coal is considered to be a medium conductor of heat with the thermal conductivity of anthracite being on the order of 5−9 × 10−4 kcal/s cm/°C while the thermal conductivity of monolithic bituminous coal falls in the range of 4−7 × 10−4 kcal/s/cm/°C. For example, the thermal conductivity of pulverized coal is lower than that of the corresponding monolithic coal. For example, the thermal conductivity of pulverized bituminous coal falls into the range of 2.5−3.5 × 10−4*f*; kcal/s cm/°C.

The thermal conductivity of coal generally increases with an increase in the apparent density of the coal as well as with volatile matter content, ash content, and temperature. In addition, the thermal conductivity of the coal parallel to the bedding plane appears to be higher than the thermal conductivity perpendicular to the bedding plane.

There is little information about the influence of water on the thermal conductivity of coal, but since the thermal conductivity of water is markedly higher than that of coal (about three times), the thermal conductivity of coal could be expected to increase if water is present in the coal.

8.5 PLASTIC AND AGGLUTINATING PROPERTIES

Plasticity refers to the melting and bonding behavior of the coal and: (1) is an indication of the initial softening, chemical reaction, gas liberation, and resolidification process within the coke oven, (2) is an important requirement in the coke blend and is required for end product coke strength, and (3) the fluidity of the plastic stage is a major factor in determining what proportions of a coal is used in a proportions of a coal used in a blend.

When coal is heated, an unstable intermediate phase (*metaplast*) is formed after the moisture is driven from the coal. This intermediate phase is responsible for the plastic behavior of coal. On further heating, a cracking process takes place in which tar is vaporized and nonaromatic groups are split off followed by recondensation and formation of semi-coke.

When coal or a blend of coals is converted to coke in slot-type ovens, two principal layers of plastic coal are formed parallel to the oven walls. As carbonization proceeds, the plastic layers move progressively inward eventually meeting at the oven center. It is within these plastic layers that the processes which result in particulate coal being converted into porous, fused semi-coke take place. The semi-coke undergoes further devolatization and contracts which results in fissures in the final coke product.

All coals undergo chemical changes when heated but there are certain types of coal that also exhibit physical changes when subjected to the influence of heat. These particular types of coals are generally known as *caking coals* whereas the remaining coals are referred to as *noncaking coals*.

Caking coals pass through a series of physical changes during the heating process insofar as they soften, melt, fuse, swell, and resolidify within a specific temperature range. This temperature has been called the *plastic range* of coal and thus the physical changes that occur within this range have been termed the *plastic properties* (*plasticity*). The caking tendency of coals increases with the volatile matter content of the coal and reaches a maximum in the range 25–35% w/w volatile matter but then tends to decrease. In addition, the caking tendency of coal is generally high in the 81–92% w/w carbon coals (with a maximum at 89% carbon); the caking tendency of coal also increases with hydrogen content but decreases with oxygen content and with mineral matter content.

When noncaking (nonplastic) coal is heated, the residue is pulverent and noncoherent. On the other hand, the caking coal produces a residue that is coherent and has varying degrees of friability and swelling. In the plastic range, caking coal particles have a tendency to form agglomerates (cakes) and may even adhere to surfaces of process equipment, thereby giving rise to reactor plugging problems. Thus, the plastic properties of coal are an important means of projecting and predicting how coal will behave under various process conditions as well as assisting in the selection of process equipment. For example, the plasticity of coal is beneficial in terms of the production of metallurgical coke but may have an adverse effect on the suitability of coal for conversion to liquids and gases. As an example, the Lurgi gasifier is unable to adequately gasify caking coals unless the caking properties are first nullified by a prior oxidative treatment.

The plastic behavior of coal is of practical importance for semi-quantitative evaluation of metallurgical coal and coal blends used in the production of coke for the steel industry. When bituminous coals are heated in the absence of air over the range 300–550 °C (570–1020 °F), volatile materials are released and the solid coal particles soften (to become a plastic-like mass) that swells and eventually resolidifies. Thus, the plastic properties of coal are an important means of projecting and predicting how coal will behave under various process conditions as well as assisting in the selection of process equipment. For example, the plasticity of coal is a beneficial property in terms of the production of metallurgical coke but may have an adverse effect on the suitability of coal for conversion to liquids and gases (Chadeesingh, 2011; Speight, 2013a, 2013b). As an example, the Lurgi gasifier is unable to adequately gasify caking coals unless the caking properties are first nullified by a prior oxidative treatment.

8.5.1 Test Methods

The Gieseler test is a standard test method in which attempts the actual extent of the plasticity of fluidity attained is measured. The Giesler test is used to characterize coals with regard to thermo plasticity and is an important method used for coal blending for commercial coke manufacture. The maximum fluidity determined by the Gieseler is very sensitive to weathering (oxidation) of the coal.

Briefly, the Giesler plastometer (ASTM D2639) is a vertical instrument consisting of a sample holder, a stirrer with four small rabble arms attached at its lower end with the means of (1) applying a torque to the stirrer, (2) heating the sample that includes provision for controlling temperature and rate of temperature rise, and (3) measuring the rate of turning of the stirrer.

A sample of −60 mesh coal is packed in the sample holder; the holder is completely filled and the rabble arms of the stirrer are all in contact with the coal. The apparatus is then immersed in the heating bath and a known torque applied to the stirrer. During the initial heating, no movement of the stirrer occurs but as the temperature is raised the stirrer begins to rotate. With increasing temperature, the stirrer speed increases until at some point the coal resolidifies and the stirrer is halted (Berkowitz, 1979).

In the procedure (ASTM D2639), the sample is air dried prior to preparation and the temperature should not exceed 15 °C (27°F) above room temperature and drying should not be continued to the extent that oxidation of the coal occurs and the plastic properties of the coal are not altered by oxidation. The apparatus is then immersed in the heating bath and a known torque applied to the stirrer. During the initial heating no movement of the stirrer occurs but as the temperature is raised the stirrer begins to rotate. With increasing temperature, the stirrer speed increases until at some point the coal resolidifies and the stirrer is halted (Figure 8.5). The plastic properties of the sample are then measured by the resistance to motion of the fluid mass in the plastometer.

Discrepancies have been noted in results obtained with the Gieseler coal plastometer. For example, Gieseler plasticity tests performed on coking coals showed that increased maximum fluidities were associated with greater retort immersion depths (distance from center of solder bath to center of coal charge), which were

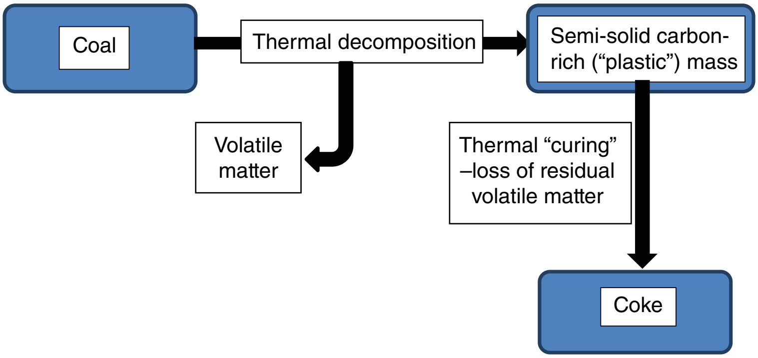

Figure 8.5 Plasticity of coal. *Source*: Adapted from Berkowitz, 1979.

reportedly caused by increased melting and volatilization rates. To achieve satisfactory inter-laboratory agreement for Gieseler plasticity data, tests must be conducted using the same standard and considering oxidation effects such as those from coal storage and transport, which rapidly lower coal plasticity.

8.5.2 Data Handling and Interpretation

Testing with a Gieseler plastometer (ASTM D2639) yields a semi-quantitative measurement of the plastic property or apparent melting of coal when heated under prescribed conditions in the absence of air. The chemical nature of the constituents that account for a coal's plastic properties is not known. The material thought to be responsible for the plastic properties of coal has been successfully removed from coal by solvent extraction, leaving a nonplastic residue. Such residue has been rendered plastic by returning to it the extracts obtained by the solvent extraction. No definite relationship has been established between the amount of extract and the plastic properties of the coal.

Data usually obtained with the Giesler plastometer are (1) softening temperature (ST) (the temperature at which stirrer movement is equal to 0.5 dial divisions per minute), which may be characterized by other rates but if so the rate must be reported, (2) maximum fluid temperature (FT) (the temperature at which stirrer movement reaches maximum rate in terms of dial divisions per minute), (3) solidification temperature (the temperature at which stirrer movement stops), and (4) maximum fluidity (the maximum rate of stirrer movement in dial divisions per minute).

The values normally determined with the Gieseler plastometer are: (1) *initial ST*, which is the temperature at which the dial movement reaches 1.0 dial division per minute—100 dial divisions = one complete revolution of the stirrer may be characterized by other rates, but if so, rate must be reported, (2) *maximum fluidity temperature*, which is the temperature at which the dial pointer movement (stirrer revolutions) reaches the maximum rate, (3) *solidification temperature*, which is the temperature at which the dial pointer movement stops, and (4) *maximum fluidity*, which is the maximum rate of dial pointer movement in dial divisions per minute.

Giesler data are used primarily for assessing coking properties and, furthermore, there is the additional capability that maximum fluidity data can also be used in selecting coals for blending to produce desirable metallurgical coke. For example, if a coal of low maximum fluidity is to be used for making coke, it may be necessary to blend with it a coal of higher fluidity.

The plasticity of individual coal macerals has also received some attention but the investigations can be complicated by the difficulties encountered in the isolation of the macerals in the "pure" state. However, there are reports of the behavior of the macerals. Thus, exinite tends to be quite plastic, with a low softening point, wide plastic range, high fluidity in the plastic state, and a high degree of swelling. This is understandable because exinite is a hydrogen-rich maceral and contains up to 70% volatile matter when isolated from high-volatile coal. It is almost impossible to plasticize fusinite insofar as this maceral is a fossil charcoal, which is hard and friable; vitrinite generally shows an intermediate plasticity behavior (Speight, 2013a).

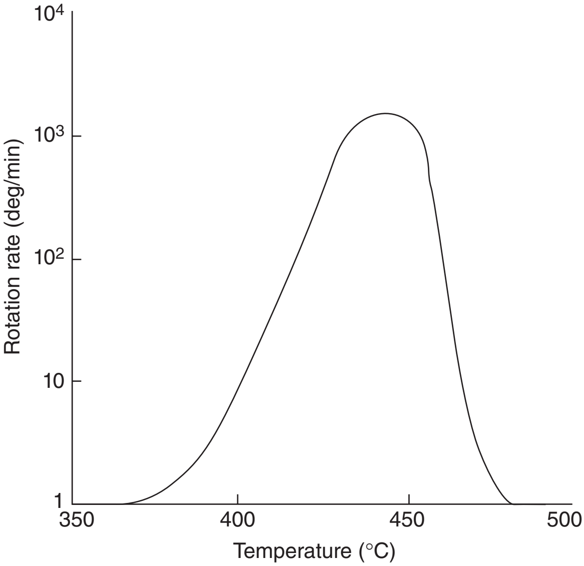

Figure 8.6 Schematic representation of the thermal decomposition of coal.

Although it is possible to formulate the general stages that occur up to and during the plastic stage of coal, the exact mechanism of coal fusion is not completely understood. There appears to be little doubt that the process is concerned with the production and/or liberation of liquid tars within the coal.

In terms of the elemental composition of coal, there is a relative hydrogen deficiency, but there are theories that admit to the presence of hydrogen-rich liquid (and mobile) hydrocarbons that are enclosed within the coal matrix and which are often (erroneously) called *bitumen* and which should not be confused with the bitumen (natural asphalts) that occur in various deposits throughout the world (Speight, 1990, 2013a, 2014). The application of heat results in the liberation of these hydrocarbon liquids and forms other hydrocarbons (*thermo-bitumen*) by scission of hydrocarbon fragments from the coal structure, and the overall effect is the formation of a high-carbon coke and a hydrocarbon tar, the latter being responsible for the fluidity of the mass. With increased heating, the tar partly volatilizes and partly reacts to form non-fluid material ultimately leading to the coke residue (Figure 8.6).

When coal is heated in a vacuum, the plastic range is generally reduced substantially, perhaps because of the rapid evaporation of the bituminous hydrocarbons that are reputedly responsible for the fluidity of the plastic coal. Heating coal to the plastic range followed by rapid cooling yields coal with a lower softening point (if plasticized a second time) and this has been ascribed to the presence of liquid in the coal that arose from the first heating.

An additional property of coal that is worthy of mention at this time is the softening point, which is generally defined as the temperature at which the particles of coal begin to melt and become rounded. The softening point indicates the onset of the plasticity stage and is (as should be anticipated) a function of the volatile matter content of coal. For example, coal with 15% volatile matter will have a softening point of the order of 440 °C (825 °F), which will decrease to a limiting value of circa 340 °C (645 °F) for coal with 30% volatile matter. The material thought to be responsible for conferring that the plastic properties on coal can be removed by solvent extraction to leave a nonplastic residue (Pierron and Rees, 1960). Plastic properties can be restored to the coal recombining the solvents extracts with the insoluble residue.

The plastic properties of coal are sensitive to the oxidation or weathering of coals, which can have a marked effect in decreasing the maximum fluidity. In fact, prolonged oxidation may completely destroy the fluidity of a coal. To reduce oxidation, samples should be tested soon after collection or, if delay is unavoidable, storage under water or in a nonoxidizing atmosphere such as nitrogen is advisable. If the maximum fluidity of the coal is decreased, the extensive oxidation may have completely destroyed the fluidity of coal. Samples should be tested as soon as possible after they are collected and should be stored under water or in a nonoxidizing atmosphere if there is to be a delay before they are tested. Proper packing around the stirrer in the plastometer is an important step in the measurement of plastic properties. Some coals may not pack easily due to their weathered condition or to the size consist of the sample. An excess of very fine coal makes the test sample hard to pack.

Some problems associated with the equipment used are the rate of heating, surface area of the rabble arms on the stirrer, and the manner in which torque is applied. The standard rate of heating influences values obtained in the test, with maximum fluidity being influenced the most. Heating rates higher than the standard lead to higher fluidity values and lower rates of heating produce lower fluidity values. The plastometer must be thoroughly cleaned after each test. Frequent use and cleaning wear away the stirrer and the rabble arms, gradually decreasing their surface area. As a result, high maximum fluidity values will be obtained. When new, the rabble arms have a total surface area of 136 mm^2. When the surface area decreases to 116 mm^2 (usually after 30–40 tests), the rabble arms should be discarded.

Although it is possible to formulate the general stages that occur up to and during the plastic stage of coal, the exact mechanism of coal fusion is not completely understood. There appears to be little doubt that the process is concerned with the production and/or liberation of liquid tars within the coal. In terms of the elemental composition of coal, there is a relative hydrogen deficiency, but there are theories that admit to the presence of hydrogen-rich liquid (and mobile) hydrocarbons that are enclosed within the coal matrix and which are often (erroneously) called *bitumen* and which should not be confused with the bitumen that occur in various deposits throughout the world (Speight, 1990, 2013a, 2014). The application of heat results in the liberation of these hydrocarbon liquids and forms other hydrocarbons (*thermobitumen*) by scission of hydrocarbon fragments from the coal structure, and the overall effect is the formation of a high-carbon coke and a hydrocarbon tar, the latter being responsible for the fluidity of the mass. With increased heating, the tar partly volatilizes and partly reacts to form non-fluid material ultimately leading to the coke residue.

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The material thought to be responsible for conferring that the plastic properties on coal can be removed by solvent extraction to leave a nonplastic residue (Pierron and Rees, 1960). Plastic properties can be restored to the coal recombining the solvents extracts with the insoluble residue. The fluid behavior or plasticity of coal in the temperature range 300–550 °C (572–1022 °F) is widely used to estimate coking characteristics and may be important for predicting coal properties with respect to coal conversion processes.

The primary use of plastic property data is for assessing the coking properties of coals. Maximum fluidity values are most often used in this respect, but the plastic range of coals has also been used as a guide for blending coals for carbonization. The plastic range is the temperature between the softening and the solidification temperature. Plastic property data should not be interpreted too closely. These data are probably more useful when applied to low fluid, less strongly coking coals than in assessing differences in the coking characteristics of high fluid, more strongly coking coals.

The *agglomerating index* is a grading index based on the nature of the residue from a 1-g sample of coal when heated at 950 ± 20 °C (1740 ± 35 °F) in the volatile matter determination (ASTM D3175). The index has been adopted as a requisite physical property to differentiate semi-anthracite from low-volatile bituminous coal and also high-volatile C bituminous coal from subbituminous A coal (Table 8.3). From the standpoint of the caking action of coal in coal-burning equipment the agglomerating index has some interest. For example, coals having indexes NAa or NAb, such as anthracite or semi-anthracite, certainly do not give any problems from caking while those coals having a Cg index are, in fact, the high-caking coals.

The agglomerating (or agglutinating) tendency of coal may also be determined by the Roga test (ISO 335), and the Roga index (calculated from the abrasion properties when a mixture of a specific coal and anthracite is heated) is used as an indicator of the agglomerating tendencies of coals (Table 8.4).

TABLE 8.3 Agglomerating and Caking Properties of Coal

Designation		
Class[a]	Group	Appearance of Residue
Nonagglomerating (button shows no swelling or cell structure and will not support a 500-g weight without pulverizing)	NA, nonagglomerate	NAa, noncoherent residue
		Nab, coke cutton shows no swelling or cell structure and after careful removal from the crucible will pulverize under a 500-g weight carefully lowered onto the button
	A, agglomerate (button dull black, sintered, shows no swelling, or cell structure will support a 500-g weight without pulverizing)	Aw, weak agglomerate (buttons come out of crucible in more than one piece)
		Af, firm agglomerate (buttons come out of crucible in one piece)
Agglomerating (button shows swelling or cell structure or will support a 500-g weight without pulverizing)	C, caking (button shows swelling or cell structure)	Cp, poor caking (button shows slight swelling with small cells, has slight gray luster)
		Cf, fair caking (button shows medium swelling and good cell structure; has characteristic metalic luster)
		Cg, good caking (button shows strong swelling and pronounced cell structure with numerous large cells and cavities; has characteristic metallic luster)

[a] Agglomerating index: Coals that in the volatile matter determination produce either an agglomerate button that will support a 500-g weight without pulverizing or a button showing swelling or cell structure shall be considered agglomerating from the standpoint of classification.

TABLE 8.4 Plastic Properties of Coal

Coal Type	Swelling Index	Dilation (%)	Roga Index
Noncaking	0	0	0–5
Weakly caking	1–2	0	5–20
Medium caking	2–4	0–40	20–50
Strongly caking	>4	>50	>50

TABLE 8.5 Free Swelling Index of Coal

Rank	Coal	Free-Swelling Index
High-volatile C	Illinois No. 6	3.5
High-volatile B	Illinois No. 6	4.5
High-volatile B	Illinois No. 5	3.0
High-volatile A	Illinois No. 5	5.5
High-volatile A	Eastern	6.0–7.5
Medium-volatile	Eastern	8.5
Low-volatile	Eastern	8.5–9.0

Source: Adapted from Baughman, 1978, page 176.

8.6 FREE SWELLING INDEX

The free swelling index (FSI) of coal is a measure of the increase in volume of a coal when it is heated (without restriction) under prescribed conditions (ASTM D720; ISO 335). The ISO test (ISO 335) called *Roga test* measures mechanical strength rather than size profiles of coke buttons; another ISO test (ISO 501) gives a crucible swelling number of coal.

8.6.1 Test Method

The test for the FSI of coal (ASTM D720) requires that several l-g samples of coal are heated under prescribed conditions to produce buttons of coke. The shape, or profile, of the buttons (Table 8.5) determines the FSI of the coal. Anthracites do not usually fuse or exhibit a FSI whereas the FSI of bituminous coals will increase as the rank increases from the high-volatile C bituminous coal to the low-volatile bituminous coal. The results may be used as an indication of the caking characteristic of the coal when burned as a fuel. This test is not recommended as a method for the determination of expansion of coals in coke ovens.

In the test method (ASTM D720), a weighed amount (~1 g) of the sample is placed in a translucent silica crucible with a prescribed size and shape and the sample is leveled in the crucible by light tapping on a hard surface. The cold crucible is then lowered into a special furnace and heated to 800 ± 10 °C (1472 ± 18 °F) in 1 min and 820 ± 5 °C (1508 ± 9 °F) in 1 min. The test can be made with either gas or electric heating. The button formed in the crucible is then compared to a chart of standard profiles and corresponding swelling index numbers. Three to five buttons are made for each sample and the average of the profile numbers is taken as the FSI. The shape, or profile, of the buttons (Table 8.5) determines the FSI of the coal. Anthracite does not usually fuse or exhibit a FSI whereas the FSI of bituminous coal will increase as the rank increases from the high-volatile C bituminous coal to the low-volatile bituminous coal.

Some problems associated with the method are the proper heating rate, oxidation or weathering of the coal sample, and an excess of fine coal in the analysis sample. Failure to achieve the proper temperature in the furnace or, more important, the proper heating rate for the sample in the crucible leads to unreliable results. Uneven heat distribution along the walls of the crucible may also cause erratic results. Oxidation or weathering of the coal sample leads to a low FSI. To minimize oxidation and the effects on the FSI, samples should be tested as soon as possible after they are collected and prepared. If oxidation of the coal is suspected, the test should be repeated on a known fresh sample of the same coal.

The size consistency of the analysis sample may influence the FSI values of some coals. There is evidence that, for many coals, an excess of fine coal (100–200 mesh) may cause FSI values to be as much as two index numbers high. The amount of fine coal in the analysis sample should be kept at a minimum for this test (and others). Reducing the coal from a large particle size to a small particle size in one step tends to produce a high concentration of fine coal. The reduction of coal samples should be carried out in an appropriate number of steps to avoid this.

In another test method (ASTM D5515), a dilatometer is used to measure the swelling of bituminous coal. The test method is limited in applicability to coal that has a FSI ≤ 1 (ASTM D720). The principle of this test method is that the final volume of char obtained at the conclusion of a standard dilatation test is dependent on the mass of coal in the coal pencil and on the radius of the retort tube. This test method incorporates a procedure that determines the mass of air-dried coal in the coal pencil; that provides a means to measure the average retort tube radii; and that employs a means to report coal expansion on an air dried coal weight basis. The value of the dilatation properties of coals may be used to predict or explain the behavior of a coal or blends during carbonization or in other processes such as gasification and combustion.

Other test methods used to determine the swelling properties of bituminous coals include the Ruhr test method (ISO 8264) and Audibert-Arnu (ISO 349) test method. However, these two test methods provide consistently different values for percent dilatation and percent contraction. Percent contraction and dilatation values obtained using the Audibert-Arnu test method are higher and lower respectively than those obtained using the Ruhr test method. These differences have been attributed to trimming the length of the coal pencil from different ends. The Audibert-Arnu test method specifies that the wider end of the coal pencil be trimmed while the Ruhr test method specifies that the narrower end of the coal pencil be trimmed.

The Roga test (ISO 335) measures mechanical strength rather than size profiles of coke buttons; another test (ISO 501) gives a crucible swelling number of coal. The nature of the volume increase is associated with the plastic properties of coal (Loison et al., 1963) and, as might be anticipated, coals which do not exhibit plastic properties when heated do not, therefore, exhibit free swelling. Although this relationship between free swelling and plastic properties may be quite complex, it is presumed that when the coal is in a plastic (or semi-fluid) condition the gas bubbles formed as a part of the thermal decomposition process within the fluid material cause the swelling phenomenon which, in turn, is influenced by the thickness of the bubble walls, the fluidity of the coal, and the interfacial tension between the fluid material and the solid particles that are presumed to be present under the test conditions.

The FSI can also be used as an indication of the extent of oxidation or weathering of coals. However, these are not as sensitive to weathering as the calorific value.

8.6.2 Data Handling and Interpretation

The results from a test may also be used as an indication of the caking characteristics of the coal when it is burned as a fuel. The volume increase can be associated with the plastic properties of coal; coals that do not exhibit any plastic properties when heated do not show free swelling. It is believed that gas formed by thermal decomposition while the coal is in a plastic or semi-fluid condition is responsible for the swelling. The amount of swelling depends on the fluidity of the plastic coal, the thickness of bubble walls formed by the gas, and interfacial tension between the fluid and solid particles in the coal. When these factors cause more gas to be trapped, greater swelling of the coal occurs.

The FSI of bituminous coals generally increases with an increase in rank (Table 8.5). Values for individual coals within a rank may vary considerably. The values for the lower-rank coals are normally less than those for bituminous coals, while anthracite does not fuse and shows no swelling value. Other effects which can influence the FSI of coal include the weathering (oxidation) of the coal. Hence, it is advisable to test coal as soon as possible after collection and preparation. There is also evidence that the size of the sample can influence the outcome of the free swelling test; an excess of fine (−100 mesh) coal in a sample has reputedly been responsible for excessive swelling to the extent that the FSI numbers can be up to two numbers higher than is the true case.

The FSI of coal is believed to be of some importance in assessing the coking properties of coal, but absolute interpretation of the data is extremely difficult. In general terms, the FSI of bituminous coals generally increases with an increase in rank (Rees, 1966) but the values for individual coals within a rank may vary considerably. The values for the lower rank coals are normally less than those for bituminous coals; anthracite does not fuse and shows no swelling value. Furthermore, a coal exhibiting a FSI of 2, or less, will most likely not be a good coking coal whereas a coal having a FSI of 4, or more, may have good coking properties.

The test for the FSI is an empirical one, and values of the FSI can be used to indicate the coking characteristics of coal when burned as a fuel. However, these values are not always sufficiently reliable for use as parameters in a classification system. FSI values have been considered useful as an indication of the tendency of coals to form objectionable “coke trees” when burned in certain types of equipment, particularly equipment with underfeed stokers. The decline in the use of underfeed stokers in coal burning equipment along with adjustments of combustion conditions have minimized the problems due to coke tree formation. The use of FSI test data for help in solving this problem has also declined.

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8.7 ASH FUSIBILITY

Ash produced from coal (Chapter 5) is the noncombustible residue that remains after all the combustible material has been burned. It is a complex mixture that results from chemical changes that take place in the components of the coal mineral matter. The composition of coal ash varies extensively just as the composition of coal mineral matter varies.

The ash fusibility test method (ASTM D1857) is designed to simulate as closely as possible the behavior of coal ash when it is heated in contact with either a reducing or an oxidizing atmosphere. The test is intended to provide information on the fusion characteristics of the ash. It gives an approximation of the temperatures at which the ash remaining after the combustion of coal will sinter, melt, and flow. Sintering is the process by which the solid ash particles weld together without melting. The temperature points are measured by observation of the behavior of triangular pyramids (cones) prepared from coal ash when heated at a specified rate in a controlled atmosphere. The critical temperature points are: (1) the *initial deformation temperature (IT)*, which is the temperature at which the first rounding of the apex of the cone occurs, (2) the *ST*, which is the temperature at which the cone has fused down to a spherical lump in which the height is equal to the width of the base, (3) the *hemispherical temperature (HT)*, which is the temperature at which the cone has fused down to a hemispherical lump at which point the height is one-half the width of the base, and (4) the *FT*, which is the temperature at which the fused mass has spread out in a nearly flat layer with a specified maximum height.

Furthermore, in terms of the determination of the IT, any shrinkage or warping of a cone can be ignored if the tip remains sharp (Figure 8.7).

8.7.1 Test Methods

The test method for determining the fusibility of coal ash (ASTM D1857) covers the observation of the temperatures at which triangular pyramids (cones) prepared from coal and coke ash attain and pass through certain defined stages of fusing and flow when heated at a specified rate in controlled, mildly reducing, and where desired, oxidizing atmospheres.

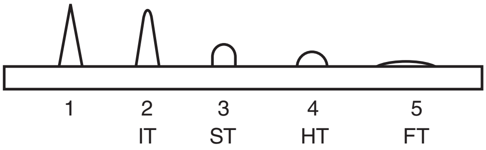

Figure 8.7 Critical temperature points. *Source*: Adapted from ASTM, 2004.

In the test method (ASTM D1857; ISO 540), coal passing a number 60 (250 μm) sieve (analysis sample prepared in accordance with method D 2013) is heated gradually to a temperature of 800–900 °C (1472–1652 °F) to remove most of the combustible material. The ash is ground in an agate mortar to pass a number 200 (75 μm) sieve, spread on a suitable dish, and ignited in a stream of oxygen for approximately 1 h at 800–850 °C (1472–1562 °F). Enough coal is used to produce 3–5 g of ash. The ash is mixed thoroughly and moistened with a few drops of dextrin binder and worked into a stiff plastic mass. The mass is then formed into a cone using a cone mold. The cones are dried, mounted on a refractory base, and heated at a specified rate in a gas-fired or electrically heated furnace under either oxidizing or reducing conditions.

In gas-fired furnaces, regulating the ratio of air to combustible gas controls the atmosphere. For reducing conditions an excess of gas over air is maintained and for oxidizing conditions an excess of air over gas is maintained. Hydrogen, hydrocarbons, and carbon monoxide produce a reducing atmosphere, while oxygen, carbon dioxide, and water vapor are considered to be oxidizing gases. For a mildly reducing atmosphere, the ratio by volume of reducing gases to oxidizing gases must be maintained between the limits of 20–80 and 80–20 on a nitrogen-free basis. In a gas-fired furnace, this ratio may be difficult to achieve at high temperatures while maintaining the required temperature rise. For an oxidizing atmosphere, the volume of reducing gases present must not exceed 10%.

In electrically heated furnaces, a mixture of 60% v/v carbon monoxide and 40% v/v ± 5% v/v carbon dioxide produces a reducing atmosphere in the furnace. A regulated stream of air produces an oxidizing atmosphere.

Proper control of the atmosphere surrounding the test specimen is probably the greatest issue encountered in determining ash fusibility, particularly when a reducing atmosphere is used. A mildly reducing atmosphere is specified, since it is believed that this more closely approximates conditions existing in fire beds when coal is burned in several types of combustion equipment. Lower ST values are obtained with a mildly reducing atmosphere than in either strongly reducing or oxidizing atmospheres. With a mildly reducing atmosphere the iron in the ash is present predominantly in the ferrous state, whereas in a strong reducing atmosphere some of the iron may be in the metallic state. In an oxidizing atmosphere, the iron is in the ferric state. Both ferric iron and metallic iron increase the refractory quality of the ash, resulting in higher fusion temperatures. ST values may vary by as much as 150–200 °C (302–392 °F), depending on the atmosphere in which the test is made.

In preparing ash for the fusibility test, it is important that the coal is spread out in a thin layer and that adequate circulation of air be maintained during burning. All iron must be converted to the ferric state and all combustible matter must be removed. A low initial heating temperature and a slow heating rate tend to minimize the retention of sulfur as sulfates in the ash. Following the burning in air, pulverizing the ash and burning it in oxygen will ensure complete conversion of iron to the ferric state and that all combustible material is burned.

8.7.2 Data Handling and Interpretation

Ash fusibility values are often specified in coal contracts because they are believed to be a measure of the tendency of coal ash to form clinkers. STs probably are used most often for this purpose. For instance, if it is desirable to have the ash fuse into a large clinker that could be easily removed, then coal with a ST low enough to allow the ash to fuse would be chosen. However, the ash should not soften at a temperature too low, as it may become fluid enough to run through the fire bed and solidify below it, making the ash harder to remove. Coal with high STs produce ash with relatively small particle size rather than fused masses. Initial deformation and FTs may also be useful, depending on the type of combustion equipment to be used for burning coal and the manner in which the ash is to be removed.

In practice, types of burning equipment, rate of burning, temperature and thickness of the fire bed, distribution of ash-forming minerals in the coal, and viscosity of the molten ash may influence ash behavior more than do the laboratory-determined ash fusibility characteristics. The correlation of the laboratory test with the actual utilization of coal is only approximate, due to the relative homogeneity of the laboratory test sample compared to the heterogeneous mixture of ash that occurs when coal is burned. Conditions that exist during the combustion of coal are so complex that they are impossible to duplicate completely in a small-scale laboratory test. Therefore, the test should be considered only as an empirical one and the data should be considered qualitative and should not be over-interpreted.

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9

MECHANICAL PROPERTIES

9.1 INTRODUCTION

In contrast to the proximate analysis, ultimate (elemental) analysis and certain of the physical properties, the mechanical properties of coal have been little used. However, these properties are of importance and should be of consideration in predicting coal behavior during mining, handling, and preparation.

Most of the ancillary mechanical and physical tests used to characterize coals and often included in classification schemes were developed in support of efforts to identify coals for coke making. As unique property that sets coking coal apart from other coal types is the caking ability (Chapter 2). There has been much effort to characterize the swelling, contracting, and thermoplastic properties of coals using techniques that allow for the comparison of different coals and how these properties influence coke production and quality. Laboratory tests such as the crucible or free swelling index, Gray-King coke type, Roga Index, Audibert-Arnu dilatometer, and Gieseler plastometer provide some means of evaluating the relative strength of swelling, degree of contraction, and how fluid a coal will become under heating conditions similar to those encountered during coke making.

