PRACTICAL BOILER WATER TREATMENT

Including Air Conditioning Systems

LEO I. PINCUS

McGraw-Hill Book Company

Practical
Boiler Water Treatment

INCLUDING AIR-CONDITIONING SYSTEMS

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Preface

The author's aim is to fill a long-felt need for a book that gives practical information on internal boiler water treatment and the treatment of circulating water in air-conditioning systems. Every effort has been made to present these subjects simply and clearly, so that the reader with a limited knowledge of water treatment can understand them.

The fundamentals of water treatment chemistry are covered in the first three chapters. A practical step-by-step outline showing how to plan and control the internal treatment of the water in boilers or air-conditioning systems is given in Chap. 4. Chapters 5 and 6 will interest those do-it-yourselfers who find it profitable to construct their own equipment or calculate for themselves their water requirements. The remainder of the book deals with practical methods for the solution of boiler water and air-conditioning-cooling-water problems.

The ideas and methods presented in this book have been tried and tested by the author during his 29 years of experience in this field. No suggestion is made that these are the only workable plans. Some are original; some have been adapted from technical literature; and some were developed from information furnished by associates in the field.

It should be stated that this book is not intended to supersede the services offered by qualified water treatment service companies or consultants. It will, however, help the user of such services to be more selective in choosing the most desirable plan for his needs.

The author wishes to express his appreciation to his associates at Water Service Laboratories for their helpful suggestions. Acknowledgment is also extended to Robert H. Marks, special projects editor of *Power* magazine, who reviewed the entire text and rendered valuable recommendations for its improvement.

Leo I. Pincus

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Practical Boiler Water Treatment

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The Chemistry of Water

Water is one of the most essential and abundant substances in nature. Three-quarters of the earth's surface is covered with water, and in the form of vapor, water is an indispensable part of the atmosphere. The chemical formula for water is H_2O or HOH. When pure it is colorless in thin layers and does not have any taste or odor.

1-1. Cycle of Water in Nature. The heat from the sun shining down on oceans, rivers, and lakes evaporates some water into the atmosphere. Wind currents carry the resulting water vapor over the land. When enough cooling takes place in the upper air the vapor condenses and precipitates as rain. Thanks to the sun and wind this process is repeated again and again.

Pure water is actually a rarity in nature. Oceans, rivers, lakes, streams, and wells—all contain various amounts of minerals picked up from the earth as well as acids and gases taken from the atmosphere. Even rain water is not completely pure. As rain falls to earth it dissolves carbon dioxide and other soluble gases present in the air. Part of this water sinks into the earth and collects in underground wells and streams. The remainder runs over the ground and finds its way back into various surface water supplies.

1-2. Water, the Universal Solvent. Water is perhaps the best-known universal solvent. Running over and through the earth it intimately mixes with the many minerals present such as limestone, salts, and gypsum. Some of these mineral solids are dissolved by the water. The mixture of water and mineral salts is called a *water solution.* Water is the solvent, and the substances dissolved in it are known as the *solute.*

1-3. Impurities in Water and Their Effect on Its Use. You have often heard it said that "One man's bread may be another man's poison." This is certainly true for all users of water. A municipality is vitally interested in delivering pure water to the community. Pure in this case means pure only to the extent that the water will not cause disease. Mineral salts or other substances in water do not have to be removed by a municipality unless they have a bearing on sanitary conditions for drinking purposes. But mineral salts are objectionable for many other important water uses, including bathing, cooking, washing clothes, generating power, heating buildings, processing materials, and manufacturing.

Water that is fit to drink can be highly corrosive to pipelines and other expensive metal equipment or can have a tendency to deposit some of its mineral salts. Mineral deposits are extremely troublesome. If not removed or prevented in the first place, they can clog pipelines, heat-exchange equipment, and boiler tubes. Scaled or corroded equipment certainly does not operate properly. Since deposits are poor conductors they impede heat transfer through metallic surfaces. Boiler explosions have been caused by excessive scale in boiler tubes. So clogging is also potentially dangerous.

Before water is put to use, all substances dissolved in the water should be carefully studied. If any are harmful some method of water treatment must be devised to avoid trouble from these particular elements.

1-4. The Basics of Chemistry. Chemistry is the study of the composition of substances, their properties, and changes in composition that can take place. To help simplify this study chemists have developed and used a language of their own. An explanation of the rudiments of this language follows to help those not well acquainted with chemistry understand the chemical terms used in water treatment.

1-5. Substance—Element—Atom. A *substance* is a particular kind of material whose specimens all show the same properties. Glass, iron, rust, gold, sugar, common salts, and water are familiar examples of substances with specific properties. The same basic substance can be used to make a variety of different objects. For example, cups, saucers, windowpanes, and microscope lenses may all be made from glass.

An *element* is a substance that cannot be decomposed into simpler substances by our present ordinary chemical methods. Familiar examples of elements are iron, copper, oxygen, gold, silver, mercury, aluminum, sulfur, and carbon. When the limit of chemical division of an element is reached, the remaining small particles are called *atoms*.

1-6. Symbols—Atomic Weight. The language of chemistry is written with *symbols*. They are the alphabet of the language. Each element or atom has a representative letter or two, such as Ca for calcium and Na for sodium (from its Latin name, natrium). For an understanding of the subject matter of chemistry it is necessary first to become familiar with all these symbols.

Each element has well-defined properties. One of these is its

Table 1-1. Common Elements, Their Symbols and Atomic Weights

Symbol	Atomic weight	Name of element	Symbol	Atomic weight	Name of element
Al	27.0	Aluminum	Fe	55.8	Iron
As	74.9	Arsenic	Mg	24.3	Magnesium
Br	79.9	Bromine	Mn	54.9	Manganese
Ca	40.1	Calcium	O	16.0	Oxygen
C	12.0	Carbon	N	14.0	Nitrogen
Cl	35.5	Chlorine	P	31.0	Phosphorus
Cu	63.6	Copper	K	39.1	Potassium
F	19.0	Fluorine	Si	28.1	Silicon
H	1.0	Hydrogen	Na	23.0	Sodium
I	126.9	Iodine	S	32.1	Sulfur

relative combining weight with other elements. Since the weight of each element in a chemical reaction does not change, the symbols also stand for a given unit weight. This can be called the *chemical unit weight* of the element. These unit weights are based upon relative combining weights of the elements and are known as *atomic weights.*

1-7. Radicals. Two elements often hold together as a group or radical during reactions, passing unchanged from one substance to another. For all practical purposes they act as a single element. This kind of grouping is called a *radical.* The unit weight of a radical equals the sum of the atomic weight of all its elements. The small subscript indicates the number of atoms of the element in the radical. For example, the unit weight of the carbonate (CO_3) radical is found by adding the atomic weight of all the carbon and oxygen present. Using Table 1-1 we find that carbon has an atomic weight of 12 and oxygen, 16. So the unit weight of the radical then equals 60 (add 12 to 16 times 3).

Table 1-2. Common Radicals, Their Symbols and Chemical Unit Weights

Symbol	Unit weight	Name of radical	Symbol	Unit weight	Name of radical
CO_3	60.0	Carbonate	OH	17.0	Hydroxide
HCO_3	61.0	Bicarbonate	PO_4	95.0	Phosphate
NO_3	62.0	Nitrate	SO_4	96.1	Sulfate
NH_4	18.0	Ammonium	SO_3	80.1	Sulfite

1-8. Compounds—Molecules. Two or more elements may combine to form a new substance or chemical *compound.* Whenever this happens the proportion by weight is always the same. The basic principle is called the law of definite or constant proportions. For example, 2 lb of hydrogen always combines with 16 lb of oxygen to form 18 lb of water. When the limit of chemical division of a compound is reached the small particles remaining are called *molecules.*

1-9. Formula—Combining Weight—Molecular Weight. *Formulas* are equivalent to words in the language of chemistry. The chemical formula for a compound is written by simply joining the symbols of two or more chemical elements which make up a compound. Symbols represent the various elements in the formula. Subfigures attached to any element stand for the number of unit weights needed for chemical combination with the other elements in the formula.

Weight relationships in a given formula do not change. The sum of the atomic weight of each element multiplied by its attached subfigure gives the formula weight. This is the *molecular weight* of the compound. For example, the formula for water is H_2O. This means that two atoms of hydrogen (atomic weight 1) unite with one atom of oxygen (atomic weight 16) to form one molecule of water with a molecular weight of 18. The *combining-weight* relationship is then 2 parts of hydrogen to 16 of oxygen to form 18 of water. This ratio holds whether the quantities are measured in pounds, ounces, grams, or chemical unit weights. It can be checked by burning 2 lb of pure hydrogen in an unlimited supply of pure oxygen. Only 16 lb of oxygen will react to produce 18 lb of water.

1-10. Valence. Chemistry would be quite a cumbersome science if we had to compute all these weight relationships every time a formula is written. To simplify the matter, hydrogen and chlorine are taken as the base elements. The combining power of all elements is then compared with these two base elements in whole number units, either equal to or greater than 1. This number is called the *valence* of the element or radical. Valence is, therefore, a whole number that tells how many atoms of hydrogen or chlorine will combine with or displace one atom of the given element.

Not all elements combine with each other. The atom itself is a small planetary universe, containing electrically charged particles called *protons* and *electrons*. The way in which these electrically charged particles are combined within the atom determines whether another atom is attracted or repelled. The valence assigned to some elements is positive and others have a negative value. Two atoms with the same valence or electrical charge will repel each other. They will not form compounds. But a positive-valence atom is attracted to an atom with a negative valence. They will combine to form a new compound.

Table 1-3. Valence of Elements and Radicals

Valence of 1		Valence of 2		Valence of 3		Valence of 4
Plus	Minus	Plus	Minus	Plus	Minus	Plus and minus
H	OH	Ca	O	Fe	PO_4	C
Na	NO_3	Fe	SO_4	Al	N in NH_3	Si
NH_4	Cl	Mg	SO_3	Cr	As in AsH_3	
Ag	I	Zn	CO_3	Sb		
Hg	ClO_3	Cu	S			

NOTE: Some elements have more than one valence and may also be both positive and negative.

In certain cases a number of elements have more than one valence. But do not let this confuse you. It is possible for an atom of iron to combine with three atoms of chlorine. But this does not mean that maximum combining capacity is exercised for all compounds of iron. Iron may combine with two atoms of chlorine. To use an analogy, a man may have $3 in his pocket, but this does not mean that he has to spend it all at once.

It is easy to write a chemical formula when the charge and valence of the element or radical are known. Here are the rules:

1. Write the positive symbols first.

2. When a positive atom or radical combines with a negative element of the same valence, the formula is simply written by joining the symbols without subfigures.

Formula	*Valence of positive and negative elements*
NaCl	1
$CaCO_3$	2
$AlPO_4$	3

3. Now take the case of a positive element or radical combining with a negative element or radical of different valence. Just place a

small subfigure to the right of the element or radical showing the number of atoms of lower valence needed to combine with the atoms of higher valence.

Element	Valence	Radical	Valence	Combined formula
Na	1	CO_3	2	Na_2CO_3
Ca	2	Cl	1	$CaCl_2$

Table 1-4 gives the formulas of various common chemical compounds of interest to those studying water-conditioning problems.

Table 1-4. Molecular Weights and Formulas of Common Chemicals

Chemical name	Molecular weight	Chemical formula
Sodium chloride	58.5	NaCl
Calcium carbonate	100.1	$CaCO_3$
Magnesium carbonate	84.3	$MgCO_3$
Sodium carbonate	106.0	Na_2CO_3
Sodium bicarbonate	84.0	$NaHCO_3$
Sodium sulfate	142.1	Na_2SO_4
Sodium hydroxide	40.0	NaOH
Calcium hydroxide	74.1	$Ca(OH)_2$
Magnesium hydroxide	58.3	$Mg(OH)_2$
Sodium nitrate	85.0	$NaNO_3$
Trisodium phosphate	164.0	Na_3PO_4
Disodium phosphate	142.0	Na_2HPO_4
Monosodium phosphate	120.0	NaH_2PO_4
Sodium silicate	122.1	Na_2SiO_3
Calcium silicate	116.1	$CaSiO_3$
Magnesium silicate	100.4	$MgSiO_3$
Calcium chloride	111.0	$CaCl_2$
Magnesium chloride	95.2	$MgCl_2$
Calcium bicarbonate	162.1	$Ca(HCO_3)_2$
Magnesium bicarbonate	146.3	$Mg(HCO_3)_2$
Aluminum chloride	133.3	$AlCl_3$
Aluminum sulfate	342.1	$Al_2(SO_4)_3$

1-11. Equations. In the language of chemistry equations are equivalent to sentences. The combination of symbols and formulas in an equation is the way that the chemist expresses his ideas about chemical changes or reactions. These equations show the reacting substances, products formed, and relative weights involved. But they do not specify all the conditions necessary for reaction, nor do they tell how rapidly or to what extent the reaction takes place.

1-12. Balancing Equations. Remember when writing chemical equations for the usual reaction that matter is neither created nor destroyed. So the relative number of molecules of reacting substances should equal the relative number of molecules of the products formed. This means that every equation must be balanced to correctly indicate the relative number of molecules involved.

For example, it is well known that carbon burns in air or oxygen. The product of this burning is carbon dioxide. Now let us write the equation for this in chemical symbols. The oxygen molecule is always represented as O_2.

$$C + O_2 = CO_2 \text{ (completely balanced)} \tag{1-1}$$

This equation is already in balance. It tells us that one atom of carbon reacts with two atoms of oxygen (left side of the equation) to form carbon dioxide (right side of the equation). The carbon dioxide contains one atom of carbon and two atoms of oxygen. This equals the amount found on the left side of the equation. The equation also reveals that 12 g (pounds, ounces, molecular, or other unit weights) of carbon reacts with 32 g of oxygen to form 44 g of carbon dioxide. (See Table 1-1, Common Elements, Their Symbols and Atomic Weights.)

Hydrogen burning in air is another example of a common chemical reaction. The product formed in this case is water. The hydrogen molecule is always written as H_2. Here is how the equation is written with chemical symbols.

$$H_2 + O_2 = H_2O \text{ (unbalanced)} \tag{1-2}$$

This equation is not balanced. There are two atoms of oxygen on the left side and only one atom of oxygen on the right side. The first step in adjusting this inequality is to prefix a 2 to the H_2O molecule on the right side of the equation. The oxygen molecules on both sides are now in balance.

$$H_2 + O_2 = 2H_2O \text{ (partially balanced)} \qquad (1\text{-}3)$$

But the over-all equation is still not in complete balance. There are still four hydrogen atoms on the right and only two hydrogen atoms on the left. Next prefix a 2 to the H_2 on the left side.

$$2H_2 + O_2 = 2H_2O \text{ (completely balanced)} \qquad (1\text{-}4)$$

There are now four hydrogen atoms and two oxygen atoms on each side, which brings the equation into complete balance.

1-13. Meaning of Equations. Equations represent many diversified ideas. To the chemist interested in manufacture or development of new products, equations represent the reactions needed to synthesize a new substance. To an engineer involved in maintaining desired chemical conditions in a process, equations stand for optimum conditions, the quantity of chemicals needed, or the results of chemical analysis.

Analytical chemistry uses equations to express the results of a chemical analysis. This branch of chemistry is subdivided into two main classes. The first is qualitative analysis to determine the presence or absence of any elements or group of elements. The second is quantitative analysis to find the amounts of each chemical element or group present.

1-14. Acids, Bases, and Salts. Most of the substances found in water are from the mineral kingdom and the study of these substances is classified as *inorganic chemistry*. In this field all substances fall into three main classifications: *acids*, *bases*, and *salts*.

All acids contain hydrogen, although not all hydrogen compounds are acids. Acid solutions in water ordinarily taste sour, release carbon dioxide from carbonates, and react with most metals to displace hydrogen. This last property of an acid solution often explains why metal equipment is severely corroded by one water supply and not affected by another. An acid water supply, of course, is the more corrosive. Here are some typical reactions of acids with other substances:

$2HCl$	+	$CaCO_3$	=	$CaCl_2$	+	H_2O	+	CO_2
Hydrochloric acid		Calcium carbonate		Calcium chloride		Water		Carbon dioxide
$2HCl$	+	Fe	=	$FeCl_2$	+	H_2		
Hydrochloric acid		Iron		Ferrous chloride		Hydrogen		

Bases or alkalies are compounds of a metal with oxygen and hydrogen. They will neutralize acids. The reaction between an acid and a base forms a salt. The other product is water. But remember that salts are also formed in several other ways.

Table 1-5. Common Acids, Bases, and the Salts They Form

Base		*Acid*		*Salt*		*Water*
$NaOH$	+	HCl	=	$NaCl$	+	HOH
Sodium hydroxide		Hydrochloric acid		Sodium chloride		
$Ca(OH)_2$		H_2SO_4	=	$CaSO_4$	+	$2HOH$
Calcium hydroxide		Sulfuric acid		Calcium sulfate		
KOH	+	HNO_3	=	KNO_3	+	HOH
Potassium hydroxide		Nitric acid		Potassium nitrate		

1-15. Ions and Ionic Theory. The quick and easy exchange of radicals and elements in a water solution indicates that acids, bases, and salts decompose into radicals as soon as they are dissolved. Pure water itself is a poor conductor of electricity. But a water solution containing an acid, base, or salt is a very good conductor. From this we deduce that acids, bases, and salts in water solution dissociate into atoms or groups of atoms carrying charges of electricity. These electrically charged atoms are called *ions.* They have either a negative or a positive charge. Even the water itself dissociates slightly into hydrogen and hydroxyl ions.

In terms of the *ionic theory* an acid is any substance that yields hydrogen ions in a water solution. And a base is any substance that yields hydroxyl ions (OH) in the water. This theory makes it easy to follow most chemical reactions in water. For example, under the right conditions, the following mineral salts found in many natural water supplies form scale on industrial equipment.

$$Ca(HCO_3)_2 \qquad CaSO_4 \qquad Mg(HCO_3)_2 \qquad MgSO_4$$

In a water solution these compounds will ionize to yield:

Ca (calcium ions with two positive charges)
Mg (magnesium ions with two positive charges)
HCO_3 (bicarbonate ions with one negative charge)
SO_4 (sulfate ions with two negative charges)

Some of the harmful ions can be removed by chemical treatment. The chemicals below react with these minerals to form a compound which is practically insoluble in water.

NaOH	Na_2CO_3	Na_3PO_4
Caustic soda	Soda ash	Trisodium phosphate

When dissolved in water they produce four different ions:

Na (sodium ions with one positive charge)
OH (hydroxyl ions with one negative charge)
CO_3 (carbonate ions with two negative charges)
PO_4 (phosphate ions with three negative charges)

The positive sodium ion of the treating chemical reacts with the negative radical of the scale-forming salt in the water. The negative radical of the treating chemical then reacts with the positive radical of the scale-forming compound. This ionic exchange takes place immediately. As a result the scale-forming compound is destroyed and a harmless salt generally takes its place.

1-16. Common Chemical Ionic Reactions in Water Treatment. Ionic reactions that take place when water is heated:

$$\begin{aligned} Ca(HCO_3)_2 + \text{heat} &= CaCO_3 + H_2O + CO_2 \\ Mg(HCO_3)_2 + \text{heat} &= MgCO_3 + H_2O + CO_2 \\ 2NaHCO_3 + \text{heat} &= Na_2CO_3 + H_2O + CO_2 \\ Na_2CO_3 + H_2O + \text{heat} &= 2NaOH + CO_2 \end{aligned}$$

(boiling under pressure)

Ionic reactions when soda ash and caustic soda are added to water:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$
$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$

Ionic reactions of soda ash and caustic soda with phosphates:

$$Na_2CO_3 + 2Na_2HPO_4 = 2Na_3PO_4 + H_2O + CO_2$$
$$Na_2CO_3 + NaH_2PO_4 = Na_3PO_4 + H_2O + CO_2$$
$$NaOH + Na_2HPO_4 = Na_3PO_4 + H_2O$$
$$2NaOH + NaH_2PO_4 = Na_3PO_4 + 2H_2O$$

Ionic reactions when trisodium phosphate is added to water:

$$3Ca(HCO_3)_2 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 6NaHCO_3$$
$$3Mg(HCO_3)_2 + 2Na_3PO_4 = Mg_3(PO_4)_2 + 6NaHCO_3$$
$$3CaCO_3 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3Na_2CO_3$$
$$3MgCO_3 + 2Na_3PO_4 = Mg_3(PO_4)_2 + 3Na_2CO_3$$
$$3CaSO_4 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3Na_2SO_4$$
$$3MgSO_4 + 2Na_3PO_4 = Mg_3(PO_4)_2 + 3Na_2SO_4$$

2

The Chemical Examination of Water

2-1. Common Analytical Methods. There are four principal methods commonly used for the chemical examination of water. These methods are classified as (1) gravimetric, (2) volumetric, (3) colorimetric, and (4) turbidimetric.

Gravimetric Analysis. This method is based on the exact separation and weighing of a compound of the desired element. A highly sensitive analytical balance must be used. In general the procedure is tedious, time-consuming, and beyond the scope of anyone but a well-trained analyst. Other methods are much simpler and more easily adaptable for use in plant chemical control.

Volumetric Analysis. In volumetric analysis chemical reagents are added in the form of *standard solutions* to avoid weighing minute quantities of chemical. Standard solution is added from a measuring burette to a given volume of the water under test. The volume of the water sample will vary with the test and may be 25, 50, or 100 ml. The burette is a long, narrow, graduated, cylindrical glass container. It has a glass cock at the bottom to control the dropping of measured amounts of the known standard solution into the water sample under test. This procedure is known as *titration*. Usually the first step is to add a few drops of a specific color indicator to the water. Then the titration is carried out by slowly adding standard solution until the indicator reveals a definite visual change in the sample. This is known as the *end point* of the titration. It is the point at which an equivalent amount of known standard solution has been added to a measured amount of the water sample. Each fraction of a milliliter used in the titration is proportional to the unknown amount of a particular ion in the water. Since strength of the standard solution is known, concentration of this ion in the sample is easily obtained. Just multiply the burette reading by the correct chemical factor. Figure 2-1 shows the equipment needed for a typical titration.