However, the mechanical properties of coal are of value as a means of predicting the strength of coal and its behavior in mines when the strength of coal pillars and stability of coal faces are extremely important factors. The mechanical properties of coal are also of value in areas such as coal winning (for the design and operation of cutting machinery), comminution (design and/or selection of mills), storage (flow properties,

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failure under shear), handling (shatter and abrasion during transport), as well as in many other facets of coal technology (Yancey and Geer, 1945; Brown and Hiorns, 1963; Evans and Allardice, 1978; van Krevelen, 1993; Gale, 1998).

It is also advantageous to know the mechanical properties of coal to assist with *in situ* coal gasification technology (Shoemaker et al., 1977). The surface and subsurface environmental impact of *in situ* coal gasification may be predicted by utilizing the thermo-mechanical-structural properties of the *in situ* materials. The most serious structural mechanics related problems of underground coal gasification are those dealing with surface subsidence, roof stability, and coal permeability thermo-mechanical changes. The ensuing subsurface environmental consequences include possible gas leakage, water contamination, water in flux into the combustion zone, and heat loss to the overburden. Control of the underground coal gasification process rate advancement, its stability, and surface and subsurface subsidence response is believed to be primarily due to the thermally induced strain and in situ stresses. In addition, coalbed permeability in the swelling bituminous coals are also influenced. Hence, the basic structural and constitutive properties of the *in situ* materials must be known in order to predict the effects of a gasification scheme with regard to roof collapse, coal fracturing, porosity, permeability, and surface subsidence (Shoemaker et al., 1977).

Thermo-mechanical data also become useful in understanding the basic mechanisms involved in mass and energy transport and mechanical-structural effects in gasification processes. For example, decreased permeability immediately after initiation of a burn is generally assumed to be due to the swelling and effervescent nature (bubbling of tar products into the fissures) of the coal at elevated temperatures. The tars products, along with the swelling of the coal, tend to restrict the outward movement (reduce permeability) of the combustion front around a borehole or cavity as well as inhibit a forward burn along a borehole. However, the swelling, effervescent and coalescent nature of the coal can become an asset in control of channeling (by-passing) in some gasification processes insofar as the fluidized coal will be forced into the channels by the pressure of the fractured roof (overburden) and the swelling of the coal.

In addition, coal ash is often seen as a benefit in engineering programs, especially when the ash possesses mechanical strength or other advantageous properties. For example, some coal fired boilers segregate lighter fly ash from the heavier bottom ash that falls to the bottom of the combustion unit during the combustion process. The physical properties of the segregated ash differ because of the different sizes and shapes of fly ash as compared to bottom ash. Therefore, the environmental regulations differentiate between several potential beneficial uses of the coal fly ash and bottom ash because of the different properties. The pH of the coal ash is less important for foundation engineering purposes than the other mechanical properties of the coal ash, but may be considered in the design process for any given usage.

In general, coal ashes can be classified according to the source of the ash, such as bituminous coal ash or anthracite coal ash source as well as segregated or unsegregated fly and bottom ash; coal ash gradation in which the ash is classified according to the size of the ash particles; and other coal ash properties, such as pH, (relative acidity or alkalinity) relevant to the proposed use.

9.2 STRENGTH

Interest in the compressive strength of coal arises mainly from the relationship to the strength of coal pillars used for roof support in mines, such as the construction of room-and-pillar mines (Holland, 1964; Choi and McCain, 1980; Jeromel et al., 2010; Oraee et al., 2010; Speight, 2013a).

The compressive strength of coal is a most difficult property to investigate by experimental means because of variability of coal properties laterally as well as vertically in the seam but also because invariably it will have one set of cracks or planes of weakness and often three sets of cracks or planes of weakness approximately normal to each other, namely, face cleavage, butt cleavage and bedding planes (Holland, 1964). Furthermore, in some coal seams there may be two sets of joints (instead of one set of joints – butt and face cleavages) or even more. Such occurrences do have the advantage of conferring linear elasticity (to short time stresses) and the point of failure in ordinary test specimens under load is easy to detect.

The structural strength of mine pillars, however, has been of interest to mining engineers ever since deep mining became common practice. As a result, many tests of the compressive strength of coal have been made – briefly these tests indicate that the compressive strength of bituminous coal tested in 3″ cubes varies between about 1000 and 7000 psi when loaded perpendicular to the bedding and between 800 and 5000 psi when loaded parallel to the bedding. In the case of anthracite, the compressive strength varies between about 1200 and 7000 psi when tested as 2-inch cubes.

There are different methods for estimating coal strength and hardness: compressive strength, fracture toughness, or grindability, all of which show a trend relative to rank, type, grade, and petrography of the coal (Callicott, 1956; Hower, 1998; Bagherieh et al., 2008). The measurement of coal strength is affected by the size of the test specimen, the orientation of stress relative to banding, and the confining pressure of the test (Hobbs, 1964; Zipf and Bieniawski, 1988; and Medhurst and Brown, 1998; Bilim and Ozkan, 2008).

By its nature, coal is a banded material which makes it weak by comparison to most other rocks. Intact rock strength is commonly defined as the strength of the rock material that occurs between discontinuities, which in coal are closely spaced and related to lithotype banding and cleat structure. For a given rank, individual lithotypes can have large compressive strength differences owing to wide ranges in maceral composition, banding texture, and cleat density (Medhurst and Brown, 1998).

Thus, the strength of a bituminous coal specimen is influenced also by its lateral dimension, the smaller specimens showing greater strength than the larger (Table 9.1), which can be attributed to the presence in the larger specimen of fracture planes or cleats. In fact, it is the smaller samples which present a more accurate indication of the strength of the coal. A factor that probably contributes to the lower strength of

TABLE 9.1 Variation of Compressive Strength with Size

Size	Average Maximum Load
2.5–4-in. cubes	2486
7–8-in. cubes	2170
10–12-in. cubes	2008
12 × 12 × 18 in. high	1152
Approx. 30-in. cube	817
Approx. 54-in. cube	306

TABLE 9.2 Variation of Compressive Strength with Rank

Coal Rank	Compressive Strength (psi)
Anthracite	2370
	3390
	2000
	1740
Bituminous	310–2490
	500
Lignite	2190–6560

large blocks of coal tested in the laboratory is the difficulty of mining large blocks and transporting them from the mine to the laboratory without imposing strains that start disintegration along the cleats. Furthermore, the variation of compressive strength with rank of coals has been noted (Table 9.2) and a plot of strength against volatile matter shows the customary minimum to be 20–25% dry, ash-free volatile matter (Table 9.3; Figure 9.1) for compression both perpendicular and parallel to the bedding plane.

9.2.1 Test Methods

Several methods of estimating relative strength or friability or grindability utilize a porcelain jar mill in which each coal may be ground for, say, revolutions and the amount of new surface is estimated from screen analyses of the feed and of the ground product. Coals are then rated in grindability by comparing the amount of new surface found in the test with that obtained for a standard coal.

The only standard test method that is available is actually a test method for determining coke reactivity and coke strength after reaction (CSR) (ASTM D5341). This test method, describes the equipment and techniques used for determining lump coke reactivity in carbon dioxide (CO_2) gas at elevated temperatures and its strength after reaction in carbon dioxide gas by tumbling in a cylindrical chamber.

In the test method as written, a sample of dried coke of designated origin and size is reacted (at 1100 ± 5 °C, 2012 ± 9 °F) with carbon dioxide gas in a retort at a specified

TABLE 9.3 Variation of Compressive Strength with Coal Particle Size

Lump size	Maximum load (psi)	Comment
(a) General		
2.5 to 4 inch cube	2486	
7 to 8 inch cube	2170	
10 to 12 inch cube	2008	
12 x 12 x 18 inch block	1152	
30 inch cube	817	
54 inch cube	306	
(b) Bituminous coal		
3 inch cube	1000–7000	Loaded perpendicular to the bedding plane
3-inch cube	800–5000	Loaded parallel to the bedding plane
(c) Anthracite		
Inch cube	1200–7000	

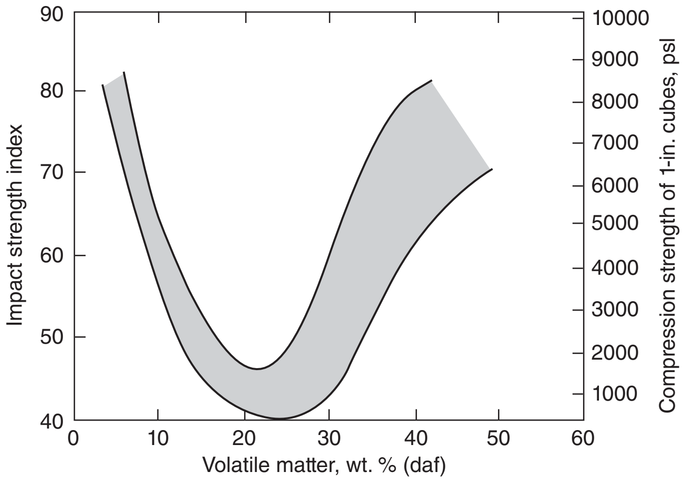

Figure 9.1 Variation of coal strength with volatile matter production. *Source*: Adapted from Brown and Hiorns, 1963, page 131.

elevated temperature for a specified length of time. Two indices, the coke reactivity index (CRI) and the CSR, are determined using the reacted coke residue. The weight loss after reaction determines the CRI. The weight retained after sieving the tumbled reacted coke in a designated number of revolutions over a designated turning rate determines the CSR. The test method if significant for coke because when coke lumps descend in the blast furnace, they are subjected to reaction with countercurrent carbon dioxide and to abrasion as they rub together and against the walls of the furnace.

These concurrent processes physically weaken and chemically react with the coke lumps, producing an excess of fines that can decrease burden permeability and result in increased coke rates and lost hot metal production. This test method is designed to measure indirectly this behavior of coke in the blast furnace.

With some modification, depending upon the coal and the data required, the test method can be applied to determining the strength of coal.

9.2.2 Data Handling and Interpretation

The most common strength characteristics of coal are involve investigations of the compressive strength and this interest arises because of the relationship to the strength of coal pillars used for roof support in mining operations. Thus, it is not surprising that many tests have arisen as a means for measuring the compressive strength of coal. The tests vary with the nature of the investigations and the coal under test to such an extent that the methodology can be questioned if it is not applied in a precise and logical manner adequate to the coal to be tested and to the task.

For example, anthracite has been tested in the form of prisms (having 2 × 2 in., 5 × 5 cm. bases that were cut parallel to the bedding planes of the coal with heights of 1, 2, and 4 in.) by the application of compression perpendicular to the bedding planes. The crushing strengths of the prisms one-inch high ranged from 3200 to 10900 psi and averaged approximately 6000 psi. Furthermore, it has also been shown that the compressive strength of coal is inversely proportional to the square root of the height of the specimen under test. However, the lateral dimension also influences the strength of bituminous coal specimen, the smaller specimens showing greater strength than the larger, which can be attributed to the presence in the larger specimen of fracture planes or cleats. In fact, it is the smaller samples that present a more accurate indication of the strength of the coal. A factor that probably contributes to the lower strength of large blocks of coal tested in the laboratory is the difficulty of mining large blocks and transporting them from the mine to the laboratory without imposing strains that start disintegration along the cleats.

The variation of compressive strength with rank of coals has been noted and a plot of strength against volatile matter shows the customary minimum to be 20–25% dry, ash-free volatile matter (Table 9.3; Figure 9.1) for compression both perpendicular and parallel to the bedding plane.

9.3 HARDNESS

The hardness of coal is often considered to be an inherent property of all coals, with hardness being a fixed value for coal. However, there are degrees of hardness within the coal sequence, as there are within various mineral sequences (Macmillan and Rickerby, 1979). As with other properties of coal, the variance in hardness depends on the composition and the nature of preservation of the original plant material that formed the coal, the amount of impurities in the coal, and the maturation conditions. Generally, the higher the value on the Mohs scale, the harder the material but the

Mohs hardness is generally too subjective for anthracite since it does not have a completely uniform internal structure and might be harder or softer in different spots. For example, when a piece of coal fractures, it appears to be softer. The hardest mineral on the scale is the diamond, while the softest is talc.

Considerable information is available on the properties of coal that relate to hardness (such as friability and grindability) but little is known of the hardness of coal as an intrinsic property.

9.3.1 Test Methods

The scratch hardness of coal can be determined by measuring the load on a pyramidal steel point required to make a scratch 100 μm in width on the polished surface of a specimen. The scratch hardness of anthracite is approximately 6 times that of a soft coal whereas pyrite is almost 20 times as hard as a soft coal (Table 9.4). Similar data were noted for anthracite and cannel coal but durain, the reputedly hard component of coal, was found to be only slightly harder than vitrain and cannel coal.

Although the resistance of coal to abrasion (or abrasive wear) may have little apparent commercial significance, the abrasiveness of coal is, on the other hand, a factor of considerable importance (Yancey et al., 1956). Often, abrasive wear results in smoother wall surfaces; therefore, designs based on an unpolished surface are usually conservative. However, abrasive wear can occasionally result in a more frictional surface, which can disrupt mass flow. When handling abrasive materials, wear tests can be performed to determine the effect on wall friction, as well as calculate the amount of wear expected.

Thus, the wear of grinding elements due to the abrasive action of coal results in maintenance charges that constitute one of the major items in the cost of grinding coal for use as pulverized fuel. Moreover, as coals vary widely in abrasiveness, this factor

TABLE 9.4 Scratch Hardness of Coal

Material	Scratch Hardness Relative to Barnsley Soft Coal
Anthracite, Great Mountain	1.70
Anthracite, Red Vein	1.75
Welsh steam	0.29
Barnsley hards	0.85
Barnsley softs	1.00
Illinois coal	1.10
Cannel	0.92
Carbonaceous shale	0.69
Shale	0.32
Pyrite	5.71
Calcite	1.92

must be considered when coals are selected for pulverized fuel plants. A standardized, simple laboratory method of evaluating the abrasiveness of coal would assist, like the standard grindability test now available, in the selection of coals suitable for use in pulverized form (Johanson and Royal, 1982). In fact, the abrasiveness of coal may be determined more by the nature of its associated impurities than by the nature of the coal substance. For example, pyrite is 20 times harder than coal and the individual grains of sandstone, another common impurity in coal, are also hard and abrasive.

In one investigation, the Vickers micro-hardness of 50 Gondwana coal samples, representing the entire coal series from peat to semi-anthracite, has been determined on the huminite/vitrinite maceral, supplemented by reflectance measurements (Mukherjee et al., 1989). A maximum value of micro-hardness was found at 0.80% reflectance, corresponding to 82.0% w/w carbon content, and a minimum at 1.68% reflectance, corresponding to 91.0% w/w carbon content – at higher rank the value increased sharply. This type of measurement may form the basis for determination of the true hardness characteristics of a coal and may serve as a useful physical parameter for the selection of coal for specific industrial use. In another method, the hardness of coal and the elastic modulus can be determined using Load and Displacement Sensing Indentation Experiments (Oliver and Pharr, 1992).

One of the most important tests for identifying mineral specimens is the Mohs hardness test, which compares the resistance of a mineral (including coal) to being scratched by ten reference minerals known as the *Mohs* (nonlinear) hardness scale. The test is useful because most specimens of a given mineral are very close to the same hardness, which can make hardness a reliable diagnostic property for most minerals. Anthracite, which has variable composition and property range (Speight, 2013a,b), has a scratch hardness at the lower end of the Mohs scale but the value does vary significantly from sample to sample.

9.3.2 Data Handling and Interpretation

Considerable information is available on the properties of coal that relate to its hardness, such as friability and grindability, but little is known of the hardness of coal as an intrinsic property. However, hardness can also be equated with friability and a test method is available to determine the friability of coal (ASTM D441, see below) that all but mirrors the test method for determining the relative measure of the resistance of coke to degradation. In this test method (ASTM D3402), a procedure for obtaining a relative measure of the resistance to degradation of coke by impact and abrasion is described. In the method as written, a sample of dry coke of designated size is tumbled in a rotating drum at a specified turning rate for a specified number of revolutions. Two indexes of its strength, the stability factor and the hardness factor, are determined by sieve analysis of the coke after treatment.

This test method can be applied to coal, remembering the reason for which the method was originally designed, and the data are applicable to coal hardness. Application of the test to coal, usually being a softer material than coke, will require some adjustment of the experimental conditions but the data can be useful in determining the hardness of coal and its possible degree of degradation during shipping and handling. These processes subject the coke to impact and abrasion and the test method is a relative measure of the resistance of coal to breakage when subjected to these degradation processes.

Although the resistance of coals to abrasion may have little apparent commercial significance, the abrasiveness of coal is, on the other hand, a factor of considerable importance. Thus, the wear of grinding elements due to the abrasive action of coal results in maintenance charges that constitute one of the major items in the cost of grinding coal for use as pulverized fuel. Moreover, as coals vary widely in abrasiveness, this factor must be considered when coals are selected for pulverized fuel plants. A standardized, simple laboratory method of evaluating the abrasiveness of coal would assist, like the standard grindability test now available, in the selection of coals suitable for use in pulverized form. Actually, the abrasiveness of coal may be determined more by the nature of its associated impurities than by the nature of the coal substance. For example, pyrite is 20 times harder than coal and the individual grains of sandstone, another common impurity in coal, are also hard and abrasive.

9.4 FRIABILITY

Friability of coal (i.e., the degree of size degradation occurs) refers to coal being readily crumbled and/or brittle, which is a measure of the strength of coal and the ability of the coal to withstand degradation in size during handling.

The friability of coal is an issue of great interest both in its scientific aspects and also from a commercial point of view to the coal industry, inasmuch as the inherent friability of a coal has a marked influence on the extent to which it is broken down, or degraded, in the numerous processes involved in mining, preparation, and marketing. To operators meeting the demands of a general market, in which the larger sizes of coal command substantially higher prices than do the smaller sizes, such degradation is very costly. Some degradation of coal during handling is unavoidable but the extent of the breakage is generally controlled by the properties of the coal (the inherent friability of the coal).

Thus, although the tendency toward breakage on handling (friability) depends on toughness, elasticity, and fracture characteristics as well as on strength, the friability test is the measure of coal strength used most frequently. For example, the coals produced in the Wyoming Powder River Basin (USA) are environmentally and economically attractive to power companies. This type of coal has made enormous inroads to power plants due to these factors regardless of any difficulties plant personnel might experience. The difficulties in handling and storing Powder River Basin coal are due to fines generation and spontaneous combustion issues.

The Powder River Basin coal is extremely friable and will break down into smaller particles virtually independent of how the coal is transported or handled. In fact, Powder River Basin is regarded as representing the extremes of handling problems: (1) dust is an issue when the coal is fine and dry and (2) plugging in bunkers and chutes is an issue when the same fine coal is wet. Once Powder River Basin coal is exposed by mining, the degradation process begins – the majority of the damage can occur in a very short time, even as short as a few days. The extent of the degradation that occurs depends in large part on the distance to the plant from the mine, that is, the time when the coal is exposed to the atmosphere during transportation. Additional factors such as crushed run of mine (CROM) size and specific handling procedures also have an impact on the degradation process. Additional decomposition occurs during handling and storage in a pile and bunker, bin or silo – the cause of the degradation could well be loss of moisture that impacts the coal both mechanically and chemically, through the generation of additional surface reaction area. The combination of the two is what makes Powder River Basin coal difficult to handle.

Friability is of interest because friable coals yield smaller proportions of the coarse sizes that may (depending on use) be more desirable and there may also be an increased amount of surface in the friable coals. This surface allows more rapid oxidation; hence conditions are more favorable for spontaneous ignition, loss in coking quality in coking coals, and other changes that accompany oxidation. These economic aspects of the friability of coal have provided the incentive toward development of laboratory friability tests.

Finally, friability and previous oxidation of the coal are also important factors in the self-heating (spontaneous combustion) process. The ease of friability exposes fresh coal surfaces to air and moisture, where oxidation and moisture adsorption can occur and so on. To complete the circle, previous oxidation makes coal more friable. Although the oxidized matter is less reactive, the porous nature of the oxidized coal makes the coal more susceptible to air and water leakage when exposed to higher pressure differentials, such as in a pile or bunker. Additionally, friability results in production of coal fines and, when dry, the dust increases the explosion hazard potential. On the other hand, if an easily-friable coal has high moisture content, handling difficulty is also increased.

During mining and coal handling operations, dust can be caused by various actions especially when the coal is easily friable. Dust levels can be controlled by spraying water, on roads, stockpiles, and conveyors. Other steps can also be taken but there is the need to monitor the dust produced as well as the potential for dust production.

The concept of a dustiness index was proposed to enable comparison among dust producing capacities of different bulk materials, such as coal (Hamilton and Knight, 1958). Dustiness estimation methods were developed with a view to establishing relative dustiness indices (BOHS, 1985; Lyons and Mark, 1994; Upton et al., 1990; Vincent, 1995; Breum et al., 1996). The objective is to provide criteria for the selection of products that will lead to less dust emissions. It is important to note, however, that different dustiness methods will produce different rank orderings.

Dust removal from coal preparation plants and mine workings is an important aspect of safety and there have been constant attempts to improve dust removal technology. As the techniques have been developed, the predictability of how coal will behave, in terms of the dust produced, under certain conditions has also been sought.

9.4.1 Test Methods

Friability is reported as the percentage reduction in the average particle size during the test. For example, if the average particle size of the tumbled coal was 75% that of the original sample, the friability would be 25%.

The tumbler test for measuring coal friability (ASTM D441) covers the determination of the relative friability of a particular size of sized coal. It affords a means of measuring the liability of coal to break into smaller pieces when subjected to repeated handling at the mine or subsequently, by the distributor or by the consumer. This test method is useful for determining the similarity of coals in respect to friability rather than for determining values within narrow limits to emphasize their dissimilarity. This test method also may serve to indicate the relative extent to which sized coals will suffer size degradation in certain mechanical feed devices. This test method may be used for differentiating between certain ranks and grades of coal and therefore the test method also useful for application to coal classification.

The method employs a cylindrical porcelain jar mill fitted with three lifters that assist in tumbling the coal. A sample (usually 1000 g) of sized coal is tumbled in the mill for a specified time at a specified number of revolutions per minute. The coal is then removed and screened and the friability is reported as the percentage reduction in the average particle size during the test. For example, if the average particle size of the tumbled coal was 75% that of the original sample, the friability would be 25%. As with several other tests, the test parameters can be adjusted to suit the purpose of the investigation but the precise parameters must be reported with the data.

Friability (or hardness) can also be determined by the use of a drop shatter test ASTM D440) that covers the determination of the relative size stability and its complement, the friability, of sized coal. The test method affords a means of indicating the ability of coal to withstand breakage when subjected to handling at the mine and during transit. The test method is useful for determining the similarity of coals in respect to size stability and friability rather than for determining values within narrow limits in order to emphasize their dissimilarity. This test method is considered applicable for testing a selected single size of different coals, for testing different single sizes of the same coal, and for mixed sizes of the same or different coals. This test method appears best suited for measuring the relative resistance to breakage of the larger sizes of coal when handled in thin layers such as from loader to mine car, from loading boom to railroad car, and from shovel to chute. While the method may not be so well adapted for measuring the potential for coal breakage when handled in mass, as in unloading open-bottom cars or emptying bins, the test method will serve also to indicate the relative size stability of composite sizes of coal where, in commercial handling, the smaller sized pieces have a cushioning effect which tends to lessen the breakage of the larger pieces of coal. A similar drop shatter test has also been described for determining the friability of coke (ASTM D3038).

The drop shatter test has also been described for determining the friability of coal (ASTM D440) which is similar to the standard method used as a shatter test for coke (ASTM D3038). In this method, a 50-lb sample of coal (2–3 in., 4.5–7.6 cm) is dropped twice from a drop-bottom box onto a steel plate 6 ft below the box. The materials shattered by the two drops is then screened over round-hole screens with 3.0 in. (76.2 mm), 2.0 in. (50.8mm), 1.5 in. (38.1 mm), 1.0 in. (25.4 mm), 0.75 inch (19.05 mm), and 0.5 inch (12.7 mm) openings and the average particle size is determined. The average size of the material, expressed as a percentage of the size of the original sample, is termed the sizeability, and its complement, the percentage of reduction in average particle size, is termed the percentage friability. Provision is made for testing sizes other than that stipulated for the standard test to permit comparison of different sizes of the same coal.

The *dustiness index* of coal is a means of determining the relative values that represent the amount of dust produced (and friability) when coal is handled in a standard manner. A standard test method (ASTM D547) was withdrawn in 1986 and there is no replacement. Thus, in an available test method, a 50-lb sample of coal is placed on a slide plate in a metal cabinet of prescribed size. When the plate is withdrawn, the sample falls into a drawer and, after 5 s, two slides are inserted into the box. The slides collect suspended dust particles for 2 min (coarse dust) or for 10 min (fine dust). The dustiness index is reported as 40 times the gram weight of dust that has settled after either 2 min or after an additional 8 min.

9.4.2 Data Handling and Interpretation

The average size of the material, expressed as a percentage of the size of the original sample, is termed the sizeability, and its complement, the percentage of reduction in average particle size, is termed the percentage friability. Provision is made for testing sizes other than that stipulated for the standard test to permit comparison of different sizes of the same coal.

Attempts have been made to correlate the friability of coal with rank (Table 9.5). Thus, lignite saturated with moisture was found to be the least friable and friability increased with coal rank to a maximum for coals of the low-volatile bituminous coal. The friability of anthracites is comparable with that of subbituminous coal; both are stronger than bituminous coal and decidedly more resistant to breakage than some of the extremely friable semi-bituminous coals.

The relationship between the friability of coal and its rank has a bearing on its tendency to undergo spontaneous heating and ignition (Chakravorty, 1984; Chakravorty and Karr, 1986). The friable, low-volatile coals, because of their high

TABLE 9.5 Variation of Friability with Rank

Coal Rank	Number of Tests	Friability (%)
Anthracite	36	33
Bituminous (low-volatile)	27	70
Bituminous	87	43
Subbituminous A	40	30
Subbituminous B	29	20
Lignite	16	12

Source: Yancey and Geer, 1945.

rank, do not oxidize readily despite the excessive fines and the attendant increased surface they produce on handling. Coals of somewhat lower rank, which oxidize more readily, usually are relatively non-friable, hence they resist degradation in size with its accompanying increase in the amount of surface exposed to oxidation. But above all, the primary factor in coal stockpile instability is unquestionably oxidation by atmospheric oxygen whilst the role of any secondary factors such as friability is to exacerbate the primary oxidation effect (Jones and Vais, 1991).

Finally, weathering (oxidation) also causes increased friability, especially in the coal on the outer edges of a stockpile. The Hardgrove Index decreases with an increased degree of weathering. This is believed to be due to the micro-cracks and fissures that develop in the coal during oxidation and to physical weathering.

9.5 GRINDABILITY

The grindability of coal is a measure of the resistance of the coal to crushing or it is the ease with which the coal may be ground fine enough for use as pulverized fuel. Two factors that affect grindability are (1) the moisture content and (2) the mineral matter contents of the coal. In general, lignite and anthracite coals are more resistant to grinding than are bituminous coals.

The grindability of coal is a composite physical property embracing other specific properties such as hardness, strength, tenacity, and fracture. Several methods of estimating relative grindability utilize a porcelain jar mill in which each coal may be ground for, say, 400 revolutions and the amount of new surface is estimated from screen analyses of the feed and of the ground product. Coals are then rated in grindability by comparing the amount of new surface found in the test with that obtained for a standard coal.

The *grindability index* (*GI*) of coal is an important technological parameter for understanding coal behavior and assessing the relative hardness of coals of varying ranks and grades during comminution (Jensen and Fryer, 1958; Lytle et al., 1992; Vuthaluru et al., 2003; Ural and Akyildiz, 2004; Tiryaki, 2005; Jorjani et al., 2008; Özbayoğlu et al., 2008; Rattanakawin and Tara, 2012; Khoshjavan et al., 2013). However, due to the heterogeneous character of coals as regards maturity, petrological constituents, and mineral impurities as well as mechanism of comminution render such determination rather difficult, leading to poor reproducibility and repeatability of the value of the Hardgrove grindability index (HGI), which contrary to other analyses for coal characterization (Chapter 5, Chapter 6, Chapter 7, and Chapter 8). Thus, the data may be misleading results when used literally to understand and explain properties emerging from other analyses and testing. In view of such problems, attempts have been made over the years to develop correlation of the HGI with the composition of coal (Sengupta, 2002).

9.5.1 Test Methods

Grindability is an index of the relative ease with which a coal may be pulverized in comparison with coals chosen as standards. The Hardgrove method (ASTM D409;

ISO 5074) has been accepted as the standard method of grindability of coal by the Hardgrove machine. There is also a test method to determine the Hardgrove grindability index of petroleum coke (ASTM D5003) that might be applicable to extremely hard coal by the usual test method and does not produce suitable reproducibility and repeatability. Suitable modifications of the test method for petroleum coke might be required.

The Hardgrove grindability test method covers the determination of the relative grindability or ease of pulverization of coal in comparison with coal chosen as the standard. A prepared and sized sample receives a definite amount of grinding energy in a miniature pulverizer and the size consist of the pulverized product is determined by sieving. The resultant size distribution is used to produce an index relative to the ease of grinding (HGI).

High-volatile bituminous coal, sub-bituminous coal, and lignite can undergo physical change as the natural or seam moisture is released during handling and preparation. This change is often sufficient to alter the grindability characteristics that will be reported when tested in the laboratory and could produce different indices dependent on the conditions of drying and the moisture level, causing inconsistencies in repeatability and reproducibility of the data for these coals.

The test for grindability (ASTM D409; ISO 5074; Hardgrove, 1932; Edwards et al., 1980) utilizes a ball-and-ring-type mill in which a sample of closely sized coal is ground for specified number (usually, 60) revolutions after which the ground product is sieved and the GI is calculated from the amount of undersize produced using a calibration chart (Figure 9.2). The results are converted into the equivalent HGI (Table 9.6). High GI numbers indicate easy-to-grind coals. Each Hardgrove machine should be calibrated by use of standard reference samples of coal with GIs of approximately 40, 60, 80, and 110. These numbers are based on an original soft coal chosen as a standard coal whose GI was set at 100.

9.5.2 Data Handling and Interpretation

The results are converted into the equivalent HGI (Hower, 1988; Hower and Lineberry, 1988; Hower and Wild, 1988). High GI numbers indicate easy-to-grind coals. There is an approximate relationship between volatile content and grindability in the low-, medium-, and high-volatile bituminous rank coals. Among these the low-volatile coals exhibit the highest GI values, often over 100. The high-volatile coals range in GI from the mid-1950s down to the high 1930s. There is also an approximate correlation between friability and grindability. Soft, easily fractured coals generally exhibit relatively high values for the GI. ASTM has two methods for measuring friability, the Drop Shatter Test, D440, and the Tumbler Test, D441, which should be used where more than a rough indication of friability is needed.

A general relationship exists between coal grindability and rank (Figure 9.3) insofar as the easier-to-grind coals are in the medium- and low-volatile groups but, nevertheless, the relationship between grindability and rank is far too approximate to permit grindability to be estimated from coal analysis. For example, low-volatile bituminous coal usually exhibits the highest GI value over 100 whereas high-volatile coal ranges

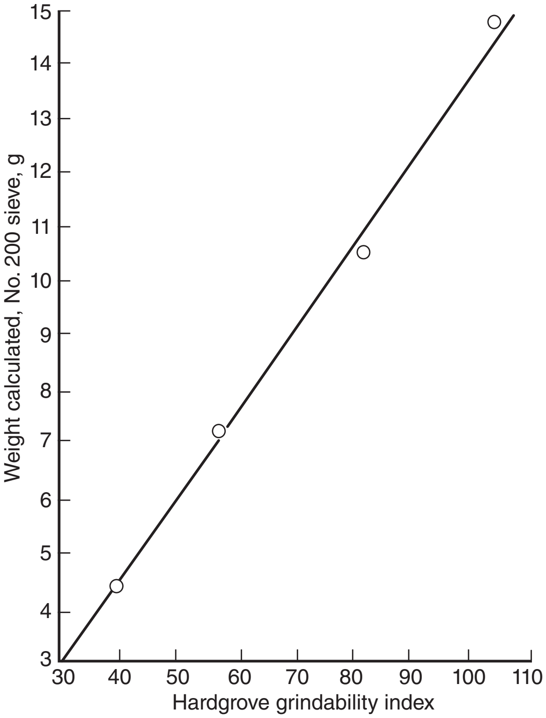

Figure 9.2 Calibration chart for the hardgrove grindability index. *Source*: Adapted from ASTM, 2013.

in GI from approximately 55 down to the 35 to 40 range. There is, however, a correlation between friability and grindability insofar as soft, easily fractured coal generally exhibits a relatively high value for the GI.

Variations in the data that fall outside of the experimental allowable limits may be due to several factors that originate during sample preparation and handling, such as (1) the sample moisture may not have been in equilibrium with the laboratory atmosphere, (2) the sample may have been over-dried or under-air-dried, (3) excessive dust loss may have occurred during screening due to a loose-fitting pan and cover on the sieve, or (4) the sample may not have had an even distribution of particles. Moisture content is particularly troublesome in some coals and causes a decrease in mean strength of the coal (White and Mazurkiewicz, 1989). The GI of coal varies from seam to seam and within the same seam.

Finally, an interesting note is the conclusions from a study of a large number of determined values of the HGI of all major types of Indian coals in has been found that the HGI of coals is mainly dependent on two factors: (1) rank of the coal and (2) the amount of mineral matter in the coal (Sinha et al., 1962). It was established that volatile matter together with the moisture of coals (both reported at 60% relative humidity and at 40 °C/104 °F) is very closely associated with the carbon content (dry

TABLE 9.6 Hardgrove Grindability Index of Coal

State	County	Bed	Mine	Hardgrove Grindability Index
Alabama	Walker	Black Creek	Drummond	46
Colorado	Fremont		Monarch No. 4	46
	Mesa		Cameo	47
Illinois	Fulton	No. 2	Sun Spot	53
	Stark	No. 6	Allendale	61
	Williamson	No. 6	Utility	57
Indiana	Pike	No. V	Blackfoot	54
Iowa	Lucas	Cherokee	Big Ben	61
Kansas	Crawford	Bevier	Clemens	62
Kentucky	Bell	High Splint	Davisburg	44
	Muhlenburg	No. 11	Crescent	55
	Pike	Elkhorn Nos. 1 and 2	Dixie	42
Missouri	Boone	Bevier	Mark Twain	62
Montana	Richland		Savage	62
New Mexico	McKinley	Black Diamond	Sundance	51
North Dakota	Burke		Noonan	38
Ohio	Belmont	No. 9	Linda	50
	Harrison	No. 8	Bradford	51
Pennsylvania	Cambria	Lower Kittaning (bituminous)	Bird No. 2	109
	Indiana	Lower Freeport (bituminous)	Acadia	83
	Schuykill	Various (anthracite)		38
	Washington	Pittsburgh	Florence	55
	Westmoreland	Upper Freeport	Jamison	65
Tennessee	Grundy	Sewance	Ramsey	59
Utah	Carbon	Castle Gate	Carbon	47
Virginia	Buchanan	Splash Dam	Harman	68
	Dickenson	Upper Banner		84
	Wise	Morris	Roda	43
West Virginia	Fayette	Sewell	Summerlee	86
	McDowell	Pocahontas No. 3	Jacobs Fork	96
	Wyoming	Powellton	Coal Mountain	58
	Wyoming	No. 2 Gas	Kopperston	70
Wyoming	Campbell	Smith/Rowland	Wyodak	59

Source: Adapted from Baughman, 1978, page 169.

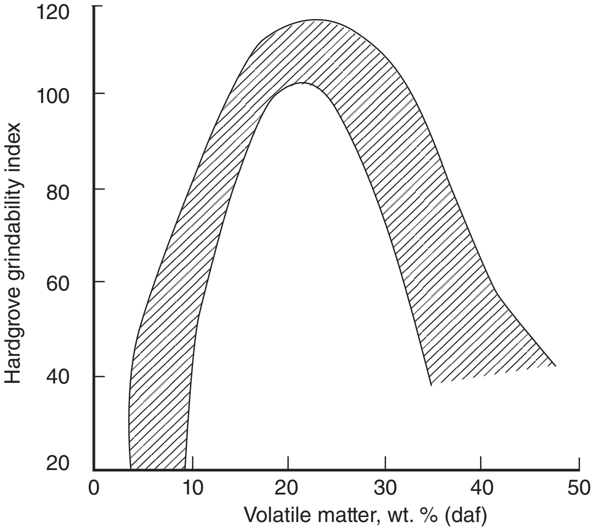

Figure 9.3 Variation of hardgrove grindability index with volatile matter. *Source*: Adapted from Berkowitz, 1979, page 91.

mineral matter free), which is one of the parameters for measuring the degree of coalification. An equation was evolved for estimating the HGI of coal from knowledge of the volatile matter plus moisture and ash (A) contents (moisture, ash, and volatile matter percentages being reported at 60% R.H. and at 40 °C basis):

$$\text{HGI} = 105 - \text{R}(1.16 + 0.002\text{R})\ 00.4\text{A}$$

This equation may be used for estimating the HGI for preliminary selection of coals for pulverized fuel fired furnaces. Furthermore, by an algebraic simplification of the original Hardgrove equation, a formula has been deduced for calculating the HGI of coals from the weight of the coal particles above 200 ASTM sieve, left after the specified Hardgrove test (and which is actually weighed), instead of from the weight of the coal particles below 200 ASTM sieve, estimated indirectly.

9.6 OTHER MECHANICAL PROPERTIES

9.6.1 Cleat Structure

Cleats are natural fractures in coal that serve as permeability avenues for darcy flow of gas and water to the well bore during production. Cleat structure is of special importance in the passage of methane through, and from coal beds as well as in the planning of underground coal gasification tests. The development of cleat and coal-seam permeability is related to the rank, type, and grade of the coal concerned.

The permeability of a coal seam, moreover, may change during gas production, due to either matrix shrinkage or cleat closure or both. Furthermore, cleats are usually perpendicular to the bedding planes (Chapter 4, Chapter 9); thus, cleat joints are usually vertical. The main system of joints is more commonly called the *face cleat* whereas a cross-system of jointing is called the *butt cleat*.

Typically, the cleat system in coal comprises two or more sets of subparallel fractures, both of which are oriented nearly perpendicular to bedding plane – the set of fractures called the *face cleat* is usually dominant and individual cleat fractures are relatively planar and persistent. The *butt cleat* is typically perpendicular to the face cleat, but the fractures tend to be discontinuous and nonplanar. Face cleat are interpreted to form perpendicular to the minimum principal axis of compressive stress. Cleat spacing has a major influence on coal bed permeability and is related to the rank of the coal rank, petrographic composition, mineral matter content, bed thickness, and tectonic history. In general, at any given rank, closer cleat spacing is associated with brighter (higher-vitrinite) coal, less mineral matter, and thinner beds (Levine, 1993). Most medium and low volatile bituminous coals will have good initial permeability if the cleats are open. Permeability can be low to nonexistent in semi-anthracite coal and anthracite coal due to the destruction of cleat.

Mineral fillings in cleat may also lead to low permeability. If a large proportion of the cleat is filled, the absolute permeability may be extremely low (Levine, 1993). Common minerals in cleat are calcite, pyrite, gypsum, kaolinite, and illite. A large acid pad is sometimes used at the beginning of a stimulation treatment in areas where calcite is prevalent in the cleat.

Thus, cleats account for most of the permeability and much of the porosity of coalbed gas reservoirs and can have a significant effect on the success of engineering procedures such as cavity stimulations. Because permeability and stimulation success are commonly limiting factors in gas well performance, knowledge of cleat characteristics and origins is essential for successful exploration and production.

A system of joint planes is often observed in coal formations and these joint planes (cleats) are usually perpendicular to the bedding planes. Thus, cleat joints are usually vertical. The main system of joints is more commonly called the *face cleat* whereas a cross-system of jointing is called the *butt cleat*. Furthermore, the cleat system in coal has a pronounced effect on the properties of a coal deposit. For example, holes drilled into coal perpendicular to the face cleat are said to yield from 2.5 to 10 times the amount of methane gas from the formation as holes drilled perpendicular to the butt cleat. Moreover, the cleat system of fracture and the frequency of cleats may determine the size of run-of-mine coal. In general, a pair of cleats will be oriented at circa 90° to each other and the orientation of the cutting elements influence the output of coal-mining machines (Figure 9.4).

Few data are available on apertures, heights, lengths, connectivity, and the relation of cleat formation to diagenesis, characteristics that are critical to permeability (Laubach et al., 1998). Moreover, recent studies of cleat orientation patterns and fracture style suggest that new investigations of even these well-studied parameters can yield insight into coal permeability.

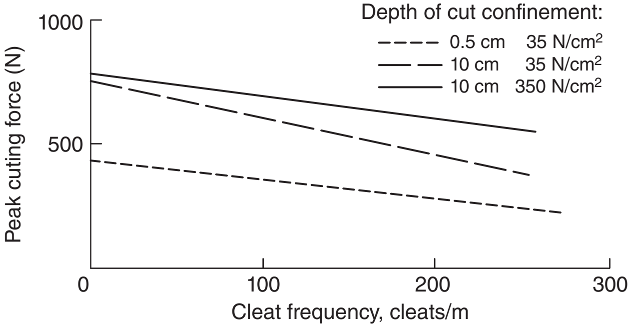

Figure 9.4 Effect of cleats on the cutting force. *Source*: Adapted from Baughman, 1978, page 171.

More effective predictions of cleat patterns will come from advances in understanding cleat origins. Although cleat formation has been speculatively attributed to diagenetic and/or tectonic processes, a viable mechanical process for creating cleats has yet to be demonstrated. Progress in this area may come from recent developments in fracture mechanics and in coal geochemistry.

It has been reported that the cleat system in coal has a pronounced effect on the properties of a coal deposit. For example, holes drilled into coal perpendicular to the face cleat are said to yield from 2.5 to 10 times the amount of methane gas from the formation as holes drilled perpendicular to the butt cleat. Furthermore, the cleat system of fracture and the frequency of cleats may determine the size of run-of-mine coal. In general, pair of cleats will be oriented at approximately 90° to each other and the orientation of the cutting elements influence the output of coal-mining machines (Figure 9.4).

Directional properties also occur in coal and these properties can affect the direction of flow of gases. For a particular coal seam, analyses of natural fracture orientation, directional permeability, directional ultrasonic velocity, and directional tensile strength (Berenbaum and Brodie, 1959) may disclose distinct coal structures that are important for gas flow through the coal (Puri and Seidle, 1992). It is of special importance in the passage of methane through and from coal beds as well as in planning of underground coal gasification tests.

9.6.2 Deformation and Flow under Stress

The rheology (deformation and flow) of coal has been studied in an effort to apply it to characteristics of coal in coal mines; coal elasticity (quality of regaining original shape after deformation under strain) has also been studied. However, it may be quite difficult to obtain meaningful measurements of coal elasticity.

For example, the heat that is generated in cutting a uniform sample (usually by means of a grinding wheel consisting of grit embedded in rubber) can cause plastic deformation of the coal surface and thereby affect the plastic properties. Water used to cool the grinding interface and to carry away particles may be absorbed by the coal and affect the elastic properties. Furthermore, discontinuities in the coal structure give a wide sample-to-sample variation.

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10

SOLVENT PROPERTIES AND SPECTROSCOPIC PROPERTIES

10.1 INTRODUCTION

Coal is an organic rock that is composed of macerals and minerals (Given, 1988; Speight, 2013 and references cited therein). The precursors to coal are as diverse as the plant chemicals themselves, with the added recognition that there may have been some evolution of these chemicals over geological time as plants, and their constituents, have evolved to modern-day counterparts. Thus, coal is a complex chemical material wherein the constituents of the original chemical precursors have undergone considerable change through chemical and physical interactions with their environment.

Identification of the constituents of complex materials, such as coal, may proceed in a variety of ways but generally can be classified into three methods: (1) spectroscopic techniques, (2) chemical techniques, and (3) physical property methods whereby various structural parameters are derived from a particular property by a sequence of mathematical manipulations. It is difficult to completely separate these three methods of structural elucidation and there must, by virtue of need and relationship be some overlap. Thus, although this review is more concerned with the use of spectroscopic methods applied to the issues of coal structure, there will also be reference to the other two related methods.

It is the purpose of this chapter to present some indication of the ability of solvents to dissolve coal as well as the spectroscopic methods that have been applied to coal analysis (Vorres, 1993 and references cited therein under the specific spectroscopic

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Handbook of Coal Analysis, Second Edition. James G. Speight.

method; Speight, 1994, 2013). However, the standard test methods are not in any great abundance but that does not stop the researcher for making such request of the analyst for spectroscopic analysis. Thus, reference to the scientific literature is necessary, keeping in mind that the focus of the references is the description of the technique and that sample preparation and sampling are of the utmost importance.

10.2 SOLVENT PROPERTIES

There are no specific test methods that apply to the solvent extraction of coal. However, procedures and protocols can be gleaned from other methods, provided that sampling and handling of the coal are in accordance with accepted standard test methods.

There are several test methods that advocate the use of solvents for various reasons and they are worthy of mention here insofar as each of the methods can be modified for application to coal.

Solvent extraction is accomplished by contacting coal with a solvent and separating the residual coal material from the solvent and the extracts (Vorres, 1993 and references cited therein). However, extraction is, typically, mass transfer limited, so thorough mixing of the solvent and coal is required. Briefly, the extraction solvent is well mixed with the coal to allow potentially soluble constituents to transfer to the solvent. The residual coal and solvent are then separated by physical methods, such as gravity decanting, filtering, or centrifuging. Distillation regenerates the solvent from the extracted material.

Nondestructive solvent extraction of coal is the extraction of soluble constituents from coal under conditions where thermal decomposition does not occur. On the other hand, solvolysis (destructive solvent extraction) refers to the action of solvents on coal at temperatures at which the coal substance decomposes and in practice relates in particular to extraction at temperatures between 300 and 400 °C (572 and 752 °F). In the present context (i.e., the solvents extraction of coal), the solvent power of the extracting liquid appears to be solely determined by the ability of the solvent to alter the coal physically (by swelling). In this respect, the most effective solvents are aromatics, phenol derivatives, naphthol derivatives, anthracene, and phenanthrene.

For the purposes of this chapter, the solvent extraction of coal is limited to those investigations and test methods that are separate from the high temperature treatment of coal with solvents in which the production of liquid products (liquefaction) is the goal.

The solvent extraction of coal has been employed for many years (Speight, 2013 and references cited therein) as a means of studying the constitution of coal with the yield and the nature of the extract dependent on the solvent type, extraction conditions, and, last but not least, the coal type (Kreulen, 1948; Francis, 1961; Dryden, 1963; Wise, 1971; Hombach, 1980; Pullen, 1983; Given, 1984; Litke et al., 1990; Blanc et al., 1991; Pickel and Gotz, 1991). The solvent extraction of coal should not be confused with the principles which lie behind coal cleaning or coal washability (Speight, 2013) even though solvents (more frequently referred to as *heavy liquids*) may be used. The approach uses a different perspective and the outcome is usually quite different.

There have been many attempts to define solvent behavior in terms of one or more physical properties of the solvent and not without some degree of success. However, it is essential to note that the properties of the coal also play an important role in defining behavior of a solvent and it has been reported that the relative solvent powers of two solvents may be reversed from one coal type to another. Thus, two properties that have found some relevance in defining solvent behavior with coal (as well as with other complex carbonaceous materials such as petroleum asphaltene constituents) are the surface tension and the *internal pressure* (Speight, 1994, page 201). However, the solvent power of primary aliphatic amines (and similar compounds) for the lower rank coals has been attributed to the presence of an unshared pair of electrons (on the nitrogen atom).

The early work on the solvent extraction of coal was focused on an attempt to separate from coal a *coking principle* (i.e., the constituents believed to be responsible for coking and/or caking properties). But solvent extraction has actually been used to demonstrate the presence in coal of material that either differed from the bulk of the coal substance or was presumed to be similar to the bulk material.

An example of the difference of the solvent extracts from the bulk material comes from a series of studies on the exhaustive extraction of coal by boiling pyridine and fractionation of the regenerated soluble solids by sequential selective extraction schemes (Speight, 2013). Subsequent analyses showed that the petroleum ether-soluble material was mostly composed of hydrocarbons (e.g., paraffins, naphthenes, and terpenes), while the ether-soluble, acetone-soluble, and acetone-insoluble fractions were resin-like substances with 80–89% carbon and 8–10% hydrogen. Indeed, this, and later work (Vahrman, 1970), led to the concept that coal is a two-component or two-phase system (Derbyshire et al., 1991; Yun et al., 1991).

One such method (ASTM D5369) describes standard procedures for extracting nonvolatile and semi-volatile organic compounds from solids such as soil, sediment, sludge, and granular waste using Soxhlet extraction. The sample must be suitable for being mixed with the sample drying agent, sodium sulfate or magnesium sulfate, to provide drying of all sample surfaces. This practice, when used in conjunction with another test method (ASTM D5368) is applicable to the determination of the total solvent extractable content (TSEC) of a soil, sediment, sludge, or granular solid waste but does depend upon the solvent chosen. However, the practice is limited to solvents having boiling points below the boiling point of water at ambient pressure. But the method does provide sample extracts suitable for analysis by various techniques such as gas chromatography with flame ionization detection (GC/FID) or gas chromatography with mass spectrometric detection (GC/MS) or any tandem mass spectrometric method (Holman, 1990).

A related test method (ASTM D5368) describes the standard procedures for gravimetrically determining the total nonvolatile and semi-volatile organic content of solvent extracts from soils or solid wastes. As written, the test method is used after a solvent extract is obtained from a soil or solid waste. For these methods to be applicable, the extraction solvent must have a boiling point less than that of water at ambient pressure. Moreover, the TSEC of a soil, sediment, sludge, or solid waste depends upon the solvent and method used for the extraction.

In both of the aforementioned cases, there may be some hesitancy because of the restrictions of the boiling point of the solvent. However, it is the method that should be considered and modified and applied accordingly to coal.

A test method for the batch extraction of treated or untreated solid waste or sludge, or solidified waste, to provide an indication of the leaching potential (ASTM D5233) is also available. The goal of this test method is to provide an extract for measurement of the concentration of various analytes and therefore, may be applied to a study of the smaller molecules that reside within the coal matrix. This test method, as written, is intended to provide an extract suitable for the measurement of the concentration of analytes that will not volatilize under the conditions of the test method and may appear to offer limitations to the use of coal but the test method does describe a procedure for performing a batch extraction of a solid. Moreover, the sampling and handling requirements that may be associated with the analysis of coal should also be applied to the method.

Once a suitable method of coal exaction has been selected, the common equipment for the method is a Soxhlet extractor, sometime fitted with a Dean and Stark adaptor. The latter allows the removal of water as a separate phase. Beyond this, and the smoking and handling constraints (remembering that coal oxidation will influence its extractability), a solvent that is suitable to the task (as defined by the objective) should be selected. In general terms, solvents for coal extraction can be grouped into four general categories: (1) nonspecific, (2) specific, (3) degrading, and (4) reactive (Williams et al., 1987). Such solvents are used in a variety of solvent-enhanced liquefaction operations. However, in terms of definition, the solvents can be described as follows (1) nonspecific solvents, (2) specific solvents, (3) degrading solvents, and (4) reactive solvents.

Nonspecific solvents extract a small amount (10%) of coal at temperatures up to about 100 °C (212 °F). The extract is thought to arise from the so-called resins and waxes that do not form a major part of the coal substance. Ethanol is an example of the nonspecific solvents. *Specific solvents* extract 20–40% of the coal at temperatures below 200 °C (392 °F) and the nature of the extract is believed to be similar to, or even represent, the original coal; pyridine is an example of such a solvent. *Degrading solvents* extract major amounts of the coal (up to more than 90%) at temperatures up to 400 °C (750 °F). This type of solvent can be recovered substantially unchanged from the solution and the solvent action is presumed to depend on mild thermal degradation of the coal to produce smaller soluble fragments; phenanthrene is an example of such a solvent. *Reactive solvents* dissolve coal by active interaction. Such solvents are usually hydrogen donors and their chemical composition is appreciably affected during the process. Furthermore, using tetralin as the example, the solvent is converted to the aromatic counterpart (in this case naphthalene) and the products from the coal can vary in composition depending upon the reaction severity and the ratio of the solvent to the coal. In addition, the extracts differ markedly in properties from those obtained with degrading solvents.

Considerable attention has been paid to the use of compressed gases and liquids as solvents for extraction processes (Schneider et al., 1980; Dainton and Paul, 1981; Bright and McNally, 1992; Kiran and Brennecke, 1992) although the law of partial pressures indicates that when a gas is in contact with a material of low volatility, the concentration of *solute* in the gas phase should be minimal and decrease with increased pressure. Nevertheless, deviations from this law occur at temperatures near the critical temperature of the gas and the concentration of solute in the gas may actually be enhanced as well as increased with pressure.

The technique of extracting virtually nonvolatile substances is particularly useful for those materials which decompose before reaching boiling point and is, therefore, well suited to the extraction of the liquids formed when coal is heated to about 400 °C (750 °F). Thus, supercritical gas/fluid extraction affords a means of recovering the liquid products when they are first formed, avoiding undesirable secondary reactions (such as coke formation), and yields of extract up to 25% or 30% have been recorded.

While the yields of extract may be lower than can be obtained with some liquid solvents and the use of high pressures might appear to be disadvantageous, there are nevertheless two positive features related to supercritical gas/fluid extraction of coal: (1) the extracts have lower molecular weights (about 500 compared to greater than 2000) and higher hydrogen content and may, presumably, be more readily converted to useful products; and (2) solvent removal and recovery is more efficient, that is, a pressure reduction has the ability to precipitate the extract almost completely.

10.2.1 Action of Specific Solvents

In general circumstances, unless solvolysis is involved, the more common organic solvents, such as benzene, alkylbenzene derivatives, methanol, acetone, chloroform, and diethyl ether, dissolve little of the true coal substance and usually extract only that material that is occluded within the coal matrix.

The effect of pyridine on coal has been known since the late days of the nineteenth century and extensive follow-up studies were carried out to determine the comparative extractability of pyridine and chloroform (Wender et al., 1981). These studies, as well as later work (Given, 1984) showed that significant yields of extracts, often as high as 35–40%, can be obtained by using pyridine, certain heterocyclic bases, or primary aliphatic amines (which may, but need not, contain aromatic or hydroxyl substituents). Secondary and tertiary aliphatic amines are often much less effective insofar as more than one alkyl group on the amine appears to present steric problems that interfere with the interaction between the solvent and the coal.

In the higher rank bituminous coals, alpha- and beta-naphthol are both effective solvents but for sub-bituminous coal, beta-naphthol may produce even less extract than phenanthrene but alpha-naphthol may extract as much is 83% w/w of the coal. Ring compounds, such as phenanthrene, appear to be superior for extracting bituminous coals of medium rank.

Many organic liquids have been suspected of exercising more than a solvent action on coal. An indication of chemical interaction is the observation that the total weight of products sometimes exceeds the original weight of coal, although up to about 5% may be the result of strong adsorption of solvents on the residue and extract. With mixed solvents, the potential for interaction may be increased.

Mixtures of the higher ketones and formamide derivatives have been reported to be considerably better solvents for coal (82% C) than either of the pure components. Mixtures worthy of note are acetophenone-monomethylformamide and methylcyclohexanone-dimethylformamide (equimolecular proportions). Thus, some solvent pairs may show enhanced solvent power whereas others may behave independently in admixture.

10.2.2 Influence of Coal Rank

Coal rank has a considerable influence on the nature and the amount of extracts obtained by the solvent extraction of coal (Speight, 2013 and references cited therein). In addition, the soluble products of the extraction, whether they be called extracts or (incorrectly) bitumen vary according to the means by which they are obtained.

10.2.2.1 Benzene-Type Solvents The results of extracting coals with benzene and benzene/ethanol mixtures have been reported (Table 10.1), but only a broad general trend appears to emerge from these observations. Thus, it appears that for coals with more than 88% carbon content for less than 25% volatile matter the amount of extract obtainable decreases rapidly; with coals of carbon content lower than this limit, no definite trend with rank appears to be evident.

10.2.2.2 Nitrogen-Containing Solvents The first systematic work on the extraction of coal using nitrogen-containing solvents (e.g., pyridine) resulted in the production of substantial amounts of extract which were then further fractionated to produce

TABLE 10.1 Extraction of Coal Using Aromatic-Hydro-Aromatic Solvents

Yield	Solvent	Details
Increasing with decreasing rank	Naphthalene	
	Hydrogenated pitch	
	Anthracene oil, retene, pyridine	10 coals, 14.6–43.7% volatile matter, pronounced peak in 30–40% range with rapid decrease below about 20% volatile matter
	Neutral tar oil	Indication of flat maximum between 25 and 40% volatile matter, but points very scattered
	Tetralin	Yield increasing with increasing rank, then decreasing
	Phenanthrene	Coals from lignite to anthracite maximum at coal of 84.4% C

Source: Adapted from Dryden, 1963.

TABLE 10.2 Extraction of Coal Using Nitrogen-Containing Solvents

Yield	Solvent	Details
Increasing with decreasing rank	Pyridine	Two coals of 90.4 and 88.5% C
	Ethylenediamine	British bright bituminous and anthracite coals, 78–94% C; particularly rapid decrease in yield between 85 and 88% C
Exhibiting no correlation	Pyridine	South Wales coals, maximum extraction at 30% volatile matter

a series of fractions based on their solubility/insolubility in different solvents – the solubility of coal is also subject to any chemical changes caused in the coal by chemical reactions (Miyake et al., 1984; Speight, 2013).

Since that time, a general correlation between yield of extract and carbon content has been reported for ethylenediamine (Table 10.2). Various other amine solvents (e.g., monoethanolamine) show similar behavior insofar as the extract yield may decrease markedly with increase in rank for coals under 85% carbon. On the other hand, the yield of extract using solvents such as benzylamine, piperidine, and pyridine may show much less variation with rank and the effectiveness of many solvents may decrease markedly for coal having more than 88% carbon.

Thus, it is possible to deduce several preferred options in the solvent extraction of coals using the so-called specific solvents. For example, the yield of extract usually decreases (but may, on occasion, increase) with an increase in the carbon content of the coal over the range 80 to circa 87% carbon. However, use of a solvent such as pyridine may produce anomalous results and the petrographic composition of the coal may also have an effect. For coals having more than approximately 81% carbon the yield of extract is diminished to such an extent that only negligible yields of extracts are noted for coals having more than approximately 93% carbon.

There is a relationship between yield of the extract and the saturation sorption or imbibition of solvent that is independent of the rank coal or the particular amine solvent. An adsorption isotherm for ethylenediamine vapor on an 82% carbon coal exhibited three main features: (1) chemisorption up to 3–6% adsorbed; (2) a fairly normal sorption isotherm from the completion of chemisorption up to a relative pressure of at least 0.8; and (3) a steeply rising indefinite region near saturation which corresponded to observable dissolution of the coal.

10.2.3 Influence of Petrographic Composition

It is generally recognized that vitrain is the most soluble constituent of any particular coal whereas fusain is the least soluble. Indeed, early work on the liquefaction of coal by dissolution in a solvent showed that even at temperatures of the order of 400 °C

(750 °F) fusain is, to all intents and purposes, insoluble. Under these aforementioned conditions, durain did show some response to the solvent but still did not match the solubility of vitrain.

10.2.4 Analysis of Coal Extracts

There is, on occasion and depending upon the circumstances, the need to analyze the extracts that have been retrieved from coal by the use of various solvents. This assumes that sufficient material has been isolated to proceed with the analysis. The caveat is, of course, that all of the solvent used from the extraction procedure has been removed from the extracts. If not, it may be removed by the use of fractionation techniques applied to the extracts and corrections will need to be applied to determine the correct yield of the extract fractions. In order to fractionate, the extracts into a variety of sub-fractions, the nature of the coal must be taken into account as well as the nature of the chemicals extracted from the coal.

The literature abounds with reports of the fractionation of extracts from coal, more specifically to the liquids and solids produced by various coal liquefaction processes (Speight, 2013 and references cited therein). However, to accomplish the sub-fractionation of the coal extracts, it is preferable to apply (with nay modifications noted) a suite of the standard test methods that are often applied to petroleum and its residue (Speight, 2014, 2015). However, before application of any sub-fractionation procedure to coal extracts, it may be necessary to *stabilize* the extracts (at a foxed temperature and pressure) to ensure that losses of potentially volatile constituents do not occur during the sub-fractionation procedure. Once the extracts have been stabilized, it is in order to proceed.

The common methods that are used to determine composition generally rely upon chromatographic fractions using an adsorbent, although other methods are available and since discussion of these methods are available in detail elsewhere (Speight, 2001), it is not the intent to present the detail here. Only a brief outline is given and the most convenient example to use relates to the methods applied to the composition of residual fuel oil that might bear a relationship to the extracts obtained from coal.

The test methods of interest for the analysis of coal extracts include tests that measure chemical composition. The preeminent test methods are those that are applied to a measurement of the asphaltene content. The issue with coal extracts is that the presence of asphaltene constituents in the extracts is solvent dependent. However, assuming that a test is necessary to determine whether Asphaltenes constituents are present, there are several test methods available.

The asphaltene fraction (ASTM D893; ASTM D2007; ASTM D3279; ASTM D4124; ASTM D6560) is the highest molecular weight and most complex fraction. In any of the methods for the determination of the asphaltene content, the sample is mixed with a large excess (usually >30 volumes hydrocarbon per volume of sample) low-boiling hydrocarbon such as *n*-pentane or *n*-heptane. For an extremely viscous sample, a solvent such as toluene may be used prior to the addition of the low-boiling hydrocarbon but an additional amount of the hydrocarbon (usually >30 volumes hydrocarbon per volume of solvent) must be added to compensate for the presence of the solvent. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage (% w/w) of the original sample.

In any of these tests, different hydrocarbons (such as *n*-pentane or *n*-heptane) will give different yields of the asphaltene fraction and if the presence of the solvent is not compensated by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present in large excess, the yields of the asphaltene fraction will vary and will be erroneous (Speight, 2014a).

Another method, not specifically described as an asphaltene separation method, is designed to remove pentane-insoluble or heptane-insoluble constituents by membrane filtration (ASTM D4055). In the method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-μm membrane filter. The flask, funnel, and the filter are washed with pentane to completely transfer any particulate matter onto the filter after which the filter (with the particulate matter) is dried and weighed to give the pentane insoluble constituents as a percent by weight of the sample. Particulate matter in the extracts can also be determined by membrane filtration (ASTM D2276, ASTM D5452, ASTM D6217).

The composition of the extracts will vary and is dependent on coal rank and the solvent employed for the extraction. Nevertheless, the composition of the extracts can be reported in the form of four or five major fractions as deduced by adsorption chromatography (Speight, 2001).

Column chromatography is generally used for compositional analyses (ASTM D2007, ASTM D2549). The former method (ASTM D2007) advocates the use of adsorption on clay and clay-silica gel followed by elution of the clay with pentane to separate saturates; elution of clay with acetone-toluene to separate polar compounds; and elution of the silica gel fraction with toluene to separate aromatic compounds. The latter method (ASTM D2549) uses adsorption on a bauxite-silica gel column. Saturates are eluted with pentane; aromatics are eluted with ether, chloroform, and ethanol.

10.3 SPECTROSCOPIC PROPERTIES

The mode of origin of coal dictates that it is a heterogeneous material consisting both carbonaceous and inorganic material. The organic structure of coal can be regarded as consisting of heterogeneous aromatic structures, with aromaticity increasing from low to high rank coals. The organic part of coal also contains sulphur, oxygen, and nitrogen in functional groups.

10.3.1 Infrared Spectroscopy

Of all the physical techniques, infrared (IR) spectroscopy gives the most valuable information about the constitution of organic materials. Indeed, qualitative information about specific structural and functional elements can often be deduced even though the spectra are too complex for individual compound analysis. In regard to quantitative evaluation of the constituents of coal by IR spectroscopy, the presence of mineral matter offers a constraint insofar as distortion of the peaks arising from the organic constituents is inevitable.

In addition, one of the issues, as it relates to coal science, is the absence of specific standard test methods that can be applied to the investigation of coal properties by IR spectroscopy, as well as by other spectroscopic methods. There are, however, test methods that are applicable to the IRs analytical technique that should be followed when the method is applied to coal analysis.

One test method (ASTM D1655) is available in which are described the standard practices for IR multivariate quantitative analysis for turbine fuels and does allow the potential for presentation to other fuels. These practices cover a guide for the multivariate calibration of IR spectrometers used in determining the physical or chemical characteristics of materials. These practices are applicable to analyses conducted in the near infrared (NIR) spectral region (roughly 780–2500 nm) through the mid infrared (MIR) spectral region (roughly 4000–400 cm^{-1}). While the practices described deal specifically with MIR and NIR analysis, much of the mathematical and procedural detail contained herein is also applicable for multivariate quantitative analysis done using other forms of spectroscopy. These practices cover techniques that are routinely applied in the NIR and MIR spectral regions for quantitative analysis. The practices outlined cover the general cases for coarse solids and for fine ground solids but do require the use of a computer for data collection and analysis. Considering the complexity of coal, a computerized data collection system is a benefit. This method should be used in conjunction with the test method that relates to the techniques that are most often used in IR quantitative analysis and are associated with the collection and analysis of data on a computer are included as well as practices that do not use a computer (ASTM E168).

In addition, the test method that covers the standard practice for general techniques for obtaining IR spectra for qualitative analysis (ASTM E 1252) is also valuable. This test method covers the spectral range from 4000 to 50 cm^{-1} and includes techniques that are useful for qualitative analysis of liquid, solid, and vapor-phase samples by IR spectrometric techniques for which the amount of sample available for analysis is not a limiting factor. These techniques are often also useful for recording spectra at frequencies higher than 4000 cm^{-1}, in the NIR region. A separate method (ASTM E334) is available for use in analyzing microgram quantities of samples by IR spectrophotometric techniques.

In all cases, specific test methods (ASTM E168; ASTM E573; ASTM E1252) should be consulted for theoretical aspects of the methodology, for general techniques of sample preparation, and for data workup and calculations.