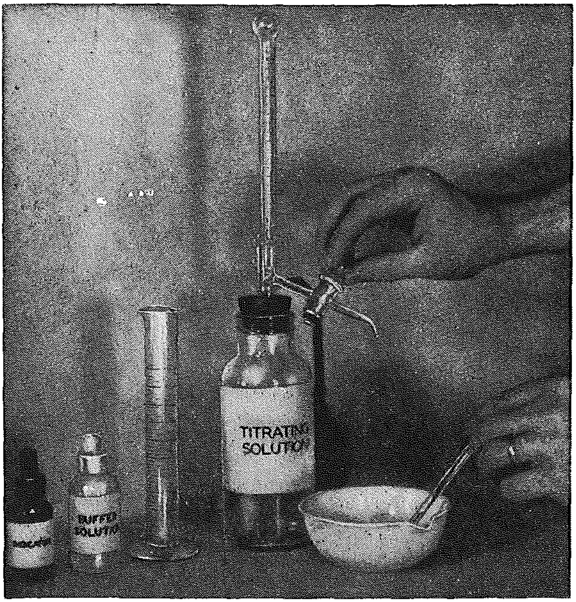


FIG. 2-1. Using a measuring burette, chemist titrates sample to violet-blue end point. Water sample is in the porcelain casserole. Graduated cylinder, buffer solution, and indicator complete the materials needed to run test. (*Courtesy of* Power *magazine.*)

EXAMPLE 1. Determine how much alkalinity is present in a sample of water. Test equipment available includes a burette containing 0.05 *N* sulfuric acid (known-strength solution) and methyl orange indicator.

First add two drops of the methyl orange indicator to a 25-ml sample of the water under test. The solution will turn yellow. Now slowly add the 0.05 *N* sulfuric acid solution, constantly stirring, until the faintest pink coloration appears in the water sample. This indicates the end point of the reaction. Under these conditions, alkalinity in parts per million calcium carbonate equals the total milliliters of 0.05 *N* sulfuric acid consumed, multiplied by 100.

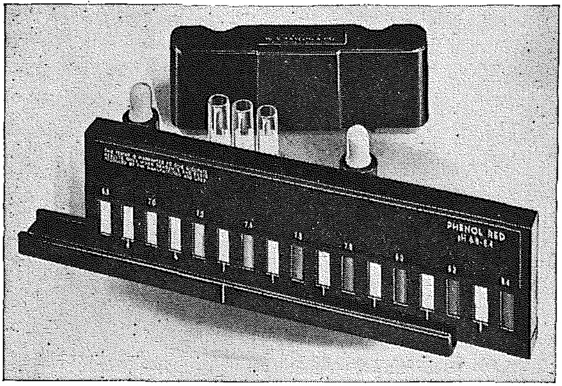


FIG. 2-2. Basic pH slide comparator outfit consisting of base and slide, two vials of indicator solution with 0.5-ml pipettes, five 5-ml test tubes, brush, and instructions. The pH of specially prepared water sample is obtained by color-matching it with the various test samples. (*Courtesy of W. A. Taylor & Co.*)

Colorimetric Analysis. Colorimetric methods of analysis are based on the fact that small amounts of specific chemical reagents added to a given volume of water will develop color. This color is proportional to the unknown amount of chemical in the water. Various color standards representing known chemical concentrations are available. These are visually compared with the colored sample. The concentration in the sample equals that of the matching standard. To simplify the matching operation and do away with the tedious work of making up known color standards, various instruments have been designed to indicate a color reading on a graduated scale. These instruments, called *colorimeters*, are ideal for colorimetric analysis. Figure 2-2 shows a comparator outfit employed to determine pH.

Table 2-1. Minimum Equipment Needed for Volumetric Analysis

Equipment	Size	Purpose
Graduated cylinders or pipettes	10 to 100 ml	Measuring out water samples
Erlenmeyer flasks, beakers, or porcelain casseroles	100 to 250 ml	Holding water samples
Burettes, plain or automatic	10 to 50 ml	Dispensing standard chemical solutions
Filter paper, glass funnels, wooden funnel support	12.5 to 18.5 cm	Filtering samples of water
Clamps and ring stands	Standard	Holding plain burettes or wooden funnel racks
Stirring rods, fused at both ends	4 in. long	Mixing water samples in casserole or beaker during titration

Turbidimetric Analysis. Turbidimetric methods of analysis make use of the fine precipitate formed when small amounts of specific reagents are added to a given volume of water. The amount of precipitate formed is proportional to the unknown concentration of the desired ion. Since light passing through the solution is obstructed by this precipitate, it gives a quantitative measure of the amount of precipitate present. Various special instruments called *turbidimeters* are used to obtain quickly turbidimetric measurements on water samples.

2-2. Setting Up a Plant Laboratory. The great majority of industrial-plant operators realize that control by proper water testing is the key to efficient water conditioning. They fully understand that it is to their advantage to make as many water control tests as possible. Since relatively few plants have complete or extensive laboratory facilities, outside analytical work is usually needed. One good arrangement is to delegate responsibility for the water treatment program to one individual. This person can then be authorized to send water samples to an outside laboratory at regular intervals to supplement the plant test work.

When investigating the actual needs of a water-testing laboratory you will find a large variety of glassware, chemical reagents, and equipment available from the many scientific and chemical supply houses. There are also many special test kits in both portable and cabinet form. In setting up the plant laboratory, get the advice of an experienced chemist. Give serious consideration to the purchase of complete test kits before trying to assemble reagents and chemical apparatus piecemeal. These kits are both compact and convenient to use. When colorimetric or turbidimetric procedures are required, be sure to make use of the many special testing outfits designed for each individual test. They are very easy to operate, are reasonable in cost, and come

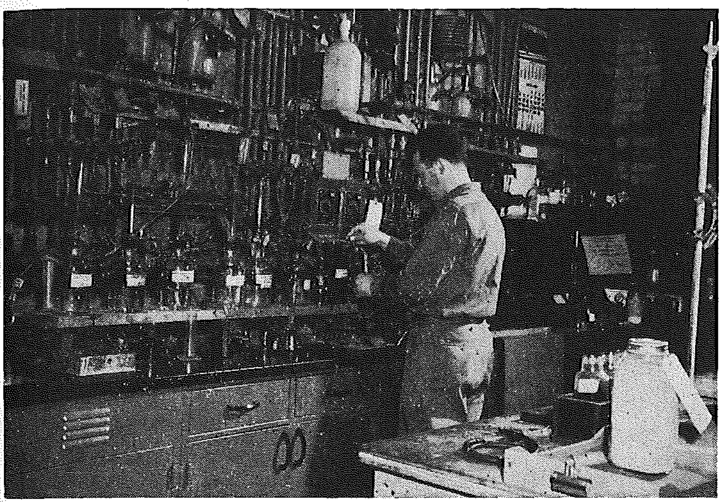


FIG. 2-3. Water-treating room at a large power plant features complete laboratory receiving sample lines from various parts of the plant. (*Courtesy of Consolidated Edison Company of New York.*)

complete with reagents and step-by-step operating instructions. Most of the simpler test procedures for plant control are based on volumetric methods. Reagents and apparatus needs vary with each specific test. But volumetric tests in general call for the items listed in Table 2-1, Figure 2-3 shows a very complete water-testing laboratory used by a large public utility. At the other end of the scale are portable test sets, such as that shown in Fig. 2-4 designed to make all the normal tests required for boiler feed water. A portable testing outfit of the colorimetric type is shown in Fig. 2-5.

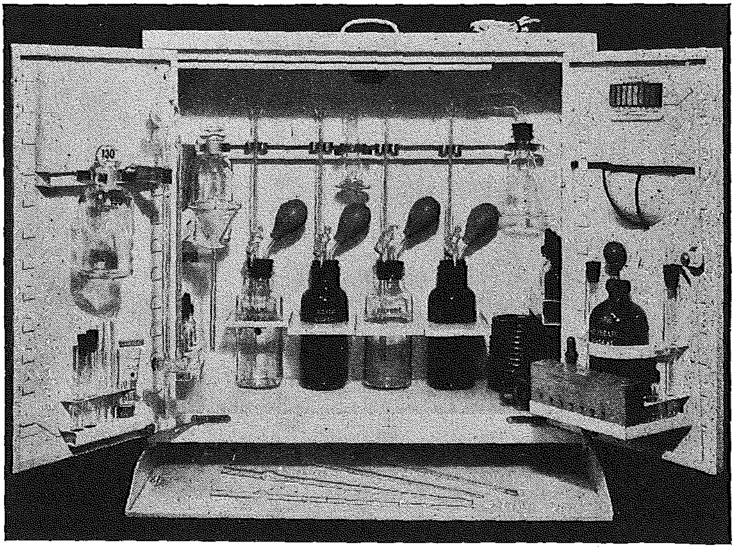


FIG. 2-4. Portable cabinet test set for boiler water analysis including pH, phosphate, hardness, alkalinity, chlorides, sulfite, and dissolved oxygen. (*Courtesy of TruTest Laboratories, Inc.*)

2-3. Expressing the Results of a Chemical Analysis. The same test results can be reported in various ways. The method used depends upon the application of the analytical results and perhaps the personal preferences of the chemist. Some of these methods are illustrated in Tables 2-2 to 2-4. The various terms used in these tables will be defined in detail later in the chapter. Note that seemingly different analyses may actually represent water with the same chemical composition.

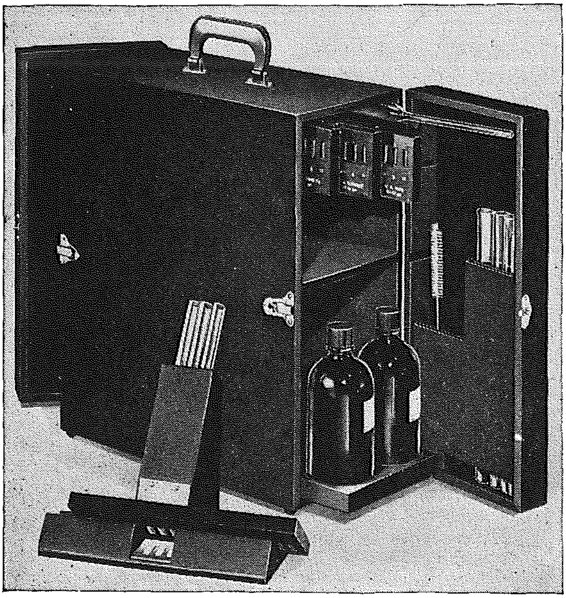


Fig. 2-5. Portable water analyzer case complete with water analyzer base, slides, and accessories. Determinations are made colorimetrically by placing the prepared sample in the middle tube and moving the slide until a color match is obtained. (*Courtesy of W. A. Taylor & Co.*)

If left to his own discretion any chemist or technician analyzing a water sample can report the results of this analysis to suit his own convenience. Of course the units and forms of expression used must be consistent for any given analysis. This can be very confusing to anyone not well versed in water chemistry and unfamiliar with the different methods of expression in common use. Several technical groups have tried to clarify this by setting standards for recording the results of water analyses. These standards have been set by the American Public Health Association (APHA),

Table 2-2. Ionic Form.
Individual Metal and Acid Radicals Reported in the Form of Ions as They Exist in Water

Ions	Ppm	Gpg	Epm
Calcium, Ca	19	1.1	0.95
Magnesium, Mg	7	0.4	0.57
Sodium, Na	3	0.2	0.13
Bicarbonate, HCO_3	62	3.6	1.02
Sulfate, SO_4	22	1.3	0.46
Chloride, Cl	6	0.3	0.17
Silica, SiO_2	2	0.1	0.07

Table 2-3. Modified Ionic Form.
Calcium, Magnesium, and Bicarbonate Ions Reported as Equivalent Calcium Carbonate

Water analysis	*Ppm*
Total hardness as $CaCO_3$	77
Calcium hardness as $CaCO_3$	48
Magnesium hardness as $CaCO_3$	29
Alkalinity as $CaCO_3$	51
Sulfates as SO_4	22
Chlorides as Cl	6
Silica as SiO_2	2

Table 2-4. Hypothetical or Probable Combinations

Water analysis	*Gpg*
Calcium bicarbonate, $Ca(HCO_3)_2$	4.5
Magnesium bicarbonate, $Mg(HCO_3)_2$	0.2
Magnesium sulfate, $MgSO_4$	1.6
Magnesium chloride, $MgCl_2$	0.1
Sodium chloride, NaCl	0.5
Silica, SiO_2	0.1

the American Chemical Society (ACS), and the American Society of Testing Materials (ASTM). Test procedures and the calculation of results that appear throughout this book are in accordance with the accepted standards of these societies.

2-4. Units of Concentration. The amounts of mineral constituents usually found in water are extremely small. In fact, on a percentage basis the amount of mineral present is much less than 1 per cent. This is the main reason why water analysis results must be expressed in other ways that are more descriptive for such small quantities.

Parts per Million (*PPM*). The most general accepted method for expressing unit concentration of a chemical in water analysis is in parts per million. One part per million means that one unit weight of a substance is dissolved in one million of the same weight units of water. For example, one ounce in one million ounces of water, one gram in one million grams of water, and one pound in one million pounds of water are all equal to one part per million. But one pound of a substance in one million gallons of water is *not* equal to one part per million since the units of pounds and gallons are not the same. Reporting analyses in parts per million simplifies calculations and comparison with data published in water treatment literature.

Grains per U.S. Gallon (*GPG*). In the past this unit was very popular when the results of water analysis were reported for industrial use. Some older laboratories still prefer to record their analyses in these terms. But it is now almost common practice to use the more convenient parts per million unit. One grain per U.S. gallon equals 17.1 ppm. To convert grains per U.S. gallon to parts per million, multiply by 17.1. To convert parts per million to grains per U.S. gallon, divide by 17.1.

Equivalents per Million (*EPM*). This unit is not generally encountered in ordinary plant control work, but it is frequently used by trained water chemists. The unit equivalents per million facilitates any chemical calculations needed to determine the amount of the various water-treating chemicals used in a water-conditioning process. The unit is also a useful tool when checking accuracy of a complete water analysis. The equivalent or chemical combining weight of a compound, element, or radical is the molecular weight of that substance divided by the valence. The concept of valence has been covered in Chap. 1. The concentration in equivalents per million is easy to obtain. Just divide concentration in parts per million by the chemical equivalent weight. Table 2-5 is very handy in making this conversion. It gives the

Table 2-5. Conversion Factors.
Formulas, Molecular Weights, and Equivalent Weights

Chemical name	Chemical formula	Molecular weight	Equivalent weight
Cations:			
Aluminum	Al	27.0	9.0
Ammonium	NH_4	18.0	18.0
Barium	Ba	137.4	68.7
Calcium	Ca	40.1	20.0
Copper	Cu	63.6	31.8
Hydrogen	H	1.008	1.0
Magnesium	Mg	24.3	12.2
Sodium	Na	23.0	23.0
Anions:			
Bicarbonate	HCO_3	61.0	61.0
Carbonate	CO_3	60.0	30.0
Chloride	Cl	35.5	35.5
Hydroxide	OH	17.0	17.0
Nitrate	NO_3	62.0	62.0
Phosphate-tribasic	PO_4	95.0	31.7
Phosphate-dibasic	HPO_4	96.0	48.0
Phosphate-monobasic	H_2PO_4	97.0	97.0
Sulfate	SO_4	96.1	48.0
Sulfite	SO_3	80.1	40.0
Compounds:			
Aluminum sulfate	$Al_2(SO_4)_3$	342.1	57.0
Aluminum hydroxide	$Al(OH)_3$	78.0	26.0
Sodium aluminate	$Na_2Al_2O_4$	163.9	27.3
Barium sulfate	$BaSO_4$	233.4	116.7
Calcium bicarbonate	$Ca(HCO_3)_2$	162.1	81.1
Calcium carbonate	$CaCO_3$	100.1	50.0
Calcium chloride	$CaCl_2$	111.0	55.5
Calcium hydroxide	$Ca(OH)_2$	74.1	37.1
Calcium sulfate	$CaSO_4$	136.1	68.1
Calcium phosphate	$Ca_3(PO_4)_2$	310.3	51.7
Magnesium bicarbonate	$Mg(HCO_3)_2$	146.3	73.2
Magnesium carbonate	$MgCO_3$	84.3	42.2
Magnesium chloride	$MgCl_2$	95.2	47.6
Magnesium hydroxide	$Mg(OH)_2$	58.3	29.2
Magnesium phosphate	$Mg_3(PO_4)_2$	262.9	43.8

Table 2-5. Conversion Factors (continued).
Formulas, Molecular Weights, and Equivalent Weights

Chemical name	Chemical formula	Molecular weight	Equivalent weight
Compounds *Cont.:*			
Magnesium sulfate	$MgSO_4$	120.4	60.2
Silica	SiO_2	60.1	30.0
Sodium bicarbonate	$NaHCO_3$	84.0	84.0
Sodium carbonate	Na_2CO_3	106.0	53.0
Sodium chloride	NaCl	58.5	58.5
Sodium hydroxide	NaOH	40.0	40.0
Sodium nitrate	$NaNO_3$	85.0	85.0
Trisodium phosphate	$Na_3PO_4 \cdot 12H_2O$	380.2	126.7
Disodium phosphate	Na_2HPO_4	142.0	47.3
	$Na_2HPO_4 \cdot 12H_2O$	358.2	119.4
Sodium sulfate	Na_2SO_4	142.1	71.0
Water	H_2O	18.0	9.0

formula, molecular weight, and equivalent weight of all the common substances usually encountered in water chemistry.

If the chemical analysis of a water sample is correct, the sum of cations in equivalents per million approximately equals the sum of the anions in equivalents per million. Comparing these sums gives a quick check on the accuracy of the analysis. When this check is made, silica, iron, and other constituents that occur in small amounts are usually not taken into consideration.

EXAMPLE 2. In Table 2-2 the individual cation and anion components are tabulated. These data can be used to check whether or not the analysis is substantially correct.

Cations		*Anions*	
Ca	0.95	HCO_3	1.02
Mg	0.57	SO_4	0.46
Na	0.13	Cl	0.17
	1.65		1.65

The sum of the cations (1.65) equals the sum of the anions. Therefore, the analysis is correct.

Pounds per Thousand Gallons (*lb per 1,000 gal*). This is a very practical unit of measurement. Most water-conditioning processes are continuous and the chemical doses added to the water are usually computed in terms of the pounds necessary to treat 1,000 gal of water. The equivalent of 120 ppm is one pound per thousand gallons. To convert parts per million to pounds per thousand gallons, divide by 120. To convert pounds per thousand gallons to parts per million, multiply by 120.

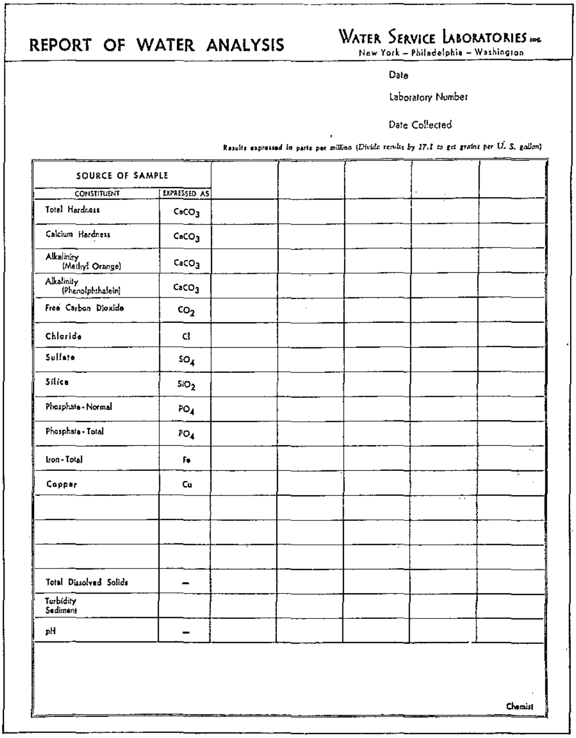
Grams per Liter (*g per liter*). Generally chemists use the metric system in making chemical tests or preparing standard solutions for volumetric analysis. Weights are expressed as grams, milligrams (one-thousandth of a gram), or kilograms (1,000 g). Volumes are expressed as liters, milliliters, or cubic centimeters (one-thousandth of a liter). For all practical purposes the milliliter and cubic centimeter mean the same thing in water treatment. One gram per liter equals 1,000 ppm. To convert grams per liter to parts per million, simply multiply by 1,000. To convert parts per million to grams per liter, divide by 1,000. Since one milligram is equal to one-thousandth of a gram, one milligram per liter equals one part per million. Table 2-6 tabulates the relation of these units of concentration.

Table 2-6. Relation of Units Used to Measure Concentration

Units of concentration	lb per 1,000 gal	g per liter	Ppm	Gpg
1 lb per 1,000 gal....	1.0	0.12	120	7.0
1 g per liter.........	8.3	1.0	1,000	58.3
1 ppm.............	0.0083	0.001	1.0	0.0583
1 gpg..............	0.143	0.017	17.1	1.0

2-5. Forms of Expression. The mineral salts dissolved in water are principally carbonates, sulfates, and chlorides of calcium, magnesium, and sodium. The actual chemical analysis determines each of the elements or radicals separately, without indicating how they are combined. In fact, once these minerals dissolve in water no one can be sure just how they were chemically combined originally.

Ionic Form. (See Table 2-2.) This is an exact form of analysis in which the personal opinion of the analyst does not enter. Individual constituents are reported separately in the form of ions as they exist in water. The ionic form is highly recommended as the standard form for expressing the results of a water analysis.



REPORT OF WATER ANALYSIS

WATER SERVICE LABORATORIES INC.
New York – Philadelphia – Washington

Date

Laboratory Number

Date Collected

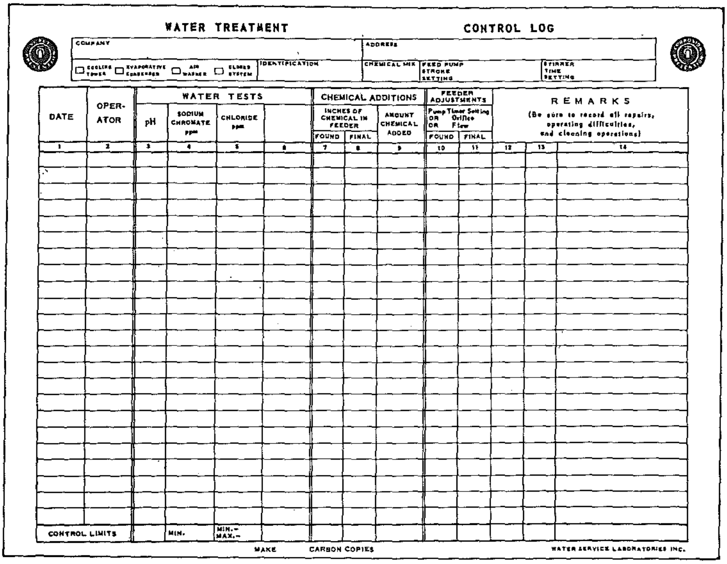
Results expressed in parts per million (*Divide results by 17.1 to get grains per U. S. gallon*)

SOURCE OF SAMPLE						
CONSTITUENT	EXPRESSED AS					
Total Hardness	$CaCO_3$					
Calcium Hardness	$CaCO_3$					
Alkalinity (Methyl Orange)	$CaCO_3$					
Alkalinity (Phenolphthalein)	$CaCO_3$					
Free Carbon Dioxide	CO_2					
Chloride	Cl					
Sulfate	SO_4					
Silica	SiO_2					
Phosphate - Normal	PO_4					
Phosphate - Total	PO_4					
Iron - Total	Fe					
Copper	Cu					
Total Dissolved Solids	–					
Turbidity Sediment						
pH	–					

Chemist

FIG. 2-6. Typical modified ionic form used to report the results of water analysis. Note that the data are called for in terms of parts per million.