From the results of IR spectroscopic investigations, it has been established (Speight, 1978, 1994) that coal contains various aliphatic and aromatic carbon-carbon and carbon-hydrogen functions but few, if any, isolated olefin bonds ($>C{=}C<$) and acetylene ($-C{\equiv}C-$) bonds. The assignment of absorptions in the IR spectra to various oxygen functions has also received some attention (Speight, 1978, 1994).

It has also been reported that ratio of aromatic hydrogen to total hydrogen increases with increasing rank and that at a 94% carbon content coal is completely aromatic. It has also been suggested that the percentage of the hydrogen contained in methyl groups probably lies in the range 15–25% and the methyl content decreases with increasing rank of the coal. Other observations on the aromaticity of coal come from investigations of a variety of coal fractions (in particular, the optical densities of the two peaks at circa 3030 and circa 2920 cm^{-1}).

IR absorption is one of three standard test methods for sulfur in the analysis sample of coal and coke using high-temperature tube furnace combustion methods (ASTM D4239). Determination of sulfur is, by definition, part of the ultimate analysis of coal (Chapter 6) but sulfur analysis by the IR method is also used to serve a number of interests: evaluation of coal preparation, evaluation of potential sulfur emissions from coal combustion or conversion processes, and evaluation of the coal quality in relation to contract specifications, as well as other scientific purposes. IR analysis provides a reliable, rapid method for determining the concentration of sulfur in coal and is especially applicable when results must be obtained rapidly for the successful completion of industrial, beneficiation, trade, or other evaluations.

In the method, the sample is burned in a tube furnace at a minimum operating temperature of 1350 °C (2462 °F) in a stream of oxygen to oxidize the sulfur. Moisture and particulates are removed from the gas by traps filled with anhydrous magnesium perchlorate. The gas stream is passed through a cell in which sulfur dioxide is measured by an IR absorption detector. Sulfur dioxide absorbs IR energy at a precise wavelength within the IR spectrum. Energy is absorbed as the gas passes through the cell body in which the IR energy is being transmitted: thus, at the detector, less energy is received. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of IR energy can be attributed only to sulfur dioxide whose concentration is proportional to the change in energy at the detector. One cell is used as both a reference and a measurement chamber. Total sulfur as sulfur dioxide is detected on a continuous basis. This method is empirical; therefore, the apparatus must be calibrated by the use of certified reference materials.

IR spectroscopy is also used (ASTM D5016) to determine sulfur in coal ash in conjunction high-temperature tube furnace combustion. This test method also allows the rapid determination of sulfur in the ash and may be used as an alternative test method (c.f., ASTM D1757). In the test, a weighed test portion is mixed with a promoting agent (that aids in the quantitative release of all sulfur present in the test portion as sulfur dioxide) and ignited in a tube furnace at a minimum operating temperature of 1350 °C (2462 °F) in a stream of oxygen. The combustible sulfur contained in the test portion is oxidized to gaseous oxides of sulfur. Traps filled with anhydrous magnesium perchlorate remove moisture and particulate matter. The gas stream is passed through a cell in which sulfur dioxide is measured by an IR absorption detector. Sulfur dioxide absorbs IR energy at a precise wavelength within the IR spectrum. Energy is absorbed as the gas passes through the cell body in which the IR energy is being transmitted; thus, at the detector, less energy is received. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. The absorption of

IR energy can be attributed only to sulfur dioxide whose concentration is proportional to the change in energy at the detector. One cell is used as both a reference and a measurement chamber. Total sulfur as sulfur dioxide is detected on a continuous basis.

The inception of Fourier transform (FT) methods for elucidating the nature of coal *overcame* the barriers that arose from many of the weaker absorption bands (Dyrcasz et al., 1984; Gaines, 1988; Guo et al., 1996). This allowed the collection of more well-defined spectra by careful repetition and permits further information to be obtained about the nature of the carbon-hydrogen bonding systems and the nature of the aromatic groups as well as information about the various functional groups in coal. For example, it is possible to differentiate between the oxygen species, the aliphatic species, and the substitution patterns on aromatic ring systems.

Fourier transform infrared (FTIR) spectroscopy is a widely adapted analytical technique for determining the different functional groups in coal structure (Cooke et al., 1986; Cerny, 1996; Georgakopoulos et al., 2003; Başaran et al., 2003; Debashis, 2005; Orrego et al., 2010; Manoj and Kunjomana, 2012; Manoj, 2013, 2014). The technique is applicable to both the organic and inorganic part of the coal. The method by which the spectra can be subtracted one from the other, allows the distinguishing of one coal from another by characteristic functional groups. Furthermore, this technique can be used to show the presence of aromatic and aliphatic structures as well as heteroatomic functions (mainly oxygenated). The method is also useful for determining the presence of minerals, is presently a useful technique for coal analysis characterization and thus can play a vital role in various utilization procedures of coal. Mineral matter in coal is considered as detrimental in coal utilization, preparation, and transportation. Coal preparation (Chapter 11) is aimed at reducing the quantity of mineral matter and the efficient use of methods chosen depends on its concentration (Speight, 2013). Prior to the structural analysis, demineralization is essential, because minerals, silica in particular, would distort the functional groups which in turn affect the prominent characteristics of coals.

In addition, some of the emphasis has been on changes that occur during coalification, weathering, and conversion. Major findings include identifying the presence of two-ring and three-ring condensed aromatic systems possibly linked through quinone-type and furan-type bridges. There has also been the interesting revelation of the relative lengths of alkyl chains in different coals (shorter in coking coal compared to non-coking coal).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in the NIR range is a technique able to determine moisture, ash, volatile matter, fixed carbon, heating value and percentage of carbon, hydrogen, nitrogen, and sulfur in coal samples (Andrés and Bona, 2005). The resultant spectra can be correlated to coal properties using partial least squares (PLSs) regression. Moreover, a principal component analysis (PCA) of the full set of samples suggested the use of more homogeneous sample sets and the data obtained for a homogeneous set improved the prediction ability of the procedure.

10.3.2 Nuclear Magnetic Resonance

Magnetic resonance spectroscopy has a considerable history of being applied to the issue of coal structure, rank, and type (Botto and Sanada, 1992, 1993; Suggate and Dickinson, 2004). However, as a historical beginning, the structural types in coal were first determined by means of statistical structural analysis (Francis, 1961). One of the first methods to supersede the statistical methods was based on proton (^{1}H) magnetic resonance that provided a quantitative distribution of the hydrogen types in coal (Bartle, 1988; Maciel et al., 1993).

In an early publication on the subject, it was reported that in a high-rank coal, 33% of the hydrogen atoms occurred in methylene groups of bridge and alicyclic structures while in a low-rank coal 67% of the hydrogen occurred in this form and/or in long chains. The nuclear magnetic resonance spectra of the products obtained from the vacuum carbonization of coal have also been studied and it was concluded that the nonaromatic hydrogen occurred almost exclusively on saturated carbon atoms as aliphatic, alicyclic, or hydroaromatic structures.

Nuclear magnetic resonance spectroscopy has proved to be of great value in fossil fuel research because it allows rapid and nondestructive determination of the total hydrogen content and distribution of hydrogen among the chemical functional groups present (Bartle and Jones, 1978; Retcofsky and Link, 1978; Petrakis and Edelheit, 1979; Snape et al., 1979; Davidson, 1980, 1986; Cookson and Smith, 1987; Bartle, 1988; Kershaw, 1989; Botto and Sanada, 1992; Meiler and Meusinger, 1992; Botto and Sanada, 1993). However, coal is a structurally diverse material and caution is to be exercised in the definition of chemical shift expectations. Thus, if structural definition is to be successful, the chemical shift relationships applied to coal, and to coal-derived products, should be lacking in any ambiguity. Sample complexity will usually introduce a variety of ambiguities.

Like IR spectroscopy, specific test methods for recording the nuclear magnetic resonance spectroscopy of coal do not exist. It is necessary, therefore, to adapt other methods to the task at hand, provided the necessary sample preparation protocols and instrumental protocols for recording magnetic resonance spectra are followed to the letter as proposed and described for IR spectroscopy (Section 1.0).

One particular test method (ASTM D5292) is designed to determine aromatic carbon contents of hydrocarbon oils by high resolution nuclear magnetic resonance spectroscopy using high-resolution nuclear magnetic resonance, provided the sample is completely soluble in chloroform and carbon tetrachloride at ambient temperature. While not specifically applicable to coal *per se*, the method can be used for coal extracts that are soluble in the aforesaid solvents. For pulse FT spectrometers, the detection limit is typically 0.1 mol% aromatic hydrogen atoms and 0.5 mol% aromatic carbon atoms. For continuous wave (CW) spectrometers, which are suitable for measuring aromatic hydrogen contents only, the detection limit is considerably higher and typically 0.5 mol% aromatic hydrogen atoms. This test method is not applicable to samples containing more than 1 mass% olefin or phenol compounds. However, this test method does not cover the determination of the percentage mass of aromatic compounds in oils since nuclear magnetic resonance signals from both saturated hydrocarbons and aliphatic substituents on aromatic ring compounds appear in the same chemical shift region. For the determination of mass or volume percent aromatics in hydrocarbon oils, chromatographic, or mass spectrometry methods can be used.

Another method (ASTM D4808) covers the determination of the hydrogen content of petroleum products, including vacuum residua, using a CW, low-resolution nuclear magnetic resonance spectrometer. Again, sample solubility is a criterion that will not apply to coal but will apply to coal extracts.

More recent work has shown that proton magnetic resonance can be applied to solid samples and has opened a new era in coal analysis by this technique (Jurkiewicz et al., 1993).

Along similar lines, carbon-13 magnetic resonance has been applied to coal and to the elucidation of the character of soluble coal fractions and other coal-derived materials (Ladner and Snape, 1978). In fact, it is the advances in carbon-13 magnetic resonance that have brought new thoughts to the chemical nature of, and structural types in, coal. The technique brought with it the innovative solid-state techniques that allowed coal to be viewed in its natural solid state without invoking the criterion of sample solubility. This removed the need for dissolution of coal fractions and the, often, tongue-in-cheek-deductions about the relationship of the soluble part of coal to the majority of the solid matrix.

The data obtained, used in conjunction with those obtained from proton magnetic resonance and from elemental analysis, indicated an typical molecule of the neutral oil to be 70% aromatic and to consist of a naphthalene ring system bearing two or three saturated side chains, each having less than three atoms. Data from the investigation of the supercritical gas extraction of coal point to a similar conclusion insofar as the structural entities can be envisaged as consisting of small aromatic ring systems, with the inclusion of hydroaromatic ring systems, and the attendant alkyl groups (predominantly methyl) as well as a variety of oxygen functions.

Carbon-13 magnetic resonance has been applied to coal and to the elucidation of structures of soluble coal fractions (Alemany et al., 1978; Bartle and Jones, 1978; Stock, 1988). The evidence from carbon-13 magnetic resonance studies of the extract of coal appears to favor the occurrence of small-ring systems. The mean structural unit appears to consist of two-to-three ring condensed aromatic systems with 40% of the available aromatic carbons bearing alkyl, phenolic, and/or naphthenic groups. Indeed, the mass spectrum of the extract indicated the presence of alkyl aromatic compounds having from one to ten or more alkyl carbons per molecule.

A derivation of the carbon-13 magnetic resonance technique, cross-polarization (CP) carbon-13 magnetic resonance offers several advantages over the conventional technique (Smith and Smoot, 1990). The results from this method have been used to indicate that the higher rank coals are indeed highly aromatic substances and the CP carbon-13 magnetic resonance could be used with confidence to determine the carbon aromaticity. The technique also offers valuable information about the oxygen distribution in coal (Franco et al., 1992).

On the subject of carbon aromaticity of coal, ^{13}C magnetic resonance spectroscopy has also found to be used in determining the fraction of carbon atoms that are in aromatic locations (f_a) as well as attempting to define the structure of the aromatic ring system. However, there is a possibility of serious underestimation of aromaticity by this method (Snape et al., 1989; Sfihi and Legrand, 1990).

The f_a data obtained from the CP spectra can also be used to estimate the size of the aromatic ring systems (Sfihi and Legrand, 1990). There are assumptions, however, that the nonaromatic carbons are mostly methylene ($-CH_2-$) groups and that the oxygen and approximately 50% of the non-aromatic carbons are directly bonded to aromatic rings. Thus, the hypothetical aromatic nuclei (H_{aru}/C_{ar}) can be estimated from the equation:

$$H_{aru}/C_{ar} = (H - 3_{ali})(2 + O)/C_{ar}$$

In this equation, where ar and ali denote atoms in aromatic and aliphatic groupings, respectively. The data also confirm a tendency for increased aromaticity with increasing rank of the coal.

The stable free radicals in coal can adversely affect the carbon-13 signal intensity. However, the quantitative reliability of the method can be greatly improved by prior treatment of coal with chemicals such as samarium (II) iodide (Stock, et al., 1988) to selectively reduce the organic free radicals. Thus, this potential error that has influenced the quantitative aspects of the method can be reduced by the use of a novel pretreatment technique as well as an appropriate standard for measurement of chemical shifts.

Carbon-13 magnetic resonance studies have also been used to investigate coal in terms of structural and dynamic heterogeneity (Tekely et al., 1990; Adachi and Nakamizo, 1993; Wind et al., 1993). Coals of different rank demonstrated significant structural differences and an increase in structural homogeneity with increase in aromaticity factor were noted. In addition, the data also indicated the presence of two phases: a macromolecular/rigid component and a molecular/mobile component. In addition, electron spin resonance spectroscopy has been used to study the effects of weathering/oxidation on the mobile and network phases of coal (Khan et al., 1988). The conclusion is that oxidation influences the hydrogen-rich (mobile) phase of coal more than it does the hydrogen-poor (network) of bituminous coal.

10.3.3 Mass Spectrometry

One of the issues that raised when data from mass spectrometry are applied to determining the character of coal is its non-volatility. However, this should not be a deterrent to using this valuable technique. It is the interpretation that is derived from the data that should be suspected. Many workers have erroneously assumed that the volatile material is truly representative of the non-volatile sample and thereby hangs the error!

Gas chromatography-mass spectroscopy as well as pyrolysis-mass spectrometry, and pyrolysis gas chromatography-mass spectroscopy of coal have enabled low molecular weight benzene derivatives, phenol derivatives, and naphthalene derivatives to be identified as well as the C_{27} and $C_{29}-C_{30}$ hopane derivatives in addition to C_{15}-sesquiterpene derivatives (Gallegos, 1978; Smith and Smoot, 1990; Blanc et al., 1991).

Curie-point pyrolysis mass spectrometry has also been valuable in providing information about the chemical types that are evolved during the thermal decomposition of coal (Tromp et al., 1988) and, by inference, about the nature of the potential chemical types in coal. However, absolute quantification of the product mixtures is not possible due to the small sample size but the composition of the pyrolysis product mix can give valuable information about the metamorphosis of the coal precursors and on the development of the molecular structure of coal during maturation. However, as with any pyrolysis, it is very important to recognize the nature and effect that any secondary reactions have on the nature of the volatile fragments, not only individually but also collectively.

Application of mass spectrometry to the identification of methyl esters of the organic acids obtained by the controlled oxidation of bituminous coal allowed the more volatile benzene carboxylic acid esters to be identified (Studier et al., 1978). These were esters of benzene tetracarboxylic acid, terepthalic acid, toluic acid, and benzoic acid. Decarboxylation of the total acid mixture was shown to afford benzene, toluene, C_2-benzene derivatives (i.e., ethylbenzene or xylene), C_3-benzene derivatives s, C_4-benzene derivatives (butylbenzene), C_5-benzene derivatives, C_7-benzene derivatives naphthalene, methylnaphthalene, C_2-naphthalene derivatives, biphenyl, methylbiphenyl, C_3-biphenyl, indane, methylindane, C_2-indane, phenanthrene, and fluorene.

Tandem mass spectrometry is also developing into an important analytical method for application to coal-derived materials (Wood, 1987). The analysis of heteroatom ring species and hydrocarbon species in coal-derived liquids offers indications of the location of the heteroatoms in, or on, ring systems as well as indications of the hydrocarbon systems.

Application of gas-chromatographic/mass spectrometric analysis to acidic/basic sub-fractions of coal-derived asphaltene constituents and concluded that the asphaltene fraction consists of one-ring and/or two-ring aromatic units which are linked by methylene chains as well as by functional groups (Koplick et al., 1984). Projection of this finding to coal itself is of interest only if it can be assumed that the inter-nuclear bonds withstood the high temperatures and were not formed as a result of secondary and tertiary (etc.) reaction. In short, the question relates to the relationship of the structural types in the asphaltene fraction to those in the original coal.

10.3.4 Ultraviolet Spectroscopy

Moreover, in the absence of any specific test methods for coal, ultraviolet spectroscopic investigations must rely on investigations applied to other substances with the criteria of sample handling and sample preparation followed assiduously. The practices to be used for recording spectra (ASTM E169) provide general information on the techniques most often used in ultraviolet and visible quantitative analysis. The purpose is to render unnecessary the repetition of these descriptions of techniques in individual methods for quantitative analysis.

One particular test method (ASTM D2008) covers the measurement of the ultraviolet absorption of a variety of petroleum products and the absorbtivity of liquids and solids, or both, at wavelengths in the region from 220 to 400 nm of the spectrum. The use of this test method implies that the conditions of measurement (wavelength, solvent if used, sample path length, and sample concentration) are specified by reference to one of the examples of the application of this test method or by a statement of other conditions of measurement.

The ultraviolet spectra of coals, examined as suspensions in potassium bromide, show an absorption band at 2650 Å that becomes more pronounced with increasing rank of the coal. This band has been assigned to aromatic nuclei and, on the basis of data obtained from comparison between the specific extinction coefficients of coal and those of standard condensed aromatic compounds, it has been concluded that the concentration of aromatic systems in coal is lower than had previously been believed.

Other investigations have led to the conclusions that coal contains benzene and naphthalene rings, heterocyclic nitrogen, cyclic ethers, hydroxyl oxygen, as well as methylene groups and may even be fairly uniform in structure. In addition, the position of the maxima in the ultraviolet spectra of coal fractions appeared to indicate a mean cluster size comparable with that obtained by other methods. Thus, there was the suggestion that low-rank coals contained small aromatic nuclei of various kinds with a gradual coalescence of the units to form much larger layers of aromatic nuclei occurring as rank increases.

Ultraviolet fluorescence spectroscopy has also been employed to investigate the nature of the aromatic systems in coal and in coal-derived products (Mille et al., 1990). Examination of the pyridine extracts produced data that were characteristic of compounds having three, four, or five condensed aromatic rings. However, it was not possible to obtain an estimation of the ring size within the insoluble coal matrix.

10.3.5 X-Ray Diffraction

The X-ray scattering from coal was the subject of several early studies, which led to the postulation that coal contains aromatic layers about 20–30 A in diameter, aligned parallel to near-neighbors at distances of about 3.5 Å.

Small-angle X-ray scattering, which permits characterization of the open and closed porosity of coal, has shown a wide size distribution and that the radius of gyration appears to be insufficient to describe the pore size. Application of the FT technique indicated that some coals have a mesoporosity with a mean size of 80–100 A radius (Guet, 1990).

10.3.6 Electron Spin Resonance

Electron spin resonance was first applied to coal during the 1950s (Ingram et al., 1954) as a method for the determination free radical species in coal. Since that time, electron spin resonance has been used to compare the data for coals of different rank and exploring the potential for relating the data to the different carbon systems as well as offering valuable information about aromaticity (Retcofsky et al., 1968; Petrakis and Grandy, 1978; Retcofsky et al., 1978; Kwan and Yen, 1979; Khan et al., 1988; Thomann et al., 1988; Nickel-Pepin-Donat and Rassat, 1990; Bowman, 1993; Sanada and Lynch, 1993).

Early work on a series of carbonized coals gave 3×10^{19} free radicals per gram (1 free radical per 1600 carbon atoms). It was also established that the free radical content of coal at first increases slowly (in the range 70–90% carbon) (Ladner and Wheatley, 1965), rises markedly (90–94% w/w C), and then decreases to limits below detectability. Thus, in a coal having 70% carbon there is one radical per 50,000 carbon atoms but this is increased to one radical per 1000 carbon atoms in coal with 94% w/w carbon.

The esr *g values* that arise from spin–orbit coupling are higher than 2.0023, which is the free electron value in the absence of spin–orbit coupling. The *g* values for vitrain and fusain decrease from low to high rank with the exception of the *g* values for vitrain from very high-rank coals; these are markedly higher. Organic free radicals have higher g values if atoms with high spin–orbit coupling constants stabilize the unpaired electron. The high g values for low-rank coals can be attributed to localization of unpaired electrons on heteroatoms. As the carbon content increases and the oxygen content decreases, the g values decrease and the radicals become localized on aromatic hydrocarbons until the g values increase again with the formation of graphitic structures by condensation of aromatic rings (Retcofsky et al., 1979).

Electron spin resonance spectra of coals usually consist of a single line with no resolvable fine structure; however, the electron nuclear double resonance (ENDOR) technique can show hyperfine interactions not easily observable in conventional esr spectra. Recently this technique has been applied to coal and it is claimed that the very observation of an ENDOR signal shows interaction between the electron and nearby protons and that the results indicate that the interacting protons are twice removed from the aromatic rings on which, it is assumed, the unpaired electron is stabilized.

10.3.7 Miscellaneous Methods

There has been a resurgence of interest in the older technique of Raman spectroscopy, especially in the coal industry where the chemistry and physics the combustion, gasification and pyrolysis of coal are of interest (Potgieter-Vermaak et al., 2011). Use of the Raman spectra of coal allows the bands to be assigned bands to the structural order of the amorphous carbons. In the case of coal analysis, the information gained by Raman investigations to describe char evolution as a function of temperature, the presence of catalysts and different gasification conditions. In addition, in order to study the inorganic matter in coal micro-Raman spectroscopy (MRS) has many advantages over other characterization techniques. With the distinct advantages that MRS has over that of other molecular characterization tools, such as powder X-ray diffraction (PXRD), FT-IR and scanning electron microscopy with X-ray detection (SEM/EDS), it is to be expected that the Raman technique will be further exploited the characterization of the inorganic matter in coal.

The electron microprobe (EMP), also known as an *electron probe microanalyzer* (*EPMA*) or *electron micro probe analyzer* (*EMPA*), is an analytical procedure that can be used to determine (nondestructively) the chemical composition of small volumes of solid materials, such as coal. The instruments work similarly to a scanning electron microscope for coal analysis (Demir et al., 1993) insofar as the sample is bombarded with an electron beam, emitting X-rays at wavelengths characteristic to the elements being analyzed. Not surprisingly, the EMP has also been used for the determination of carbon, oxygen, and nitrogen content of coal and coal macerals (Harrison, 1991; Bustin et al., 1992, 1993). The scanning proton microprobe has also been used for the analysis of mercury and other trace elements in a Kentucky coal (Hower et al., 2008).

In addition, the surface analysis of pyrite coal from the Wuda coalfield, Inner Mongolia, China, has been achieved using high-resolution time-of-flight secondary ion mass-spectrometry (Dai et al., 2003).

In order to improve the speed of coal Analyis for online work, a non-linearized multivariate dominant factor-based PLS model was applied to analyze coal properties through laser-induced breakdown spectroscopy (LIBS) (Yuan et al., 2013). The results demonstrated an overall improvement over conventional PLS method for ash content, volatile content, and calorific value measurement. Although current LIBS application results for coal proximate analysis have not met the national standard, LIBS is shown to be fully capable of providing useful information for coal combustion optimization and reliable references for coal pricing, showing LIBS has great potential for coal property analysis for coal analysis and especially analysis in the power generation industry.

Instrumental neutron activation analysis (INAA) is a versatile technique for elemental analysis because it has very low detection limits for many elements, lends itself to automation, and provides precise data for many major, minor, and trace elements in coal (Block and Dams, 1973; Ondov et al., 1975; Rowe and Steinnes, 1977a,b; Swaine, 1985). For analyses based on the measurement of long-lived nuclides ($t^{1/2}$>1 day), 30 elements can be determined routinely in most coal samples. Two additional elements can be determined in certain coals. Extension of the technique to the measurement of short-lived activities, with rapid sample transfer and short irradiation and counting times, makes possible the determination of an additional nine elements.

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11

THE NEED FOR COAL ANALYSIS

11.1 INTRODUCTION

Coal is one of the many vital commodities that contributes on a large scale to energy supply and, unfortunately to environmental pollution, including acid rain, the greenhouse effect, and *allegedly* global warming (global climate change) (Bell, 2011). Whatever the effects, the risks attached to the coal fuel cycle could be minimized by the introduction of new clean coal technologies (Speight, 2013a), remembering that there is no single substitute for coal fuel in the generation of energy. Consideration of the diversity of plant precursors that eventually form coal as well as localized variations in the maturation conditions, it is not surprising that there is a wide variation in physical and chemical properties of coals from different basins as well as lateral and depth variations within a given coal group. Moreover, in addition to the variations in the composition and behavior of the organic portion of coal, mineral matter indigenous to the plants enters the coal as well as mineral matter that arise from the erosion of rocks as rock fragments. Thus, clay, pyrite, calcite, and quartz are thus incorporated in the coals along with other minerals. These inorganic substances are an integral part of all coals and affect overall chemical and physical properties of the coals. Hence the need for a comprehensive monitoring program involving coal analysis (as well as evolution of the analytical methods) to determine the suitability of coal for use (Lyons et al., 1996; Majumder et al., 2008).

Coal analysis is often the long-lost cousin of coal technology. Many observers feel that coal analysis is used to classify coal and from that point it finds little use I coal

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Handbook of Coal Analysis, Second Edition. James G. Speight.

technology. Nothing could be further from the truth. The issue that remains as an epilog to this book is a discussion of the use of the analytical data to chart continued and future use of coal. With the expansion of industrialization, the use of coal has increased by several orders of magnitude since the early decades of the twentieth Century (Miller, 2005; Speight, 2008) requires the generation and use of property data. As was first documented writers at the discomfort of Eleanor, the wife and Queen of King Henry III of England (Chapter 2), there are undesirable side effects that accompany the use of coal. Emissions of nonindigenous chemicals into the environment or the ejection into the environment of chemicals that are indigenous but in quantities that exceed their natural occurrence are major issues.

11.2 IDENTIFICATION AND CHARACTER OF COAL

The identification and character of coal may be presented in the form of proximate analysis (Chapter 5) and ultimate analyses (Chapter 6) – a typical proximate analysis includes the moisture, ash, volatile matter, and fixed carbon – fixed carbon is actually a measure of the carbon-forming (coke-forming) propensity of coal under specific test conditions. Moreover, it is important for economic reasons to determine the moisture and mineral matter content (determined by combustion as mineral ash) of coal because they do not contribute to the heating value of a coal. In most cases, ash is an undesirable residue and a source of pollution, but for some purposes (e.g., use as a chemical feedstock or for liquefaction) the presence of mineral matter may be desirable. Most of the heat value of a coal comes from its volatile matter, excluding moisture, and fixed carbon content. For most coals, it is necessary to measure the actual amount of heat released upon combustion (expressed in British thermal units per pound or in joules per kilogram) (Chapter 8).

On the other hand, ultimate analyses are used to determine the carbon, hydrogen, sulfur, nitrogen, ash, oxygen, and moisture contents of coal. For specific applications, other chemical analyses may be employed, such as identifying the forms of sulfur present, which may occur in the form of sulfide minerals (pyrite and marcasite), sulfate minerals (gypsum), or organically bound sulfur. In other cases, the analyses may involve determining the trace elements present (e.g., mercury, chlorine) (Chapter 4, Chapter 6), which may influence the suitability of a coal for a particular purpose or help to establish methods for reducing environmental pollution (Chapter 4) (Finkelman, 2003; Kolker et al., 2006; Bhangare et al., 2011).

Coal use is a necessary part of the modern world and the need for stringent controls over the amounts and types of emissions from the use of, in the present context, coal is real. The necessity for the cleanup of coal-based process gases is real but to intimate that coal is the major cause of all our environmental concerns is unjust. Gaseous products and by-products are produced from a variety of industries (Speight, 2002; Ali et al., 2005; Mokhatab et al., 2006; Speight, 2011, 2014; Lee et al., 2015). These gaseous products all contain quantities of noxious materials that are a severe detriment to the environment and must be managed effectively through the use of analytical data (Speight and Singh, 2014).

It is predictable that coal will be the primary source of energy for the next several decades, well into the next century and therefore the message is clear: until other energy sources supplant coal, the challenge is to develop technological concepts that will provide the maximum, and environmentally efficient, recovery of energy from coal (Fulkerson et al., 1990). Furthermore, while coal occurs in various forms defined in a variety by rank or type (Chapter 2), it is not only a solid hydrocarbonaceous material with the potential to produce considerable quantities of carbon dioxide as a result of combustion. Many coals do contain considerable quantities of sulfur (Speight, 2013a,b), which opens up not only the possibility but also the reality of sulfur dioxide production (Manowitz and Lipfert, 1990; Tomas-Alonso, 2005; Speight, 2013a,b).

In this respect, coal is often considered to be a dirty fuel and is usually cited as the most environmentally obnoxious of the fossil fuels. However, coal is not necessarily as dirty fuel; perhaps coal is no dirtier than the so-called clean nuclear fuels, which have a habit of being really dirty when nuclear plants go awry. In addition, following a diesel-fuel vehicle (fuels with low-sulfur diesel) under full load and/or up an incline presents the trailing vehicle with obnoxious clouds of black (albeit-low sulfur) fumes. Recognition that coal use has been responsible for emissions (gases, liquids, and solids) that are detrimental to the environment requires a change in thinking and opens new avenues for coal use in an environmentally clean and efficient manner (Kolker et al., 2006; Kolker et al., 2009).

There are a number of processes that are being used in coal-fired power stations that improve the efficiency and environmental acceptability of coal extraction, preparation and use, and many more are under development (Bris et al., 2007). These processes are collectively known as clean coal technologies. Designation of a technology as a clean coal technology does not imply that it reduces emissions to zero or near zero. For this reason, the term has been criticized as being misleading and it might be more appropriate to refer to cleaner coal technologies (Balat, 2008a,b; Nordstrand et al., 2008).

Clean coal technologies seek to reduce harsh environmental effects by using multiple technologies to clean coal and contain its emissions (Speight, 2013a,b). When coal burns, it releases carbon dioxide and other emissions in flue gas. Some clean coal technologies purify the coal before it burns. One type of coal preparation, coal washing, removes unwanted minerals by mixing crushed coal with a liquid and allowing the impurities to separate and settle (Luttrell et al., 2000). Furthermore, the clean coal technology field is moving in the direction of coal gasification with a second stage so as to produce a concentrated and pressurized carbon dioxide stream followed by its separation and geological storage. This technology has the potential to provide what may be called zero emissions – but which, in reality, is extremely low emissions of the conventional coal pollutants, and as low-as-engineered carbon dioxide emissions. This has come about as a result of the realization that efficiency improvements, together with the use of natural gas and renewables such as wind will not provide the deep cuts in greenhouse gas emissions necessary to meet future national targets (Omer, 2008). However, at the current time, there is no single technology or combination of technologies that is capable of addressing all of the environmental or economic challenges likely to arise from continued dependence on coal as a major source of energy in the coming decades, underscoring the need to assemble and prove viable alternatives to address these challenges over the long term.

It is in these areas that coal analysis will play a fundamental and crucial role in the determination of the future of coal use. For example, with coal analysis as the basis for decision-making, clean coal technologies have been developed that cause a reduction in the emissions of several pollutants, reduce waste, and increase the amount of energy gained from each ton of coal (Nordstrand et al., 2008). These technologies include various chemical and physical treatments applied precombustion or post-combustion and may be broadly divided into processes relating either to (1) combustion efficiency or (2) pollution control.

It is not the intent of this chapter to justify the use of analytical techniques for coal identification, but to show how analytical data can assist (in fact, are necessary) in the efficient and environmentally friendly use of coal.

11.3 PHYSICAL PROPERTIES

Many of the properties of coal are strongly rank-dependent, although other factors such as maceral composition and the presence of mineral matter also influence its properties. Several techniques have been developed for studying the physical and chemical properties of coal, including density (specific gravity) measurement (Chapter 7), thermal analysis (Chapter 8), mechanical and electrical properties (Chapter 7), as well as spectroscopic properties (Chapter 10).

For example, an important property of coal is its reflectivity (also referred to as *reflectance*) (Chapter 7), which is the ability of coal to reflect light. Reflectivity is measured by shining a beam of monochromatic light (with a wavelength of 546 nm) on a polished surface of the vitrinite macerals in a coal sample and measuring the percentage of the light reflected with a photometer. Vitrinite (Chapter 1) is used because its reflectivity changes gradually with increasing rank. The reflectivity of fusinite (Chapter 1) is too high due to its origin as charcoal and liptinite tends to disappear with increasing rank. Although little of the incident light is reflected (ranging from a few tenths of a percent to 12%), the value increases with rank and can be used to determine the rank of most coals without measuring the percentage of volatile matter present. In fact, vitrinite reflectance (Chapter 7) can be used to establish bituminous coal rank and has the following advantages: (1) steady increase of vitrinite reflectance with rank, (2) independence from composition or homogeneity of the reflectance measurement, (3) independence of sample size, and (4) minimal effects of oxidation.