Modified Ionic Form. (See Table 2-3.) This is another widely used and popular form of analysis. Here again the personal opinion of the analyst does not have an influence. This differs from the ionic form in that the calcium, magnesium, and bicarbonate are reported as calcium hardness, magnesium hardness, and alkalinity in terms of equivalent calcium carbonate weight rather than actual weights. Since the molecular weight of calcium carbonate equals 100, it facilitates percentage comparisons with other compounds. In addition, both calcium and carbonate are important in hardness and alkalinity. So it has become customary to report hardness and alkalinity in terms of equivalent calcium carbonate. This common practice seems to add still another factor to an existing situation that is already confused. But it does make rapid interpretation of analytical results possible without much calculation. This is an advantage which engineers experienced in this field will not willingly give up.



WATER TREATMENT CONTROL LOG

COMPANY
ADDRESS

☐ COOLING TOWER ☐ EVAPORATIVE CONDENSER ☐ AIR WASHER ☐ CLOSED SYSTEM
IDENTIFICATION
CHEMICAL MIX
FEED PUMP STROKE SETTING
STIRRER TIME SETTING

DATE	OPERATOR	WATER TESTS				CHEMICAL ADDITIONS			FEEDER ADJUSTMENTS		REMARKS (Be sure to record all repairs, operating difficulties, and cleaning operations)		
		pH	SODIUM CHROMATE ppm	CHLORIDE ppm		INCHES OF CHEMICAL IN FEEDER		AMOUNT CHEMICAL ADDED	Pump Timer Setting OR Orifice OR Flow				
						FOUND	FINAL		FOUND	FINAL			
1	2	3	4	5	6	7	8	9	10	11	12	13	14
CONTROL LIMITS			MIN.	MIN.– MAX.–									

MAKE CARBON COPIES

WATER SERVICE LABORATORIES INC.

FIG. 2-7. Water treatment control log includes data needed to analyze operating results and make required adjustments.

Hypothetical or Probable Combinations. (See Table 2-4.) Although the actual determination of various substances in water is usually made in terms of elements or radicals, hypothetical or probable combinations are sometimes calculated. This is the least satisfactory way of reporting because it injects into the picture any personal preference of the analyst in selecting these combinations.

If it is necessary to express results as hypothetical combinations, combine the cations and anions in accordance with the following order for the purpose of uniformity:

Cations	*Anions*
Calcium	Bicarbonate
Magnesium	Carbonate
Sodium	Hydroxide
Potassium	Sulfate
	Nitrate
	Chloride

All other combinations, such as silica, iron, and the aluminum oxides, are reported as such except in special cases where a more extensive determination may be required. Water analysis results are usually reported on a standard form similar to the one shown in Fig. 2-6. Plant operating data are recorded periodically on a log sheet similar to the one shown in Fig. 2-7.

3

Water Tests

The primary purpose of every good water treatment plan is to produce and maintain the chemical composition of the water within the ideal range that will be most beneficial to both the mechanical equipment and the process. Control by chemical testing is one of the most important parts of the treatment plan. To stay within the desired range of chemical composition the water must be regularly tested. These chemical tests must be carried out by a responsible individual at the plant or by a reliable outside water treatment specialist. The kind of tests needed will vary with each treatment plan. For example, phosphates and soda ash are often added to boiler water to minimize scale and corrosion. Boiler water limits are then set up as follows: (1) pH above 11, (2) total alkalinity between 300 and 500 ppm, (3) excess phosphate as PO_4 in the range of 50 to 100 ppm, (4) total hardness of 0 ppm, and (5) chlorides as Cl between 60 and 100 ppm. The control of this treatment calls for the right equipment and simple test procedures to determine pH, alkalinity, phosphate, hardness, and chlorides. Each test used must be accurate enough to control these chemical variables in the boiler water within the prescribed limits.

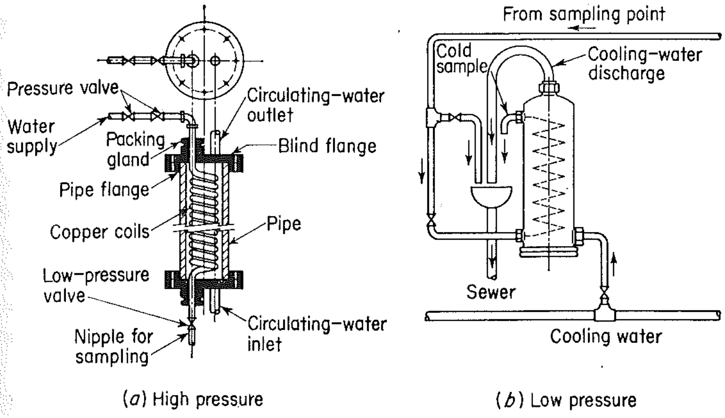
When buying equipment and standard chemical solutions for these control tests, get extra glass items such as beakers, erlenmeyer flasks, graduated cylinders, pipettes, and burettes to allow for normal breakage. A liter of standard solution is usually enough to have on hand. It is also a good idea to buy a known standard sample to periodically check whether or not the reagents and standard solutions on hand are still giving reliable results. Run through the test procedure at regular intervals using the known standard sample. If these test results do not check with the standard sample, discard the reagents one by one and substitute fresh reagents. Continue doing this until the test results check with the known standard. In some cases the test procedure itself will indicate which reagents are liable to go bad. These will need to be replaced from time to time and of course should be the first reagents discarded when a routine check shows incorrect test results.

3-1. Care of Test Equipment. In order to get accurate and reliable test results, it is very important to have clean chemical testing apparatus. Dirty and broken equipment encourages slovenly and careless testing. Be sure to wash and clean all bottles and glassware thoroughly after each use.

Measuring apparatus such as pipettes and graduated cylinders should be carefully rinsed before using, preferably with a portion of the water to be tested. Always employ the same burette for any given standard solution.

3-2. Collecting Water Samples. The tests can be no better than the water sample that is collected for analysis. So before any radical change is made in the treatment, it is always advisable to test more than one sample. The big problem is to obtain a water sample that is truly representative of the whole body of water. Unless this is done the analysis of the sample does not give a true picture of the chemical composition of the water. The time at which the sample is taken in relation to the water treatment process and the way it is taken are both extremely important.

For example, boiler water samples should be taken just before blowing the boiler down and adding treatment chemicals. The sample can be collected from a water column connection. But the line must first be cleared thoroughly by blowing down. Samples can also be taken from a continuous blowdown line. If possible always run the boiler water samples through a cooling coil. This prevents the flashing of steam when the water leaves the boiler. In most cases the sample should be cooled to room temperature to permit any suspended matter to settle on the bottom of the container. The resulting clear water is then usually suitable for testing without need for any further filtering. Cooling-coil design for high- and low-pressure boiler water sampling is shown in Fig. 3-1.



(*a*) High pressure (*b*) Low pressure

FIG. 3-1. Cooling coils for boiler water sampling. (*Taken from* Standard Methods of Water Analysis, 11*th edition, page* 39.)

Another good rule to remember in collecting water samples is to avoid the use of dead-end lines. If this is not practical, allow water to flow through the line for several minutes before the sample is actually collected. The time needed for this can be judged by feeling the pipe as the water is running through. Let the hot water run until the pipe becomes hot or let cold water run until the pipe becomes cold.

3-3. Conductivity. This is a measure of the ability of water to conduct an electric current. Pure water is highly resistant to the passage of an electric current. In other words, its conductivity is very low. When mineral salts, acids, or alkalies are added to pure water they dissociate into positive and negative ions. These in turn increase conductivity in proportion to the number of ions present. Therefore conductivity can be used as a test to determine the amount of total dissolved solids in water. The automobile battery is an example of a solution of water and sulfuric acid that actually produces an electric current and transmits it to battery terminals.

Conductance is measured in mhos, or reciprocal ohms. One mho is the conductance of a substance through which one ampere of current flows at a potential difference of one volt. This measurement is usually made with a conductivity meter calibrated to read in micromhos. The micromho is one-millionth of a mho and is more convenient to use when dealing with the low conductivities associated with most waters. The term mho is ohm spelled backward, which emphasizes the reciprocal relation between the ohm as the basic unit of electrical resistance and the mho as the basic unit of conductivity.

Conductivity measurement performs many useful jobs in the plant. The purity of steam leaving a boiler may be determined by measuring the conductivity of a condensed steam sample. This measurement reveals any solids carryover producing impure steam. Pure steam is just a relative term. What is considered pure in one plant may be very impure at another. But in most small industrial plants 5 ppm or less of solids is satisfactory. At the other end of the scale, high-pressure turbine operation demands practically complete absence of solids with residuals in the parts per billion range.

Determining total dissolved solids of boiler water or circulating cooling water by conductivity is also helpful in adjusting the blowdown rate. Usual chemical methods for this determination are time-consuming and complicated. The conductivity test procedure is quick and simple. Special techniques and skill are not needed, so routine tests can be run in a matter of minutes by the plant operator.

The conductivity meters shown in Figs. 3-2 and 3-3 illustrate some of the portable equipment now available. Figure 3-4 shows a conductivity-cell installation in a pipeline through which a bypass stream runs to give a continuous conductivity reading on this water.

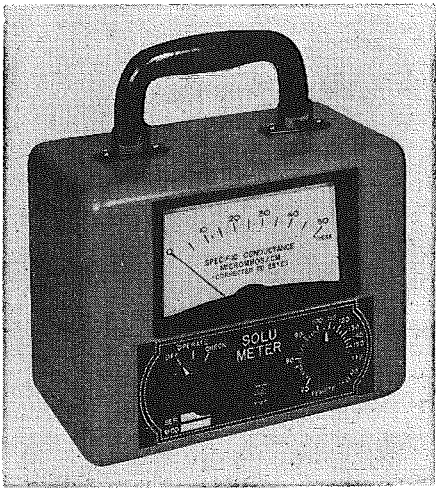


Fig. 3-2. Portable conductivity instrument, transistorized and battery-operated, is housed in gasketed, splashproof case for field use. (*Courtesy of Industrial Instruments, Inc.*)

The meter itself is basically an electrical measuring device. A Wheatstone bridge, shown in Fig. 3-5, serves as the measuring circuit. The temperature-sensitive resistance R_t provides temperature compensation. The conductivity cell immersed in the water sample forms the unknown resistance in one leg of the bridge. The change in solution conductivity changes its resistance R_x. The amplifier then actuates a balancing motor which immediately reacts to move the slider on R_4 to a new position of balance. The instrument pen moves a corresponding amount to record the new conductivity value. The conductivity cell used depends on the expected range of conductivity and the corrosive properties of the water solution.

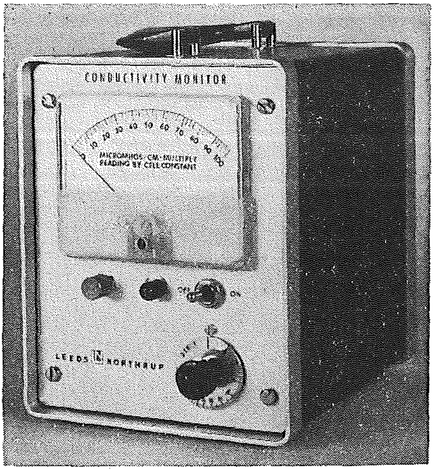


FIG. 3-3. Transistorized portable conductivity monitor that operates on 107 to 127 volts, 60 cycles, AC, is employed for a variety of solution conductivity measurements including condensate, demineralized water. (*Courtesy of Leeds & Northrup Company.*)

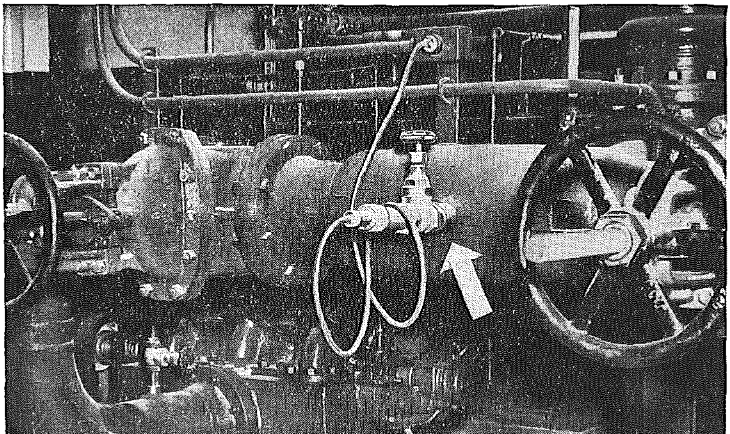


FIG. 3-4. Typical installation of conductivity cell in pipeline. The cell senses changes in conductivity and transmits signal to conductivity indicator or recorder. (*Courtesy of Minneapolis-Honeywell Regulator Company.*)

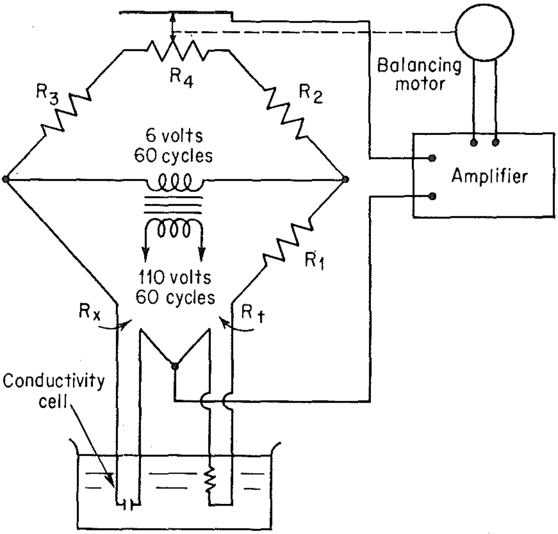


FIG. 3-5. Simplified diagram of circuit employed to measure the conductivity of water.

3-4. pH. The term pH is used to indicate the degree of acidity or alkalinity of a solution. It is measured on a pH scale just as temperature is measured on the scale of a thermometer.

We are all familiar with the common Fahrenheit thermometer. On this scale 32 is the freezing point of water. Values above and below 32 represent degrees of heat and cold, respectively. Any values higher than 32 represent an increase in heat. The higher the number, the greater the degree of heat. On the other hand, values below 32 denote a decrease in temperature. The lower the number, the greater the degree of coldness.

In similar manner the degree of acidity or alkalinity of a solution is measured by the pH scale. Instead of calling these units degrees, as in the case of the thermometer, the units in this scale are called *pH values.* It is apparent that you do not have to know the meaning of the term degree Fahrenheit to find the temperature of a solution with a thermometer. It is equally true that you do not need to know the meaning of the term pH in order to measure the degree of acidity or alkalinity of a solution.

On the pH scale a value of 7.0 represents the pH of a neutral solution. If the substance tested has a pH of 7.0, it is neither acid nor alkaline. Absolutely pure water has a pH of 7.0. Similar to the illustration of temperature on a thermometer, as pH values go from 7 to 14 the solution becomes increasingly alkaline. As the pH drops below 7 and approaches zero the solution becomes increasingly acid. The pH value then is simply a number between 0 and 14 on a scale that depicts the degree of acidity or alkalinity of a solution.

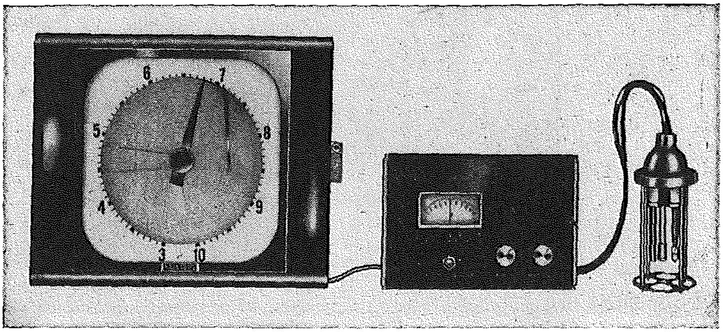


Fig. 3-6. Bristol round-chart pH recorder, Beckman pH amplifier, and pH electrode assembly team up to indicate and record pH. (*Courtesy of The Bristol Company.*)

It is interesting to note that most natural waters fall within the nearly neutral pH range of 6.0 to 8.0. Exceptions are swamp waters, with a pH of 3.0 to 5.0; mine waters, with a pH of 2.0, and natural Western brines, with a pH of 9.5. Ocean water usually has a pH in the range of 8.0 to 8.4.

The scale-forming and corrosive tendencies of a water are greatly influenced by pH. Low or acid pH favors corrosion of metallic equipment coming in contact with the water. High or alkaline pH may precipitate calcium carbonate from solution to form scale on the surfaces of pipelines, boiler tubes, heat-exchange equipment, condensers, etc.

Many chemical-treatment systems to prevent scale and corrosion rely on pH as one of the most important control factors. For example, the pH of boiler water is usually controlled at a minimum value of 10.5. This is high enough to prevent corrosion and at the same time allows precipitation of the various scale-forming salts. Water for air-conditioning systems and condenser cooling usually calls for a pH controlled in the slightly alkaline range of 7.0 to 8.5 for best corrosion protection.

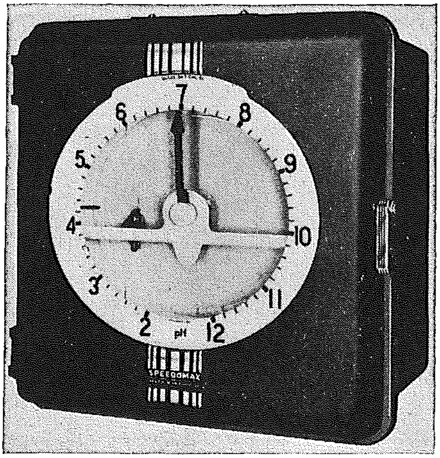


Fig. 3-7. Indicator and recorder combination continuously detects and records pH. Instrument indicates on a circular scale 28-in. calibrated circumference and simultaneously records on a round chart 9¼-in. calibrated diameter. The chart makes a complete revolution in 24 hr. (*Courtesy of Leeds & Northrup Company.*)

In general the analysis of any given water is incomplete unless the pH has been determined. The pH value is also a valuable tool in interpreting the scale-forming and corrosion tendencies of water.

Colorimetric or electrometric methods can be used to determine pH. Both methods require specialized equipment which is readily available at most laboratory supply houses. Each manufacturer of these instruments will furnish complete directions for determining pH with his particular equipment. These instructions are generally in line with accepted standard test procedures. Figures 3-6 to 3-8 illustrate some instruments of this type.

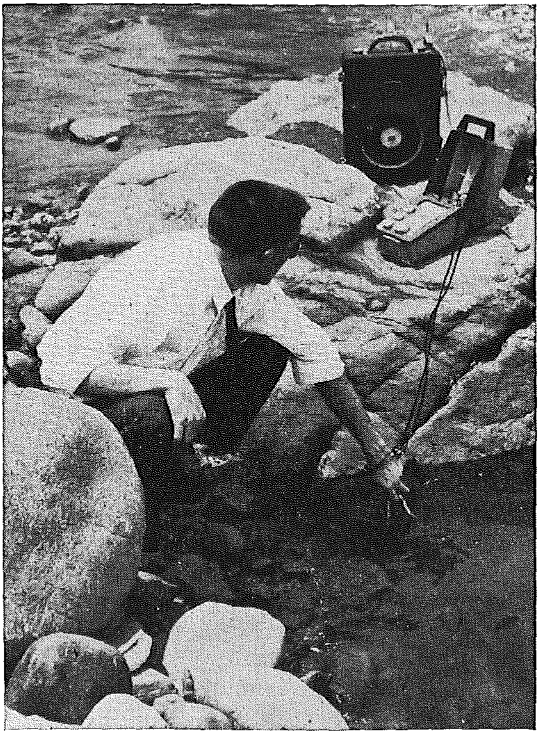


FIG. 3-8. Portable pH meters have many uses. This one is being employed on stream survey work. (*Courtesy of The Bristol Company.*)

3-5. Colorimetric pH Method. This method is based on the fact that various specially prepared *indicator* solutions (organic chemicals and dyes) give distinct colors at different pH values.

The test is made by adding a small amount of the indicator to a sample of water. The resulting color change is matched against a set of prepared standard colors. This can be done quickly in a device called a *comparator*. The pH of the sample is then read directly from the matching color standard.

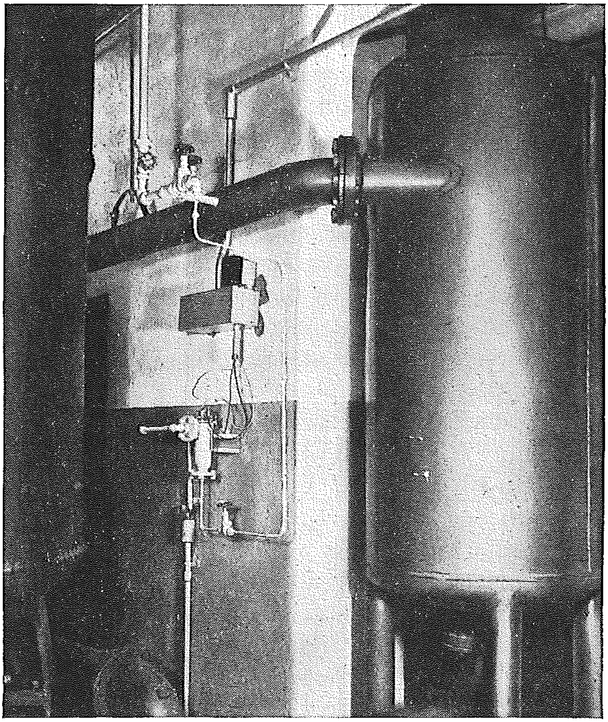


FIG. 3-9. Flow-type pH electrode receives sample of river water flowing through the pipeline. (*Courtesy of Minneapolis-Honeywell Regulator Company.*)

3-6. Electrometric pH or Glass-electrode Method. The pH meter is essentially an electrical instrument. A potentiometer measures the voltage developed across two electrodes in contact with the solution under test. The voltage of one electrode, known as a *calomel half-cell*, is fixed. The voltage of the other cell, generally a glass electrode, varies with the pH of the sample. The exact mechanical procedure for determining pH will vary slightly with the instruments furnished by different instrument manufacturers. However, the glass electrode is generally standardized by placing it in a buffer solution of known pH and adjusting the instrument to that value. The glass electrode can then be placed in the solution being measured and its pH read directly on the instrument scale. Installation of flow pH electrode is illustrated in Fig. 3-9.