In addition, coal that occurs in a sedimentary basin, which contains crude oil and/or gas reveals a close relationship between coalification and the maturation of liquid and gaseous hydrocarbons. During the initial stages of coalification (to a reflectivity of almost 0.5 and near the boundary between subbituminous and high-volatile C bituminous coal), hydrocarbon generation produces chiefly methane. The maximum generation of liquid crude oil occurs during the development of high-volatile bituminous coals (in the reflectivity range from ~0.5 to about 1.3). With increasing depth and temperature, petroleum liquids decompose and, finally, only natural gas (methane) remains. Coal reflectivity can be used to anticipate the potential for finding liquid or gaseous hydrocarbons during the exploration for crude oil.

Many coal classification systems (Chapter 2) use the percentage of volatile matter generated in the proximate analysis test method (Chapter 5) to distinguish coal ranks. For example, in the ASTM classification, high-volatile A bituminous (and higher rank coals) are classified on the basis of the volatile matter produced in the text method. Lower rank coal is classified primarily on the basis of the heat values (Chapter 8), because of the wide range in the yield of volatile matter (which may also include moisture). The agglomerating character of a coal refers to the ability of the coal to soften and swell when heated and to form a coke-like mass (Chapter 8), which is then used for steel manufacture – the most suitable coals with the preferred agglomerating properties occur in the bituminous coal rank.

Other properties, such as ash-fusion temperature (Chapter 4), and free-swelling index (a visual measurement of the amount of swelling that occurs when a coal sample is heated in a covered crucible) (Chapter 8), as well as hardness and grindability (Chapter 9), may affect coal mining and preparation, as well as the way in which a coal is utilized. The ash-fusion temperature influences furnace design and operating conditions while the free-swelling index provides preliminary information concerning the suitability of a coal for coke production. On the other hand, hardness and grindability determine the kinds of equipment used for mining, crushing, and grinding coals in addition to the amount of power consumed in their operation.

Finally, the density of coal (Chapter 7) is controlled in part by the presence of pores (porosity) (Chapter 7) that persist throughout coalification. Measurement of pore sizes and pore distribution is difficult; however, there appear to be three size ranges of pores: (1) macropores (diameter >50 nm, 50×10^{-9} m), (2) mesopores (diameter 2–50 nm), and (3) micropores (diameter <2 nm). Most of the effective surface area of a coal (~200 m^2/g) is not on the outer surface of a piece of coal but is located inside the coal in its pores. The presence of pore space is important in the production of coke, gasification, liquefaction, and the generation of high-surface-area carbon for purifying water and gases. From the standpoint of safety, coal pores may contain significant amounts of adsorbed methane that may be released during mining operations and form explosive mixtures with air. The risk of explosion can be reduced by adequate ventilation during mining or by prior removal of coalbed methane.

11.4 PRODUCTION

Coal undisturbed-in-the-ground is generally considered pose an environmental threat although the mineral matter associated with coal (Chapter 4), which is usually classed as part of the coal, can influence groundwater properties and fires in the coal seams can lead to subsidence, contamination of groundwater, and health and safety issues related to heat and emissions from the fires. Although it may be argued that coal (including the mineral matter) has been *in-situ* for millions of years and any environmental threats have long since been dissipated, the modern divergence of an aquifer and/or the occurrence of acid rain (to mention only two such possibilities) create a new paradigm and raises the potential for environmental disturbance.

From the earliest days of coal extraction, potential hazardous situations were created by the coal-mining and coal-use technologies of the time. The consequences of past irresponsible practices have been inherited today. Recent industrial expansion and the population explosion worldwide are contributing further to the pollution being brought about by the coal industry.

Coal mining has always been regarded as a dangerous industry and to a certain degree will always be so but advances in recovery technology offer the potential of safer working conditions and improved productivity while at the same time meeting the new environmental standards required by legislative regulations.

Some of the chemical processes that influence groundwater chemistry in coal-bearing strata include carbon dioxide production, silicate hydrolysis, pyrite oxidation, carbonate mineral dissolution, cation exchange, sulfate reduction, and the precipitation and dissolution of secondary minerals leading to contamination of the groundwater (Banaszak, 1980; Groenewold et al., 1981; Powell and Larson, 1985). However, coal production and use have diverse impacts on the surrounding earth and atmosphere, generating various pollutants from such stages of the coal fuel-cycle as (1) coal production, (2) coal preparation, (3) coal transportation and storage, and (4) coal utilization. In this chapter, these phases form the basis of discussion on the nature of coal pollutants and their consequent effects.

Irrespective of how it is extracted in mines and used in industry, coal produces three distinct types of pollutants: (1) gaseous, (2) liquid, and (3) solid substances, which generally demand quite different preventive or ameliorative measures. In this context, other impacts such as noise, subsidence, and waste disposal should also be classified as pollutants arising from coal use. Numerous methods have been devised to interrelate the data and to maintain environmental standards at threshold limits and thus minimize pollution damage while at the same time improving worker productivity, coal quality, and accident prevention schemes (Bostick and Daws, 1994; Bullock et al., 2002).

Coal mining has always been, and remains, a dangerous occupation. Mine atmospheres are hazardous in terms of the health and safety of miners and, although technological advancements and legislation have led to improvement in the environmental and safety aspects in mines, pollutants are still produced at significant levels from coal excavation in both surface and underground mines.

11.4.1 Dust

The production of airborne dust particles (measured though the dustiness index) (Chapter 9) is a major problem in underground mines where dust explosions with or without explosions due to released gases, are the main concern (Colinet et al., 2010). In addition, dust is not solely a localized problem since fine particles can be transported to contaminate areas far from their source.

Dust is a by-product of blasting and (in open pit mines) earth moving operations. The degree of risk is relative to the physical size of particulate matter, the humidity of air, and the velocity and direction of prevailing winds. Particle size and duration of exposure determine how far dust and droplets penetrate the respiratory tract. Inhaled fine dust remains in the alveoli, but all types of larger particles are removed by the filtering capacity of the respiratory system (Suess et al., 1985). The constituents of particulate matter (*particulates*) having a diameter less than 10 μm (particularly those in the range of 0.25–7 μm) may give rise to such respiratory diseases as chronic bronchitis and pneumoconiosis. If the dust contains silica particles, diseases such as silicosis (progressive nodular fibrosis) become a major threat to health.

11.4.2 Fugitive Emissions

The geological processes of coal formation (Chapter 1, Chapter 2) also produce methane (CH_4) and carbon dioxide (CO_2) may also be present in some coal seams. These are known collectively as seam gas and remain trapped in the coal seam until the coal is exposed and broken during mining. Methane is the major greenhouse gas emitted from coal mining and handling. The major stages for the emission of greenhouse gases for both underground and surface coal mines are: (1) mining emissions, (2) post-mining emissions, (3) low temperature oxidation of coal, (4) and spontaneous ignition of coal.

Mining emissions result from the liberation of stored gas during the breakage of coal, and the surrounding strata, during mining operations.

On occasion, when the heat produced by low temperature oxidation is trapped, the temperature rises and an active fire may result (*spontaneous combustion of coal*) and is an extreme case of coal oxidation (Chapter 8) (Speight, 2013a, 2013b). Spontaneous combustion is characterized by rapid reactions, sometimes visible flames and rapid carbon dioxide formation, and may be natural or anthropogenic.

11.4.3 Mine Waste Disposal

The waste material, which is the by-product of both underground and surface excavation operations, are a major pollution issue and disposal of these solid wastes is the most controversial aspect of coal mining. The primary environmental damage of waste piles (mines tips) are not only noise and dust from moving vehicles but also groundwater contamination, leaching of toxic and acid pollutants such as heavy metals (Chapter 4) (Bullock et al., 2002; Baruah and Khare, 2010; Speight, 2013a,b), and loss of usable land. Reclamation to some degree restores the land, but reduction in the fertility of the soil and diminished ecological habitat are slow to recover. In fact, old mine tips, inherited from unregulated past practices of dumping mine waste, are a danger to local drainage systems and may have toxic effects on human health.

Another issue related to waste disposal arose because of the oxidation of pyrite which produces acidic compounds which, with other toxic materials, can be leached into the local water supply. Simultaneously, heat produced from such chemical reactions led to spontaneous combustion of coal particles in the waste tips (Guney, 1968; McNay, 1971; Speight, 2013a,b). The potential hazards from spontaneous combustion in the spoil heaps can be substantially reduced by controlled tipping, site selection, as well as compaction of waste.

In the past, mine overburden or mine tipple was usually dumped into low-lying areas, often filling wetlands or other sources of water. This results in dissolution of some of the mineral matter (Chapter 4) which seeps into both ground and surface water causing disruption to marine habitats and deteriorate drinking water sources. In addition, pyrite (FeS_2) can form sulfuric acid (H_2SO_4) and iron hydroxide [$Fe(OH)_2$]when exposed to air and water. When rainwater washes over these rocks, the runoff can become acidified affecting local soil environments, rivers, and streams (*acid mine drainage*).

11.4.4 Subsidence

Subsidence is a costly economic impact of underground mining because it creates horizontal and vertical displacement of the surface, which generally causes structural damage to buildings, roads, and railroads as well as pipeline rupture. The factors contributing to the ground movement and ultimate surface damage are thickness, dip and depth of the coal seam, angle of draw, the nature and thickness of the overburden, and the amount of support left in the *goaf* (*goff* or *gob* – that of a mine from which the mineral has been partially or wholly removed). These effects relate not only to the mine planning but also to the mechanical properties of coal (Chapter 9).

Underground mine planning and design (using mechanical and any other necessary properties of the coal) has as its goal an integrated mine systems design, whereby coal is extracted and prepared at a desired market specification and at a minimum unit cost within acceptable social, legal, and regulatory constraints. A mining operation should be more correctly viewed as an integrated system because of the diversity of the coal properties as well as the technological processes. Planning must account for both environmental protection, beginning as early as the initial exploration, and for reclamation, which should be based on the character of the coal and the seam structure.

In addition, the transportation of spoil or tipple to the surface from an underground mine where it is then deposited in piles or rows offers a new environmental hazard. The potential for leaching materials from spoil/tipple offers a mode of environmental contamination not often recognized that that is of at least equal importance to the potential contamination from surface mining operations. Similarly the discharge of gaseous and liquid effluents from underground mining operations should be of at least equal concern to those arising from surface mining operations. Thus the environmental issues related to coal mining, be they underground or surface, operations are multifaceted (Argonne, 1990).

Another hazard that may become obvious by its presence is the spontaneous ignition and ensuing combustion of coal (Speight, 2013a,b). This usually occurs when coal is exposed to changing weather conditions and uncontrollable oxidation reaction, with the evolution of heat, ensues.

11.5 PREPARATION, TRANSPORTATION, AND STORAGE

11.5.1 Preparation

Coal preparation is an industry that has a substantial impact on the environment and refuse disposal forms a major part of this multifaceted problem (Argonne, 1990). Run-of-mine coal from underground mines goes directly to the coal washing section or preparation plants where beneficiation and removal of certain impurities associated with coal substance take place.

Thus, knowledge of the physical properties of coal is important in coal preparation and utilization (Chapter 7). For example, the density (specific gravity) of coal density ranges from approximately 1.1 to about 1.5 grams per cubic centimeter (gm/cc). Coal is slightly denser than water (1.0 gm/cc) and significantly less dense than most rock and mineral matter (e.g., shale – ~2.7 gm/cc and pyrite – FeS_2 – approximately of 5.0 gm/cc). Thus, differences in density differences make it possible to improve coal quality by removing most of the mineral matter and sulfide-rich fragments by means of heavy liquid separation processes in which materials with a density greater than approximately 1.5 gm/cc settle out while the coal floats on the surface of the liquid). Devices such as cyclones and shaker tables also separate coal particles from rock and pyrite on the basis of differences in density (Speight, 2013a,b).

Thus, physical and mechanical processes (Chapter 7, Chapter 9) based on surface characteristics or the difference in specific gravity can remove 95% w/w of the pyrite sulfur (FeS_2) in coal – this is typically (approximately) equivalent to 30–35% w/w of the total sulfur and over 50% w/w of the mineral matter content of the coal. Preparation, therefore, improves coal quality (Chapter 4, Chapter 6) (Griswold et al., 1990; Suárez-Ruiz and Ward, 2008) and hence renders the coal less environmentally destructive.

11.5.2 Transportation

Coal, after washing and upgrading, is transported to industrial centers either by rail, trucks, barges, ships, or slurry pipelines (Speight, 2013a,b). Generally, the manner of coal handling is substantially affected by particle size, particle size distribution, and moisture content (Chapter 5, Chapter 7, Chapter 9) The choice of the mode of transportation of coal may be instrumental in dealing with pollution hazards. Bulk movement of coal by methods other than road is advantageous from both the economic and environmental standpoint. Transportation by road tends to create dust, increase traffic noise and congestion, and raises the risk of accidents and injuries (Chadwick et al., 1987). In many instances, conventional railroads are preferred for the handling of coal since the large capacity wagons can be covered, sprayed by water, and wind guards and chemical binders can be used to reduce dust (Chapter 9).

Coal stockpiled near the pit-head or in close proximity to industrial sites is a potential source of dust and surface water runoffs. Regular inspection is required to monitor the rate of spontaneous combustion, which causes the emission of local scale toxic gases. Moreover, stockpiling on a large scale or over a long period arouses adverse reaction from the general public on its unsightliness and puts constraints on coal handling. These problems can, to a certain degree, be overcome by storing coal in abandoned pits or silos constructed for the purpose, but authorities still need to look into alternative optional proposals to deal with the environmental matters.

11.5.3 Storage

Storage of coal at coal preparation plants is not practiced to the same extent as it was decades ago. The active principles in reducing coal storage at coal preparation plants were (1) fugitive dust and (2) runoff control. In fact, in some areas, local environmental regulations may rule out open storage, but it should be considered at least initially, because it can be less expensive from a total cost standpoint, even with environmental controls.

On the other hand, utility coal yards at power plants often need to store coal so that in anticipation of disruption in coal delivery for the plant (such as a train derailment) often means that the plants may require several days of backup. An efficient method that has been used and still is used where environmental regulations permit such actions for storing large quantities of coal is ground placement, where stocks of 30–90 days consumption may be required.

The low temperature oxidation of coal dramatically influences and alters inherent properties. The deleterious effect that oxidation has upon the coking and caking properties of coals, through the loss of plasticity and fluidity, is well documented and, if coal is stored for a sufficiently long period (depending upon the character of the coal) there can be serious effects on the suitability of the coal for the designated use.

Proximate analysis (Chapter 5) of the oxidized coals will show any changes to the bulk properties of the coal in terms of volatile matter production and coke production and show an initial rapid loss in their volatile matter content. In addition, infrared analysis and functional group analysis (Chapter 10) will indicate whether or not the oxidation process involves the progressive removal of aliphatic functions and the inclusion of oxygen bearing functionalities within the molecular structure of the coal. In addition, for further elucidation of the chemical changes to the coal, petrographic analysis (Chapter 1) will show changes in the vitrinite reflectance value between the original coal and the oxidized coal. The suggestion from the text methods will be that coal should not be stored for prolonged periods.

In addition, in such cases where open storage is allowed, rain and snow runoff can become contaminated by chemical and bacteriological action on pyritic materials contained in the coal. Chemically, this occurs by the same series of reactions that are known to produce acid coal mine drainage and the amount of runoff is dependent upon (1) configuration of the stockpile, (2) particle size of the coal, (3) moisture content of the coal, (4) amount of rainfall, and (5) the intensity of the rain (shower or downpour). Studies indicate runoff ranges from 50% to 95% of the rainfall on the pile;

the remainder evaporates or is held in the pile. Constructing coal storage piles so as to encourage runoff and inhibit the amount of water percolating through the piles can minimize the energy wasted in driving off moisture prior to combustion and is a function of the mechanical properties of coal (Chapter 9) (Cox et al., 1977; Ripp, 1984).

11.6 UTILIZATION

Coal utilization can cause environmental problems – during the incomplete burning or conversion of coal, many compounds are produced, some of which are carcinogenic (Speight, 2013a,b).

11.6.1 Combustion

Coal utilization for power generation is of growing environmental concern, mainly due to emissions of carbon dioxide associated with the combustion process (Speight, 2013b). Although coal is only one of many sources represented by this anthropogenic carbon dioxide, the coal industry is searching for and developing technological options to mitigate its contribution to the problem.

It is essential that the correct type of coal be chosen for electricity generation. An increase of applicable coal types to coal-fired power plants is preferable in order to ensure the stable supply of coals. On the other hand, coal type has much effect on a coal-fired boiler in a thermal power plant such as keeping combustion, production of fly ash as well as sulfur oxide (SO_x) and nitrogen oxide (NO_x) emissions. An unsuitable coal type affects furnace state in the boiler and, in the worst case, damages the boiler. Currently, the suitability of coal for a power plant operation is selected on the basis of coal (such as inherent moisture, volatile matter, and caloric value,) (Chapter 5, Chapter 8) and fly ash properties, such as component and chemical composition of the fly ash (Chapter 4). On the other hand, many coal and fly ash properties affect the combustion state in a coal-fired power plant. Thus, coal and fly ash properties were used for the coal type selection. However, in order to obtain a coal type selection method for the screening, combustion test results may be required in which the candidate coal types are checked by a combustion test using a specific test furnace (Goto et al., 2011).

Furthermore, there is a large difference in the rank of the coals which can result in two completing phenomena: (1) adverse impact and (2) beneficial impact. In respect to the *adverse impact*, lower rank coal can react with the available oxygen faster and therefore impede the burnout of the higher rank coal, which tends to occur when the rank of the lower rank coal is sub-bituminous or lower and it is the main coal in the blend. In respect to the *beneficial impact*, the rapid release of the volatile mater from lower rank coal provides a hotter thermal environment, without significantly reducing the oxygen, this will aid in the combustion of the higher rank coal. This tends to occur when the lower rank coal is bituminous of good combustion performance blended with a higher rank coal of poorer combustion performance or when the lower rank coal is sub-bituminous but is a minor component in the blend. Thus coal rank or quality can have a significant impact on the operating costs of coal-fired installations. Generally, coals with low total moisture, mineral matter, and sulfur, high specific energy and good combustion performance can increase plant efficiency (Table 11.1). However, extensive analytical testing of the coal and the produced ash is required prior to the design of a plant for a new coal feedstock. This consists of laboratory and perhaps small scale tests but usually not full scale due to the expense. The design of a plant for a new coal feedstock is a difficult exercise since much of the design is reliant on empirical data from past experience on other similar coals. This can result in an inappropriate design due to an unusual coal/ash property, which is not discovered until the plant is operational – hence the need for continuous analytical monitoring. Plant modifications (if feasible) are then required which usually require an extensive and on-going analytical program.

Coal combustion also produces sulfur oxides and nitrogen oxides that react with atmospheric moisture to produce sulfuric and nitric acids (acid rain). In addition, particulate matter (fly ash) that is also produced during coal combustion can be transported by winds for many hundreds of miles and solids (bottom ash and slag) that must be disposed of. Trace elements originally present in the coal may escape as volatiles (such as chlorine and mercury) or be concentrated in the ash (such as arsenic and barium) (Chapter 4, Chapter 6). Some of these pollutants can be trapped by using such devices as electrostatic precipitators, baghouses, and scrubbers. Regardless of the means used for combustion, knowledge of the composition of the waste and acceptable methods of waste disposal are regulated.

The environmental aspects of coal combustion have been a major factor in the various processes and the movement of the fossil fuel base away from petroleum and natural gas to coal has increased the need for effluent/pollutant control for large, fossil-fueled power plants (Hart, 1981; Slack, 1981; Argonne, 1990). Very large amounts of coal are consumed in generating electricity and the emissions from power stations and similar industrial sources represents a potential, and considerable, environmental hazard. These power plants and the accompanying flue gas desulfurization processes emit effluents, which often are pollutants, and which by mere contact with the external environment or by (generally) simple atmospheric chemical transformations, may form secondary pollutants that are more harmful than the initial effluent/pollutant.

Coal-based processes involved in combustion and conversion facilities release gaseous and liquid effluents as well as solid effluents deleterious to the environment and human health. The preference can be made from the following alternatives (Clark et al., 1977): (1) identify the potential pollutants in the coal through a comprehensive analytical program, and (2) remove the potential pollutants from the process effluent, such as passing the polluted air through a series of dust collectors that filter the fine particulates.

The products of the complete combustion of coal are carbon dioxide and water. However, in the exhaust gases from any practical device, there will be, in addition to these compounds, carbon monoxide, sulfur oxides (SO_x), nitrogen oxides (NO_x), unburned hydrocarbons, and probably solid particulates (soot) with small amounts of hydrogen chloride and polycyclic organic matter. Traces of other gaseous compounds

TABLE 11.1 Summary of the Influence of Coal Properties on Combustion

Proximate analysis:

Moisture content affects boiler efficiency, fuel burn rate, flame temperature, heat transfer in the steam generator, primary air temperature requirements, and ash resistivity in electrostatic precipitators.

Ash:

The ash produced from the mineral matter affects slagging and fouling, boiler efficiency, plant availability (erosion), plant maintenance, ash disposal and particulate emissions. Ash composition influences the slagging and fouling behavior and also the performance of the fly ash collection plant. Low ash fusion temperatures may lead to slagging (deposits within the furnace chamber) or to fouling (deposits in the convective passes of a boiler).

Low ash fusibility temperatures tend to increase the slagging potential of coal ash in the furnace; although the specific nature or the ash constituents, burner design, combustion conditions and furnace design generally have a more direct or obvious influence on ash slagging behavior.

Volatile matter:

The quantity of unburnt combustibles tends to increase as volatile matter decreases if all else is fixed. Heat release rates and temperature profiles inside the boiler are also affected by volatile matter or coal reactivity. The ratio of fixed carbon to volatile matter (fuel ratio) indicates the ease of ignition but the heat content of the volatile matter is a more reliable guide to ignition; low mineral matter coals are preferable.

Moisture:

High moisture content increases transportation costs per unit of energy and may increase handling problems, depending on the clay content of the coal.

Fixed Carbon:

The fixed carbon content establishes the rank of the higher rank coals. Increase in fixed carbon requires an increase in pulverising mill product fineness for proper combustion,

Calorific Value:

The calorific value of a coal affects the boiler efficiency, annual coal tonnage requirements, auxiliary power requirements, and (indirectly) all coal-related throughputs. Calorific value decreases linearly with increase in ash and or moisture in a given coal.

Ultimate Analysis:

Gives an indication of the stoichiometric air requirements and the volume and composition of the products of combustion. The ultimate analysis also gives an indication of the combustion air requirements. The coal properties in the ultimate analysis affect boiler efficiency and auxiliary power requirements.

(*continued*)

TABLE 11.1 ***(Continued)***

Carbon:

This property influences combustion air requirement and flue gas flows.

Hydrogen:

This property also influences combustion air requirement and flue gas flows. In addition, high hydrogen contents lead to lowered boiler efficiency.

Nitrogen:

Increased nitrogen may be associated with increase in NO_x emissions depending on the form of nitrogen in the coal (i.e., volatile nitrogen versus char nitrogen). as well as other coal properties such as volatile matter; however, the principal controlling variables for NO_x emissions arc burner design and combustion conditions.

Sulfur:

The distribution of the total sulfur – organic, inorganic and sulfate – can be used to estimate SO_x emissions. High sulfur content tends to reduce ash resistivity and enhance precipitator performance. High sulfur also increases the potential for air-heater cold-end corrosion.

Ash Constituents:

Silica-Quartz:

These constituents are a measure of the abrasiveness of the coal in milling and the erosion potential of fly ash. Increased silicate content increases fly ash resistivity, which can degrade electrostatic precipitator performance.

Iron:

Iron content is a measure of slagging potential, particularly for bituminous coals. Iron content, as it compares to CaO and MgO content, is also an indicator of ash type (lignite source or bituminous coal source) and general ash behavior.

Sodium:

Increased sodium content can indicate increased slagging, fouling, and corrosion of hot-side boiler surfaces. High sodium content reduces ash resistivity in electrostatic precipitators.

Potassium:

Potassium is generally similar to sodium in its effects. High potassium content has been correlated to the potential for high alkali/iron/trisulfate corrosion in superheaters and reheaters.

Swelling Index:

Poor burnout can be associated with a high swelling index due to agglomeration and coking of particles prior to ignition and in the flame.

TABLE 11.1 ***(Continued)***

Bulk Properties:

Size Analysis:

Size analysis of coal influences the handling and dustiness characteristics of the coal. Coal having more than 30% of fine particles (<2 mm) can cause handling problems with the frequency increasing as the fines percentage increases. Wet coals containing a high proportion of fines and/or fine clay particles, could cause major handling difficulties such as hopper and chute blockages.

Grindability:

An increase in Hardgrove grindability index increases mill capacity and reduces mill power requirements. Coals with high grindability values are more likely to degrade forming fines and nuisance dust. Increasing fines content in conjunction with coal moisture can cause handling problems.

Abrasiveness:

This property is related to the content and composition of mineral constituents in the coal and the grindability of the coal. The *abrasion Index* is a measure of the abrasiveness of coal. With an increasing value indicating an increased rate of wear on mill pulverizing elements.

are also to be found. Of these principal pollutants, concern has largely been focused on sulfur dioxide and nitrogen oxides, so-called acid gases because of their apparent importance on long-term environmental effects. Carbon monoxide (CO) is generally formed by the partial combustion of carbonaceous material in a limited supply of air. Small quantities of carbon monoxide are produced by the combustion of coal and from spontaneous combustion. In the atmosphere, the carbon monoxide is eventually converted to carbon dioxide. These emissions are not considered to be a problem for environmental pollution.

Acid gases (SO_x and NO_x) emitted into the atmosphere provide the essential components in the formation of acid rain. Sulfur is present in coal as both organic sulfur and inorganic sulfur (Chapter 4, Chapter 6). During combustion, most of the sulfur is converted to sulfur dioxide with a small proportion remaining in the ash as sulfite:

$$S_{coal} + O_2 \rightarrow SO_2$$

At flame temperatures in the presence of excess air, some sulfur trioxide is also formed:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Only a small amount of sulfur trioxide can have an adverse effect as it brings about the condensation of sulfuric acid and causes severe corrosion. Although diminution of the excess air reduces sulfur trioxide formation considerably, other considerations, such as soot formation, dictate that the excess air level cannot be lowered sufficiently to eliminate sulfur trioxide entirely.

From 10% to 50% of the nitrogen inherent in the organic coal structure is converted to nitrogen oxides during combustion which also produce acidic products thereby contributing to the acid rain:

$$2N_{coal} + O_2 \rightarrow 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$4NO + O_2 + 2H_2O \rightarrow \underset{\text{Nitrous acid}}{4HNO_2}$$

$$\underset{\text{Nitric acid}}{NO_2 + H_2O \rightarrow HNO_3}$$

Nitrogen in coal (Chapter 6) also contributes significantly to the formation of gases. Of the nitrogen oxides emitted in power station flue gas, 95% is nitric oxide (NO), which oxidizes rapidly in the atmosphere to form nitrogen dioxide (NO_2) (CEE, 1981).

Very little, if anything, can be done as part of the coal pretreatment operations to eliminate nitrogen, which is a part of the organic coal structure (Speight, 2013a,b). The situation is less clear in the case of hydrogen chloride sources in coal; both organically bound chlorine and inorganic chloride salts (although it is not known that these contribute appreciably to hydrogen chloride formation during combustion) but these processes do not remove organically bound chlorine, which is a more likely precursor to hydrogen chloride in a combustion process.

However, the management of volatile matter (Chapter 5) evolution patterns also is of significance in controlling nitrogen oxide emission. Nitrogen evolving rapidly, frequently under reducing conditions, does not oxidize but converts to nitrogen. Nitrogen volatiles that evolve more slowly can exist in an oxidizing environment and formation of nitrogen oxides from these is more likely than from fuel nitrogen sources.

Furthermore, during coal combustion, the mineral matter (Chapter 4) is transformed into ash, part of which is fly ash discharged to the atmosphere as particles suspended in the flue gases and part of which is bottom ash removed from the base of the furnace (Speight, 2013a,b). Furthermore, the quantity, particle size distribution, and properties of fly ash are directly related to the combustion technique applied and the constitution and properties of the coal. Particulate matter in the form of dust, smoke, and fly ash are generated by a variety of chemical and physical processes in the combustion chamber. These effluents exhibit a range of particle size and composition – particles of relatively large size remain in the furnace, but smaller particles are emitted to the atmosphere with the flue gases.

Analytical data resulting from coal combustion in power plants show consistent and selective separation of trace elements in the various outlets of the combustion furnace in the following groups (Chadwick et al., 1987):

Group I: elements, such as Al, Ba, Ca, Ce, Cs, Fe, K, Mg, Mn, and Th, remain condensed at the temperature of coal combustion and divide equally between fly-ash and bottom ash.

Group II: elements, such as As, Cd, Cu, Pb, Sb, Se, and Zn, are volatilized and will, therefore, be depleted from the slag and bottom ash and condense out on the smaller fly-ash particles; elements, such as Cr, Ni, U, and V, display intermediate behavior between Groups I and II.

Group III: elements, such as Br, Hg, and I, are very volatile and mostly remain in the gas phase. They are depleted in all ashes. Any remainder will be associated with fly ash.

The scale of these environmental problems can be minimized, if not eliminated, by the use of comprehensive analytical programs designed for the purpose of control. Control of sulfur dioxide emissions could be accomplished by using low-sulfur content coal, blending high-sulfur coal with low, and treating coal before combustion to remove some of the sulfur. Coal washing, although mainly applied for reducing the mineral content of coal, removes up to 70% of inorganic sulfur and 40% of total sulfur.

Although not generally considered to be a major pollutant, hydrogen chloride from inorganic contaminants is gaining increasing recognition as a pollutant arising from the combustion of coal (Chapter 4, Chapter 6). Hydrogen chloride quickly picks up water from the atmosphere to form droplets of hydrochloric acid and, like sulfur dioxide, is a contributor to acid rain. However, hydrogen chloride may exert severe local effects because it does not have to undergo any chemical change to become an acid and, therefore, under atmospheric conditions involving a buildup of stack emissions in the area of a large power plant, the concentration of hydrochloric acid in rain droplets could be quite high.

The nonvolatile oxidation products of the inorganic constituents of the coal (Chapter 4) are left as ash and contribute to the formation of corrosive deposits (Reid, 1981; Argonne, 1990). When pulverized coal is used, a large proportion of the ash is carried out of the combustion chamber with the exhaust gas stream and has to be removed as completely as possible, usually by use of electrostatic precipitators.

In regard to the behavior of trace elements (Chapter 4) in coal-fired power plants, the elements have been divided into two groups, those appearing mainly in the bottom ash (elements or oxides having lower volatility) and those appearing mainly in the fly ash (elements or oxides having higher volatility). *Bottom ash* is agglomerated ash particles, formed in pulverized coal furnaces, that are too large to be carried in the flue gases and impinge on the furnace walls or fall through open grates to an ash hopper at the bottom of the furnace. Physically, bottom ash is typically gray to black in color, is quite angular, and has a porous surface structure.

Among the trace elements present in coal (Chapter 4) with recognized toxic properties, high-volatility elements (beryllium. mercury, and lead) do not form gaseous-hydrides, will condense on cooling and very likely will be almost completely removed by the aqueous condensates formed on gas cooling and/or purification. Arsenic, antimony, and selenium have lower volatility but can form gaseous hydrides, (covalent) hydrides: arsine (AsH_3), stibine (SbH_3) , and hydrogen selenide (H_2Se). These, however, have stability characteristics that preclude their formation at the temperature and pressure prevailing in the oil/gas plant gasifiers.

11.6.2 Carbonization

Coal carbonization is the process for producing metallurgical coke for use in iron-making blast furnaces and other metal smelting processes. Carbonization of coal (Speight, 2013a) entails heating coal to temperatures as high as 1100 °C (2010 °F) in the absence of oxygen in order to distill out tars and light oils (see Tar and pitch). A gaseous by-product referred to as *coke oven gas* (*COG*) along with ammonia, water, and sulfur compounds are also thermally removed from the coal.

During carbonization, coal undergoes a variety of physical and chemical changes which are often difficult to predict due to its complex and heterogeneous nature. Understanding the carbonization behavior of coal, though a careful analytical program focusing on devolatilization and swelling (Chapter 5, Chapter 8), is required in order to improve the process. The thermoplastic behavior of coal (Chapter 8) indirectly affects the process efficiency due to its effect on coke quality during carbonization, and also has an impact on coal degradation behavior.

The coke that remains from the process consists predominantly of carbon, in various crystallographic forms, but also contains the thermally modified remains of various minerals that were in the original coal (Chapter 8). These mineral remains, commonly referred to as coke ash, do not combust and are left as a residue after the coke is burned. The coke product also contains a portion of the sulfur that was originally present in the coal and can affect the combustion characteristics of the coke (leading to the emission of sulfur dioxide).

It is a common practice to pulverize coal (Chapter 9) for coke making to more than 80%, being less than 3 mm in size. In other plants, crushing of the coal takes place after the various coals have been blended. This blending is accomplished by discharging measured, either mass or volumetric, amounts of each coal into mixing bins. This may be accomplished through use of intermediate conveyor belt systems as well. The coal blend is withdrawn from the mix bins on an as-needed basis and is transported to the coal blend silo at the coke battery.