3-7. Alkalinity. Alkalinity in a water is usually composed of carbonates, bicarbonates, and hydroxides. But other ions such as borate, silicate, and phosphate also partially contribute to the total alkalinity. It is then evident that a test for alkalinity does not measure any one specific ion in the water. The total amount of alkalinity is found by titration with a standard solution of strong acid to certain pH reference points. Phenolphthalein and methyl orange indicators are used to provide these standard reference points. The phenolphthalein changes color at a pH of about 8.3 and methyl orange changes color at a pH of about 4.3.

The alkalinity of a natural water normally consists of calcium and magnesium bicarbonate. Frequently it also includes some sodium bicarbonate. Like pH, alkalinity is another important factor in determining whether a water supply has scale-forming or corrosive tendencies. High alkalinity in a water can make it unfit for use in certain industrial processes. For example, the flavor of carbonated beverages is adversely affected by high alkalinity. This means that the water supply for the carbonated-beverage industry must be carefully investigated. Alkalinity must be less than the allowable maximum, or the water must be treated to reduce it to the desired level.

High alkalinity in boiler feed water is also undesirable for many reasons. Heat in the boiler will break down the bicarbonate ions in the boiler water. This liberates carbon dioxide, which mixes with the steam coming from the boiler. When the steam condenses the carbon dioxide dissolves in the condensate to form carbonic acid. This reduces the pH and promotes corrosion of both steam lines and condensate return lines. Excessive alkalinity in boiler water also promotes carryover and contributes to caustic embrittlement (an intercrystalline cracking of boiler metal). On the other hand, if alkalinity is too low, it does not give proper protection against corrosion.

The aims of boiler water treatment include maintaining the alkalinity in a range that is (1) high enough to prevent corrosion and (2) low enough to prevent carryover of solids with the steam and not contribute to caustic embrittlement of the metal. A guide to selecting maximum allowable alkalinity is given in Table 3-1 for various boiler operating pressures. As an additional safeguard the phenolphthalein alkalinity should be maintained at 60 to 80 per cent of the total alkalinity in the boiler. In order to establish maximum safe limits for alkalinity in any particular boiler it is necessary to frequently analyze samples of condensed steam. The results of this test work will establish the boiler alkalinity level that does not contaminate the steam being produced.

Table 3-1. Boiler Water Alkalinity at Various Operating Pressures

Boiler operating pressure, psig	Total alkalinity, ppm as calcium carbonate	
	Minimum	Maximum
0–300	200	700
301–450	160	600
451–600	120	500
601–750	120	400
751–900	120	300

In systems where cooling water is circulated, total alkalinity has major importance in predicting the tendency of calcium carbonate to precipitate from the water and form scale. The higher the alkalinity, the greater is the tendency to precipitate calcium carbonate. Where acid treatment is necessary to reduce the alkalinity and prevent scale, routine tests are made for alkalinity content to regulate the rate of acid that must be fed into the cooling system.

3-8. Alkalinity Test. Alkalinity is found by titration with a standard acid solution using phenolphthalein and methyl orange indicators. Above a pH of 8.3, phenolphthalein indicator gives a red or pink color to a water solution. When pH drops to about 8.3 the indicator becomes colorless. The methyl orange indicator gives a yellow color when the pH is above 4.3. At about 4.3 pH, this indicator changes to a salmon pink. If too much acid is added to the water sample, dropping the pH well below 4.3, the color of the indicator will change to a definite pink.

3-9. Reagents Used. (1) Phenolphthalein indicator solution at 0.5 per cent strength. Dissolve 5 g of phenolphthalein in 1 liter of a 50 per cent solution of ethyl alcohol in distilled water. Neutralize with dilute sodium hydroxide (0.02 N) to a faint pink color. (2) Methyl orange indicator at 0.1 per cent strength. Dissolve 1 g of methyl orange in 1 liter of distilled water. (3) Standard sulfuric acid (0.02 N).

3-10. Phenolphthalein-alkalinity Procedure. Add four drops of phenolphthalein indicator to the water. Use a 50- to 100-ml sample, if possible, in a white porcelain casserole or an erlenmeyer flask over a white surface. Titrate with standard 0.02 N sulfuric acid until the pink coloration of the indicator just disappears.

3-11. Methyl-orange-alkalinity Procedure. Add two drops of methyl orange indicator to the same solution used to determine the phenolphthalein alkalinity. It is also possible to use another fresh 50- to 100-ml sample in a white porcelain casserole or an erlenmeyer flask over a white surface. Titrate with standard 0.02 N sulfuric acid until the color changes from yellow to pink.

3-12. Calculating Results. The parts per million of alkalinity present expressed in terms of calcium carbonate equals

$$\frac{\text{ml of } 0.02\ N \text{ sulfuric acid} \times 1{,}000}{\text{ml of sample}}$$

EXAMPLE 1. A 50-ml sample of water is titrated with standard 0.02 N sulfuric acid. To reach the phenolphthalein-color-change point, 6 ml of acid is required. The methyl-orange-color-change point is reached when 9 ml of acid is added. The phenolphthalein alkalinity is then

$$\frac{6 \times 1{,}000}{50} = 120 \text{ ppm}$$

The methyl orange alkalinity is

$$\frac{9 \times 1{,}000}{50} = 180 \text{ ppm}$$

3-13. Chloride. The chlorides of calcium, magnesium, sodium, and other metals are normally found in natural water supplies. All of these chlorides are very soluble. This explains why they usually stay in solution even when the water is evaporated and all the dissolved solids are concentrated. The concentration of chlorides before and after evaporation will reveal how much the water solution has concentrated. The test for chlorides in routine control work is used to determine how many times the dissolved solids in boiler water or cooling water are concentrating. For circulating cooling water the mathematical expression is

$$\frac{\text{Chlorides in circulating water}}{\text{Chlorides in makeup water}} = \text{number of concentrations}$$

In any industrial process where treated water is evaporated, a maximum and minimum range of concentration of dissolved salts is usually specified. To keep the number of concentrations within this range, it is usually necessary to establish and follow a blowdown schedule. The amount of blowdown needed is easily calculated from the following equation.

$$\frac{\text{Amount of system makeup, gal}}{\text{Number of concentrations allowable}} = \text{blowdown, gal}$$

The blowdown can also be expressed as a percentage of makeup in terms of chlorides. This formula is

$$\frac{\text{Chlorides in makeup water (100)}}{\text{Chlorides allowed in process water}} = \text{blowdown, per cent}$$

For example, the feed-water treatment may allow 10 concentrations of the boiler water. If chloride in the incoming feed water is 3 ppm, the boiler water will then contain 30 ppm chlorides. Blowdown then equals

$$\frac{3 \times 100}{30} = 10\%$$

If 1,000 gal of makeup is added every day, the blowdown will be 100 gal per day. Once a blowdown schedule is established, the chloride test can be used as a control monitor to tell whether or not the blowdown rate must be increased or decreased to maintain the correct number of concentrations of the boiler water.

3-14. Chloride Test—Mohr Titration Method. Chlorides are found by titration with a standard silver nitrate solution. Potassium chromate is used as the indicator. The chloride ion is preferentially precipitated by the silver nitrate as silver chloride. When all the soluble chlorides are precipitated, the silver nitrate reacts with the chromate indicator. Red silver chromate is then precipitated. The permanent appearance of this red color marks the end point of the titration.

3-15. Reagents Used. (1) Standard silver nitrate solution, 1 ml = 0.5 mg Cl, 0.0141 *N*. Dissolve 2.396 g silver nitrate in 1 liter of distilled water. (2) Standard sodium chloride solution, 1 ml = 0.5 mg Cl, 0.0141 *N*. Dissolve 8.243 g of fused sodium chloride in 500 ml of distilled water. Dilute 50 ml of this solution to 1 liter. (3) Potassium chromate indicator, 5 per cent solution. Dissolve 50 g of neutral potassium chromate in 100 ml of distilled water. Add silver nitrate solution until a slight red precipitate is formed. After letting the solution stand overnight, filter to remove the precipitate. Then dilute the filtrate to 1 liter with distilled water. (4) Hydrogen peroxide, 30 per cent solution. (5) Phenolphthalein indicator solution, 0.5 per cent (same as used for alkalinity test). (6) Sulfuric acid, 2 per cent, or acid used for the alkalinity test.

3-16. Test Procedure. If the phenolphthalein and methyl orange alkalinities have already been determined, the same sample can be used for the chloride test without further neutralization. If not, add four drops of phenolphthalein indicator to a 50-ml sample, in a white porcelain casserole or an erlenmeyer flask over a white surface. If a pink color develops, add 2 per cent sulfuric acid, drop by drop, stirring, until the pink color is just destroyed. Add 1 ml of potassium chromate indicator to the neutralized sample. This turns the solution a bright yellow. Slowly add silver nitrate solution, with constant stirring, until one drop produces a permanent color change from pure yellow to pinkish yellow.

For greatest accuracy with this test an indicator blank should be used. Titrate 50 ml of distilled water with silver nitrate solution, using 1 ml of potassium chromate indicator. Place this blank, showing the end-point color, near the sample being titrated. This will greatly aid in detection of the color change at the chosen end point. Under these conditions the blank should be about 0.2 ml. To remove color and any sodium sulfite present, boil the sample with hydrogen peroxide, filter, and cool.

If the chloride concentration is very high, it may be necessary to use a smaller sample and dilute to 50 ml with distilled water so that the concentration of chloride ion is preferably between 5 and 200 ppm.

3-17. Calculating Results. The amount of chloride present in parts per million as Cl equals

$$\frac{(\text{ml silver nitrate} - \text{ml of blank}) \times \text{AgNO}_3 \text{ in mg Cl per ml} \times 1{,}000}{\text{Vol of sample in ml}}$$

EXAMPLE 2. A 50-ml sample of water is titrated with a silver nitrate solution equivalent to 0.5 mg Cl per ml, using potassium chromate indicator. To reach the end-point color, 3.8 ml of silver nitrate is required. The blank is found to be 0.2 ml.

$$\text{Chlorides, ppm as Cl} = \frac{(3.8 - 0.2) \times 0.5 \times 1{,}000}{50} = 36$$

3-18. Total Hardness. The amount of hardness in a water is a measure of its soap-consuming capacity and its scale-forming tendencies. Dissolved calcium and magnesium compounds are the principal constituents of hardness in water. Other dissolved substances, such as aluminum, iron, manganese, and zinc, also contribute to the total hardness. The hardness of natural waters varies considerably in different sections of the country. In general the water hardness can be put into the following broad classifications:

Total hardness, ppm	*Classification*
Less than 15	Very soft water
15–60	Soft water
61–120	Medium-hard water
121–180	Hard water
More than 180	Very hard water

Natural surface waters such as those from lakes and streams are usually softer than ground or well waters in the same area.

In boiler water conditioning the hardness in water is undesirable for several reasons. It can produce sludge, mud, or scale in the boiler. In addition, hardness is the source of scale and deposits in feed-water heaters, feed lines, and economizers. For these reasons the boiler water must be treated so that the amount of hardness present in the boiler water is close to zero. This is done by adding inorganic salts such as sodium carbonate, hydroxide, and phosphate which precipitate practically all of the hardness. Various organic materials are also added frequently to aid removal of the resulting sludge from the boiler by blowdown.

Hardness in circulating cooling waters can cause scale to form in heat-exchange equipment and on any surface where the water circulates. Of course, there are many factors that influence the conditions under which the hardness salts either precipitate as scale or sludge or remain in solution. Scale formation is effectively prevented by regulating one or more of these factors. One way is to lower the pH or alkalinity of the circulating water. Another is to limit the number of concentrations of dissolved solids by blowdown. Surface-active or sequestering agents such as the polyphosphates are often added to hold the hardness in solution at concentrations higher than would normally be possible without these agents. The usual cooling-water treatment will include one or more of these methods.

Total hardness in a water can be determined by two very simple tests: the first is the *soap titration method* and the second is known as the *ethylenediaminetetraacetic acid (EDTA) titration method*. Basically the soap titration method measures the soap-consuming ability of the water. It is generally considered inferior to the EDTA test because it is not as precise or accurate and takes much longer to run. For these reasons the soap titration method is rapidly passing out of use.

3-19. Test for Total Hardness—EDTA Titration Method. The total hardness is determined by titration with a standard solution of EDTA using chrome black T, an organic dye, as an indicator. The chrome black T indicator forms a wine-red complex when even slight traces of calcium and magnesium salts are present in the water. If no calcium or magnesium is present and the pH is in the range of 8.5 to 11.5, the chrome black T solution will have a blue color. EDTA also forms a colorless complex salt with calcium and magnesium. These EDTA complex salts are more stable than the chrome black T complexes. Therefore, when sufficient EDTA is added to combine with all the calcium and magnesium in the water sample containing chrome black T, the solution will change color from wine red to blue. Unfortunately there are several substances that might be found in the water sample which may interfere with this test. Because of this a number of modifications in test reagents and procedures are available. The following method is known as the borate buffer procedure. The chemical reagents for this can be made under the supervision of a qualified chemist or can be purchased from a laboratory supply house.

Before this hardness test is run it is necessary to determine whether or not undue interference will take place. This can be checked by taking two water samples, one 50 ml and the other 25 ml diluted with distilled water to 50 ml. If the hardness of both samples differs by more than the expected experimental error, interference is indicated. If there is interference, the advice of a water treatment specialist should be sought to select the proper EDTA method for hardness testing.

3-20. Reagents Used. (1) EDTA standard titrating solution, 1 ml = 1 mg $CaCO_3$. (2) Standard calcium solution, 1 ml = 1 mg $CaCO_3$. A standard magnesium solution may be substituted for the calcium solution. (3) Chrome black T indicator solution. Dissolve 0.5 g of chrome black T in 100 ml pure triethanolamine, or pure Cellosolve, filtering if necessary. Prepare fresh solution at least once a month to prevent the titration end points from becoming obscure. (4) Buffer, inhibitor mixture, pH 12.5. Dissolve 40 g of borax, $Na_4B_4O_7 \cdot 10H_2O$, in about 800 ml of distilled water, with warming and stirring if necessary. In a separate vessel dissolve 10 g of sodium hydroxide, 10 g of Rochelle salt, $KNaC_4H_4O_6 \cdot 4H_2O$, and either 10 g of $Na_2S \cdot 9H_2O$ or 7 g of $Na_2S \cdot 5H_2O$ in 100 ml of distilled water. When both solutions are cool, mix and dilute them to 1 liter with distilled water. The buffer solution must be protected against atmospheric carbon dioxide. If this buffer mixture fails to produce a pH of 10.3 when added to the sample as described in the test or if it loses its distinctive sulfide odor, a fresh supply must be made.

3-21. EDTA Hardness Test Procedure. Place 50 ml of the water sample in a white porcelain casserole or an erlenmeyer flask. Add 1 ml of the buffer-inhibitor mixture plus one or two drops of indicator solution. If hardness is present the sample will turn red. Add the EDTA titrating solution *slowly* with continuous stirring until the last reddish tinge disappears from the solution. The final color of the indicator in solution should be blue.

Check the accuracy of this test procedure at regular intervals using 50 ml of the known standard calcium or magnesium solution.

3-22. Calculating Results. The parts per million of total hardness, expressed in terms of $CaCO_3$, equals

$$\frac{\text{Vol of EDTA titrating solution in ml} \times 1{,}000}{\text{Vol of sample in ml}}$$

EXAMPLE 3. A 50-ml sample of raw water is titrated with EDTA solution. It takes 5 ml of EDTA to reach total hardness end-point color with chrome black T indicator. The total hardness in parts per million as $CaCO_3$ is then found by substituting these values in the above formula.

$$\text{Total hardness} = \frac{5 \times 1{,}000}{50} = 100 \text{ ppm as } CaCO_3$$

3-23. Calcium Hardness. The raw, makeup, or feed water in a process is usually tested for calcium hardness in order to calculate the amount of chemicals needed for treatment. For example, phosphate is frequently used as the main conditioning chemical in internal boiler water treatment. It selectively precipitates the calcium hardness. Magnesium hardness is precipitated as the hydroxide either by the natural alkalinity of the water or by the addition of alkaline salts such as caustic soda or soda ash. The amount of phosphate needed is determined by the amount of calcium present in the water. The magnesium hardness (difference between total hardness and calcium hardness) determines how much, if any, alkaline chemical is needed.

3-24. EDTA Titration Method for Calcium Hardness. Calcium hardness is found by titration with a standard solution of EDTA using ammonium purpurate (also called murexide), an organic dye, as an indicator. At a pH of about 12 the ammonium purpurate indicator is sensitive to calcium ions and insensitive to magnesium ions. This indicator will form a pink color even with just a trace of calcium present in the water. If no calcium is present, the indicator will be purple. As in the test for total hardness, if sufficient EDTA is added to combine with all the calcium in the water sample containing ammonium purpurate, the solution will change color from pink to purple.

3-25. Reagents Used. (1) EDTA standard titrating solution, 1 ml = 1 mg calcium carbonate. (2) Standard calcium solution, 1 ml = 1 mg calcium carbonate. (3) Sodium hydroxide solution, 2.0 *N*. Dissolve 80 g of sodium hydroxide in 800 ml of distilled water. Then cool and dilute to 1 liter. (4) Ammonium purpurate indicator mixture. There are a number of ways to prepare this mixture. The most stable preparation is made by combining 0.2 g of ammonium purpurate with 100 g of sodium chloride. Mix thoroughly and grind to a 40- to 50-mesh size. Use a measuring cup to dispense this mixture. One level cup should equal 0.2 g.

3-26. EDTA Calcium Test Procedure. Place 50 ml of the water sample in a white porcelain casserole or erlenmeyer flask. Add 1 ml of 2.0 *N* sodium hydroxide to the sample and stir. Add 0.2 g of ammonium purpurate indicator mixture using a measuring cup. If calcium hardness is present the sample will turn pink. Add the EDTA titrating solution *slowly* with continuous stirring until the color changes from pink to purple. Check the end point by adding one or two more drops of EDTA solution. If the end point has been reached, no further color change will take place. Practice is necessary to spot the change in color marking the end point of the titration. Check the accuracy of this test at regular intervals using 50 ml of the known standard calcium solution.

3-27. Calculating Results. The parts per million of calcium hardness expressed in terms of $CaCO_3$ equals

$$\frac{\text{Vol of EDTA titrating solution in ml} \times 1{,}000}{\text{Vol of sample in ml}}$$

EXAMPLE 4. A 50-ml sample of raw water is titrated with EDTA solution. Using ammonium purpurate indicator, the end point is reached by adding 4 ml of EDTA. The calcium hardness in parts per million as $CaCO_3$ is then found by substituting in the above formula.

$$\text{Calcium hardness} = \frac{4 \times 1{,}000}{50} = 80 \text{ ppm as } CaCO_3$$

3-28. Sulfate. Sulfate is present in most water supplies. Water flowing through the earth picks up sulfate from beds of gypsum and shale. Some surface waters may also receive acid mine drainage which contributes to the over-all sulfate content of the water.

Sulfate can combine with the calcium in untreated boiler water to form calcium sulfate scale. Scale formation of this type in a boiler can be prevented by removing the calcium hardness. This is simpler and far more economical than trying to remove the sulfate.

The amount of sulfates dissolved in the water must be known in order to estimate the total solids present. There are several methods used to determine how much sulfate is in the water. The two most simple tests are the THQ titration method and the turbidimetric method. THQ titration just calls for the ordinary apparatus used in volumetric titrations. The turbidimetric test calls for specialized instruments like the turbidimeter or the photoelectric colorimeter.

3-29. THQ Titration for Sulfate. The sulfate present is found by titrating with a standard solution of barium chloride in an alcoholic solution using tetrahydroxyquinone (THQ) as an indicator. The barium chloride reacts with sulfate to precipitate barium sulfate. The THQ indicator in a water solution will detect the presence of excess barium ions. When there is no excess of barium ions, the color of the indicator in solution is yellow. But as soon as there is an excess of soluble barium ions, the yellow color changes to pink.

Soluble phosphate does interfere with the titration as it is usually performed. When phosphates are known to be present the test procedure must be modified.

3-30. Reagents Used. (1) Barium chloride solution, 0.025 *N*. Dissolve 3.05 g of $BaCl_2 \cdot 2H_2O$ in distilled water adding enough water to make up a total volume of 1 liter. (2) THQ indicator. Use a measuring cup to dispense the indicator. One level cup is equal to 0.2 g. (3) Ethyl or isopropyl alcohol. (4) Silver nitrate solution, 2 per cent. Dissolve 2 g of silver nitrate in 100 ml of distilled water. (5) Phenolphthalein indicator solution, 0.5 per cent. Dissolve 5 g of phenolphthalein indicator in 1 liter of a 50 per cent solution of ethyl or isopropyl alcohol in distilled water. Neutralize with dilute sodium hydroxide solution (0.02 *N*) to a faint pink color. (6) Bromcresol-green indicator solution. Dissolve 0.1 g bromcresol green in 14.3 ml of 0.01 *N* sodium hydroxide and dilute to 250 ml with distilled water. (7) Hydrochloric acid, 0.1 *N*. Dilute 8 ml of concentrated hydrochloric acid to 1 liter with distilled water.

3-31. THQ Titration Test Procedure (Phosphates Absent). Place 25 ml of the clear water sample in an erlenmeyer flask. Add four drops of phenolphthalein indicator. If the sample turns pink, add the 0.1 *N* hydrochloric acid with a dropper until the color just disappears. If the sample does not turn pink, add a dilute solution of sodium hydroxide until it does turn pink. Then neutralize with the 0.1 *N* hydrochloric acid. Add 25 ml of ethyl or isopropyl alcohol. Then add one level measure of THQ indicator (0.2 g) with the cup provided for this purpose. The solution formed has a yellow color. Slowly add the 0.025 *N* barium chloride solution, constantly stirring, until the color changes from yellow to red. A blank correction is necessary and can be obtained by following exactly the same procedure, using 25 ml of distilled water.

The end point of the titration can be sharpened by adding 2 per cent silver nitrate solution just before titrating with the barium chloride. Add 1 ml silver nitrate when the chlorides are low and 3 ml when the chlorides are high. If the solution develops an intense cherry-red color when these amounts of silver nitrate are added, discard the sample and repeat the procedure using a smaller amount of silver nitrate.

3-32. THQ Titration Procedure (Phosphate Present). Place 25 ml of the clear water sample in an erlenmeyer flask. Add four drops of bromcresol green. This will normally cause the solution to turn a green color. Add 0.1 *N* hydrochloric acid with a dropper until the color changes from green to straw. Then follow the normal test procedure, adding the alcohol and THQ indicator and then titrating with barium chloride. Preferably the blank should contain the same amount of phosphate as the sample.

3-33. Calculating Results. The parts per million of sulfate expressed as SO_4 equals

$$\frac{(\text{Vol of barium chloride in ml} - \text{amount used for blank in ml}) \times 1{,}200}{\text{Vol of sample in ml}}$$

EXAMPLE 5. A 25-ml sample of water is titrated with barium chloride solution using THQ indicator to determine the amount of sulfates present. It takes 5 ml of barium chloride to reach the end point. A blank is also run and found to be 0.2 ml. Amount of sulfates present equals

$$\frac{(5.0 - 0.2) \times 1{,}200}{25} = 230 \text{ ppm as } SO_4$$

3-34. Turbidimetric Sulfate Test. This test is based on the

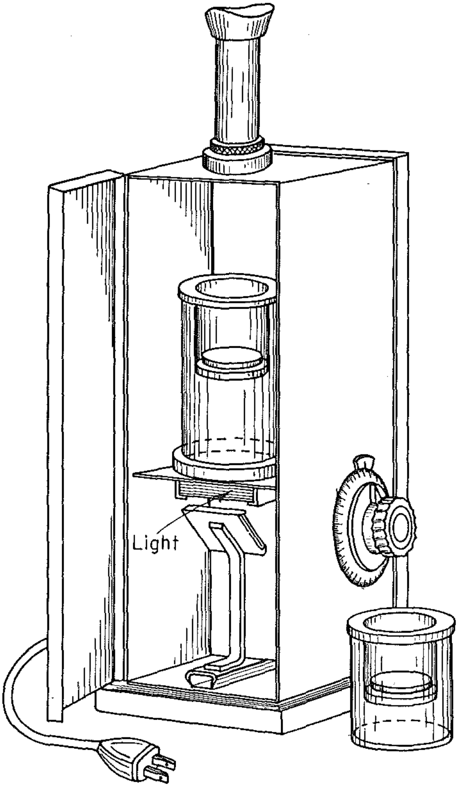


FIG. 3-10. Turbidimeter, no. 8000T. (*Courtesy of Hellige, Inc.*)

fact that barium sulfate crystals of uniform size are formed when barium chloride is added to an acid solution under controlled conditions. The turbidity developed in the solution is directly proportional to the sulfate content of the water. This turbidity can then be measured with a special instrument such as a turbidimeter or a photoelectric colorimeter that has previously been calibrated with known sulfate solutions. Since the detailed procedure differs slightly with each make of equipment, we will not attempt to describe the details of this test. These are best obtained from the operating instructions on the particular instrument involved. Figure 3-10 shows a turbidimeter frequently used for this test.

3-35. Phosphate. Phosphate is usually not found in natural waters. But chemicals containing phosphate are usually added to water for scale and corrosion control. Generally speaking, there are two classes of phosphate compounds used in water treatment: the normal (or orthophosphate) and the polyphosphate. The polyphosphates differ from the normal phosphates in that they will form soluble complex salts with calcium and magnesium. These complex compounds are not stable under all conditions and can revert to a normal-phosphate form. For example, boiling a dilute solution of the polyphosphate will hasten the reversion to normal phosphate.

Polyphosphates are used in boiler water treatment to prevent the formation of calcium carbonate deposits in the cooler feedwater lines to the boiler. But once in the boiler they revert to normal phosphate and, under favorable pH conditions, precipitate the calcium salts as tricalcium phosphate. The tricalcium phosphate in the boiler water forms a sludge which does not stick to the boiler metal like scale. This sludge can then be removed by blowdown from the boiler. In a phosphate-treated boiler water (either normal or polyphosphate) the pH should be in the range above 9.5 to ensure precipitation of tricalcium phosphate. In addition it is desirable to carry an excess soluble phosphate of about 30 to 60 ppm as PO_4. This helps drive the reaction of calcium and phosphate to completion and assures the immediate removal of any hardness entering the boiler. Therefore the test for phosphate is one of the principal control tests on treated boiler water.

Polyphosphates are also used to great advantage in cooling water systems where calcium carbonate scale formation on cooling surfaces is a major problem. Many factors influence the formation of scale in a cooling water. These include pH, alkalinity, calcium hardness, total solids, and temperature. The tendency for calcium carbonate to deposit on metallic surfaces increases with an increase in any one of these factors.

For example, water which does not form scale at 80°F may definitely deposit scale at 140°F. Conversely, there is less tendency to form scale when any of the control factors is reduced. Take the case of a cooling water that is depositing a calcium carbonate scale in the system. The pH of the water is 8.2. Adding acid to reduce the pH is often enough to control the formation of scale.

The addition of polyphosphates changes the conditions under which scale will form in a cooling water with a given pH, alkalinity, calcium hardness, total solids, and temperature. For example, consider another cooling water that is depositing calcium carbonate scale. The water composition is such that it is too costly to reduce pH, alkalinity, and the other factors that influence scale formation. But the addition of controlled amounts of polyphosphate can stabilize the water and prevent scale formation even though the other factors remain the same. For best results the unreverted polyphosphate in the cooling water should be maintained in the range of 2 to 4 ppm. If this amount does not prevent scale, some of the other factors promoting scale must be reduced regardless of cost.

Phosphates, particularly the polyphosphates, are not the most effective corrosion inhibitors. But they do reduce the amount of tuberculation. This has the advantage of keeping head losses from the products of corrosion to a minimum. About 2 to 4 ppm of unreverted polyphosphate should be maintained for best corrosion control. This treatment has been used successfully in municipal water systems to prevent *red water*.

Caustic embrittlement can be prevented in a high-pressure boiler by coordinated pH-phosphate control. With this treatment the pH value of the boiler water must never be higher than the pH of a trisodium phosphate solution containing the same quantity of PO_4.

3-36. Colorimetric Test for Orthophosphate. Practically all of the colorimetric methods for this test are based on the initial formation of phosphomolybdic acid. A prepared molybdate reagent is added to the water sample containing phosphate. Then when a reducing agent is added to the phosphomolybdic acid, a blue color is produced. The intensity of this color is proportional to the amount of phosphate present in the solution. The intensity of this blue color can be measured by:

1. Preparing a set of known standard samples and then matching these visually with the unknown water sample under test. The preparation of these standards is a tedious job and therefore this procedure is not too popular.
2. Employing a phosphate comparator. This is the simplest way for most plant engineers and is the most widely used.
3. Calibrating an electrophotometer so that it can be used to test for phosphates. This is the most accurate of the three methods and is most likely found in plants having a full-time chemist. An instrument of this type is shown in Fig. 3-11. Colorimeters can also be hooked up to a recording instrument, as shown in Fig. 3-12.

The reducing agents most widely used are aminonaphthol–sulfonic acid solution and stannous chloride. If stannous chloride is used the sensitivity of the test is greatly increased. But stannous chloride is also more subject to interference than aminonaphthol. Both these reducing agents are unstable and must be carefully stored in accordance with the test instructions.

Each manufacturer of phosphate-testing equipment furnishes the detailed instructions for determination of phosphate with his apparatus. For those who wish to use an electrophotometer, a good method is outlined in *Standard Methods for the Examination of Water, Sewage and Industrial Wastes*. This manual is published

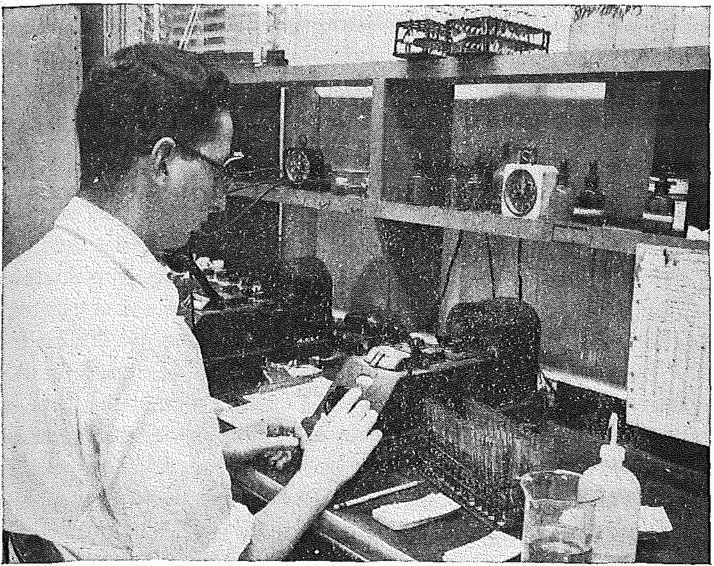


FIG. 3-11. Laboratory technician runs test with Klett-Summerson colorimeter.

jointly by the American Public Health Association, the American Water Works Association, and the Federation of Sewage and Industrial Wastes Association.

3-37. Modified Procedure for Polyphosphate Testing. Polyphosphates such as pyro-, meta-, and tripolyphosphate do not respond to the colorimetric test for orthophosphate. But these

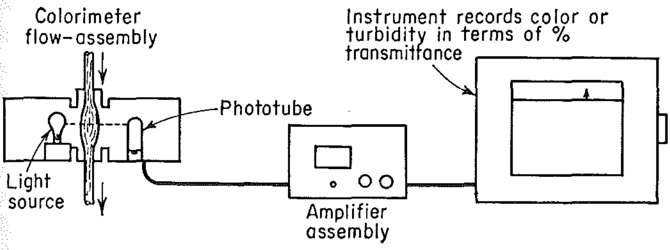


FIG. 3-12. Colorimeter flow assembly is employed in combination with amplifier and recorder to measure color or turbidity.

compounds can be converted into orthophosphate by boiling with acid. To determine the polyphosphate content originally present, the normal orthophosphate test is made on two samples. One sample is handled in the normal manner but the other is first boiled with acid. The polyphosphate content then equals the difference between these two test results.

3-38. Sulfite. Natural water supplies do not normally contain sulfite. But practically all natural waters do contain dissolved oxygen. Oxygen may also be added to process water as it flows through various items of equipment in the system. Dissolved oxygen, whether present naturally or added later, is one of the most important factors causing the corrosion of steam boilers and accessories, heat exchangers, and cooling-system equipment. Sodium sulfite is very effective in corrosion prevention because it reacts with the dissolved oxygen in the water to form sodium sulfate. With removal of the dissolved oxygen one of the most important causes of corrosion is eliminated.

Sodium sulfite is most widely used for boiler water treatment. Deaeration of feed water is regarded as absolutely essential. The bulk of the dissolved oxygen and other gases is usually removed most economically by physical means in an external deaerator. But this must be followed by chemical treatment with sodium sulfite to eliminate the last traces of oxygen in the feed water going to the boiler. In addition, an excess of 20 to 30 ppm sodium sulfite is maintained in the boiler. This gives added assurance that all the dissolved oxygen in the feed water has been eliminated.

The test for dissolved oxygen in water is fairly involved. For this reason it is not usually run on a routine basis in most plants. The sodium sulfite test is much simpler and can be easily set up for routine control. A given amount of sodium sulfite is added to the boiler water. Then a sulfite test is run to see if any excess sulfite is present. If no excess is found, more sulfite is called for immediately. If the excess sulfite is more than 30 ppm, less sulfite can be used on subsequent charges to the boiler. Thus by regular sulfite tests the amount of sodium sulfite fed to the boiler can be regulated to give the desired 30 ppm excess.

3-39. Volumetric Sulfite Test. Sulfite is determined by titration with a standard potassium iodide-iodate solution using starch as the indicator. After the sulfite completely reacts with the iodide-iodate solution, free iodine is produced. This free iodine turns the starch indicator blue, indicating the end point of the titration. Unfortunately, this method is affected by any substance in the water that can be oxidized, such as organics, sulfides, and nitrites. All of these substances will test as a sulfite and indicate a higher value of sulfite than is actually present in the water.

3-40. Reagents Used. (1) Potassium iodide-iodate solution, 1 ml = 0.5 mg SO_3. Dissolve 0.45 g of potassium iodate in about 100 ml of distilled water. Then add 4.35 g of potassium iodide and 0.31 g of sodium bicarbonate. Dilute to exactly 1 liter. (2) Hydrochloric acid, concentrated. (3) Starch indicator, 0.5 per cent solution. Weigh out 0.5 g of starch. Make a paste with distilled water. Then dilute with 100 ml of boiling distilled water. Add 0.1 g of salicylic acid to act as a preservative. To assure getting a good end point, renew the starch indicator solution about every three to five days.

3-41. Test Procedure. Make sure that the water sample has been freshly drawn with as little contact with air as possible. Do not filter the sample. Place 0.5 ml of concentrated hydrochloric acid in a casserole and add 100 ml of the water to be tested. Then add 1 ml of the starch indicator and stir. Continue stirring and titrate with standard potassium iodide-iodate solution until a permanent faint-blue color develops. This blue color marks the end point.

3-42. Calculating Results. The amount of sulfite present expressed as parts per million of SO_3 equals

$$\frac{\text{Vol of potassium iodide-iodate used in ml} \times 500}{\text{Vol of sample in ml}}$$

EXAMPLE 6. A 100-ml sample of boiler water is titrated with potassium iodide-iodate solution. Starch is used as the indicator to determine the amount of sulfite present in the sample. The blue color of the end point is reached by adding 6 ml of iodide-iodate. The quantity of sulfite present in terms of SO_3 is then

$$\frac{6 \times 500}{100} = 30 \text{ ppm}$$

3-43. Chromate. Chromate is another substance not usually found in natural water. But chemicals containing chromate are often added to water circulating in heat-exchange and cooling equipment for corrosion control. Chromate is one of the most effective corrosion inhibitors available for cooling towers, evaporative condensers, air washers, heating boilers, and closed hot- and cold-water systems.

The amount of chromate required for best protection varies considerably. Temperature of the water, chloride content, and pH are three of the most important influences. The higher the temperature and the greater the amount of chlorides in the water, the higher is the concentration of chromate needed for corrosion protection. The amount of chromate is not affected by pH when it is in the range above 7.0. But if the pH is lower than 7.0, higher concentrations of chromate may be required. The following table is a rough guide to the concentration of chromate needed for adequate corrosion protection.

Amount of Na_2CrO_4, ppm	Water temperature, °F	Chlorides	Minimum pH
200	Up to 120	....	6.5
500	Above 120	....	7.0
1,750	....	$CaCl_2$ brine (20–25 per cent solution)	
3,500	....	NaCl brine (20–25 per cent solution)	

The actual amount of chromate needed to retard corrosion can also be found by immersing some clean steel in a sample of the treated water for a reasonable period of time.

Routine testing for chromate is essential for proper control when chromates are employed for corrosion protection. In the range of chromate concentrations used for corrosion control, the amount of chromate can be judged by comparing its yellow color with that of solutions of known strength. Many standard test kits are available for this purpose.

3-44. Colorimetric Test for Chromate. The amount of chromate in the water sample is found by comparing a sample of acidified chromate-treated water with a series of known standards of the same acidified chromate solutions. A photoelectric colorimeter, calibrated to read chromate concentration directly, can also be used effectively.

3-45. Reagents Used. (1) Chromate solution containing 1,000 ppm chromate as sodium chromate. This is needed as a base to prepare 100, 200, 500, and 1,000 ppm standards for visual comparison. (2) Hydrochloric acid, three parts concentrated hydrochloric acid to two parts of distilled water.

3-46. Preparing Known Standard Solutions. (1) 1,000 ppm chromate solution as sodium chromate. Dissolve 1.2 g of K_2CrO_4 (potassium chromate) in distilled water or clear tap water and make up to a total volume of 1 liter. (2) 100 ppm chromate standard. Dilute 10 ml of 1,000 ppm solution with distilled or clear tap water to a total volume of 100 ml. (3) 200 ppm chromate standard. Dilute 20 ml of 1,000 ppm solution with distilled or clear tap water to a total volume of 100 ml. (4) 500 ppm chromate standard. Dilute 50 ml of 100 ppm solution with distilled or clear tap water to a total volume of 100 ml. (5) Pour 50 ml of each standard solution into a 2-oz French square bottle. Add 1 ml of hydrochloric acid reagent. Cap and label each bottle to indicate the parts per million of chromate present.

3-47. Test Procedure. Pour 50 ml of the water sample containing chromate into a clean 2-oz French square bottle. Then add 1 ml of hydrochloric acid reagent. Compare and match the color intensity with that of the prepared standards. If the color intensity is greater than 1,000 ppm standard, dilute the sample solution with distilled or clear tap water. Then use the dilution factor to calculate the correct chromate concentration of the sample.

EXAMPLE 7. A 50-ml sample of chromate-treated brine has a more intense color than the 1,000 ppm chromate standard. A 25-ml sample of the chromate-treated brine is then diluted with clear tap water to 50 ml and acid reagent is added. Compared with the 1,000 ppm standard this sample is now slightly lighter in color. This indicates that the chromate concentration is more than 1,000 ppm but less than 2,000 ppm. By varying the amount of dilution the range for comparison can be narrowed down to any desired concentration. To further narrow the range, 20 ml of clear tap water is added to 30 ml of the chromate-treated brine. Comparison with the 1,000 ppm standard reveals that the sample is darker. This again indicates that the chromate content of the brine is more than 1,667 ppm but less than 2,000 ppm.

4

A Blueprint for Efficient Water Treatment

The primary aim of chemical water treatment is to change the composition of the water in a process so that it is no longer harmful to either the process or the equipment. The first step is to select an ideal range of chemical composition desired in the water. Then it is necessary to calculate the amounts of treating chemical needed to produce and maintain this condition on a continuous basis.

A great deal has been written on determining the ranges of chemical composition needed for the various industrial processes employing water. But there is very little information available on how this can be accomplished in practice. As a result, water treatment is frequently started on a trial-and-error basis and quite often falls far short of the desired results.

There is a basic difference between any *hit-or-miss* plan and a well-planned method of water treatment. This difference lies in the amount of effort put into the plan to account for all the important items which go into and out of the over-all process. We are all familiar with the fact that matter can be neither created nor destroyed by the usual chemical processes. Therefore the input to the system must balance all of the output. This balance applies to all the water that enters, leaves, or remains in the apparatus or system. It also applies to each chemical element originally in the water and to any chemical elements which may be added to treat it.

The importance of keeping continuous records of everything going into and out of the process can hardly be overemphasized. This continuous record will show whether or not the treatment is being maintained within the ideal range. It will also pinpoint any sudden or abnormal change in the process water or in the treatment and establish the immediate need for checking the essential elements of both. Once the cause of such an upset is tracked down, corrective action can then be taken. Perhaps the chemical composition of the water or the amount of chemicals used for treatment has changed. Experience shows that many sudden upsets in the system balance are caused by unsuspected troubles with mechanical equipment that can readily be fixed. An automatic float may be stuck or a valve may not be holding. Water may be leaking from the system through corroded pipes or equipment. Excess water may be entering the system through leaks in submerged coils or other heat-transfer apparatus.

By correction of all these mechanical faults the normal system balance can be restored without changing the established dose of treating chemicals. In each case the trouble is quickly brought to light and corrective steps can be taken.

The material balance for some water treatment processes is very simple and makes the solution of these problems relatively easy. But in most cases the over-all process must be examined in great detail following a definite plan of attack. The most logical way to begin is with a general survey.

4-1. The Survey. The first step is a survey of the process. This can be compared to the medical doctor's preliminary examination and case history that he compiles before treating each patient. The actual survey of the process should include as many facts as possible such as those given in the following outline:

1. Equipment data
    - *a.* Size and manufacturer's rating
    - *b.* Detailed description of its purpose
    - *c.* Physical condition of the equipment: is it scaled or corroded? are there any leaks, etc.?
    - *d.* Enough data to calculate the gallons of water that each specific piece of equipment contains
    - *e.* Type and size of auxiliary equipment
    - *f.* Type and size of chemical feeds
2. Operating conditions
    - *a.* Operating pressures, temperatures, actual loads, hours of operation, etc.
    - *b.* Enough data so that volume of water entering, leaving, or remaining in the process can be calculated
    - *c.* Extent of operating troubles caused by scale, corrosion, clogging, foaming, priming, etc.
3. Chemical reactions involved in the process
    - *a.* Because of dissolved salts in the raw (untreated) water
    - *b.* Because of water treatment

Actually very few plants have the complete set of direct-reading instruments needed to give all of the quantitative data required by this kind of survey. In order to get this information for a survey the most practical means available must be employed. A knowledge of certain simple chemical tests, empirical formulas, and some elementary mathematics is very helpful. The use of these tools is taken up in Chap. 5.

4-2. Flow Diagram of the Process. Use the survey data to prepare a set of simple line sketches similar to Figs. 4-1 to 4-4. These drawings show each item of equipment, give operating data, and trace the various streams of material through the process. Each flow is properly labeled with the pertinent data such as weights, volumes, temperatures, pressures, and chemical reactions that are collected in the survey. In order to make these diagrams easy to read and understand the following symbols are used:

C = concentration of any salt or element in the water; this can be expressed in lb per 1,000 gal
V = vol of water, gal
W = weight of any salt or element in the water; this can be expressed in lb

Subscripts to each of these symbols are used to give additional information. For example, odd-numbered subscripts indicate flow entering the main piece of equipment. All the even-numbered subscripts then stand for flow leaving the main piece of equipment. The subscript *m* indicates that the symbol refers to the water contained in the main piece of equipment. Other lettered subscripts will be defined as they are used.

4-3. Material Balance. The flow diagram can be very helpful in setting up the various individual material balances and at the same time will focus attention on every detail of the process. After this kind of study is made, those streams or flows that have a negligible influence on the problem and its solution can be discarded.