Furthermore, when coal is heated (carbonized) in a coke oven, hydrocarbon-based gas (coal carbonization gas) is generated. The coal carbonization gas passes through the upper space of the coke oven chamber (oven top space) and is exhausted from the oven and sent to the succeeding process. Since the oven top space is a high temperature atmosphere (820–950 °C, 1500–1740 °F), the coal carbonization gas is subject to thermal decomposition there, causing carbon to deposit on the surface of the refractory bricks that make up the coke oven chamber. If the amount of carbon deposits becomes excessive, it not only reduces the effective volume of the coke oven chamber, thereby reducing productivity, but also increases the resistance of the coke when it is pushed out of the chamber. Thus, excessive carbon deposits can be an impediment to stable operation of the coke oven battery (Nakagawa et al., 2006). When both coal carbonization gas and fine coal are present (measured as the dustiness index; Chapter 9), the carbon deposition rate increases in quadratic function manner relative to the fine coal concentration. In addition, a laboratory experiment was conducted to evaluate the dusting characteristics of various charging coals and formulated them in terms of HGI, coal particle size, moisture content, and oil addition rate. Furthermore, by combining the results of the present experiment and the conventional equation on the rate of carbon deposition from coal carbonization gas, a formula was produced for estimating the rate of carbon deposition when both coal carbonization gas and fine coal are present.

11.6.3 Liquefaction

The potential exists for generation of significant levels of atmospheric pollutants from a coal liquefaction facility – these pollutants include coal dust, combustion products, fugitive organics, and fugitive gases (Table 11.2). The fugitive organics and gases could include carcinogenic polynuclear organics and toxic gases such as metal carbonyls, hydrogen sulfides, ammonia, sulfurous gases, and cyanides (Speight, 2013a,b).

A major source of emissions from the coal dissolution and liquefaction operation is the atmospheric vent on the slurry mix tank (Speight, 2013a). The slurry mix tank is used to mix the coal feedstock with the recycle solvent. Gases dissolved in the recycle solvent stream under pressure will flash from the solvent as it enters the unpressurized slurry mix tank. These gases can contain hazardous volatile organics and acid gases. Control techniques proposed for this source include scrubbing, incineration, or venting to the combustion air supply for either a power plant or a process heater.

11.6.4 Gasification

Coal gasification offers one of the most versatile methods to convert coal into electricity, hydrogen, and other valuable energy-related products (Chadeesingh, 2011; (Speight, 2013a, 2013b). In the gasifier, coal is typically exposed to steam and carefully controlled amounts of air or oxygen under high temperatures and pressures. Under these conditions, chemical reactions are initiated that typically produce a mixture of carbon monoxide, hydrogen, and other gaseous compounds.

The gas produced by gasification can contain one or more of contaminants such as ash, char, alkali metals, nitrogen compounds, polynuclear aromatic compounds, tar, sulfur-containing compounds (including hydrogen sulfide) and (on occasion) chlorine-containing compounds. The identity and amount of these contaminants depend on the gasification process and the type of coal (Chapter 2, Chapter 5, Chapter 6). Co-gasification of coal with biomass results (depending on the type of biomass) in a change in the composition of the emissions as the ash may contain

TABLE 11.2 Summary of the Sources of Pollutants from a Coal Liquefaction Plant

Source	Pollutant
Gases	Ammonia
	Acid gas
	Carbonyl sulfide
	Carbon disulfide
Lock hopper vent gas	Carbon monoxide
	Hydrogen cyanide
	Aromatic amines
	Aliphatic hydrocarbons
	Benzene derivatives
	Phenol derivatives
	Nitrogen heterocycles
Gasifier	Carbon monoxide
	Acid gas
	Hydrogen sulfide
	Carbonyl sulfide
	Carbon disulfide
Ash/slag	Mineral dust
	Fly ash
Catalyst regenerator	Catalyst dust
Combustor	Sulfur oxides
	Carbon monoxide
	Carbon dioxide
Product storage	Aromatic amines
	Aliphatic hydrocarbons
	Benzene derivatives
	Phenol derivatives
	Nitrogen heterocycles
	Polycyclic aromatic hydrocarbons

higher proportions of heavy metals (Balat, 2008a,b; Speight, 2013b). A major concern with these feedstocks is the potential for heavy metals (Chapter 4) to leach into the environment following ash disposal.

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GLOSSARY

Abandoned workings: sections, panels and other areas that are not ventilated and examined in the manner required for work places.

Abutment: (1) the weight of the rocks above a narrow roadway is transferred to the solid coal along the sides, which act as abutments of the arch of strata spanning the roadway; (2) the weight of the rocks over a longwall face is transferred to the front abutment, that is, the solid coal ahead of the face and the back abutment, that is, the settled packs behind the face.

Accessed: coal deposits that have been prepared for mining by construction of portals, shafts, slopes, drifts, and haulage ways; by removal of overburden; or by partial mining.

Acid drainage: the runoff of acidic liquids from coal production waste piles. Such runoff can contaminate ground and surface waters.

Acid deposition or acid rain: a mixture of wet and dry *deposition* (deposited material) from the atmosphere containing higher than typical amount of nitric and sulfuric acids.

Acid gas: hydrogen sulfide (H_2S) or carbon dioxide (CO_2).

Acid mine drainage: any acid water draining or flowing on, or having drained or flowed off, any area of land affected by mining.

Acid mine water: mine water that contains free sulfuric acid, mainly due to the weathering of iron pyrites.

Handbook of Coal Analysis, Second Edition. James G. Speight.

Acid rain: a solution of acidic compounds formed when sulfur and nitrogen oxides react with water droplets and airborne particles.

Acre-foot (acre-ft): the volume of coal that covers 1 acre at a thickness of 1 ft (43,560 ft^3; 1,613.333 yd^3; 1,233.482 m^3). The weight of coal in this volume varies according to rank.

Acre-inch (acre-in.): the volume of coal that covers 1 acre at a thickness of 1 in. (3,630 ft^3; 134.44 yd^3; 102.7903 m^3). The weight of coal in this volume varies according to rank.

Active workings: any place in a mine where miners are normally required to work or travel and which are ventilated and inspected regularly.

Adit: a nearly horizontal passage from the surface by which a mine is entered and dewatered; a blind horizontal opening into a mountain, with only one entrance.

Advance: mining in the same direction, or order of sequence; first mining as distinguished from retreat.

Afterdamp: gases remaining after an explosion in a mine consisting of carbon dioxide, carbon monoxide, nitrogen, and hydrogen sulfide; the toxic mixture of gases left in a mine following an explosion caused by firedamp (methane), which itself can initiate a much larger explosion of coal dust.

Agglomerating: coal that, during volatile matter determinations, produces either an agglomerate button capable of supporting a 500-g weight without pulverizing or a button showing swelling or cell structure.

Agglomeration: formation of larger coal or ash particles by smaller particles sticking together.

Airshaft: A vertical shaft in which air is blown down through the various sections of the underground mine. The air is generated by a large fan on the surface providing oxygen for the miners below.

Air split: the division of a current of air into two or more parts.

Airway: any passage through which air is carried. This is also known as an air course.

Anemometer: an instrument for measuring air velocity.

Angle of dip: the angle at which strata or mineral deposits are inclined to the horizontal plane.

Angle of draw: this angle is assumed to bisect the angle between the vertical and the angle of repose of the material and is 20° for flat seams; for dipping seams, the angle of break increases, being 35.8° from the vertical for a 40° dip; the main break occurs over the seam at an angle from the vertical equal to half the dip.

Angle of repose: the maximum angle from horizontal at which a given material will rest on a given surface without sliding or rolling.

Anthracene oil: the heaviest distillable coal tar fraction, with distillation range 270–400 °C (520–750 °F), containing creosote oil, anthracene, phenanthrene, carbazole, and so on.

Anthracite (hard coal): a hard, black, shiny coal very high in fixed carbon and low in volatile matter, hydrogen, and oxygen; a rank class of non-agglomerating coals as defined by the American Society for Testing and Materials having more than 86% fixed carbon and less than 14% volatile matter on a dry, mineral-matter-free basis; this class of coal is divisible into the semi anthracite, anthracite, and meta-anthracite groups on the basis of increasing fixed carbon and decreasing volatile matter.

Anthracosis: *see* **Black lung**.

Anthraxylon: US Bureau of Mines term for vitrinite viewed by transmitted light.

Anticline: an upward fold or arch of rock strata.

Aquifer: a water-bearing formation through which water moves more readily than in adjacent formations with lower permeability.

Arching: fracture processes around a mine opening, leading to stabilization by an arching effect.

Area (of an airway): average width multiplied by average height of airway, expressed in square feet.

Ash: the noncombustible residue remaining after complete coal combustion; the final form of the mineral matter present in coal.

Ash analysis: percentages of inorganic oxides present in an ash sample. Ash analyses are used for evaluation of the corrosion, slagging, and fouling potential of coal ash. The ash constituents of interest are silica (SiO_2) alumina (Al_2O_3), titania (TiO_2), ferric oxide (Fe_2O_3), lime (CaO), magnesia (MgO), potassium oxide (K_2O), sodium oxide (Na_2O), and sulfur trioxide (SO_3). An indication of ash behavior can be estimated from the relative percentages of each constituent.

Ash free: a theoretical analysis calculated from basic analytical data expressed as if the total ash had been removed.

Ash-fusion temperatures: a set of temperatures that characterize the behavior of ash as it is heated. These temperatures are determined by heating cones of ground, pressed ash in both oxidizing and reducing atmospheres.

As-received basis: represents an analysis of a sample as received at a laboratory.

As-received moisture: the moisture present in a coal sample when delivered.

Attritus: a microscopic coal constituent composed of macerated plant debris intimately mixed with mineral matter and coalified. US Bureau of Mines usage, viewed by transmitted light.

Auger: a rotary drill that uses a screw device to penetrate, break, and then transport the drilled material (coal).

Auger mining: mining generally practiced but not restricted to hilly coal-bearing regions of the country that uses a machine designed on the principle of the auger, which bores into an exposed coal seam, conveying the coal to a storage pile or bin for loading and transporting. May be used alone or in combination with conventional surface mining. When used alone, a single cut is made sufficient to expose the coal seam and provide operating space for the machine. When used in combination with surface mining, the last cut pit provides the operating space.

Auxiliary operations: all activities supportive of but not contributing directly to mining.

Auxiliary ventilation: portion of main ventilating current directed to face of dead end entry by means of an auxiliary fan and tubing.

Azimuth: a surveying term that references the angle measured clockwise from any meridian (the established line of reference); the bearing is used to designate direction; the bearing of a line is the acute horizontal angle between the meridian and the line.

Back: the roof or upper part in any underground mining cavity.

Backfill: the operation of refilling an excavation. Moreover, the material placed in an excavation in the process of backfilling.

Baghouse: an air pollution control device that removes particulate matter from flue gas, usually achieving a removal rate above 99.9%.

Barrel: liquid volume measure equal to 42 US gals, commonly used in measuring petroleum or petroleum products.

Barren: said of rock or vein material containing no minerals of value, and of strata without coal, or containing coal in seams too thin to be workable.

Barricading: enclosing part of a mine to prevent inflow of noxious gasses from a mine fire or an explosion.

Barrier: something that bars or keeps out. Barrier pillars are solid blocks of coal left between two mines or sections of a mine to prevent accidents due to inrushes of water, gas, or from explosions or a mine fire.

Beam: a bar or straight girder used to support a span of roof between two support props or walls.

Beam building: the creation of a strong, inflexible beam by bolting or otherwise fastening together several weaker layers. In coal mining, this is the intended basis for roof bolting.

Bearing: a surveying term used to designate direction. The bearing of a line is the acute horizontal angle between the meridian and the line. The meridian is an established line of reference. Azimuths are angles measured clockwise from any meridian.

Bearing plate: a plate used to distribute a given load. In roof bolting, the plate used between the bolt head and the roof.

Bed: a stratum of coal or other sedimentary deposit.

Bedrock: the rock material directly above and below the coal seam.

Beehive oven: a dome-shaped oven not equipped to recover the by-product gas and liquids evolved during the coking process.

Belt conveyor: a looped belt on which coal or other materials can be carried and which is generally constructed of flame-resistant material or of reinforced rubber or rubber-like substance.

Belt Feeder (Feeder breaker): a crawler-mounted surge bin often equipped with a crusher or breaker and used in room-and-pillar sections positioned at the end of the section conveyor belt. It allows a quick discharge of the shuttle car. It sizes the coal and a built-in conveyor feeds it at an appropriate rate onto the conveyor belt.

Belt idler: a roller, usually of cylindrical shape, which is supported on a frame and which, in turn, supports or guides a conveyor belt. Idlers are not powered but turn by contact with the moving belt.

Belt take-up: a belt pulley, generally under a conveyor belt and inby the drive pulley, kept under strong tension parallel to the belt line. Its purpose is to automatically compensate for any slack in the belting created by start-up.

Bench: the surface of an excavated area at some point between the material being mined and the original surface of the ground, on which equipment can sit, move, or operate. A working road or base below a high wall, as in contour stripping for coal.

Beneficiation: the treatment of mined material, making it more concentrated or richer; *see* **Physical coal cleaning**.

Berm: a pile or mound of material capable of restraining a vehicle.

Binder: a streak of impurity in a coal seam.

Bit: the hardened and strengthened device at the end of a drill rod that transmits the energy of breakage to the rock—the size of the bit determines the size of the hole; a bit may be either detachable from or integral with its supporting drill rod.

Bituminous (soft) coal: a relatively soft dark brown to black coal, lower in fixed carbon than anthracite but higher in volatile matter, hydrogen, and oxygen; a rank class of coals as defined by the American Society for Testing and Materials (ASTM) high in carbonaceous matter, having less than 86% fixed carbon, and more than 14% volatile matter on a dry, mineral-matter-free basis and more than 10,500 Btu on a moist, mineral-matter-free basis. This class may be either agglomerating or non-agglomerating and is divisible into the high-volatile C, B, A; medium; and low volatile bituminous coal groups on the basis of increasing heat content and fixed carbon and decreasing volatile matter.

Blackdamp: a deadly gas that is caused from coal burning in an atmosphere which lacks oxygen; mostly a mixture of carbon dioxide and nitrogen found in mines after fires and explosions.

Black lung (anthracosis): a respiratory disease caused by prolonged inhalation of coal dust.

Blasting agent: any material consisting of a mixture of a fuel and an oxidizer.

Blasting cap: a detonator containing a charge of detonating compound, which is ignited by electric current or the spark of a fuse. Used for detonating explosives.

Blasting circuit: electric circuits used to fire electric detonators or to ignite an igniter cord by means of an electric starter.

Bleeder or bleeder entries: special air courses developed and maintained as part of the mine ventilation system and designed to continuously move air-methane mixtures emitted by the gob or at the active face away from the active workings and into mine-return air courses.

Blue gas: a mixture consisting chiefly of carbon monoxide and hydrogen formed by action of steam on hot coal or coke.

Boghead coal: same as cannel coal except that algal remains can be seen under the microscope.

Boiler slag: a molten ash collected at the base of slag tap and cyclone boilers that is quenched with water and shatters into black, angular particles having a smooth glassy appearance.

Bolt torque: the turning force in foot-pounds applied to a roof bolt to achieve an installed tension.

Bone coal or bone: impure coal that contains much clay or other fine-grained detrital mineral matter; the term bone coal has been erroneously used for cannel coal, canneloid coal, and well cemented to metamorphosed coaly mudstone and (or) claystone. Bone coal has also been applied to carbonaceous partings; the term *impure coal* accompanied by adjective modifiers such as *silty*, *shaly*, or *sandy* is the preferred usage because the definition of bone coal does not specify the type or weight percentages of impurities.

Borehole: any deep or long drill-hole, usually associated with a diamond drill.

Boss: any member of the managerial ranks who is directly in charge of miners (e.g., shift-boss, face-boss, fire-boss).

Bottom: floor or underlying surface of an underground excavation.

Bottom ash: consists of agglomerated ash particles formed in pulverized coal boilers that are too large to be carried in the flue gases and impinge on the boiler walls or fall through open grates to an ash hopper at the bottom of the boiler. Bottom ash is typically gray to black in color, is quite angular, and has a porous surface structure.

Box-type magazine: a small, portable magazine used to store limited quantities of explosives or detonators for short periods of time at locations in the mine which are convenient to the blasting sites at which they will be used.

Brattice or brattice cloth: fire-resistant fabric or plastic partition used in a mine passage to confine the air and force it into the working place; also termed *line brattice*, *line canvas*, or *line curtain*.

Break line: the line that roughly follows the rear edges of coal pillars that are being mined; the line along which the roof of a coal mine is expected to break.

Breakthrough: a passage for ventilation that is cut through the pillars between rooms.

Bridge carrier: a rubber-tire-mounted mobile conveyor, about 10 m long, used as an intermediate unit to create a system of articulated conveyors between a mining machine and a room or entry conveyor.

Bridge conveyor: a short conveyor hung from the boom of mining or lading machine or haulage system with the other end attached to a receiving bin that dollies along a frame supported by the room or entry conveyor, tailpiece—as the machine boom moves, the bridge conveyor keeps it in constant connection with the tailpiece.

Bright coal: US Bureau of Mines term for a combination of clarain and vitrain with small amounts of fusain.

Briquetting: a process of applying pressure to coal fines, with or without a binder, to form a compact or agglomerate.

British thermal unit (Btu): the quantity of heat required to raise the temperature of one pound of water one °F at, or near, its point of maximum density of 39.1 °F (equivalent to 251.995 g calories; 1,054.35 J; 1.05435 kJ; 0.25199 kcal).

Brow: a low place in the roof of a mine, giving insufficient headroom.

Brushing: digging up the bottom or taking down the top to give more headroom in roadways.

Btu: British thermal unit; a measure of the energy required to raise the temperature of one pound of water one degree Fahrenheit.

Bug dust: the fine particles of coal or other material resulting from the boring or cutting of the coal face by drill or machine.

Bump (or burst): a violent dislocation of the mine workings which is attributed to severe stresses in the rock surrounding the workings.

Burn line: the contact between burned and unburned coal in the subsurface. In the absence of definitive information, the subsurface position of a burn line is assumed to be vertically below the surface contact between unaltered and altered rocks.

Butt cleat: a short, poorly defined vertical cleavage plane in a coal seam, usually at right angles to the long face cleat.

Butt entry: a coal mining term that has different meanings in different locations—it can be synonymous with panel entry, sub-main entry, or in its older sense it refers to an entry that is *butt* onto the coal cleavage (i.e., at right angles to the face).

Cage: a rectangular transporting device used to haul mine cars (pit cars) loaded with coal or dirt and rock from the earth below. The cage was also used to transport miners, mules and supplies to and from the workplace below.

Cage: a person who worked at the cages loading and unloading the mine cars etc. on to the cages.

Calorie: the quantity of heat required to raise 1 g of water from 15 to 16 °C; a calorie is also termed gram calorie or small calorie (equivalent to 0.00396832 Btu; 4.184 J; 0.001 kg calorie).

Calorific value: the quantity of heat that can be liberated from one pound of coal or oil measured in Btu/lb.

Cannel coal: predominately durain with lesser amounts of vitrain than splint coal and small quantities of fusain. Spores can be seen under the microscope.

Canopy: a protective covering of a cab on a mining machine.

Cap: a miner's safety helmet; a highly sensitive, encapsulated explosive that is used to detonate larger but less sensitive explosives.

Cap block: a flat piece of wood inserted between the top of the prop and the roof to provide bearing support.

Car: a railway wagon, especially any of the wagons adapted to carrying coal, ore, and waste underground.

Car-dump: the mechanism for unloading a loaded car.

Carbide bit: a cutting or drilling bit for rock or coal, made by fusing an insert of molded tungsten carbide to the cutting edge of a steel bit shank.

Carbonization: a process whereby coal is converted to coke by devolatilization.

Carbon monoxide: a colorless, odorless, very toxic gas formed by incomplete combustion of carbon, as in water gas or producer gas production.

Carburetted blue gas: *see* **Water gas**.

Cast: a directed throw; in strip-mining, the overburden is cast from the coal to the previously mined area.

Certified: describes a person who has passed an examination to do a required job.

Chain conveyor: a conveyor on which the material is moved along solid pans (troughs) by the action of scraper crossbars attached to powered chains.

Chain pillar: the pillar of coal left to protect the gangway or entry and the parallel airways.

Check curtain: a sheet of brattice cloth hung across an airway to control the passage of the air current.

Chock: large hydraulic jacks used to support roof in longwall and shortwall mining systems.

Clarain: a macroscopic coal constituent (lithotype) known as bright-banded coal, composed of alternating bands of vitrain and durain.

Clastic rocks: rocks composed of fragments (clasts) of preexisting rock; may include sedimentary rocks as well as to transported particles whether in suspension or in deposits of sediment.

Clastic dike: a vertical or near-vertical seam of sedimentary material that fills a crack in and cuts across sedimentary strata—the dikes are found in sedimentary basin deposits worldwide; dike thickness varies from millimeters to meters and the length is usually many times the width.

Clay vein: a fissure that has been infilled as a result of gravity, downward-percolating ground waters, or compactional pressures which cause unconsolidated clays or thixotropic sand to flow into the fissure.

Clean Air Act Amendments of 1990: a comprehensive set of amendments to the federal law governing US air quality; the Clean Air Act was originally passed in 1970 to address significant air pollution problems in our cities and the 1990 amendments broadened and strengthened the original law to address specific problems such as acid deposition, urban smog, hazardous air pollutants and stratospheric ozone depletion.

Clean Coal Technologies: a number of innovative, new technologies designed to use coal in a more efficient and cost-effective manner while enhancing environmental protection; technologies include: fluidized-bed combustion, integrated gasification combined cycle, limestone injection multi-stage burner, enhanced flue gas desulfurization (or *scrubbing*), coal liquefaction and coal gasification.

Cleats: natural opening-mode fractures in coal beds which account for most of the permeability and much of the porosity of coalbed gas reservoirs.

Coal: an organic rock; a stratified combustible carbonaceous rock, formed by partial to complete decomposition of vegetation; varies in color from dark brown to black; not fusible without decomposition and very insoluble.

Coal bed methane (coalbed methane): methane adsorbed to the surface of coal; often considered to be a part of the coal seam.

Coal dust: particles of coal that can pass a No. 20 sieve.

Coal gas: the mixture of volatile products (mainly hydrogen, methane, carbon monoxide, and nitrogen) remaining after removal of water and tar, obtained from carbonization of coal, having a heat content of 400–600 Btu/ft^3.

Coal gasification: production of synthetic gas from coal.

Coalification: those processes involved in the genetic and metamorphic history of the formation of coal deposits from vegetable matter.

Coal liquefaction: conversion of coal to a liquid.

Coal measures: strata containing one or more coal beds.

Coal province: an area containing two or more coal regions.

Coal mine: an area of land and all structures, facilities, machinery, tools, equipment, shafts, slopes, tunnels, excavations, and other property, real or personal, placed upon, under, or above the surface of such land by any person, used in extracting coal from its natural deposits in the earth by any means or method, and the work of preparing the coal so extracted, including coal preparation facilities; the British term is *colliery* or (in northern areas) *pit*.

Coal preparation/washing: the treatment of coal to reject waste. In its broadest sense, preparation is any processing of mined coal to prepare it for market, including crushing and screening or sieving the coal to reach a uniform size, which normally results in removal of some non-coal material. The term coal preparation most commonly refers to processing, including crushing and screening, passing the material through one or more processes to remove impurities, sizing the product, and loading for shipment. Many of the processes separate rock, clay, and other minerals from coal in a liquid medium; hence the term washing is widely used. In some cases, coal passes through a drying step before loading.

Coal rank: indicates the degree of coalification that has occurred for a particular coal. Coal is formed by the decomposition of plant matter without free access to air and under the influence of moisture, pressure, and temperature. Over the course of the geologic process that forms coal—coalification—the chemical composition of the coal gradually changes to compounds of lower hydrogen content and higher carbon content in aromatic ring structures. As the degree of coalification increases, the percentage of volatile matter decreases and the calorific value increases. The common ranks of coal are anthracite, bituminous, subbituminous, and brown coal/lignite.

Coal region: an area containing one or more coal fields.

Coal reserves: measured tonnages of coal that have been calculated to occur in a coal seam within a particular property.

Coal sampling: the collection and proper storage and handling of a relatively small quantity of coal for laboratory analysis. Sampling may be done for a wide range of purposes, such as: coal resource exploration and assessment, characterization of the reserves or production of a mine, to characterize the results of coal cleaning processes, to monitor coal shipments or receipts for adherence to coal quality contract specifications, or to subject a coal to specific combustion or reactivity tests related to the customer's intended use. During predevelopment phases, such as exploration and resource assessment, sampling typically is from natural outcrops, test pits, old or existing mines in the region, drill cuttings, or drilled cores. Characterization of a mine's reserves or production may use sample collection in the mine, representative cuts from coal conveyors or from handling and loading equipment, or directly from stockpiles or shipments (coal rail cars or barges). Contract specifications rely on sampling from the production flow at the mining or coal handling facility or at the load-out, or from the incoming shipments at the receiver's facility. In all cases, the value of a sample taken depends on its being representative of the coal under consideration, which in turn requires that appropriate sampling procedures be carefully followed.

For coal resource and estimated reserve characterization, appropriate types of samples include (alphabetically):

Bench sample**:** a face or channel sample taken of just that contiguous portion of a coalbed that is considered practical to mine, also known as a *bench*; For example, bench samples may be taken of minable coal where impure coal that makes up part of the geologic coalbed is likely to be left in the mine, or where thick partings split the coal into two or more distinct minable seams, or where extremely thick coal beds cannot be recovered by normal mining equipment, so that the coal is mined in multiple passes, or benches, usually defined along natural bedding planes.

Column sample**:** a channel or drill core sample taken to represent the entire geologic coalbed; it includes all partings and impurities that may exist in the coalbed.

Composite sample**:** a recombined coalbed sample produced by averaging together thickness-weighted coal analyses from partial samples of the coalbed, such as from one or more bench samples, from one or more mine exposures or outcrops where the entire bed could not be accessed in one sample, or from multiple drill cores that were required to retrieve all local sections of a coal seam.

Face channel or channel sample**:** a sample taken at the exposed coal in a mine by cutting away any loose or weathered coal then collecting on a clean surface a sample of the coal seam by chopping out a channel of uniform width and depth; a face channel or face sample is taken at or near the working face, the most freshly exposed coal where actual removal and loading of mined coal is taking place. Any partings greater than 3/8 in. and/or mineral concretions greater than ½ in. thick and 2 in. in maximum diameter are normally discarded from a channel sample so as better to represent coal that has been mined, crushed, and screened to remove at least gross non-coal materials.

Coal seam: a layer, vein, or deposit of coal. A stratigraphic part of the earth's surface containing coal.

Coal tar: the condensable distillate containing light, middle, and heavy oils obtained by carbonization of coal. About 8 gal of tar is obtained from each ton of bituminous coal.

Coal upgrading: generally refers to upgrading technology that removes moisture and certain pollutants from lower-rank coals such as sub-bituminous coal and lignite by raising the calorific value; upgrading technologies are typically precombustion treatments and/or processes that alter the characteristics of a coal before it is burned; the product is often referred to as *refined coal*; may also refer to gasification and liquefaction processes in which the coal is upgraded to a gaseous or liquid product.

Coal washing: the process of separating undesirable materials from coal based on differences in densities; pyrite (FeS_2) is heavier and sinks in water—coal is lighter and floats.

Coal zone: a series of laterally extensive and (or) lenticular coal beds and associated strata that arbitrarily can be viewed as a unit; generally, the coal beds in a coal zone are assigned to the same geologic member or formation.

Coarse coal: coal pieces larger than ½ mm in size.

Cogeneration: a process by which electricity and steam, for space heating or industrial-process heating, are produced simultaneously from the same fuel.

Coke: a gray, hard, porous, and coherent cellular-structured combustible solid, primarily composed of amorphous carbon; produced by destructive distillation or thermal decomposition of certain bituminous coal that passes through a plastic state in the absence of air.

Coke-oven gas: a medium-Btu gas, typically 550 Btu/ft^3, produced as a by-product in the manufacture of coke by heating coal at moderate temperatures.

Colliery: British name for coal mine.

Column flotation: a precombustion coal cleaning technology in which coal particles attach to air bubbles rising in a vertical column—the coal is then removed at the top of the column.

Comminution: breaking, crushing, or grinding of coal, ore, or rock.

Competent rock: rock which, because of its physical and geologic characteristics, is capable of sustaining openings without any structural support except pillars and walls left during mining (stalls, light props, and roof bolts are not considered structural support).

Compliance coal: a coal or a blend of coals that meets sulfur dioxide emission standards for air quality without the need for flue gas desulfurization.

Concretion: a volume of sedimentary rock in which mineral cement fills the spaces between the sediment grains; often ovoid or spherical in shape, although irregular shapes also occur.

Contact: the place or surface where two different kinds of rocks meet; applies to sedimentary rocks, as the contact between a limestone and a sandstone, for example, and to metamorphic rocks; and it is especially applicable between igneous intrusions and their walls.

Continuous miner: a mechanical mining machine consisting of a cutting head, a coal-gathering device, a chain conveyor with flexible loading boom, and a crawler-equipped chassis. Its function is to excavate the mineral and to load it onto shuttle cars or continuous-haulage systems. It is electrically powered, with a hydraulic subsystem for auxiliary functions. Power is supplied through a trailing cable.

Contour: a line on a map that connects all points on a surface having the same elevation.

Contour mining (contour stripping): the removal of overburden and mining from a coal seam that outcrops or approaches the surface at approximately the same elevation in steep or mountainous areas.

Core drilling: the process by which a cylindrical sample of rock and other strata is obtained through the use of a hollow drilling bit that cuts and retains a section of the rock or other strata penetrated.

Core sample: a cylinder sample generally 1–5 in. diameter drilled out of an area to determine the geologic and chemical analysis of the overburden and coal.

Cover: the overburden of any deposit.

Creep: the forcing of pillars into soft bottom by the weight of a strong roof; in surface mining, a very slow movement of slopes downhill.

Crib: a roof support of prop timbers or ties, laid in alternate cross-layers, log-cabin style; it may or may not be filled with debris and is also may be called a chock or cog.

Cribbing: the construction of cribs or timbers laid at right angles to each other, sometimes filled with earth, as a roof support or as a support for machinery.

Crop coal: coal at the outcrop of the seam; usually considered to be of inferior quality due to partial oxidation, but this is not always the case.

Crossbar: the horizontal member of a roof timber set supported by props located either on roadways or at the face.

Crosscut: a passageway driven between the entry and its parallel air course or air courses for ventilation purposes; also, a tunnel driven from one seam to another through or across the intervening measures; sometimes called *crosscut tunnel* or *breakthrough*; in vein mining, an entry perpendicular to the vein.

Cross entry: an entry running at an angle with the main entry.

Crusher: a machine for crushing rock or other materials—among the various types of crushers are the ball mill, gyratory crusher, Handsel mill, hammer mill, jaw crusher, rod mill, rolls, stamp mill, and tube mill.

Cutter, Cutting machine: a machine, usually used in coal, that will cut a 10–to 15-cm slot which allows room for expansion of the broken coal; also applies to the man who operates the machine and to workers engaged in the cutting of coal by prick or drill.

Cycle mining: a system of mining in more than one working place at a time, that is, a miner takes a lift from the face and moves to another face while permanent roof support is established in the previous working face.

Cyclone: a cone-shaped air-cleaning apparatus which operates by centrifugal separation that is used in particle collecting and fine grinding operations.

Cyclone collectors: an equipment in which centrifugal force is used to separate particulates from a gas stream.

Cyclone firing: refers to slagging combustion of coarsely pulverized coal in a cylindrical (cyclone) burner. Some wet-bottom boilers are not cyclone-fired. The primary by-product is a glassy slag referred to as boiler slag.

Demonstrated reserves: a collective term for the sum of coal in both measured and indicated resources and reserves.

Dense media (heavy media): liquids, solutions, or suspensions having densities greater than that of water.

Dense-media separation: a coal-cleaning method based on density separation, using a heavy-media suspension of fine particles of magnetite, sand, or clay.

Dense medium: a dense slurry formed by the suspension of heavy particles in water; used to clean coal.

Depleted resources: resources that have been mined; includes coal recovered, coal lost-in-mining, and coal reclassified as subeconomic because of mining.

Deposit: mineral deposit or ore deposit is used to designate a natural occurrence of a useful mineral, or an ore, in sufficient extent and degree of concentration to invite exploitation.

Depth: the vertical depth below the surface; in the case of incline shafts and boreholes it may mean the distance reached from the beginning of the shaft or hole, the borehole depth, or the inclined depth.

Descending-bed system: gravity downflow of packed solids contacted with upwardly flowing gases—sometimes referred to as *fixed-bed* or *moving-bed* system.

Detectors: specialized chemical or electronic instruments used to detect mine gases.

Detonator: a device containing a small detonating charge that is used for detonating an explosive, including, but not limited to, blasting caps, exploders, electric detonators, and delay electric blasting caps.

Development mining: work undertaken to open up coal reserves as distinguished from the work of actual coal extraction.

Devolatilization: the removal of vaporizable material by the action of heat.