Figure 4-1 shows the various water streams entering and leaving the process. The total volume in gallons entering the system must equal the total number of gallons leaving as long as the volume that remains in the process is constant. The flows on this diagram are lettered so that the volume balance to and from the main item of equipment can be expressed mathematically:

$$V_1 + V_3 \text{ (water input)} = V_2 + V_4 \text{ (water output)}$$

This assumes that the total amount of water in the system V_m remains constant. In this equation

V_1 = raw water entering the equipment every day (input), gal
V_3 = process water returned daily (input), gal
V_2 = water going to waste every day (output), gal
V_4 = process water leaving the equipment every day (output), gal
V_m = water normally held in the equipment, gal

EXAMPLE 1. In this case the main equipment in the flow diagram is a boiler. The amount of raw water entering (before any chemical treatment in the process) is 500 gal per day. Condensate returning to the boiler also equals 500 gal a day. Blowdown to waste from the boiler is 100 gal daily. The boiler itself while operating contains 1,000 gal of water at all times. How much water does this boiler evaporate in a day? The solution is easily obtained by substituting these data in the input equals output formula:

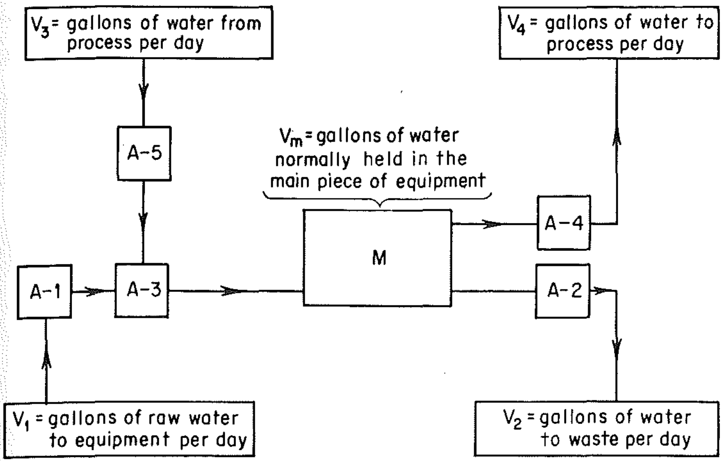


FIG. 4-1. Flow diagram with material balance in gallons of water.

NOTES: 1. M represents the main item of equipment. A-1, A-2, A-3, A-4, and A-5 are auxiliary equipment in the cycle such as pumps, tanks, and heaters.

2. *Raw water* is the term commonly used to indicate water "as received" before treatment. In this flow diagram it stands for water taken direct from the mains before chemical treatment.

$$\begin{aligned} V_1 + V_3 &= V_2 + V_4 \\ 500 + 500 &= 100 + V_4 \\ V_4 &= 900 \text{ gal per day evaporation} \end{aligned}$$

Figure 4-2 shows changes that take place in the chemical characteristics of the raw water as it goes through the process. These changes may affect the equipment or the over-all operation. For example, the raw water entering a given boiler contains sodium chloride, calcium sulfate, and calcium bicarbonate. Due to evaporation, the sodium chloride concentrates 20 times, indicating that all the solids have increased 20 times. However, the calcium sulfate concentrates only 10 times. Half of it precipitates from the boiler water, indicating that scale is forming on the tubes. The calcium bicarbonate, under heat and pressure, breaks up to form carbon dioxide and an insoluble calcium carbonate deposit which must be removed regularly by blowdown.

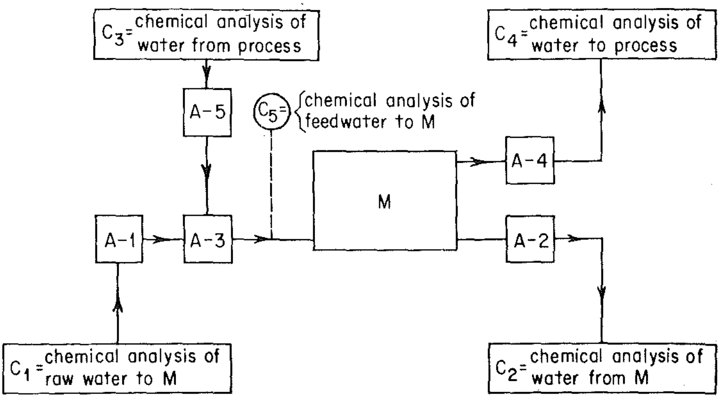


FIG. 4-2. Flow diagram with chemical balance of the raw-water changes.

NOTES: 1. M represents the main item of equipment. A-1, A-2, A-3, A-4, and A-5 are auxiliary equipment in the cycle such as pumps, tanks, and heaters.

2. The term *feed water* stands for a mixture of the raw water and water returning from the process.

In Fig. 4-2 the amount of each chemical constituent entering the process must be accounted for in order to obtain a material balance. The input will then equal the output as long as the amount that remains in the process is constant. The various flows are lettered to help simplify this kind of chemical balance. But remember that a chemical water analysis is made in terms of the concentration of each constituent in the water at the point of analysis. For a complete material balance the chemical analysis is tied together with the volume data of Fig. 4-1. The combined concentration and volume data are easily expressed mathematically. Assuming that the amounts of both water and chemicals held in the process do not change, the formula is

$$\underbrace{C_1V_1 + C_3V_3}_{\text{Total input}} = \underbrace{C_2V_2 + C_4V_4}_{\text{Total output}} \tag{4-1}$$

If the feed water is a fairly constant combination of raw water and water returning from process, the formula can be simplified to

$$C_5(V_1 + V_3) = C_2V_2 + C_4V_4 \tag{4-2}$$

C_1 = chemical analysis of raw water entering the process
C_2 = chemical analysis of water in the main item of equipment M or leaving M as waste
C_3 = chemical analysis of water returning from process to M
C_4 = chemical analysis of water going to process from M
C_5 = chemical analysis of the feed water to M

EXAMPLE 2. Water from the boiler system in Example 1 is chemically analyzed for chloride with the following results:

Raw water to boiler	$C_1 = 4$ ppm
Water in the boiler	$C_2 = 20$ ppm
Condensate returns to the boiler	$C_3 = 0$ ppm
Total feed water to the boiler	$C_5 = 2$ ppm
Steam leaving the boiler	$C_4 = 0$ ppm

Prove that the chloride input to the system equals the chloride output. How many pounds of chlorides enter the system every day with the makeup?

The simplest way to check the chloride balance is first to change all the terms in Eqs. (4-1) and (4-2) to a common system of units. Convert the parts per million of chlorides at any given point in the system to the more familiar pounds per gallon. Just divide the parts per million of chlorides by 120,000. The volume of water in gallons per day multiplied by the pounds per gallon of chlorides gives the pounds per day of chlorides at that particular point in the system. In this example

$C_1 = 0.0000333$ lb per gal
$C_2 = 0.000167$ lb per gal
$C_3 = 0$
$C_4 = 0$
$C_5 = 0.0000167$ lb per gal

Now substitute these values in Eq. (4.2).

$$\begin{aligned} C_5 \times (V_1 + V_3) &= C_2V_2 + C_4V_4 \\ 0.0000167 \times (500 + 500) &= (0.000167 \times 100) + (0 \times 900) \\ 0.0167 \text{ lb per day} &= 0.0167 \text{ lb per day} \end{aligned}$$

Therefore the amount of chlorides entering and leaving the boiler system balances out at 0.0167 lb per day.

The raw-water chloride input is C_1V_1 or 0.0000333×500. This also equals 0.0167 lb per day. This numerical example also emphasizes why the chemist prefers to use a unit such as parts per million rather than the familiar pound unit for water analysis. The pound units contain so many zeros that they are very awkward to handle.

The survey and the resulting flow diagrams (Figs. 4-1 and 4-2) will usually provide enough information to diagnose any water trouble in the process needing correction. In like manner the medical doctor diagnoses the patient's ills and then uses all his training and experience to prescribe treatment suited to the individual needs of each patient. Prescribing suitable water treatment also requires training and a lot of experience. Chemicals must be selected from those available and the desired range of chemical composition in the treated water must be defined. If there is any doubt about the kind of treatment needed the services of a competent water treatment specialist should be obtained.

There are two basic methods of adding and controlling the treating chemicals needed to properly condition water in a given process: they are the *batch method* and the *continuous method.*

4-4. The Batch Method of Treatment. With the batch method the chemical balance is always computed around the volume of water contained in the main piece of equipment. The prescribed amounts of treating chemicals are added to the main body of water. Then the water is tested to see if the proper concentration has been reached. Tests are run at regular intervals to make sure that the desired levels are maintained. Additional treating chemicals are then added as needed.

The following basic equation is used to compute the amount of treating chemical needed at any particular moment for the batch method of treatment:

$$W = C \times V \tag{4-3}$$

where C = concentration of chemical desired in the water, lb per 1,000 gal
V = vol of water treated, gal
W = weight of treating chemical added to the water, lb

The concentration of chemical desired in the water is usually reported in parts per million or grains per U.S. gallon and therefore must be converted into pounds per thousand gallons.

The over-all chemical balance of treating chemicals for the batch method is outlined in Fig. 4-3. Various lettered subscripts are used to help simplify interpretation of the data. The descriptive subscripts used in this flow diagram have the following meanings:

a = added to the water or equipment
d = desired in the water
f = found in the water
e = wasted in outgoing water or from the equipment
m = main body of water
ma = added to main body of water or main item of equipment
md = desired in the main body of water
mf = found in main body of water
r = reacts with salts in the water

This flow diagram can be used in several ways to compute the amount of treating chemical needed in a given process.

4-5. Batch Method 1. This is actually the simplest treating method. A definite concentration of treating chemical is added to a known volume of water. The treating chemical does not react with any salts in the water.

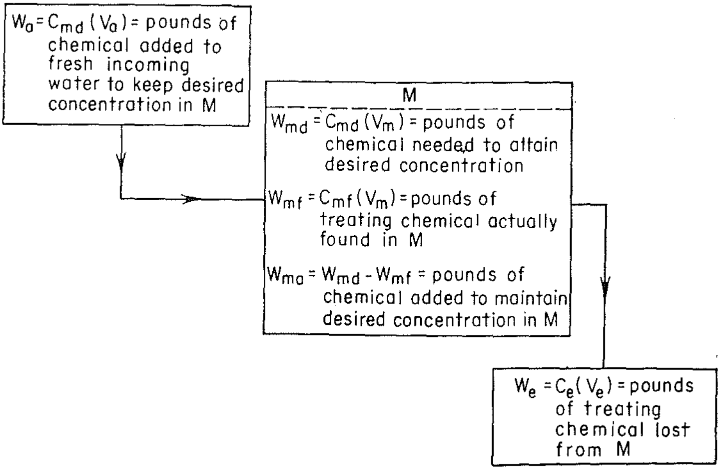


FIG. 4-3. Chemical balance of treating chemicals—batch method.
Glossary of terms:

W = pounds of chemical
V_a = vol of water added to M, gal
V_e = vol of water lost from M, gal
V_m = vol of water in M, gal
C_{md} = concentration of treating chemicals desired in M, lb per 1,000 gal
C_{mf} = concentration of treating chemicals found in M, lb per 1,000 gal
C_e = concentration of treating chemicals lost from M, lb per 1,000 gal
C_r = concentration of treating chemicals reacting with salts in water

NOTE: These chemical balances hold when the treating chemical does not react with the water. If it does react, add C_r to the concentration factor in each equation. For example:

$$W_{md} = (C_r + C_{md})V_m$$

EXAMPLE 3. A boiler contains 5,000 gal of water (V_m). The water in the boiler must be treated with enough anhydrous sodium chromate (W_{md}) to produce an initial concentration of 480 ppm sodium chromate (C_{md}). In addition, the amount of sodium chromate in the boiler water must not be allowed to fall below 240 ppm (C_{mf}). How much anhydrous sodium chromate is needed to produce the initial concentration of 480 ppm? How much treating chemical (W_{ma}) is needed to bring the concentration up from 240 to 480 ppm?

The amount of anhydrous sodium chromate needed initially can be calculated from Eq. (4-3).

$$W_{md} = C_{md}(V_m)$$

Since 120 ppm is equal to 1 lb per thousand gallons, 480 ppm of anhydrous sodium chromate equals 4 lb per thousand gallons. By the same token, 240 ppm is equal to 2 lb per thousand gallons.

C_{md} = 4.0 lb per 1,000 gal
V_m = 5,000 gal
W_{md} = amount of treating chemical needed in lb to produce the initial concentration of 480 ppm sodium chromate in the water
W_{md} = 4.0 lb per 1,000 gal (5,000 gal)
= 20 lb

Therefore, the initial treatment of the 5,000 gal of boiler water calls for 20 lb of anhydrous sodium chromate.

Equation (4-3) can also be used to determine the amount of chromate needed to raise the concentration in the boiler from 240 ppm back to 480 ppm.

$$W_{ma} = C_{ma}(V_m)$$

C_{ma} is the amount of treating chemical needed to raise the concentration from 240 ppm (C_{mf}) to 480 ppm (C_{md}). By definition

$$C_{ma} = C_{md} - C_{mf}$$

This expression can be substituted in Eq. (4-3) for C_{ma}.

$$W_{ma} = (C_{md} - C_{mf})V_m \tag{4-4}$$

C_{mf} = 2.0 lb per 1,000 gal
W_{ma} = amount of treating chemical in lb to raise the concentration from 240 to 480 ppm
W_{ma} = (4.0 lb per 1,000 gal − 2.0 lb per 1,000 gal) × 5,000 gal
= 10 lb

Therefore, increasing the concentration from 240 to 480 ppm in 5,000 gal of boiler water requires the addition of 10 lb of anhydrous sodium chromate.

4-6. Batch Method 2. Again, a definite amount of treating chemical is added to a known volume of water in a vessel. But in this case the treating chemical reacts with salts in the water. The first step in solving this problem is to calculate the amount of treating chemical consumed in the reaction. Then the concentration of treating chemical that must be maintained in the vessel is selected. The quantity of treating chemical needed is computed from these two values for the given volume of water being treated.

EXAMPLE 4. A boiler contains 5,000 gal of water (V_m). An analysis of the water reveals that it contains 100 ppm calcium sulfate which will react with 80 ppm of trisodium phosphate (C_r). How much trisodium phosphate must be added to the water in this boiler to produce an initial concentration of 200 ppm trisodium phosphate (C_{md})?

The figure of 80 ppm trisodium phosphate is given at this point to illustrate the effect of treating chemicals that react with the water. Therefore it is not necessary to discuss the combining-weight relationships of these chemicals in detail. The chemical reaction is

$$3CaSO_4 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3Na_2SO_4$$

Three times the molecular weight of calcium sulfate reacts with twice the molecular weight of trisodium phosphate (see Sec. 1-16). This is the same as saying that 408 ppm calcium sulfate reacts with 328 ppm trisodium phosphate (see Tables 1-1 and 1-2 for weights of elements and radicals). Therefore, in the same proportion, 100 ppm calcium sulfate reacts with 80 ppm trisodium phosphate.

The amount of trisodium phosphate needed to produce an initial concentration of 200 ppm trisodium phosphate in the boiler is calculated by setting up Eq. (4-3) in the following way:

$$W_{md} = (C_r + C_{md})V_m \qquad (4\text{-}5)$$

$(C_r + C_{md})$ is the total concentration needed to produce the 200 ppm trisodium phosphate wanted in the boiler.

C_r = 0.67 lb per 1,000 gal (80 ppm trisodium phosphate)
C_{md} = 1.67 lb per 1,000 gal (200 ppm trisodium phosphate)
V_m = 5,000 gal of water in the boiler
W_{md} = amount of treating chemical in lb needed to produce 200 ppm trisodium phosphate in the boiler water

$$\begin{aligned} W_{md} &= 0.67 + 1.67 \text{ lb per 1,000 gal (5,000 gal)} \\ &= 11.7 \text{ lb} \end{aligned}$$

The initial treatment of 5,000 gal of water in the boiler therefore calls for 11.7 lb of trisodium phosphate.

4-7. The Continuous Method of Treatment. With this method the fixed volume of water in the equipment is usually of secondary importance. The most important changes are those taking place in the water as it goes into and out of the equipment. The over-all balance is based on the fact that the input streams must equal the output streams. The correct amount of treating chemical is added continuously to the incoming-water stream. The concentration of chemical in the main body of water is then checked to see if the desired level has been reached. Enough time is allowed for the main body of water to reach a stable or equilibrium condition. Then tests are performed at regular intervals to make sure that the correct concentration is maintained. If it is too high or too low, the input and output balance should be checked and the treatment adjusted to compensate.

The following basic equation is used to compute the amount of treating chemicals needed in the continuous treatment:

$$\underset{\text{Water in}}{C_o(V_o)} = \underset{\text{Water out}}{C_e(V_e)} \qquad (4\text{-}6)$$

Subscript o = all odd-numbered subscripts in Fig. 4-4
Subscript e = all even-numbered subscripts in Fig. 4-4

The continuous method of treatment is shown in schematic form in Fig. 4-4. All the odd-numbered subscripts in this flow diagram indicate incoming streams of water. The even-numbered subscripts represent the outgoing streams of water. Like the batch method this flow diagram can be used in several ways to calculate the amounts of treating chemical required.

General Plan for the Continuous Method. One common method is to add a definite concentration of treating chemicals (C_2) to a fixed volume of water in a boiler, evaporator, or other apparatus. Water enters the equipment at a constant rate (V_1). Treating chemical (W_1) is added to the incoming water at a given concentration (C_1 for chemicals which do not react with salts in the water and $C_r + C_1$ for those chemicals that do react with the incoming water). The total water input usually consists of raw water plus some steam condensate returned for reuse. In the case of a boiler or evaporator, the water evaporates at a rate

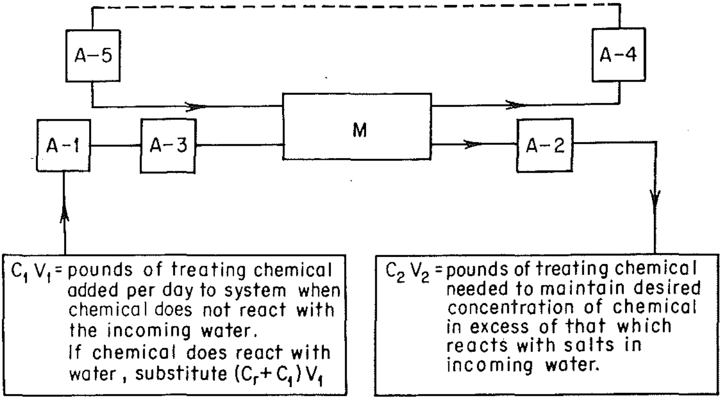


FIG. 4-4. Chemical balance of treating chemicals—continuous-flow method. *Glossary of terms:*

C_r = concentration of treating chemical that reacts with salts in the incoming water, lb per 1,000 gal
C_1 = concentration of treating chemical desired in excess of C_r in the incoming water, lb per 1,000 gal (Other treating chemicals may be represented by odd numbers, C_3, C_5, etc.)
V_1 = vol of incoming water, gal per day
C_2 = concentration of treating chemical needed in equipment, lb per 1,000 gal
V_2 = vol of water going to waste, gal per day

proportional to the water entering. The steam or vapor formed is equivalent to distilled water in purity. All the salts and chemicals present in the incoming water remain in the equipment and concentrate. This build-up of salt concentration is controlled by removing water (blowdown) from the boiler at a fixed rate (V_2) that is proportional to the incoming water rate. If the treating chemicals do not react with the salts in the water, Eq. (4-6) can be set up in the following way:

$$W = C_1V_1 = C_2V_2 \tag{4-7}$$

where W = treating chemical added to the incoming water, lb per day
C_1 = concentration of treating chemical needed in the incoming water, lb per 1,000 gal
V_1 = vol of incoming water, gal per day
C_2 = concentration of treating chemical wanted in the equipment and therefore found in the water going to waste as blowdown
V_2 = vol of water going to waste, gal per day

In Eq. (4-7) the value of C_2 is usually known. C_2 is the concentration of treating chemical that must be maintained in the equipment. Operating conditions fix V_1 and V_2. Equation (4-7) can then be solved for either W or C_1.

If any substances in the water do react with the treating chemicals, the first step is to write out the chemical reaction involved. Then calculate the concentration of treating chemical (C_r) that is changed or removed from the water by the reaction. The amount of treating chemical needed to meet these conditions is

$$W = (C_r + C_1)V_1 \tag{4-8}$$

where W = treating chemical added to the incoming water, lb per day
C_r = concentration of treating chemical that reacts with salts in the incoming water, lb per 1,000 gal
C_1 = concentration of treating chemical wanted in the incoming water in excess of C_r, lb per 1,000 gal

In Eq. (4-8) V_1 is usually fixed by operating conditions. The value of C_r is obtained by studying the chemical reactions involved. The unknown is usually C_1. Equation (4-7) can be used to find the value of C_1 without computing C_r.

$$C_1V_1 = C_2V_2 \tag{4-7}$$

The value of C_2 is usually known. It is the concentration of treating chemical that must be maintained in the equipment. Operating conditions will usually fix V_1 and V_2. Since three of the four items in Eq. (4-7) are known, we can solve for C_1. Then we can substitute this value in Eq. (4-8) and solve for W.

EXAMPLE 5. A boiler plant operates under the following conditions. The quantity of raw water entering the boiler equals 500 gal per day (V_1). Condensate returned is 500 gal per day. Blowdown amounts to 100 gal per day (V_2). The volume of water in the boiler is 1,000 gal under all conditions. The concentration needed in the boiler (C_2) is 200 ppm trisodium phosphate. An analysis of the raw water shows the presence of 100 ppm calcium sulfate which reacts with 80 ppm trisodium phosphate as previously explained in Example 4. How much trisodium phosphate is needed to maintain the desired 200 ppm concentration in the boiler? Equations (4-7) and (4-8) are used to solve this problem.

$$C_1V_1 = C_2V_2 \tag{4-7}$$

$$W = (C_r + C_1)V_1 \tag{4-8}$$

C_1 = concentration of treating chemical desired in the raw water in terms of lb per 1,000 gal
V_1 = 500 gal of raw water per day going to the boiler
C_2 = 200 ppm or 1.67 lb per 1,000 gal
V_2 = 100 gal of blowdown per day
C_r = 80 ppm trisodium phosphate or 0.67 lb per 1,000 gal

First solve for C_1 in Eq. (4-7).

$$\begin{aligned} C_1 \times 500 \text{ gal per day} &= 1.67 \text{ lb per 1,000 gal} \times 100 \text{ gal per day} \\ &= 0.334 \text{ lb per 1,000 gal} \end{aligned}$$

Then use Eq. (4-8) to solve for W.

$$W = (0.67 + 0.334) \text{ lb per 1,000 gal} \times 500 \text{ gal per day}$$

$$W = 0.502 \text{ lb per day}$$

Therefore, we need 0.502 lb per day of trisodium phosphate to maintain a concentration of 200 ppm trisodium phosphate in the boiler.