Dewatering: the removal of water from coal by mechanical equipment such as a vibrating screen, filter, or centrifuge.

Diffusion: blending of a gas and air, resulting in a homogeneous mixture; blending of two or more gases.

Diffuser fan: a fan mounted on a continuous miner to assist and direct air delivery from the machine to the face.

Dilute: to lower the concentration of a mixture; in this case the concentration of any hazardous gas in mine air by addition of fresh intake air.

Dilution: the contamination of ore with barren wall rock in stopping.

Dip: the inclination of a geologic structure (bed, vein, fault, etc.) from the horizontal; dip is always measured downwards at right angles to the strike.

Dipping strata: strata which have a pronounced downdip; the strata that form either side of the typical petroleum anticline are often referred to as dipping strata.

Direct hydrogenation: hydrogenation of coal without use of a separate donor solvent hydrogenation step.

Downcast: air forced down into the mine below, by way of the airshaft which is adjacent to the escape shaft.

Dragline: an excavating machine that uses a bucket operated and suspended by means of lines or cables, one of which hoists or lowers the bucket from a boom; the other, from which the name is derived, allows the bucket to swing out from the machine or to be dragged toward the machine for loading. Mobility of draglines is by crawler mounting or by a walking device for propelling, featuring pontoon-like feet and a circular base or tub. The swing of the machine is based on rollers and rail. The machine usually operates from the highwall.

Drainage: the process of removing surplus ground or surface water either by artificial means or by gravity flow.

Draw slate: a soft slate, shale, or rock from approximately 1–10 cm thick and located immediately above certain coal seams, which falls quite easily when the coal support is withdrawn.

Drift: a horizontal passage underground. A drift follows the vein, as distinguished from a crosscut that intersects it, or a level or gallery, which may do either.

Drift mine: an underground coal mine in which the entry or access is above water level and generally on the slope of a hill, driven horizontally into a coal seam.

Drill: a machine utilizing rotation, percussion (hammering), or a combination of both to make holes; if the hole is much over 0.4 m in diameter, the machine is called a borer.

Drilling: the use of such a machine to create holes for exploration or for loading with explosives.

Dry, ash-free (daf) basis: a coal analysis basis calculated as if moisture and ash were removed.

Drying: the removal of water from coal by thermal drying, screening, or centrifuging.

Dull coal: coal that absorbs rather than reflects light, containing mostly durain and fusain lithotypes.

Dummy: a bag filled with sand, clay, etc., used for stemming a charged hole.

Dump: to unload; specifically, a load of coal or waste; the mechanism for unloading, for example, a car dump (sometimes called tipple); or, the pile created by such unloading, for example, a waste dump (also called heap, pile, tip, spoil pike).

Durain: a macroscopic coal constituent (lithotype) that is hard and dull gray in color.

Ebullating-bed reactor: a system similar to a fluidized bed but operated at higher gas velocities, such that a portion of the solids is carried out with the up-flowing gas.

Electrostatic precipitation: separation of liquid or solid particles from a gas stream by the action of electrically charged wires and plates.

Electrostatic precipitator (ESP): collection of coal combustion fly ash requires the application of an electrostatic charge to the fly ash, which then is collected on grouped plates in a series of hoppers. Fly ash collected in different hoppers may have differing particle size and chemical composition, depending on the distance of the hopper from the combustor. The ESP ash may also be collected as a composite.

Endothermic reaction: a process in which heat is absorbed.

Entrained flow system: solids suspended in a moving gas stream and flowing with it.

Entry: an entrance into a series of dugout tunnels and/or passageways in the mine below.

Equilibrium moisture: the moisture capacity of coal at 30 °C (86 °F) in an atmosphere of 95% relative humidity.

Escape shaft: a stairway reaching from the bottom of the mine to the top of the mine used in case of an emergency.

Excluded minerals: minerals that may be mined with the coal but are not an intrinsic part of the coal.

Exinite: a microscopic coal constituent (maceral) or maceral group containing spores and cuticles. Appears dark gray in reflected light.

Exothermic reaction: a process in which heat is evolved.

Exploration: the search for mineral deposits and the work done to prove or establish the extent of a mineral deposit. *Alt:* prospecting and subsequent evaluation.

Explosive: any rapidly combustive or expanding substance; the energy released during this rapid combustion or expansion can be used to break rock.

Extraction: the process of mining and removal of cal or ore from a mine.

Face: the solid unbroken surface of a coal bed that is at the advancing end of the mine workplace.

Face cleat: the principal cleavage plane or joint at right angles to the stratification of the coal seam.

Face conveyor: a conveyor used on longwall mining faces and consisting of a metal trough with an integrated return channel. Steel scrapers attached to an endless round link or roller-type chain force through the trough any material deposited inside the trough by the mining machine. Spill plates and guides for mining equipment are attached. For flexibility and ease of installation the conveyor is made up of 5-ft sections. Commonly, two electrically powered drives (one on each end) move chain, scrapers (flights), and material along.

Face supports: hydraulically powered units used to support the roof along a longwall face. They consist of plates at the roof and floor and 2–6 hydraulic cylinders that press these plates against the respective surfaces with forces of 200–800 tons.

Factor of safety: the ratio of the ultimate breaking strength of the material to the force exerted against it—if a rope will break under a load of 6000 lb, and it is carrying a load of 2000 lb, its factor of safety is 3 (6000 divided 2000).

Fall: a mass of roof rock or coal which has fallen in any part of a mine.

Fan, auxiliary: a small, portable fan used to supplement the ventilation of an individual working place.

Fan, booster: a large fan installed in the main air current, and thus in tandem with the main fan.

Fan signal: an automation device designed to give alarm if the main fan slows down or stops.

Faults: the fractures in the rock sequence along which strata on each side of the fracture appear to have moved, but in different directions; a slip-surface between two portions of the earth’s surface that have moved relative to each other; a failure surface and is evidence of severe earth stresses.

Fault zone: a fault, instead of being a single clean fracture, may be a zone hundreds or thousands of feet wide; the fault zone consists of numerous interlacing small faults or a confused zone of gouge, breccia, or mylonite.

FBC materials: unburned coal, ash, and spent bed material used for sulfur control. The spent bed material (removed as bottom ash) contains reaction products from the absorption of gaseous sulfur oxides (SO_2 and SO_3).

FGD materials: derived from a variety of processes used to control sulfur emissions from boiler stacks. These systems include wet scrubbers, spray dry scrubbers, sorbent injectors, and a combined sulfur oxide (SO_x) and nitrogen oxide (NO_x) process. Sorbents include lime, limestone, sodium-based compounds, and high-calcium coal fly ash.

Fill: typically any material that is put back in place of the extracted coal—sometimes to provide ground support.

Fine coal: coal pieces less than ½ mm in size.

Fines: the content of fine particles, usually less than c in., in a coal sample.

Firedamp: an explosive mixture of carbonaceous gases, mainly methane, formed in coal mines by the decomposition of coal.

Fissure: an extensive crack, break, or fracture in the rocks.

Fixed-bed system: *see* **Descending-bed system**.

Fixed carbon: the combustible residue left after the volatile matter is driven off. In general, the fixed carbon represents that portion of the fuel that must be burned in the solid state.

Float-and-sink analysis: separation of crushed coal into density fractions using a series of heavy liquids. Each fraction is weighed and analyzed for ash and often for sulfur content. Washability curves are prepared from these data.

Flocculants: water-soluble or colloidal chemical reagents that when added to finely dispersed suspensions of solids in water, promote the formation of flocs of the particles and their rapid settlement.

Floor: the layer of rock directly below a coal seam or the floor of a mine opening.

Flue gas desulfurization (FGD or scrubbing): the removal of sulfur oxides

Flue gas desulfurization (FGD): is removal of the sulfur gases from the flue gases (stack gases) of a coal-fired boiler—typically using a high-calcium sorbent such as lime or limestone. The three primary types of FGD processes commonly used by utilities are wet scrubbers, dry scrubbers, and sorbent injection.

Fluidity: the degree of plasticity exhibited by a sample of coal heated in the absence of air under controlled conditions, as described in ASTM Standard Test Methods D1812 and D2639.

Fluidization: *see* **fluidized-bed system**.

Fluidized-bed combustion (FBC): accomplishes coal combustion by mixing the coal with a sorbent such as limestone or other bed material. The fuel and bed material mixture is fluidized during the combustion process to allow complete combustion and removal of sulfur gases. Atmospheric FBC (AFBC) systems may be bubbling (BFBC) or circulating (CFBC). Pressurized FBC (PFBC) is an emerging coal combustion technology.

Fluidized-bed system: solids suspended in space by an upwardly moving gas stream.

Fluid temperature (ash fluid temperature): the temperature at which the coal ash becomes fluid and flows in streams.

Fly ash: airborne bits of unburnable ash that are carried into the atmosphere by stack gases; coal ash that exits a combustion chamber in the flue gas and is captured by air pollution control equipment such as electrostatic precipitators, baghouses, and wet scrubbers.

Folded strata: strata that are bent or curved as a result of permanent deformation.

Formation: any assemblage of rocks which have some character in common, whether of origin, age, or composition. Often, the word is loosely used to indicate anything that has been formed or brought into its present shape.

Fouling: the accumulation of small, sticky molten particles of coal ash on a boiler surface.

Fracture: a general term to include any kind of discontinuity in a body of rock if produced by mechanical failure, whether by shear stress or tensile stress. Fractures include faults, shears, joints, and planes of fracture cleavage.

Free moisture (surface moisture): the part of coal moisture that is removed by air-drying under standard conditions approximating atmospheric equilibrium.

Free swelling index: a measure of the agglomerating tendency of coal heated to 800 °C (1470 °F) in a crucible. Coals with a high index are referred to as coking coals; those with a low index are referred to as free-burning coal.

Friability: the tendency of coal particles to break down in size during storage, transportation, or handling; quantitatively expressed as the ratio of average particle size after test to average particle size before test, times 100.

Friable: easy to break, or crumbling naturally. Descriptive of certain rocks and minerals.

Froth flotation: a process for cleaning coal fines in which separation from mineral matter is achieved by attachment of the coal to air bubbles in a water medium, allowing the coal to gather in the froth while the mineral matter sinks.

Fusain: a black macroscopic coal constituent (lithotype) that resembles wood charcoal; extremely soft and friable. Also, US Bureau of Mines term for mineral charcoal seen by transmitted light microscopy.

Fuse: a cord-like substance used in the ignition of explosives—black powder is entrained in the cord and, when lit, burns along the cord at a set rate; a fuse can be safely used to ignite a cap, which is the primer for an explosive.

Fusinite: a microscopic coal constituent (maceral) with well-preserved cell structure and cell cavities empty or occupied by mineral matter.

Gallery: a horizontal or a nearly horizontal underground passage, either natural or artificial.

Gasification: conversion of coal to gas.

Gasification, underground (in situ gasification): a method of utilizing coal by burning in place and extracting the released gases, tars, and heat.

Gas purification: gas treatment to remove contaminants such as fly ash, tars, oils, ammonia, and hydrogen sulfide.

Gob: the term applied to that part of the mine from which the coal has been removed and the space more or less filled up with waste; also, the loose waste in a mine which is also called *goaf*.

Global climate change: usually refers to the gradual warming of the earth caused by the greenhouse effect; believed to be the result of man-made emissions of greenhouse gases such as carbon dioxide, chlorofluorocarbons (CFC) and methane, although there is no agreement among the scientific community on this controversial issue.

Goal sizes: in the coal industry, the term *5 in. to ¾ in.* means all coal pieces between 5 in. and ¾ in. at their widest point. *Plus 5 in.* means coal pieces over 5 in. in size; *1 ½ in. to 0* or *−1 ½ in.* means coal pieces 1 ½ in. and under.

Grade: a term indicating the nature of coal as mainly determined by the sulfur content and the amount and type of ash; not recommended for use in coal resource estimations; definitive statements as to the contents and types of sulfur and ash are preferable—statements indicating high, medium, or low grade are inappropriate without documentation; *see* **Quality**.

Grain: in petrology, that factor of the texture of a rock composed of distinct particles or crystals which depends upon their absolute size.

Granular bed filters: an equipment that uses a bed of a separate, closely packed solids as the separation medium.

Gravity separation: the treatment of coal particles that depends mainly on differences in specific gravity of particles for separation.

Green energy: an energy that can be extracted, generated, and/or consumed without any significant negative impact to the environment.

Grindability index: a number that indicates the ease of pulverizing a coal in comparison to a reference coal. This index is helpful in estimating mill capacity. The two most common methods for determining this index are the Hardgrove Grindability Method and Ball Mill Grindability Method. Coals with a low index are more difficult to pulverize.

Grizzly: a course screening or a scalping device that prevents oversized bulk material from entering a material transfer system; constructed of rails, bars, beams.

Ground control: the regulation and final arresting of the closure of the walls of a mined area; the term generally refers to measures taken to prevent roof falls or coal bursts.

Ground pressure: the pressure to which a rock formation is subjected by the weight of the superimposed rock and rock material or by diastrophic forces created by movements in the rocks forming the earth's crust; such pressures may be great enough to cause rocks having a low compressional strength to deform and be squeezed into and close a borehole or other underground opening not adequately strengthened by an artificial support, such as casing or timber.

Gunite: a cement applied by spraying to the roof and sides of a mine passage.

Hard coal: coal with a heat content greater than 10,260 Btu/lb. on a moist ash-free basis. Includes anthracite, bituminous, and the higher-rank subbituminous coals.

Hardgrove grindability index: the weight percent of coal retained on a No. 200 sieve after treatment as specified in ASTM Standard Test Method D409.

Haulage: the horizontal transport of ore, coal, supplies, and waste; the vertical transport of the same is called hoisting.

Haulageway: any underground entry or passageway that is designed for transport of mined material, personnel, or equipment, usually by the installation of track or belt conveyor.

Headframe: the structure surmounting the shaft which supports the hoist rope pulley, and often the hoist itself.

Heading: a vein above a drift; an interior level or airway driven in a mine; in longwall workings—a narrow passage driven upward from a gangway in starting a working in order to give a loose end.

Head section: a term used in both belt and chain conveyor work to designate that portion of the conveyor used for discharging material.

Heat of combustion, heat value: the amount of heat obtainable from coal expressed in British thermal units per pound, joules per kilogram, kilojoules or kilocalories per kilogram, or calories per gram: to convert Btu/lb to kcal/kg, divide by 1.8. To convert kcal/kg to Btu/lb, multiply by 1.8.

Heaving: applied to the rising of the bottom after removal of the coal; a sharp rise in the floor is called a *hogsback*.

Heavy media: *see* **Dense media**.

Heavy oil: a heavy coal tar fraction with distillation range usually 250–300 °C (480–570 °F), containing naphthalene and coal tar bases.

High temperature tar: the heavy distillate from the pyrolysis of coal at a temperature of about 800 °C (1470 °F).

High-volatile bituminous coal: three related rank groups of bituminous coal as defined by the American Society for Testing and Materials which collectively contain less than 69% fixed carbon on a dry, mineral-matter-free basis; more than 31% volatile matter on a dry, mineral-matter-free basis; and a heat value of more than 10,500 Btu per pound on a moist, mineral-matter-free basis.

Highwall: the unexcavated face of exposed overburden and coal in a surface mine or the face or bank on the uphill side of a contour strip mine excavation.

Highwall mining: a highwall mining system consists of a remotely controlled continuous miner which extracts coal and conveys it via augers, belt, or chain conveyors to the outside; the cut is typically a rectangular, horizontal cut from a highwall bench, reaching depths of several hundred feet or deeper.

Hogsback: a sharp rise in the floor of a seam.

Hoist: a drum on which hoisting rope is wound in the engine house, as the cage or skip is raised in the hoisting shaft.

Hoisting: the vertical transport coal or material.

Horizon: in geology, any given definite position or interval in the stratigraphic column or the scheme of stratigraphic classification; generally used in a relative sense.

Horseback: a mass of material with a slippery surface in the roof; shaped like a horse's back.

Hydraulic: of or pertaining to fluids in motion. Hydraulic cement has a composition which permits it to set quickly under water. Hydraulic jacks lift through the force transmitted to the movable part of the jack by a liquid. Hydraulic control refers to the mechanical control of various parts of machines, such as coal cutters, loaders, etc., through the operation or action of hydraulic cylinders.

Hydrocyclone: hydraulic device for separating suspended solid particles from liquids by centrifugal action. Cyclone action splits the inlet flow, a small part of which exits via the lower cone, the remainder overflowing the top of the cylindrical section. Particles are separated according to their densities, so that the denser particles exit via the cone underflow and less dense particles exit with the overflow.

Hydrogasification: reaction of carbonaceous material such as coal with hydrogen to produce methane.

Hydrogenation: chemical reaction in which hydrogen is added to a substance.

Hydrology: the science that relates to the water systems of the earth.

Hydrophilic: possessing polar surfaces that are readily wetted by water; literally, water-loving.

Hydrophobic: possessing nonpolar surfaces that are not wetted by water; literally, water-hating.

Igneous intrusions: an intrusion into another geologic formation that occurs when magma cools and solidifies before it reaches the surface; coal and associated strata may have been intruded by once molten igneous rocks forcibly injected into the sedimentary sequence from below.

Impure coal: coal having 25 wt% or more, but less than 50 wt% ash on the dry basis (ASTM, 1981; D-2796, p. 344); impure coal having more than 33 weight percent ash is excluded from resource and reserve estimates unless the coal is cleanable to less than 33 wt% ash; *see* **Bone coal**.

Inby: in the direction of the working face.

Incline: any entry to a mine that is not vertical (shaft) or horizontal (adit). Often incline is reserved for those entries that are too steep for a belt conveyor (+17° −18°), in which case a hoist and guide rails are employed. A belt conveyor incline is termed a slope. *Alt:* Secondary inclined opening, driven upward to connect levels, sometimes on the dip of a deposit; also called *inclined shaft*.

Included minerals: minerals that are part of the coal particle and matrix.

Incompetent: applied to strata, a formation, a rock, or a rock structure not combining sufficient firmness and flexibility to transmit a thrust and to lift a load by bending.

Indicated coal resources: coal for which estimates of the rank, quality, and quantity have been computed partly from sample analyses and measurements and partly from reasonable geologic projections; the points of observation are ½ to 1 ½ miles apart. Indicated coal is projected to extend as an ½ mile wide belt that lies more than ¼ mile from the outcrop or points of observation or measurement.

Indirect hydrogenation: coal is first gasified to make a synthesis gas. The gas is then passed over a catalyst to produce methanol or paraffinic hydrocarbons.

Inferred coal resources: coal in unexplored extensions of the demonstrated resources for which estimates of the quality and size are based on geologic evidence and projection; quantitative estimates are based largely on broad knowledge of the geologic character of the deposit and for which there are few, if any, samples or measurements—the estimates are based on an assumed continuity or repletion of which there is geologic evidence; this evidence may include comparison with deposits of similar type; bodies that are completely concealed may be included if there is specific geologic evidence of their presence; the points of observation are 1 ½ to 6 miles apart.

Inferred reserves (unproved reserves): the term *inferred reserves* is commonly used in addition to, or in place of, *potential reserves*.

Initial deformation temperature (ash initial deformation temperature): the temperature at which coal begins to fuse and become soft.

In situ: in the natural or original position. Applied to a rock, soil, or fossil when occurring in the situation in which it was originally formed or deposited.

Intake: the passage through which fresh air is drawn or forced into a mine or to a section of a mine.

Intermediate section: a term used in belt and chain conveyor network to designate a section of the conveyor frame occupying a position between the head and foot sections.

Immediate roof: the roof strata immediately above the coalbed, requiring support during the excavation of coal.

Isopach: a line, on a map, drawn through points of equal thickness of a designated unit. Synonym for isopachous line; isopachyte.

Jackleg: a percussion drill used for drifting or stopping that is mounted on a telescopic leg which has an extension of about 2.5 m. The leg and machine are hinged so that the drill need not be in the same direction as the leg.

Jackrock: a caltrop or other object manufactured with one or more rounded or sharpened points, which when placed or thrown present at least one point at such an angle that it is peculiar to and designed for use in puncturing or damaging vehicle tires; jackrocks are commonly used during labor disputes.

Jigs: machines that produce stratification of the particles in a bed or particles of differing densities by repeated differential agitation of the bed, the heaviest particles migrating to the lowest layer. The jigging action may be carried out in air or with the bed immersed in water or other liquids.

Job Safety Analysis (JSA): a job breakdown that gives a safe, efficient job procedure.

Joint: a divisional plane or surface that divides a rock and along which there has been no visible movement parallel to the plane or surface.

Kettle bottom: a smooth, rounded piece of rock, cylindrical in shape, which may drop out of the roof of a mine without warning. The origin of this feature is thought to be the remains of the stump of a tree that has been replaced by sediments so that the original form has been rather well preserved.

Kerf: the undercut of a coal face.

Lamp: the electric cap lamp worn for visibility; also, the flame safety lamp used in coal mines to detect methane gas concentrations and oxygen deficiency.

Layout: the design or pattern of the main roadways and workings—the proper layout of mine workings is the responsibility of the manager aided by the planning department.

Lift: the amount of coal obtained from a continuous miner in one mining cycle.

Light oil: a coal tar and coal gas fraction with distillation range between 80 and 210 °C (175–410 °F) containing mainly benzene with smaller amounts of toluene and xylene.

Lignite: a brownish-black woody-structured coal, lower in fixed carbon and higher in volatile matter and oxygen than either anthracite or bituminous coal—similar to the *brown coal* of Europe and Australia; a class of brownish-black, low-rank coal defined by the American Society for Testing and Materials as having less than 8300 Btu on a moist, mineral-matter-free basis; in the United States, lignite is separated into two groups: Lignite A (6300–8300 Btu) and lignite B (<6300 Btu).

Liquefaction: the conversion of coal into nearly mineral-free hydrocarbon liquids or low-melting solids by a process of direct or indirect hydrogenation at elevated temperatures and pressures and separation of liquid products from residue by either filtration or distillation or both.

Liquefied petroleum gas (LPG): a mixture of propane and butane.

Lithology: the character of a rock described in terms of its structure, color, mineral composition, grain size, and arrangement of its component parts; all those visible features that in the aggregate impart individuality of the rock; lithology is the basis of correlation in coal mines and commonly is reliable over a distance of a few miles.

Lithotypes: coal lithotypes represent the macrostructure of coal and are, in fact, descriptive of the coal.

Load: to place explosives in a drill hole; also, to transfer broken material into a haulage device.

Loader: a crawler-mounted unit equipped with a coal-gathering device mounted to an inclined feed plate at the front side. A chain conveyor with an articulated loading boom discharges the coal at the opposite end into shuttle cars or any other conveying systems. It is used primarily on conventionally mined room-and-pillar sections and resembles a continuous miner without the cutting head.

Loading machine: any device for transferring excavated coal into the haulage equipment.

Loading pocket: transfer point at a shaft where bulk material is loaded by bin, hopper, and chute into a skip.

Long ton: a unit of weight in the US Customary System and in the United Kingdom equal to 2240 lb (1.0160469 metric tons; 1.1200 short tons; 1016.0469 kg).

Longwall mining: a mining method in which a large rectangular section of coal is removed in one continuous operation. Equipment is installed along one side of the section (the longwall face) and the coal is removed in slices 2–4 ft thick. The excavated area behind the equipment is allowed to cave.

Loose coal: coal fragments larger in size than coal dust.

Low-Btu gas: a nitrogen-rich gas with a heat content of 100–200 Btu/ft^3 produced in gasification processes using air as the oxygen source. The air-blown form of producer gas.

Low voltage: up to and including 660 V by federal standards.

LPG: *see* **Liquefied petroleum gas**.

Maceral: microscopic petrographic units of coal.

Main entry: a main haulage road. Where the coal has cleats, main entries are driven at right angles to the face cleats.

Main fan: a mechanical ventilator installed at the surface; operates by either exhausting or blowing to induce airflow through the mine roadways and workings.

Manhole: a safety hole constructed in the side of a gangway, tunnel, or slope in which miner can be safe from passing locomotives and car. This is also called a refuge hole.

Man trip: a carrier of mine personnel, by rail or rubber tire, to and from the work area.

Manway: an entry used exclusively for personnel to travel form the shaft bottom or drift mouth to the working section; it is always on the intake air side in gassy mines. This is also, a small passage at one side or both sides of a breast, used as a traveling way for the miner, and sometimes, as an airway, or chute, or both.

Measured coal resources: coal for which estimates of the rank, quality, and quantity have been computed from sample analyses and measurements from closely spaced and geologically well-known sample sites, such as outcrops, trenches, mine workings, and drill holes. The points of observation and measurement are so closely spaced and the thickness and extent of coals are so well defined that the tonnage is judged to be accurate within 20% of true tonnage. Although the spacing of the points of observation necessary to demonstrate continuity of the coal differs from region to region according to the character of the coal beds, the points of observation are no greater than ½ mile apart. Measured coal is projected to extend as a ¼-mile wide belt from the outcrop or points of observation or measurement.

Meridian: a surveying term that establishes a line of reference. The bearing is used to designate direction. The bearing of a line is the acute horizontal angle between the meridian and the line. Azimuths are angles measured clockwise from any meridian.

Metallurgical coal: coal used in the steelmaking process to manufacture coke; metallurgical coal; an informally recognized name for bituminous coal that is suitable for making coke by industries that refine, smelt, and work with iron—other uses are space heating, blacksmithing, smelting of base metals, and power generation; generally, metallurgical coal has less than 1% sulfur and less than 8% ash on an as-received basis—most premium metallurgical coal is low- to medium-volatile bituminous coal.

Methane: a potentially explosive gas formed naturally from the decay of vegetative matter, similar to that which formed coal. Methane, which is the principal component of natural gas, is frequently encountered in underground coal mining operations and is kept within safe limits through the use of extensive mine ventilation systems.

Methane monitor: an electronic instrument often mounted on a piece of mining equipment, that detects and measures the methane content of mine air.

Microlithotypes: the microscopic analogs of the coal lithotypes and, hence, represent a part of the fine microstructure of coal; associations of coal macerals with the proviso that the *associations* should occur within an arbitrary minimum bandwidth (50 μ, 50 × 10 mm).

Middlings: coal of an intermediate specific gravity and quality.

Methanation: a process for catalytic conversion of 1 mole of carbon monoxide and 3 moles of hydrogen to 1 mole of methane and 1 mole of water.

Middle (carbolic or creosote) oil: a coal tar fraction with a distillation range of 200–270 °C (390–520 °F), containing mainly naphthalene, phenol, and cresols.

Mine development: the term employed to designate the operations involved in preparing a mine for ore extraction. These operations include tunneling, sinking, cross-cutting, drifting, and raising.

Mined land: land with new surface characteristics due to the removal of minable commodities by surface-mining methods and subsequent surface reclamation.

Mine mouth electric plant: a coal burning electric-generating plant built near a coal mine.

Miner: a person who is engaged in the business or occupation of extracting ore, coal, precious substances, or other natural materials from the earth's crust.

Mineral: an inorganic compound occurring naturally in the earth's crust, with a distinctive set of physical properties, and a definite chemical composition.

Mineral matter: the solid inorganic material in coal.

Mineral-matter-free basis: a theoretical analysis calculated from basic analytical data expressed as if the total mineral matter had been removed; used in determining the rank of a coal.

Misfire: the complete or partial failure of a blasting charge to explode as planned.

Moisture: the total moisture content of a sample customarily determined by adding the moisture loss obtained when air-drying the sample and the measured moisture content of the dried sample. Moisture does not represent all of the water present in coal, as water of decomposition (combined water) and hydration are not given off under standardized test conditions.

Molten bath gasifier: a reaction system in which coal and air or oxygen with steam are contacted underneath a pool of liquid iron, ash, or salt.

Mountain top removal (mountaintop removal): a form of surface mining in which the summit or summit ridge of a mountain is removed in order to permit easier access to coal seams; after the coal is extracted, the overburden is either put back onto the ridge to approximate the original contours of the mountain or dumped elsewhere, often in neighboring valleys; generally associated with coal mining in the Appalachian Mountain areas.

Moving-bed system: *see* **Descending-bed system**.

Mud cap: a charge of high explosive fired in contact with the surface of a rock after being covered with a quantity of wet mud, wet earth, or sand, without any borehole being used. This is also termed adobe, dobie, and sandblast (illegal in coal mining).

Multiple-seam mining: mining in areas where several seams are recovered from the same area.

Natural gas: a naturally occurring gas with a heat content over 1000 Btu/ft^3, consisting mainly of methane but also containing smaller amounts of the C_2–C_4 hydrocarbons as well as nitrogen, carbon dioxide, and hydrogen sulfide.

Natural ventilation: ventilation of a mine without the aid of fans or furnaces.

Nip: a device at the end of the trailing cable of a mining machine used for connecting the trailing cable to the trolley wire and ground.

Oil agglomeration: treatment of a suspension of fine coal particles suspended in water with a light hydrocarbon oil so that the particles are preferentially collected by the oil, which separates as a floating pasty agglomerate and can be removed by skimming. First developed as a method for recovering fine coal particles by Trent in 1914.

Open end pillaring: a method of mining pillars in which no stump is left; the pockets driven are open on the gob side and the roof is supported by timber.

Open-pit mining: surface mining, a type of mining in which the overburden is removed from the product being mined and is dumped back after mining; may refer specifically to an area from which overburden has been removed, which has not been filled.

Outby; outbye: a distance nearer to the shaft and hence farther from the working face, toward the mine entrance, and the opposite of inby.

Outcrop: an area at which a coal seam is naturally exposed at the surface.

Overburden: the earth, rock, and other materials that lie above the coal seam.

Overcast (undercast): enclosed airway which permits one air current to pass over (under) another without interruption.

Oxidized coal: bituminous coal, the properties of which have been fundamentally modified as a result of chemisorption of oxygen in the air or oxygen dissolved in groundwater. The chemisorption is a surface phenomenon rarely detectable by chemical analysis but usually detectable by petrographic examination. It reduces the affinity of coal surfaces for oil and seriously impairs coking, caking, and agglutinating properties.

Panel: a coal mining block that generally comprises one operating unit.

Panic bar: a switch, in the shape of a bar, used to cut off power at the machine in case of an emergency.

Parting: a layer or stratum of non-coal material in a coal bed which does not exceed the thickness of coal in either the directly underlying or overlying benches.

Peat: partially carbonized plant matter, formed by slow decay in water.

Percentage extraction: the proportion of a coal seam which is removed from the mine. The remainder may represent coal in pillars or coal which is too thin or inferior to mine or lost in mining. Shallow coal mines working under townships, reservoirs, etc., may extract 50%, or less, of the entire seam, the remainder being left as pillars to protect the surface. Under favorable conditions, longwall mining may extract from 80% to 95% of the entire seam. With pillar methods of working, the extraction ranges from 50% to 90% depending on local conditions.

Percussion drill: a drill, usually air powered, that delivers its energy through a pounding or hammering action.

Permissible: that which is allowable or permitted. It is most widely applied to mine equipment and explosives of all kinds that are similar in all respects to samples that have passed certain tests of the MSHA and can be used with safety in accordance with specified conditions where hazards from explosive gas or coal dust exist.

Permit: as it pertains to mining, a document issued by a regulatory agency that gives approval for mining operations to take place.

Petrography: a branch of coal petrology specifically deals with the analysis of the maceral composition and rank of coal and therefore plays an essential role in predicting coal behavior.

Petrology: the study of the organic and inorganic constituents of coal and their transformation via metamorphism.

Physical coal cleaning: a processes that employ a number of different operations, including crushing, sizing, dewatering and clarifying, and drying, which improve the quality of the fuel by regulating its size and reducing the quantities of ash, sulfur, and other impurities. In this text, the term coal cleaning is synonymous with the terms coal preparation, beneficiation, and washing.

Pick: a tool for loosening or breaking up coal or dirt consisting of a slightly curved bar at both ends and fitted onto a long handle.

Piggy-back: a bridge conveyor.

Pillar: an area of coal left to support the overlying strata in a mine; sometimes left permanently to support surface structures.

Pillar robbing: the systematic removal of the coal pillars between rooms or chambers to regulate the subsidence of the roof; also termed *bridging back the pillar*, *drawing the pillar*, or *pulling the pillar*.

Pinch: a compression of the walls of a vein or the roof and floor of a coal seam so as to *squeeze out* the coal.

Pinning: Roof bolting.

Pipeline gas: a methane-rich gas with a heat content of 950–1050 Btu/ft^3 compressed to 1000 psi.

Pit: used in reference to a specifically describable area of open-cut mining. May be used to refer to only that part of the open-cut mining area from which coal is being actively removed or may refer to the entire contiguous mined area; also used in Britain to refer to a mine.

Pit Car: a small railroad-type car approximately 6 × 3 in size, used to haul coal, dirt and rock.

Pitch: the inclination of a seam; the rise of a seam; also, the nonvolatile portion of coal tar.

Plan: a map showing features such as mine workings or geological structures on a horizontal plane.

Plasticity: a property of certain coals when heated in the absence of air. For a relative and a semiquantitative method for determining the relative plastic behavior of coal, refer to ASTM Standard Test Methods D2639 and D1812, respectively.

Pneumoconiosis: a chronic disease of the lung arising from breathing coal dust.

Portal: the structure surrounding the immediate entrance to a mine; the mouth of an adit or tunnel.