4-8. The Control Record. When the chemical charge is put into the water, the changes in composition are best followed by making routine analysis checks on a periodic basis. The most essential part of every good water treatment plan is to keep a running record of these analyses and any other factors that influence the over-all process balance. This kind of control can be readily compared to the clinical approach in medicine. The hospital keeps detailed charts and records of each patient's temperature, pulse rate, blood count, medication, diet, etc. Any abnormality in these factors warns the doctor that something is wrong. He can then act immediately to find the cause of the trouble and take corrective measures.

Figure 4-5 shows a typical water treatment control record. It consists of two essential parts. The permanent data describe the normal expected operating conditions. The other regular entries cover those factors that affect the treatment balance. These include water input, water output, chemical dosages fed to the process, and the chemical analysis of changing elements in the water which affect the treatment.

The control record is a valuable tool that helps the plant operator maintain treatment within the desired maximum and minimum limits. It indicates when the amounts of treating chemical must be increased or decreased. It also helps the operator decide when to adjust such items as blowdown or bleed rates that affect the concentration of salts in evaporative equipment or a boiler. Whenever the control records reveal a sudden change in chemical composition of the water, the operator must be on the alert for trouble. The direction of this change is usually a clue to what has happened. Operating conditions most affected by such a change should be checked closely. Once the cause of the trouble is found, corrective action can be taken. If the operator still cannot find the cause of the trouble, at least he knows it is time to call for the help of a consultant.

Name of company..
Specific equipment under treatment..
Size or capacity of equipment..

Normal Operating Data

Hours operation..............Water input..................Water output......................
Type treatment..............................Dosages normally used...............................
Concentration of treating chemicals desired in the water..........................
..............................Maximum..............................Minimum..............................
Concentration of salts normally desired in the water (if evaporative equipment)..............................Maximum..............................Minimum..............................
Special data..
....

Date and time	Water input	Water output	Dosage used	Chemical analysis			Remarks
				Item A	Item B	Item C	

FIG. 4-5. Typical form of water treatment control record.

EXAMPLE 6. A typical control record for a low-pressure steam-heating boiler shows an abnormal rise in the chloride content of the boiler water. What is the probable cause and how can it be corrected? Since there is no apparent change in the normal operating conditions, the operator knows something is actually wrong. Chlorides are not changed by heat or normal boiler water reactions. The operator is well aware of this since he has been checking chlorides regularly as a guide to the concentrations of all salts in the boiler water.

Therefore the rise in chlorides means that a general rise in total dissolved solids must be taking place in the boiler water. This means that there has been an increase in the amount of raw-water makeup entering the boiler. Since total boiler input consists of raw water and condensate, it appears that all of the normal condensate returns are not getting back to the boiler.

A careful check of the steam and condensate-return system reveals a leak in one of the return pipes. This leak is repaired and the chloride concentration in the boiler water falls back to its normal level. Thus the control record helps correct a bad operating condition which might otherwise go undetected.

5

Practical Ways of Finding Capacity, Blowdown, and Makeup

In almost every water-conditioning problem it is necessary to find out how much water is held in each item of equipment. We also need to know how much water enters, leaves, or remains in the process on a daily, hourly, or some other unit-of-time basis. Quite often a small or even a medium-sized plant does not have the right measuring instruments available to obtain this information. Water meters and gauges placed in the right locations will give most of the needed data. But if these instruments are not readily available, the water volumes and flow rates must be measured some other way. This chapter outlines various practical methods which will help you obtain the required information in the absence of instruments and gauges.

5-1. Determining the Holding Capacity of a Vessel or Tank. Most of the equipment usually found in a plant can be classified as either rectangular, cylindrical, conical, circular, or some combination of these various shapes. Figure 5-1 lists the formulas needed to calculate the volume of some of the common shapes. The formula given for cylindrical-tank volume is good only when the tank is in a vertical position or is completely filled with water. Figure 5-2, universal tank capacity scales, can be used to calculate the gallons of water in a horizontal tank when it is partially filled with water.

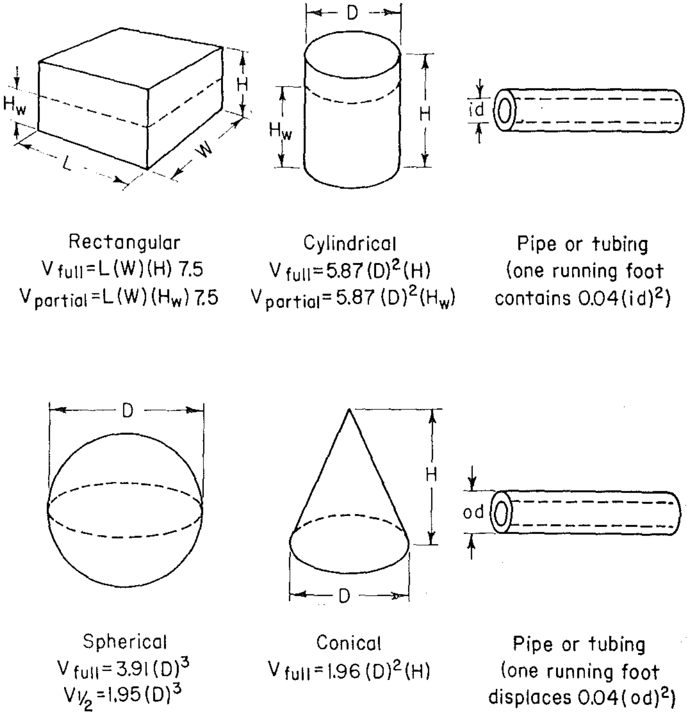


FIG. 5-1. Gallons of water common shapes hold or displace.

L = length, ft
W = width, ft
H = height, ft
D = diameter, ft
H_w = height to water line, ft
id = inside diameter, in.
od = outside diameter, in.

These scales give the volume of liquid contained in a horizontal tank with flat vertical ends. Figure 5-1 gives the formula for calculating the total volume of cylindrical tanks with flat ends. But this formula does not apply when it is necessary to calculate the contents of a partially filled horizontal tank. In that case the first step is to take soundings of the partly filled tank to determine the actual depth of liquid. Then express this depth as a per cent of the tank diameter (depth divided by diameter multiplied by 100). Enter the scales in Fig. 5-2 with this number to obtain the volume occupied by the liquid as a percentage of the total tank volume.

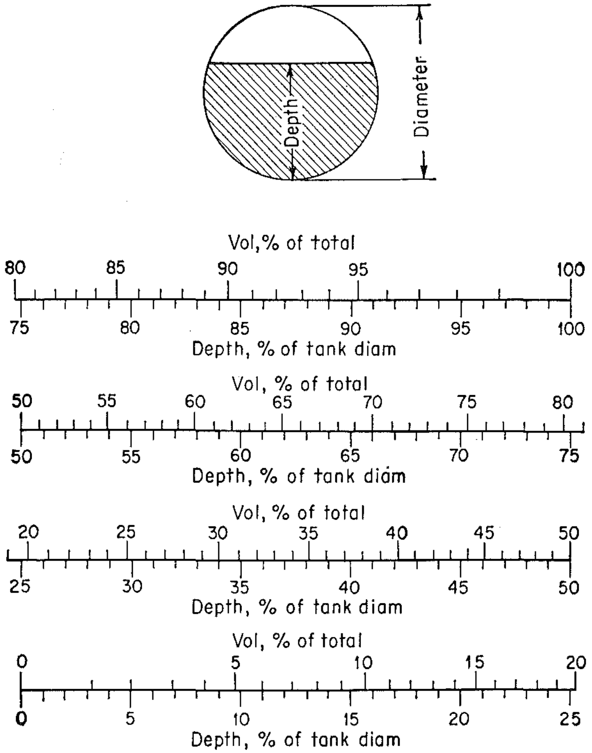


FIG. 5-2. Universal tank capacity scales.

EXAMPLE 1. A horizontal cylindrical tank has an inside diameter of 7 ft and is 10 ft long. The depth of water in the tank is 4 ft.

How many gallons of water are in the partly filled tank?

Total capacity of tank = $5.87 \times 7^2 \times 10 = 2{,}880$ gal
Tank depth as a per cent of tank diameter = $\frac{4}{7} \times 100 = 57.1$ per cent
Corresponding vol from scales in Fig. 5-2 = 59.0 per cent
Vol of liquid in tank = $2{,}880 \times \frac{59}{100} = 1{,}700$ gal

Usually plant equipment is physically some combination of the various basic shapes described in Fig. 5-1. In general the volume of the largest-shaped section is calculated first. All the equipment taking up room inside this particular section decreases the final volume. Any equipment added to this section increases the final volume. For example, a rectangular tank has a bank of heat-exchange tubes that maintain the water at a given temperature. In this case the volume of water held in the tank equals the total volume of water calculated from its dimensions without tubes minus the volume of water actually displaced by these tubes.

EXAMPLE 2. A rectangular tank holds the water needed for a certain process. The tank itself is 5 ft long by 6 ft wide by 8 ft high. Normally the depth of water in the tank is only 6 ft. There are 80 cylindrical tubes along the lower portion of the tank. Each of these tubes is 5 ft long with an inside diameter of 1⅞ in. and an outside diameter of 2 in. How much water does the tank hold when it is filled to the usual 6-ft level?

If the tank did not contain any tubes the quantity of water present would be

$$L \times W \times H_w \times 7.5 = \text{water vol, gal}$$
$$5 \times 6 \times 6 \times 7.5 = 1{,}350 \text{ gal}$$

The tank actually contains 400 ft of tubes (80 times 5) in the bottom of the tank. They displace a volume of water equal to

$$0.04 \times \text{od}^2 \times 400 = \text{water displaced, gal}$$
$$0.04 \times 2^2 \times 400 = 64 \text{ gal}$$

The amount of water actually held in the tank at the 6-ft level is then 1,350 minus 64, or 1,286 gal of water.

The water tube boiler is a typical example of a vessel combining many shapes. It usually consists of one or more cylindrical drums with numerous cylindrical tubes. The volume of water held in a boiler of this type is readily calculated from the information contained in Figs. 5-1 and 5-2.

1. If the boiler drums are vertical or completely filled, the amount of water in each cylindrical drum is found from the formula in Fig. 5-1. If the drums are horizontal, use Fig. 5-2.
2. The volume of water contained in all the circulating tubes is then calculated from the formula in Fig. 5-1 and equals $0.04\ id^2 \times$ number of running feet.
3. The total volume of water held in the water tube type of boiler equals that held in the drums plus all the water contained in the circulating tubes.

5-2. Empirical Formulas Based on Cubical Dimensions. Some low-pressure heating boilers are rectangular and others are cylindrical. It would be extremely complicated to add or subtract the variety of shapes which are frequently a part of the water side of this type of boiler. Experience has shown that this is not necessary. By substitution of a general factor into the formula for a rectangle or a cylinder, the gallons of water contained in a specific type of boiler can be estimated for normal operating conditions. Table 5-1 lists several empirical formulas which have been found very useful for low-pressure heating boilers.

Table 5-1. Empirical Formulas Giving the Number of Gallons of Water Contained in Various Boilers

Type of boiler	*Formula*
Cast iron sectional	$L \times W \times H_w \times 3$
Steel fire tube	$3 \times D^2 \times L$
Rectangular self-encased water tube	$L \times W \times H_w \times 1.6$

NOTE: D is the diameter of the shell. All other dimensions are as shown in Fig. 5-1.

5-3. Measuring Vessel Volume Experimentally. There are three methods of experimentally determining the gallons of water contained in a particular piece of equipment. These are classified as (1) the direct method, (2) the indirect method, and (3) the chemical tracer method.

5-4. The Direct Method. First completely empty the vessel that is being measured. Then add known amounts of water from another smaller vessel.

EXAMPLE 3. A boiler is used to generate steam for heating. How many gallons of water does the boiler hold at normal operating level? A cylindrical tank measuring 2 ft in diameter by 2 ft high is available, and it can be connected to the suction side of the feed-water pump.

According to the formula in Fig. 5-1, the full volume of the cylindrical measuring tank is 47 gal ($5.87 \times 2^2 \times 2$). Since the volume occupied by the water in the boiler is greater at higher temperatures, note the operating level in the gauge glass under steaming conditions. Then allow the water to cool to room temperature and again note the level in the gauge glass. Then proceed as follows:

1. Empty the boiler.
2. Fill the measuring tank with water.
3. Pump the 47 gal of water in the measuring tank directly into the boiler using the boiler feed pump.
4. Repeat steps 2 and 3 until the water in the boiler is at normal operating level in the gauge glass at room temperature. If it takes 20 tank fills to bring the water up to the desired level, the quantity of water in the boiler is then 20 times 47, or 940 gal.

5-5. The Indirect Experimental Method. This method consists in filling the vessel at a constant rate of flow and noting the time that it takes to fill it completely. The mathematical expression is

$$Q_n = T \times V \qquad (5\text{-}1)$$

where Q_n = vol of water held by the vessel at normal operating level, gal
T = total time to fill the vessel, min
V = rate of flow into the vessel, gpm

EXAMPLE 4. How many gallons of water does an open odd-shaped tank hold when it is filled to a point that is 4 in. from the top? A hose can be attached to a nearby 1-in. pipeline and used to deliver water to the tank. In addition this pipeline has a handy gate valve for regulating the flow of water.

With the aid of a 5-gal pail, adjust the gate valve to deliver about 20 gpm. At this flow it takes 15 sec to fill the 5-gal pail. Once the rate is set, use the hose to fill the empty tank. Note the time that is required. At the 20-gpm rate it takes 30 min to fill the tank to a point 4 in. from the top.

$$\begin{aligned} Q_n &= T \times V \\ &= 30 \text{ min} \times 20 \text{ gpm} \\ &= 600 \text{ gal} \end{aligned}$$

Therefore the tank normally holds 600 gal of water when filled to a point 4 in. below the top.

5-6. The Chemical Tracer Method. This method is based on putting a measured quantity of an unreactive foreign element into the volume of water to be measured. The resulting concentration of the tracer element in the body of water is then found by chemical analysis. The mathematical expression for this relationship is

$$V_n = \frac{W_t}{C_t} \tag{5-2}$$

where V_n = vol of vessel, gal

W_t = exact weight of tracer element, lb (or oz)

C_t = concentration of the tracer element, lb per 1,000 gal (or oz per 1,000 gal)

The tracer element added to the water does not have to be one that is completely absent from the water itself. However, if the tracer is already present the actual amount should be negligible. This requirement is satisfied when the final concentration of the tracer element is at least ten times greater than the original concentration of this element in the water. Another important consideration is that the tracer element should not react with the water or any other element in the water under the actual conditions of this test.

When the chloride or nitrate content of the water in the vessel is not too high, salts like sodium chloride (common table salt) or sodium nitrate (saltpeter) can be used as the chemical tracer.

Tables 5-2 and 5-3 are helpful when it is necessary to choose the correct amount of tracer needed to increase the chloride (Cl) or nitrate (NO_3) any desired amount in a given water supply.

EXAMPLE 5. A boiler is used at a plant for heating. With the aid of a chemical tracer, find out how much water the boiler holds at normal operating level. Use sodium nitrate as the tracer element. The nitrate present in the boiler water itself is 2 ppm.

Table 5-2. Sodium Chloride Tracer Chart

Vol of water contained in the vessel, gal	Chloride (Cl) increase in the vessel, ppm								
	100	150	200	250	300	350	400	450	500
	Amount of salt added to the vessel, oz								
100	2	3.5	4.5	5.5	6.5	7.5	9	10	11
200	4.5	6.5	9	11	13	15.5	17.5	20	22
300	6.5	10	13	16.5	20	23	26.5	29.5	33
400	9	13	17.5	22	26.5	31	35	39.5	44
500	11	16.5	22	27.5	33	38.5	44	49.5	55
600	13	19.5	26	32.5	39	46	52.5	59	66
700	15.5	23	30.5	38	46	53.5	61	69	77
800	17.5	26	35	44	52.5	61.5	70	78.5	88
900	19.5	29.5	39.5	49	59	69	79	88.5	99
1,000	22	33	44	55	66	77	88	99	110
1,200	26	39	52.5	65.5	78.5	92	105	118	131
1,400	30.5	46	61	76.5	92	107	122	138	153
1,600	35	52.5	70	87.5	105	122	140	158	175
1,800	39.5	59	78.5	98.5	118	138	158	178	197
2,000	43.5	65.5	87.5	110	132	154	176	197	219

Add 10 oz of sodium nitrate to the boiler water under normal operating conditions. Allow enough time to ensure complete mixing of the tracer with the entire volume of boiler water. Then analyze the boiler water for nitrate content. Under these conditions the nitrate in the boiler expressed as NO_3 is 62 ppm, for a net nitrate increase of 60 ppm. Table 5-3 shows that 10 oz of sodium nitrate gives a 60 ppm nitrate increase in 900 gal of water.

Table 5-3. Sodium Nitrate Tracer Chart

Vol of water contained in the vessel, gal	Nitrate (NO_3) increase in the vessel, ppm									
	20	40	60	80	100	120	140	160	180	200
	Amount of sodium nitrate ($NaNO_3$) added to vessel, oz									
100	0.5	0.75	1.25	1.50	1.75	2	2.5	3	3	3.5
200	0.5	1.5	2	3	3.5	4.5	5	6	6.5	7
300	1	2	3.5	4.5	5.5	6.5	7.5	9	10	11
400	1.5	3	4.5	6	7	8.5	10	11.5	13	14
500	2	3.5	5.5	7.5	9	11	13	14.5	16.5	18
600	2	4.5	6.5	9	11	13	15.5	17.5	20	22
700	2.5	5	7.5	10	13	15.5	18	20.5	23	25.5
800	3	6	8.5	11.5	14.5	17.5	20	23	26	29
900	3.5	6.5	10	13	16.5	20	23	26.5	30	33
1,000	3.5	7	11	14	18	22	25.5	29	33	36.5
1,200	4.5	9	13	17.5	22	26.5	31	35	39.5	44
1,400	5	10	15.5	20.5	25.5	30.5	35.5	41	46	51
1,600	6	11.5	17.5	23.5	29	35	41	47	52.5	58.5
1,800	6.5	13	20	26.5	33	39.5	46	53	59.5	66
2,000	7	14.5	22	29	36.5	44	51	58.5	65.5	73

Therefore the heating boiler in this case holds 900 gal of water at normal operating level.

5-7. Application of Chemical Tracers to Find Blowdown or Other Water Losses. The use of a chemical tracer to determine the amount of blowdown or other water losses from a vessel is not difficult. Just follow these steps:

1. First determine the normal average concentration of tracer in the water before adding the tracer element.
2. Next add the right amount of tracer chemical to the water. Use enough to give a final concentration at least 10 times greater than the average normally found in the vessel itself.

3. After mixing the tracer thoroughly with the water, determine the final concentration of the chemical tracer. This step automatically determines the number of gallons held in the vessel.

4. Make an analysis for the tracer element in the water on a regular basis. This can be done before each blowdown or at least once a day. Keep the level of water in the vessel constant by adding fresh water to replace any that is lost by blowdown. The tracer element lost this way is not replaced by the incoming fresh water, and gradually the tracer element in the water is diluted. This loss of chemical tracer is directly proportional to the amount of water lost by blowdown. Prepare a table showing the per cent loss of tracer chemical during each interval of analysis. Then use this table to calculate the average per cent loss of tracer element.

5. The amount of water lost by blowdown equals the number of gallons of water held in the vessel multiplied by the average per cent loss of tracer chemical.

EXAMPLE 6. A boiler is used at a plant for generating steam. How much water is lost from the boiler by blowdown? The operating schedule calls for blowdown regularly once a day. The amount equals 3 in. of water as measured by the gauge glass. For several weeks before the test the chloride content of the boiler water is analyzed daily. These records show an average chloride content of 20 ppm expressed as Cl. Since the concentration of chlorides is low, sodium chloride can be used as the tracer chemical to determine the amount of blowdown.

Add enough sodium chloride tracer to give a minimum final concentration at least 10 times greater than the average chloride content of 20 ppm in the boiler water. Best results will be obtained with a concentration in the range of 400 to 500 ppm Cl. Table 5-2 shows that 11 oz of sodium chloride is required for every 100 gal of boiler water to increase the chloride content of the boiler water by 500 ppm. As a trial measure add 22 oz of sodium chloride tracer to the boiler. After allowing a reasonable time for mixing, analyze the boiler water for chloride. This test shows an actual chloride content of 120 ppm, or a net increase of 100 ppm. On this basis the boiler holds about 1,000 gal of water.

However, not enough tracer chemical has been added. The chloride concentration should be around 500 ppm. Table 5-2 also shows that 110 oz of sodium chloride tracer is needed to get 500 ppm Cl in 1,000 gal of water. Therefore another 88 oz of sodium chloride is needed in the boiler water. After adding and mixing the additional salt, again test the boiler water for chlorides. Then each day, just before blowing down the boiler, take a boiler water sample and run the chloride test. The results of this typical test, covering a five-day period, are shown in Table 5-4.

Table 5-4. Loss of Chloride Tracer in Per Cent

Day	Chloride, ppm		Daily Cl loss	
	Total	Due to salt added	Ppm	%
1st	510	490	0	
2d	450	430	60	12
3d	400	380	50	11
4th	365	345	35	8.7
5th	330	310	35	9.6

Total Cl loss for 5 days........ 41.3%
Average daily Cl loss*........ 10.3%

* Computed thus: $\frac{12 + 11 + 8.7 + 9.6}{4} = 10.3\%$

Table 5-4 shows that 110 oz of sodium chloride increases the chloride content of the boiler water exactly 490 ppm. From Table 5-2 we find that the boiler holds about 1,000 gal of water. With 10 per cent average daily blowdown from a 1,000-gal boiler, the daily blowdown loss is 100 gal of water.

5-8. Determining the Amount of Makeup Water to a Vessel. There are various ways to determine the amount of makeup water to a vessel when there is no meter on the makeup water line. These methods can be classified as either *direct* or *indirect*.

5-9. The Direct Experimental Method. This is based on adding all the makeup requirements from a series of smaller vessels whose volumes have previously been calibrated. A typical hookup is shown in Fig. 5-3.