Portal bus: a track-mounted, self-propelled personnel carrier that holds 8–12 people.

Post: the vertical member of a timber set.

Potential reserves: reserves of coal that are believed to exist in the earth.

Power shovel: a large machine for digging, the digging part of which is a bucket as the terminal member of an articulated boom. Power to the bucket is supplied through hydraulic cylinders or cables.

Precision: a measure of the maximum random error or deviation of a single observation. It may be expressed as the standard error or a multiple thereof, depending on the probability level desired.

Preheating (coke making): the heating of coal in a preheating column to 180–300 °C (355–570 °F) to dry off all the moisture and leave a hot, dry fluid coal that can be charged by gravity or pipeline.

Preparation: the process of upgrading run-of-mine coal to meet market specifications by washing and sizing.

Preparation (coke making): fine grinding of coal to ensure adequate fusion of the particles. Usual practice is to grind the coal so that 65–85% will pass through a c-in. screen opening.

Preparation plant: a place where coal is cleaned, sized, and prepared for market.

Pretreatment: mild oxidation of coal to eliminate caking (agglomeration) tendencies.

Primary roof: the main roof above the immediate top. Its thickness may vary from a few to several thousand feet.

Primer (booster): a package or cartridge of explosive which is designed specifically to transmit detonation to other explosives and which does not contain a detonator.

Producer gas: mainly carbon monoxide with smaller amounts of hydrogen, methane, and variable nitrogen, obtained from partial combustion of coal or coke in air or oxygen, having a heat content of 110–160 Btu/ft^3 (air combustion) or 400–500 Btu/ft^3 (oxygen combustion).

Prop: a coal mining term for any single post used as roof support. Props may be timber or steel; if steel—screwed, yieldable, or hydraulic.

Proven reserves: coal reserves that are actually found (proven), usually by drilling and coring.

Proximate analysis: the determination by prescribed methods of moisture, volatile matter, fixed carbon (by difference), and ash; unless specified, proximate analyses do not include determinations of sulfur or phosphorous or any determinations other than those named; proximate analyses are reported by percent and on as-received, moisture-free, and moisture- and ash-free bases. Pulverized coal combustion refers to any combustion process that uses very finely ground (pulverized) coal in the process.

Pyrite: a hard, heavy, shiny, yellow mineral, iron disulfide (FeS_2), generally in cubic crystals; also called iron pyrites, fool's gold, sulfur balls—the most common sulfide found in coal mines.

Quality: an informal classification of coal relating to its suitability for use for a particular purpose. Refers to individual measurements such as heat value, fixed carbon, moisture, ash, sulfur, phosphorus, major, minor, and trace elements, coking properties, petrologic properties, and particular organic constituents. The individual quality elements may be aggregated in various ways to classify coal for such special purposes as metallurgical, gas, petrochemical, and blending use; *see* Grade.

Raise: a secondary or tertiary inclined opening, vertical or near-vertical opening driven upward form a level to connect with the level above, or to explore the ground for a limited distance above one level.

Ramp: a secondary or tertiary inclined opening, driven to connect levels, usually driven in a downward direction, and used for haulage.

Rank: a complex property of coals that is descriptive of their degree of coalification (i.e., the stage of metamorphosis of the original vegetal material in the increasing sequence peat, lignite, subbituminous, bituminous, and anthracite).

Rank of coal: the classification of coal by degree of hardness, moisture and heat content. *Anthracite* is hard coal, almost pure carbon, used mainly for heating homes. *Bituminous coal* is soft coal. It is the most common coal found in the United States and is used to generate electricity and to make coke for the steel industry. *Subbituminous coal* is a coal with a heating value between bituminous and lignite. It has low fixed carbon and high percentages of volatile matter and moisture. *Lignite* is the softest coal and has the highest moisture content. It is used for generating electricity and for conversion into synthetic gas. In terms of Btu or heat content, anthracite has the highest value, followed by bituminous, subbituminous and lignite.

Raw coal: run-of-mine coal that has been treated by the removal of tramp material, screening, or crushing.

Reclamation: the process of reconverting mined land to its former or other productive uses.

Recoverable reserves (coal): unmined coal deposits that can be removed by current technology, taking into account economic, legal, political and social variables.

Recovery: the proportion or percentage of coal or ore mined from the original seam or deposit.

Red dog: a nonvolatile combustion product of the oxidation of coal or coal refuse. Most commonly applied to material resulting from in situ, uncontrolled burning of coal or coal refuse piles. It is similar to coal ash.

Reduction ratio: the ratio between the feed top size and the product top size; the ratio between the feed and product sizes.

Regulator: a device (wall, door) used to control the volume of air in an air split.

Refined coal: *see* **Coal upgrading**.

Repeatability: the closeness of agreement between test results carried out by one person with one instrument in one laboratory.

Replicate: a measurement or observation that is part of a series performed on the same sample.

Reproducibility: the measure of agreement between test results carried out by more than one person with more than one instrument in more than one laboratory.

Reserve: that portion of the identified coal resource that can be economically mined at the time of determination. The reserve is derived by applying a recovery factor to that component of the identified coal resource designated as the reserve base.

Resin bolting: a method of permanent roof support in which steel rods are grouted with resin.

Resources: concentrations of coal in such forms that economic extraction is currently or may become feasible. Coal resources broken down by identified and undiscovered resources. Identified coal resources are classified as demonstrated and inferred. Demonstrated resources are further broken down as measured and indicated. Undiscovered resources are broken down as hypothetical and speculative.

Respirable dust: dust particles 5 μ or less in size.

Respirable dust sample: a sample collected with an approved coal mine dust sampler unit attached to a miner, or so positioned as to measure the concentration of respirable dust to which the miner is exposed, and operated continuously over an entire work shift of such miner.

Retreat mining: a system of robbing pillars in which the robbing line, or line through the faces of the pillars being extracted, retreats from the boundary toward the shaft or mine mouth.

Return: the air or ventilation that has passed through all the working faces of a split.

Return idler: the idler or roller underneath the cover or cover plates on which the conveyor belt rides after the load which it was carrying has been dumped at the head section and starts the return trip toward the foot section.

Rib: the side of a pillar or the wall of an entry. The solid coal on the side of any underground passage. Same as rib pillar.

Rider: a thin seam of coal overlying a thicker one.

Ripper: a coal extraction machine that works by tearing the coal from the face.

Rob: to extract pillars of coal previously left for support.

Robbed out area: that part of a mine from which the pillars have been removed.

Roll: (1) a high place in the bottom or a low place in the top of a mine passage, (2) a local thickening of roof or floor strata, causing thinning of a coal seam.

Roll protection: a framework, safety canopy, or similar protection for the operator when equipment overturns.

Roof: the stratum of rock or other material above a coal seam; the overhead surface of a coal working place; *see* **Back or Top**.

Roof bolt: a long steel bolt driven into the roof of underground excavations to support the roof, preventing and limiting the extent of roof falls. The unit consists of the bolt (up to 4 ft long), steel plate, expansion shell, and pal nut. The use of roof bolts eliminates the need for timbering by fastening together, or laminating, several weaker layers of roof strata to build a beam.

Roof fall: a coal mine cave-in especially in permanent areas such as entries.

Roof jack: a screw- or pump-type hydraulic extension post made of steel and used as temporary roof support.

Roof sag: the sinking, bending, or curving of the roof, especially in the middle, from weight or pressure.

Roof stress: unbalanced internal forces in the roof or sides, created when coal is extracted.

Roof support: posts, jacks, roof bolts and beams used to support the rock overlying a coal seam in an underground mine. A good roof support plan is part of mine safety and coal extraction.

Roof trusses: a combination of steel rods anchored into the roof to create zones of compression and tension forces and provide better support for weak roof and roof over wide areas.

Room-and-pillar mining: a mining method in which a designated area is divided into regular-shaped coal pillars through the parallel development of entries and cross-cuts. After the area is so developed, the remaining pillars are mined by slicing them into smaller pillars.

Room neck: the short passage from the entry into a room.

Round: planned pattern of drill holes fired in sequence in tunneling, shaft sinking, or stopping. First the cut holes are fired, followed by relief, lifter, and rib holes.

Royalty: the payment of a certain stipulated sum on the mineral produced.

Rubbing surface: the total area (top, bottom, and sides) of an airway.

Run-of-mine coal: raw coal as it leaves the mine prior to any type of crushing or preparation.

Safety fuse: a train of powder enclosed in cotton, jute yarn, or waterproofing compounds, which burns at a uniform rate; used for firing a cap containing the detonation compound which in turn sets off the explosive charge.

Safety lamp: a lamp with steel wire gauze covering every opening from the inside to the outside so as to prevent the passage of flame should explosive gas be encountered.

Safety pillar: a large unmined area left between a mining section and mine openings designated for long-term use. It is laid out to absorb the abutment loads created by the mining activity and to prevent any adverse effects on the openings designated for long-term use.

Sampling: cutting a representative part of an ore (or coal) deposit, which should truly represent its average value.

Sandstone: a sedimentary rock consisting of quartz sand united by some cementing material, such as iron oxide or calcium carbonate.

Scaling: removal of loose rock from the roof or walls. This work is dangerous and a long bar (called a scaling bar) is often used.

Scoop: a rubber tired-, battery- or diesel-powered piece of equipment designed for cleaning runways and hauling supplies.

Scrubbers: any of several forms of chemical/physical devices that remove sulfur compounds formed during coal combustion. These devices, technically known as flue gas desulfurization systems, combine the sulfur in gaseous emissions with another chemical medium to form inert sludge, which must then be removed for disposal; *see* **Flue gas desulfurization**.

Seam: underground layer of coal or other mineral of any thickness.

Secondary roof: the roof strata immediately above the coalbed, requiring support during the excavating of coal.

Section: a portion of the working area of a mine.

Selective mining: the object of selective mining is to obtain a relatively high-grade mine product; this usually entails the use of a much more expensive stopping system and high exploration and development costs in searching for and developing the separate bunches, stringers, lenses, and bands of ore.

Self-contained breathing apparatus: a self-contained supply of oxygen used during rescue work from coal mine fires and explosions; same as SCSR (self-contained self-rescuer).

Self-rescuer: a small filtering device carried by a coal miner underground, either on his belt or in his pocket, to provide him with immediate protection against carbon monoxide and smoke in case of a mine fire or explosion. It is a small canister with a mouthpiece directly attached to it. The wearer breathes through the mouth, the nose being closed by a clip. The canister contains a layer of fused calcium chloride that absorbs water vapor from the mine air. The device is used for escape purposes only because it does not sustain life in atmospheres containing deficient oxygen. The length of time a self-rescuer can be used is governed mainly by the humidity in the mine air, usually between 30 min and 1 h.

Severance: the separation of a mineral interest from other interests in the land by grant or reservation. A mineral dead or grant of the land reserving a mineral interest, by the landowner before leasing, accomplishes a severance as does his execution of a mineral lease.

Shaft: a deep vertical passage used to enter the mine below; a shaft has to be *sunk* or dug out until the vein of coal is reached. When a coal vein or layer was found, then the digging began in a mainly horizontal direction to follow the vein.

Shaft mine: an underground mine in which the main entry or access is by means of a vertical shaft.

Shale: a rock formed by consolidation of clay, mud, or silt, having a laminated structure and composed of minerals essentially unaltered since deposition.

Shale parting (shale break): typically a layer of shale in a coal seam that runs parallel to the bedding plane of the seam.

Sheave: a large pulley used to guide a cable. Sheaves at the mine were placed at the highest point of the tipple called the headframe. These sheaves guided the cables that raised and lowered the cages.

Shortwall mining: a mining method with a panel layout similar to longwall mining but at a panel width reduced by approximately 50%. It uses continuous-mining equipment for coal cutting and haulage and a specially designed hydraulic roof support.

Shovel: an excavating or coal-loading machine that uses a bucket mounted on and operated by means of a handle or dipper stick that moves longitudinally on gears and is lifted or lowered by cable. The entire machine is mounted on crawlers for mobility, and the upper structure is mounted on rollers and rail for swing or turn.

Shuttle car: a rubber-tired vehicle used to haul coal from the continuous miner or loader to a belt feeder or conveyor belt. It is usually electrically powered, with the power supplied through a trailing cable. Some new models are equipped with diesel engines.

Side slope: the slope of the sides of a canal, dam, or embankment. It is customary to name the horizontal distance first as 1.5–1.0 or frequently 1½:1, meaning a horizontal distance of 1.5–1 ft vertical.

Silicosis: a respiratory disease (fibrosis of the lung) caused by the prolonged inhalation of silica dust.

Sinking: the process by which a shaft is driven.

Skid: a track-mounted vehicle used to hold trips or cars from running out of control. Also it is a flat-bottom personnel or equipment carrier used in low coal.

Skip: a car being hoisted from a slope or shaft.

Skipjack: a triggering mechanism that causes mine cars (pit cars) to dump its load of coal or rock to a designated area at the mine.

Slack: small coal; the finest-sized soft coal, usually less than one inch in diameter.

Slag: the nonmetallic product resulting from the interaction of flux and impurities in the smelting and refining of metals.

Slag cyclone: the primary combustion chamber for a cyclone-fired boiler. Ash from the coal melts in the cyclone and is removed as a slag.

Slagging: the accumulation of coal ash on the wall tubes of a coal-fired boiler furnace, forming a solid layer of ash residue and interfering with heat transfer.

Slag pile: a significant amount of dirt and rock excavated from the earth below that is dumped into a pile.

Slate: a miner’s term for any shale or slate accompanying coal. Geologically, it is a dense, fine-textured, metamorphic rock, which has excellent parallel cleavage so that it breaks into thin plates or pencil-like shapes.

Slate bar: the proper long-handled tool used to pry down loose and hazardous material from roof, face, and ribs.

Slickenside: a smooth, striated, polished surface produced on rock by friction.

Slip: a fault. A smooth joint or crack where the strata have moved on each other.

Slope: primary inclined opening, connection the surface with the underground workings.

Slope mine: an underground mine with an opening that slopes upward or downward to the coal seam.

Slot oven: a long, narrow refractory chamber charged with coal heated in the absence of air by adjacent heating flues. Ovens are arranged in batteries with heating flues between each pair, like books on a shelf. Typical ovens are 457 mm wide, 12–15 m long, and 4–6 m high.

Sloughing: the slow crumbling and falling away of material from roof, rib, and face.

Slurry: a mixture of pulverized insoluble material and water.

Slurry pipeline: a pipeline that can transport a coal-water mixture for long distances.

Solid: mineral that has not been undermined, sheared out, or otherwise prepared for blasting.

Sounding: knocking on a roof to see whether it is sound and safe to work under.

Spad: a flat spike hammered into a wooden plug anchored in a hole drilled into the mine ceiling from which is threaded a plumbline. The spad is an underground survey station similar to the use of stakes in marking survey points on the surface. A pointer spad, or sight spad, is a station that allows a mine foreman to visually align entries or breaks from the main spad.

Span: the horizontal distance between the side supports or solid abutments along sides of a roadway.

Sparging: bubbling a gas into the bottom of a pool of liquid.

Specific energy: the energy per unit of throughput required to reduce feed material to a desired product size.

Specific gravity: the ratio of weight per unit volume of a substance to the weight of the same unit volume of water.

Splint coal: US Bureau of Mines term for durain with some vitrain and clarain and small amount of fusain.

Split: any division or branch of the ventilating current; also, the workings ventilated by one branch. Also, to divide a pillar by driving one or more roads through it.

Split coal: coal that is disturbed by layers of other geologic material, usually layers of shale.

Spoil: the overburden or non-coal material removed in gaining access to the coal or mineral material in surface mining.

Spontaneous combustion: the self-ignition of coal through oxidation under very specific conditions. Different types of coal vary in their tendency toward self-ignition.

Spragger: a person whose occupation is to apply braking to the mine cars below by means of placing wood blocks or wedges underneath the wheels to prevent them from rolling down slight grades.

Square mile-foot: the volume of coal (27,878,400 ft^3; 789,428.38 m^3; 1,032, 533.33 yd^3) that covers 1 square mile to a thickness of 1 foot; the weight of coal varies according to the rank.

Squeeze: the settling, without breaking, of the roof and the gradual upheaval of the floor of a mine due to the weight of the overlying strata.

Stack gas: the product gas evolved during complete combustion of a fuel.

Stage loader: a chain conveyor of a design similar to the face conveyor. It provides a connection between the face conveyor and the section conveyor belt.

Steeply inclined: said of deposits and coal seams with a dip of from 0.7 to 1 rad (40–60°).

Stemming: the noncombustible material used on top or in front of a charge or explosive.

Stinkdamp: a mine gas containing a high proportion of hydrogen sulfide.

Stoker firing: the combustion of coal on a grate, which may be stationary or moving.

Strike: the direction of the line of intersection of a bed or vein with the horizontal plane; the strike of a bed is the direction of a straight line that connects two points of equal elevation on the bed; also the withdrawal of labor by miners and their associates.

Strip mine: refers to a procedure of mining that entails the complete removal of all material from over the product to be mined in a series of rows or strips; this is also referred to as *open cut*, *open pit*, or *surface mine*.

Stripping: the removal of earth or non-ore rock materials as required to gain access to the ore or mineral materials wanted. The process of removing overburden or waste material in a surface mining operation.

Stripping ratio: the unit amount of spoil or waste (overburden) that must be removed to gain access to a similar unit amount of ore or mineral material.

Stump: any small pillar.

Subbituminous coal: a glossy-black-weathering and nonagglomerating coal that is lower in fixed carbon than bituminous coal, with more volatile matter and oxygen; a rank class of nonagglomerating coals having a heat value content of more than 8300 Btu's and less than 11,500 Btu's on a moist, mineral-matter-free basis—this class of coal is divisible on the basis of increasing heat value into the subbituminous C, B, and A coal groups.

Subsidence: the gradual lowering of the surface area over an extended period of time as a result of an underground excavation.

Substitute natural gas: *see* **Synthetic natural gas**.

Subsurface water: water that occurs beneath the surface of the earth in a liquid, solid, or gaseous state; consists of suspended water and groundwater.

Sulfur (total sulfur): sulfur found in coal as iron pyrites, sulfates, and organic compounds. It is undesirable because the sulfur oxides formed when it burns contribute to air pollution and sulfur compounds contribute to combustion-system corrosion and deposits.

Sulfur forms: the analytical percentage by weight of coal sulfate, pyritic, and organic sulfur.

Sump: the bottom of a shaft, or any other place in a mine, that is used as a collecting point for drainage water.

Sumping: to force the cutter bar of a machine into or under the coal. This is also called a sumping cut or sumping in.

Support: the all-important function of keeping the mine workings open. As a verb, it refers to this function; as a noun it refers to all the equipment and materials—timber, roof bolts, concrete, steel, etc.—that are used to carry out this function.

Surface mine: a mine in which the coal lies near the surface and can be extracted by removing the covering layers of rock and soil.

Surface mining: a mining method whereby the overlying materials are removed to expose the mineral for extraction; *see also* **Strip mine**.

Suspension: weaker strata hanging from stronger, overlying strata by means of roof bolts.

Sustainable energy: the provision of energy that meets the needs of the present without compromising the ability of future generations to meet their needs; sources include renewable energy sources and, in the near term because of the wealth of reserves, coal, and oil shale.

Sweetened gas: gas from which acid (sour) gases such as H_2 S and CO_2 have been removed.

Syncline: a fold in rock in which the strata dip inward from both sides toward the axis; the opposite of anticline.

Syncrude: synthetic crude oil produced by pyrolysis or hydrogenation of coal or coal extracts.

Syngas: *see* **Synthesis gas**.

Synthesis gas (syngas): approximately 2:1 molar mixture of hydrogen and carbon monoxide with varying amounts of carbon dioxide.

Synthetic (substitute) natural gas: pipeline-quality gas that is interchangeable with natural gas (mainly methane).

Tail gas: residual gas leaving a process; gas produced in a refinery and not usually required for further processing.

Tailgate: a subsidiary gate road to a conveyor face as opposed to a main gate. The tailgate commonly acts as the return airway and supplies road to the face.

Tailpiece: also known as foot section pulley. The pulley or roller in the tail or foot section of a belt conveyor around which the belt runs.

Tail section: a term used in both belt and chain conveyor work to designate that portion of the conveyor at the extreme opposite end from the delivery point. In either type of conveyor, it consists of a frame and either a sprocket or a drum on which the chain or belt travels, plus such other devices as may be required for adjusting belt or chain tension.

Tension: the act of stretching.

Ten-Wheeler: an old time train locomotive consisting of ten wheels, also referred to as a 4–6–0, four small wheels up front near the pilot (cow catcher) and six larger wheels under the middle of the loco and zero wheels at the rear or under the cab where the engineer sat.

Tertiary: lateral or panel openings (e.g., ramp, crosscut).

Through-steel: a system of dust collection from rock or roof drilling. The drill steel is hollow and a vacuum is applied at the base, pulling the dust through the steel and into a receptacle on the machine.

Timber: a collective term for underground wooden supports.

Timbering: the setting of timber supports in mine workings or shafts for protection against falls from roof, face, or rib.

Timber set: a timber frame to support the roof, sides, and sometimes the floor of mine roadways, or shafts.

Tipple: originally the place where the mine cars were tipped and emptied of their coal; still used in that sense, although now more generally applied to the surface structures of a mine, including the preparation plant and loading tracks. The tracks, trestles, screens, and so on at the entrance to a colliery where coal is screened and loaded.

Ton: a short or net ton is equal to 2000 lb; a long or British ton is 2240 lb; a metric ton is approximately 2205 lb.

Top: a mine roof; *see* **Back**.

Top size: the smallest sieve size upon which is retained a total of less than 5% w/w of a total sample.

Torque wrench: a wrench that indicates, as on a dial, the amount of torque (in units of foot-pounds) exerted in tightening a roof bolt.

Town gas: a gaseous mixture of coal gas and carbureted water gas manufactured from coal with a heat content of 600 Btu/ft^3.

Toxic spoil: acid spoil with pH below 4.0; also spoil having amounts of minerals, such as aluminum, manganese, and iron, that adversely affect plant growth.

Trace element: any element present in minute quantities, such as lead and mercury.

Trackman: person whose duty it was to lay railroad track to selected areas wherein miners could conveniently load the pit cars with coal.

Tractor: a battery-operated piece of equipment that pulls trailers, skids, or personnel carriers. This is also used for supplies.

Tram: used in connection with moving self-propelled mining equipment. A tramming motor may refer to an electric locomotive used for hauling loaded trips or it may refer to the motor in a cutting machine that supplies the power for moving or tramming the machine.

Transfer: a vertical or inclined connection between two or more levels and used as an ore pass.

Transfer point: location in the materials handling system, either haulage or hoisting, where bulk material is transferred between conveyances.

Trapper: a person, usually of a young age, who opened and closed doors down below in the mine for drivers. The doors down below were used to guide the downcast or airflow to desired areas of the mine.

Tumbling-bed gasifier: an apparatus in which coal is lifted vertically in a revolving cylinder and dropped through an axially flowing stream of oxygen and steam.

Two-stage gasification: partial gasification or pyrolysis in a first step followed by complete gasification of the resultant char in a second step.

Trip: a train of mine cars.

Troughing idlers: the idlers, located on the upper framework of a belt conveyor, which support the loaded belt. They are so mounted that the loaded belt forms a trough in the direction of travel, which reduces spillage and increases the carrying capacity of a belt for a given width.

Tunnel: a horizontal, or near-horizontal, underground passage, entry, or haulageway, that is open to the surface at both ends. A tunnel (as opposed to an adit) must pass completely through a hill or mountain.

Ultimate analysis: the analytical percentage by weight of coal carbon, hydrogen, nitrogen, sulfur, oxygen, and ash; the determination by prescribed methods of the ash, carbon, hydrogen, nitrogen, oxygen (by difference), and sulfur contents—quantities of each analyzed substance are reported by percentage for the following conditions: as-received, dried at 105 °C (221 °F), and moisture-and ash-free.

Undercut: to cut below or undermine the coal face by chipping away the coal by pick or mining machine; in some localities the terms *undermine* or *underhole* are used.

Underground mine: also known as a *deep mine*; usually located several hundred feet below the earth's surface, an underground mine's coal is removed mechanically and transferred by shuttle car or conveyor to the surface.

Underground mining: the extraction of coal or its products from between enclosing rock strata by underground mining methods, such as room and pillar, longwall, and shortwall, or through in situ gasification.

Underground station: an enlargement of an entry, drift, or level at a shaft at which cages stop to receive and discharge cars, personnel, and material. An underground station is any location where stationary electrical equipment is installed. This includes pump rooms, compressor rooms, hoist rooms, battery-charging rooms.

Undiscovered reserves: reserves that are yet to be discovered; the term and the associated *speculative data* are often used in reserve estimation.

Unit train: a long train of between 60 and 150 or more hopper cars, carrying only coal between a single mine and destination; a railway train designated to achieve economies of scale by transporting a single commodity (such as coal), loading fully and operating nonstop.

Universal coal cutter: a type of coal cutting machine which is designed to make horizontal cuts in a coal face at any point between the bottom and top or to make shearing cuts at any point between the two ribs of the place. The cutter bar can be twisted to make cuts at any angle to the horizontal or vertical.

Unproved reserves: *see* **Inferred reserves**.

Upcast shaft: a shaft through which air leaves the mine.

Valuation: the act or process of valuing or of estimating the value or worth; appraisal.

Vein(coal): a layer of coal found in the earth; the deeper the vein, the older and better quality of coal.

Velocity: the rate of airflow in lineal feet per minute.

Ventilation: the provision of a directed flow of fresh and return air along all underground roadways, traveling roads, workings, and service parts.

Violation: the breaking of any state or federal mining law.

Virgin: unworked; untouched; often said of areas where there has been no coal mining.

Vitrain: a macroscopic coal constituent (lithotype) that appear as brilliant black bands of uniform appearance and greater than 10^{-2} mm thick.

Vitrinite: a microscopic coal constituent (maceral) that appears translucent by transmitted light and gray in reflected light; termed anthraxylon when viewed by transmitted light.

Void: a general term for pore space or other openings in rock. In addition to pore space, the term includes vesicles, solution cavities, or any openings either primary or secondary.

Volatile matter: hydrogen, carbon monoxide, methane, tar, other hydrocarbons, carbon dioxide, and water obtained on coal pyrolysis; those products, exclusive of moisture, given off as gas and vapor, determined by definite prescribed methods (ASTM D2361; ASTM D3761; ASTM D3175; ASTM D3176; ASTM D3178; ASTM D3179).

Vortex flow: the whirling motion of a gas stream in a round vessel that causes separation by downward flow of solid or liquid particulates contained in the gas.

Washability analysis: a procedure used in a laboratory before preparation plant design to determine the cleaning processes to be employed and used during normal operation to evaluate the performance of the cleaning equipment and the amenability of the raw coal feed to the cleaning processes chosen.

Washout: the sudden erosion of soft soil or other support surfaces by a gush of water; if a washout occurs in a crater-like formation it is a sinkhole.

Waste: rock or mineral which must be removed from a mine to keep the mining scheme practical, but which has no value.

Water (carbureted blue) gas: a mixture of carbon monoxide and hydrogen formed by the action of air and then steam on hot coal or coke and enriched with hydrocarbon gases from the pyrolysis of oils.

Water gauge (standard U-tube): an instrument that measures differential pressures in inches of water.

Weathering: the action of air and water on coal in surface stockpiles, causing size reduction, oxidation, and decreases of any caking or coking properties.

Wedge: a piece of wood tapering to a thin edge and used for tightening in conventional timbering.

Weight: fracturing and lowering of the roof strata at the face as a result of mining operations, as in *taking weight*.

White damp: carbon monoxide, CO. A gas that may be present in the afterdamp of a gas- or coal-dust explosion, or in the gases given off by a mine fire; also one of the constituents of the gases produced by blasting. Rarely found in mines under other circumstances. It is absorbed by the hemoglobin of the blood to the exclusion of oxygen. One-tenth of 1% (0.001) may be fatal in 10 min.

Width: the thickness of a lode measured at right angles to the dip.

Winning: the excavation, loading, and removal of coal or ore from the ground; winning follows development.

Winze: secondary or tertiary vertical or near-vertical opening sunk from a point inside a mine for the purpose of connecting with a lower level or of exploring the ground for a limited depth below a level.

Wire rope: a steel wire rope used for winding in shafts and underground haulages. Wire ropes are made from medium carbon steels. Various constructions of wire rope are designated by the number of strands in the rope and the number of wires in each strand. The following are some common terms encountered: airplane strand, cable-laid rope, cane rope, elevator rope, extra-flexible hoisting rope, flat rope, flattened-strand rope, guy rope, guy strand, hand rope, haulage rope, hawser, hoisting rope, lang lay rope, lay, left lay rope, left twist, non-spinning rope, regular lay, reverse-laid rope, rheostat rope, right lay, right twist, running rope, special flexible hoisting rope, standing rope, towing hawser, transmission rope.

Working: when a coal seam is being squeezed by pressure from roof and floor, it emits creaking noises and is said to be *working*; this often serves as a warning to the miners that additional support is needed.

Working face: any place in a mine where material is extracted during a mining cycle.

Working place: from the outby side of the last open crosscut to the face.

Workings: the entire system of openings in a mine for the purpose of exploitation.

Working section: from the faces to the point where coal is loaded onto belts or rail cars to begin its trip to the outside.

COMMON CONVERSION FACTORS USED IN COAL TECHNOLOGY

To Convert	To	Multiply By
Acres	hectares	0.4047
Acres	square feet	43,560
Acres	square miles	0.001562
Acres	square feet	43,560
Acre foots	barrels	7758.0
Atmosphere	centimeters of mercury	76
Atmosphere	torr	760
Atmosphere	mm Hg	760
Atmosphere	psia	14.686
Atmosphere	inches Hg	29.91
Atmosphere	bars	1.0133
Atmosphere	feet H_2O	33.899
Barrel (oil)	US gallons	42
Barrel	cubic feet	5.6146
Barrel	lbs water @ 60 °F	350
Barrel per day	cubic centimeters/second	1.84
Btu	foot pounds	778.26

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To Convert	To	Multiply By
Btu/lb	kcal/kgm	1.8
Btu/lb	kJ/kgm	2.33
Btu/hour	horsepower	0.0003930
Btu	kilowatt-hour	0.0002931
Btu/hour	watts	0.2931
Centimeters	inches	0.3937
Centimeters	feet	0.03281
Cubic foot	cubic meters	0.0283
Cubic foot	cubic centimeters	28,317
Cubic foot	gallons	7.4805
Cubic meters	cubic feet	35.3145
Cubic meters	cubic yards	1.3079
Cubic yards	cubic meters	0.7646
Density of water @ 60 °F	gram/cubic centimeter	0.999
Density of water @ 60 °F	lb/cu ft	62.367
Density of water @ 60 °F	Lb/US gallon	8.337
Feet	meters	0.3048
Feet	miles (nautical)	0.0001645
Feet	miles (statute)	0.0001894
Gallons (US)	liters	3.7853
Gallon	cubic inches	231
Gallon	cubic centimeters	3,785.4
Gallon	cubic feet	0.13368
Grams	ounces (avoirdupois)	0.0353
Grams	pounds	0.002205
Hectares	acres	2.4710
Inches	millimeters	25.4000
Inches	centimeters	2.5400
Kilograms	pounds (avdp)	2.2046
Kilograms	pounds (troy)	2.679
Kilometers	miles	0.6214
Kilowatt-hour	Btu	3412
Liters	gallons (US)	0.2642
Liters	pints (dry)	1.8162
Liters	pints (liquid)	2.1134
Liters	quarts (dry)	0.9081
Liters	quarts (liquid)	1.0567
Meters	feet	3.2808
Meters	miles	0.0006214
Meters	yards	1.0936
Metric tons	tons (long)	0.9842

To Convert	To	Multiply By
Metric tons	tons (short)	1.1023
Miles	kilometers	1.6093
Miles	feet	5280
Miles (nautical)	miles (statute)	1.1516
Miles (statute)	miles (nautical)	0.8684
Millimeters	inches	0.0394
Ounces (avoirdupois)	grams	28.3495
Ounces (avoirdupois)	pounds	0.0625
Ounces (liquid)	pints (liquid)	0.0625
Ounces (liquid)	quarts (liquid)	0.03125
Ounces (troy)	ounces (avoirdupois)	1.09714
Pints (dry)	liters	0.5506
Pints (liquid)	liters	0.4732
Pints (liquid)	ounces (liquid)	16
Pounds (troy)	kilograms	0.3782
Pounds (avoirdupois)	kilograms	0.4536
Pound	grams	453.59
Pound	ounces	16
1 psi	kPa	6.895
Quarts (dry)	liters	1.1012
Quarts (liquid)	liters	0.9463
Quarts (liquid)	ounces (liquid)	32
Square feet	square meters	0.0929
Square kilometers	square miles	0.3861
Square meters	square feet	10.7639
Square meters	square yards	1.1960
Square miles	square kilometers	2.5900
Square mile	acres	640
Square yards	square meters	0.8361
Tons (long)	metric tons	1.016
Tons (short)	metric tons	0.9072
Tons (long)	pounds	2240
Tons (short)	pounds	2000
Torr	atmospheres	0.001316
Torr	mm Hg	1
Yards	meters	0.9144
Yards	miles	0.0005682

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