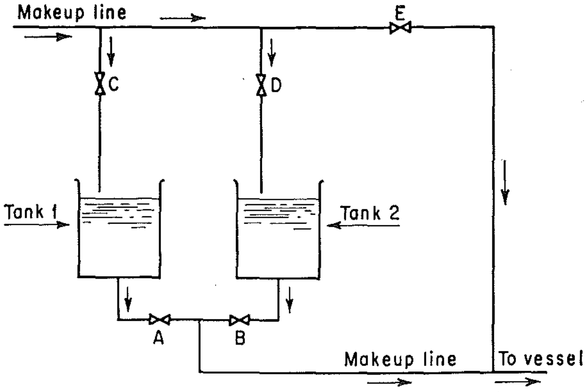


FIG. 5-3. Typical hookup of small makeup-measuring tanks to a large vessel.

1. Open valves C and D to fill tanks 1 and 2.
2. Feed makeup to vessel from tank 1 by closing valve E and opening valve A.
3. Switch feed from tank 1 to tank 2 by closing valve A and opening valve B.
4. Repeat, alternately filling and emptying tanks 1 and 2.

The following description explains how the two small calibrated measuring tanks in Fig. 5-3 are used to find the amount of makeup water needed for a larger vessel:

1. Fill both tanks with a measured amount of water.
2. Feed all the makeup to the large vessel from tank 1 first. When this tank is empty, add more makeup from tank 2.
3. Refill the empty tank while the other is feeding makeup to the large vessel.
4. The total number of times each tank is emptied per day multiplied by the gallons of water each tank holds will give the total amount of makeup water during the course of the day.

EXAMPLE 7. A boiler is used for steam generation. How much makeup water is used per day? Two 50-gal cylindrical tanks are available and are hooked up as shown in Fig. 5-3.

Both tanks are filled with water to the 50-gal level. As makeup water is needed, tank 1 is emptied first and then tank 2. Both tanks are filled and emptied 10 times during the day. Therefore, the total makeup to the boiler is 50 × 10 × 2 or 1,000 gal per day.

5-10. Determining Makeup to a Boiler from Fuel Consumption. This is an indirect approximate method. It is based on determining the total steam evaporated per day (or any other unit of time) from the amount of fuel (pounds or gallons) used per day. The raw water and the feed water are first analyzed for chloride content. This gives the amount of makeup as a percentage of the total steam evaporated from the boiler.

The relationship between the pounds of fuel used and the total steam evaporated on a daily basis at any given installation is conveniently expressed by mathematical formula. The pounds of water evaporated per pound of fuel equals

$$\frac{\text{Btu per lb of fuel} \times \text{boiler and furnace efficiency}}{\text{Heat input per lb of steam produced}} \tag{5-2}$$

The first item in Eq. (5-2), Btu per pound of fuel, is constant for each grade or type of fuel used. It stands for the number of heat units in that particular fuel. The term Btu is an abbreviation for *British thermal unit.* It is actually the amount of heat needed to raise the temperature of one pound of water one degree Fahrenheit. Table 5-5 gives some typical fuel-heating values.

The second item in Eq. (5-2), boiler and furnace efficiency, is about constant for each individual installation. It is the ratio of heat in the fuel that actually produces steam divided by the total heat in the fuel. Typical values of efficiency are given in Table 5-5.

The third item in Eq. (5-2), heat input for each pound of steam produced, can be found from the simplified steam data given in Tables 5-6 and 5-7 and from Fig. 5-4.

Using all these data in conjunction with Fig. 5-4 the pounds of water evaporated per pound of fuel can be quickly determined.

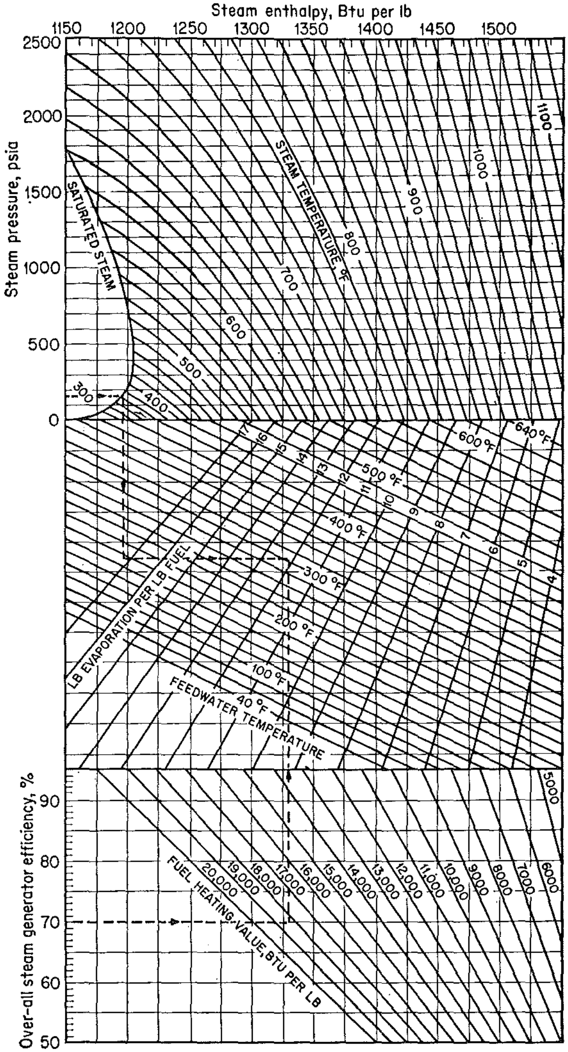


FIG. 5-4. Quick-figuring chart for determining pounds evaporation per pound fuel.

Table 5-5 also gives values for the pounds of water evaporated per pound of fuel when the heat input for each pound of steam produced is 970.4 Btu. This quantity is the equivalent evaporation of dry steam from and at 212°F at 14.7 psia and is generally used for comparing boiler performance. The 970.4 Btu value is listed in the steam data in Table 5-6. It equals the difference between the total heat of the saturated steam vapor and the heat of the saturated liquid at 212°F.

Table 5-5. Some Typical Fuel-heating and Efficiency Values

Fuel used	Firing method	Boiler and furnace efficiency, %	Heat value, Btu per lb	Evaporation, lb water per lb fuel, from and at 212°F
Soft coal.	Stoker	70	13,400	9.7
Hard coal . . .	Hand	60	11,500	7.1
#2 oil.	Automatic	70	19,400	14.0
#6 oil.	Automatic	70	18,300	13.2

NOTE: Number 2 oil weighs around 7.1 lb per gal. Number 6 oil weighs around 8.2 lb per gal.

The total pounds of water evaporated per pound of fuel is determined from either Eq. (5-2), Table 5-5, or Fig. 5-4. This in turn is used to compute the total pounds of water evaporated per day by substituting in the following equations:

$$W_e/\text{day} = W_e \text{ per lb fuel} \times \text{lb fuel per day}$$
$$W_e/\text{day} = (W_m + W_c)/\text{day}$$

where W_e = total water evaporated in the boiler, lb
W_m = makeup water to the boiler, lb
W_c = condensate returned to the boiler, lb

By chemical analysis for the chloride content of both the makeup and the feed water (mixture of makeup and returned condensate), the per cent feed water due to the makeup can be calculated. This

Table 5-6. Steam Tables Simplified

1. Saturation pressures

Absolute pressure, psi	Temperature, °F	Specific vol		Enthalpy ("heat")		
		Saturation liquid	Saturation vapor	Saturation liquid	Evaporation	Saturation vapor
0.50	79.58	0.01608	641.4	47.6	1048.8	1096.4
1.0	101.74	0.01614	333.6	69.7	1036.3	1106.0
2.0	126.08	0.01623	173.73	94.0	1022.2	1116.2
3.0	141.48	0.01630	118.71	109.4	1013.2	1122.6
4.0	152.97	0.01636	90.63	120.9	1006.4	1127.3
5.0	162.24	0.01640	73.52	130.1	1001.0	1131.1
6.0	170.06	0.01645	61.98	138.0	996.2	1134.2
7.0	176.85	0.01649	53.64	144.8	992.1	1136.9
8.0	182.86	0.01653	47.34	150.8	988.5	1139.3
9.0	188.28	0.01656	42.40	156.2	985.2	1141.4
10	193.21	0.01659	38.42	161.2	982.1	1143.3
14.7	212.00	0.01672	26.80	180.0	970.4	1150.4
15	213.03	0.01672	26.29	181.1	969.7	1150.8
20	227.96	0.01683	20.089	196.2	960.1	1156.3
25	240.07	0.01692	16.303	208.5	952.1	1160.6
30	250.33	0.01701	13.746	218.8	945.3	1164.1
40	267.25	0.01715	10.498	236.0	933.7	1169.7

2. Saturation temperatures

Temperature, °F	Absolute pressure, psi	Specific vol		Enthalpy ("heat")		
		Saturation liquid	Saturation vapor	Saturation liquid	Evaporation	Saturation vapor
32	0.08854	0.01602	3306	0.00	1075.8	1075.8
35	0.09995	0.01602	2947	3.02	1074.1	1077.1
40	0.12170	0.01602	2444	8.05	1071.3	1079.3
45	0.14752	0.01602	2036.4	13.06	1068.4	1081.5
50	0.17811	0.01603	1703.2	18.07	1065.6	1083.7
55	0.2141	0.01603	1430.7	23.07	1062.7	1085.8
60	0.2563	0.01604	1206.7	28.06	1059.9	1088.0
65	0.3056	0.01605	1021.4	33.05	1057.1	1090.2
70	0.3631	0.01606	867.9	38.04	1054.3	1092.3
75	0.4298	0.01607	740.0	43.03	1051.5	1094.5
80	0.5069	0.01608	633.1	48.02	1048.6	1096.6
85	0.5959	0.01609	543.5	53.00	1045.8	1098.8
90	0.6982	0.01610	468.0	57.99	1042.9	1100.9
95	0.8153	0.01612	404.3	62.98	1040.1	1103.1
100	0.9492	0.01613	350.4	67.97	1037.2	1105.2
105	1.1016	0.01615	304.5	72.95	1034.3	1107.3
110	1.2748	0.01617	265.4	77.94	1031.6	1109.5

50	281.01	0.01727	8.515	250.1	924.0	1174.1
60	292.71	0.01738	7.175	262.1	915.5	1177.6
70	302.92	0.01748	6.206	272.6	907.9	1180.6
80	312.03	0.01757	5.472	282.0	901.1	1183.1
90	320.27	0.01766	4.896	290.6	894.7	1185.3
100	327.81	0.01774	4.432	298.4	888.8	1187.2
110	334.77	0.01782	4.049	305.7	883.2	1188.9
120	341.25	0.01789	3.728	312.4	877.9	1190.4
130	347.32	0.01796	3.455	318.8	872.9	1191.7
140	353.02	0.01802	3.220	324.8	868.2	1193.0
150	358.42	0.01809	3.015	330.5	863.6	1194.1
160	363.53	0.01815	2.834	335.9	859.2	1195.1
170	368.41	0.01822	2.675	341.1	854.9	1196.0
180	373.06	0.01827	2.532	346.1	850.8	1196.9
190	377.51	0.01833	2.404	350.8	846.8	1197.6
200	381.79	0.01839	2.288	355.4	843.0	1198.4
250	400.95	0.01865	1.8438	376.0	825.1	1201.1
300	417.33	0.01890	1.5433	393.8	809.0	1202.8
350	431.72	0.01913	1.3260	409.7	794.2	1203.9
400	444.59	0.0193	1.1613	424.0	780.5	1204.5
450	456.28	0.0195	1.0320	437.2	767.4	1204.6
500	467.01	0.0197	0.9278	449.4	755.0	1204.4
600	486.21	0.0201	0.7698	471.6	731.6	1203.2
700	503.10	0.0205	0.6554	491.5	709.7	1201.2
800	518.23	0.0209	0.5687	509.7	688.9	1198.6
900	531.98	0.0212	0.5006	526.6	668.8	1195.4
1000	544.61	0.0216	0.4456	524.4	649.4	1191.8
1200	567.22	0.0223	0.3619	571.7	611.7	1183.4
1500	596.23	0.0235	0.2765	611.6	556.3	1167.9

115	1.4709	0.01618	231.9	82.93	1028.7	1111.6
120	1.6924	0.01620	203.27	87.92	1025.8	1113.7
125	1.9420	0.01622	178.61	92.91	1022.9	1115.8
130	2.2225	0.01625	157.34	97.90	1020.0	1117.9
135	2.5370	0.01627	138.95	102.9	1017.0	1119.9
140	2.8886	0.01629	123.01	107.9	1014.1	1122.0
145	3.281	0.01632	109.15	112.9	1011.2	1124.1
150	3.718	0.01634	97.07	117.9	1008.2	1126.1
155	4.203	0.01637	86.52	122.9	1005.2	1128.1
160	4.741	0.01639	77.29	127.9	1002.3	1130.2
165	5.335	0.01642	69.19	132.9	999.3	1132.2
170	5.992	0.01645	62.06	137.9	996.3	1134.2
175	6.715	0.01648	55.78	142.9	993.3	1136.2
180	7.510	0.01651	50.23	147.9	990.2	1138.1
185	8.383	0.01654	45.31	152.9	987.2	1140.1
190	9.339	0.01657	40.96	157.9	984.1	1142.0
200	11.526	0.01663	33.64	168.0	977.9	1145.9
210	14.123	0.01670	27.82	178.1	971.6	1149.7
212	14.696	0.01672	26.80	180.0	970.4	1150.4
220	17.186	0.01677	23.15	188.1	965.2	1153.4
240	24.969	0.01692	16.323	208.3	952.2	1160.5
260	35.429	0.01709	11.763	228.6	938.7	1167.3
280	49.203	0.01726	8.645	249.1	924.7	1173.8
300	67.013	0.01745	6.466	269.6	910.1	1179.7
350	134.63	0.01799	3.342	321.6	870.7	1192.3
400	247.31	0.01864	1.8633	375.0	826.0	1201.0
450	422.6	0.0194	1.0993	430.1	774.5	1204.6
500	680.8	0.0204	0.6749	487.8	713.9	1201.7
550	1045.2	0.0218	0.4240	549.3	640.8	1190.0

Table 5-7. Steam Tables Simplified

3. Superheated steam

Absolute pressure, psi (saturation temperature)		Saturation liquid	Saturation vapor	Temperature, °F								
				300	400	500	600	700	800	900	1000	1200
15	v	0.02	26.29	29.91	33.97	37.99	41.99	45.98	49.97	53.95	57.93	65.89
(213.03)	h	181.1	1150.8	1192.8	1239.9	1287.1	1334.8	1383.1	1432.3	1482.3	1533.1	1637.5
20	v	0.02	20.09	22.36	25.43	28.46	31.47	34.47	37.46	40.45	43.44	49.41
(227.96)	h	196.2	1156.3	1191.6	1239.2	1286.6	1334.4	1382.9	1432.1	1482.1	1533.0	1637.4
40	v	0.017	10.498	11.040	12.628	14.168	15.688	17.198	18.702	20.20	21.70	24.69
(267.25)	h	236.0	1169.7	1186.8	1236.5	1284.8	1333.1	1381.9	1431.3	1481.4	1532.4	1637.0
60	v	0.017	7.175	7.259	8.357	9.403	10.427	11.441	12.449	13.452	14.454	16.451
(292.71)	h	262.1	1177.6	1181.6	1233.6	1283.0	1331.8	1380.9	1430.5	1480.8	1531.9	1636.6
80	v	0.018	5.472	......	6.220	7.020	7.797	8.562	9.322	10.077	10.830	12.332
(312.03)	h	282.0	1183.1	......	1230.7	1281.1	1330.5	1379.9	1429.7	1480.1	1531.3	1636.2
100	v	0.018	4.432	......	4.937	5.589	6.218	6.835	7.446	8.052	8.656	9.860
(327.81)	h	298.4	1187.2	......	1227.6	1279.1	1329.1	1378.9	1428.9	1479.5	1530.8	1635.7
150	v	0.018	3.015	......	3.223	3.681	4.113	4.532	4.944	5.352	5.758	6.564
(358.42)	h	330.5	1194.1	......	1219.4	1274.1	1325.7	1376.3	1426.9	1477.8	1529.4	1634.7
200	v	0.018	2.288	......	2.361	2.726	3.060	3.380	3.693	4.002	4.309	4.917
(381.79)	h	355.4	1198.4	......	1210.3	1268.9	1322.1	1373.6	1424.8	1476.2	1528.0	1633.7
250	v	0.0187	1.8438	......	......	2.151	2.427	2.688	2.942	3.192	3.439	3.928
(400.95)	h	376.0	1201.1	......	......	1263.4	1318.5	1371.0	1422.7	1474.5	1526.6	1632.7
300	v	0.0189	1.5433	......	......	1.7675	2.005	2.227	2.442	2.652	2.859	3.269
(417.33)	h	393.8	1202.8	......	......	1257.6	1314.7	1368.3	1420.6	1472.8	1525.2	1631.7

Table 5-7. Steam Tables Simplified (Continued)

3. Superheated steam

Absolute pressure, psi (saturation temperature)		Saturation liquid	Saturation vapor	Temperature, °F								
				300	400	500	600	700	800	900	1000	1200
400	v	0.0193	1.1613	......	......	1.2851	1.4770	1.6508	1.8161	1.9767	2.134	2.445
(444.59)	h	424.0	1204.5	......	......	1245.1	1306.9	1362.7	1416.4	1469.4	1522.4	1629.6
500	v	0.0197	0.9278	......	......	0.9227	1.1591	1.3044	1.4405	1.5715	1.6996	1.9504
(467.01)	h	449.4	1204.4	......	......	1231.3	1298.6	1357.0	1412.1	1466.0	1519.6	1627.6
600	v	0.0201	0.7698	......	......	0.7947	0.9463	1.0732	1.1899	1.3013	1.4096	1.6208
(486.21)	h	471.6	1203.2	......	......	1215.7	1289.9	1351.1	1407.7	1462.5	1516.7	1625.5
800	v	0.0209	0.5687	......	......	......	0.6779	0.7833	0.8763	0.9633	1.0470	1.2088
(518.23)	h	509.7	1198.6	......	......	......	1270.7	1338.6	1398.6	1455.4	1511.0	1621.4
1000	v	0.0216	0.4456	......	......	......	0.5140	0.6084	0.6878	0.7604	0.8294	0.9615
(544.61)	h	542.4	1191.8	......	......	......	1248.8	1325.3	1389.2	1448.2	1505.1	1617.3
1500	v	0.0235	0.2765	......	......	......	0.2815	0.3719	0.4352	0.4893	0.5390	0.6318
(596.23)	h	611.6	1167.9	......	......	......	1174.5	1287.2	1363.8	1429.3	1490.1	1606.8
2000	v	0.0257	0.1878	......	......	......	......	0.2489	0.3074	0.3532	0.3935	0.4668
(635.82)	h	671.7	1135.1	......	......	......	......	1240.0	1335.5	1409.2	1474.5	1596.1
2500	v	0.0287	0.1307	......	......	......	......	0.1686	0.2294	0.2710	0.3061	0.3678
(668.13)	h	730.6	1091.1	......	......	......	......	1176.8	1303.6	1387.8	1458.4	1585.3
3000	v	0.0346	0.0858	......	......	......	......	0.0984	0.1760	0.2159	0.2476	0.3018
(695.36)	h	802.5	1020.3	......	......	......	......	1060.7	1267.2	1365.0	1441.8	1574.3
3206.2	v	0.0503	0.0503	......	......	......	......	......	0.1583	0.1981	0.2288	0.2806
(705.40)	h	902.7	902.7	......	......	......	......	......	1250.5	1355.2	1434.7	1569.8

is expressed as

$$\text{Makeup in per cent} = \frac{\text{Cl in feed water}}{\text{Cl in raw water}} \times 100$$

The pounds of makeup water per day then equals

$$\text{Total lb water evaporated per day } \frac{\text{Cl in feed water}}{\text{Cl in makeup water}} \tag{5-3}$$

The amount of makeup water in gallons is easily found by dividing the answer in pounds by 8.34.

EXAMPLE 8. A boiler generates steam at 135 psi (149.7 psia). The average temperature of the incoming feed water is 180°F. The fuel oil used is number 6. Find the pounds of evaporation per pound of fuel oil.

The steam tables at 150 psia show a steam enthalpy of 1194.1 Btu per pound of saturated vapor. Enter the chart, Fig. 5-4, at this pressure. Cross over to 1194.1 Btu and then down 180°F feed-water temperature. Then draw a horizontal line across the chart at this point. Next, reenter the chart at 70 per cent efficiency (see Table 5-5) and cross over to 18,300 Btu heating value (see Table 5-5). Then draw a vertical line up from this point to meet the horizontal line at 12.2 lb evaporation per pound of fuel.

EXAMPLE 9. In the previous example the boiler burned 500 gal or 4,100 lb of number 6 fuel per day. The total water evaporated is therefore 50,020 lb. Chemical analysis of the makeup shows a chloride content of 12 ppm. The average amount of chloride in the feed water is 6 ppm. How much makeup is added in gallons per day?

With Eq. (5-3) the quantity of makeup water is easily determined.

$$\text{Makeup per day} = 50{,}020 \times 6/12 = 25{,}010 \text{ lb}$$

This is equivalent to 3,000 gal of water per day.

5-11. Determining Makeup from the Rated Boiler Horsepower. This is an indirect method giving only approximate results. It is based on the fact that all boilers were formerly given horsepower rating. This boiler horsepower equals the evaporation of 34.5 lb of water per hour with feed water at 212°F. It is equivalent to 4 gal of water evaporated per hour.

Under operating conditions in those days the boilers were designed so that 10 sq ft of heating surface was considered equal to 1 boiler hp. But in later years the use of high evaporative rates and the addition of water walls, economizers, and air preheaters in the boiler became common practice. These changes made the term boiler horsepower almost meaningless when calculated from heating surface. The actual amount of water evaporated per hour is greater than that indicated by rated horsepower. In order to account for this difference, the term *per cent* rating came into use. A boiler rating of 100 per cent means that water is evaporated at the rate of 4 gal per hour for every 10 sq ft of heating surface. Most boilers today operate well above 100 per cent rating. If the rated horsepower of the boiler, the per cent rating, and per cent makeup are all known, the amount of makeup is estimated as follows:

$$\text{Water evaporation, gal per hour} = \text{boiler hp rating} \times 4 \times \frac{\%\ \text{rating}}{100} \qquad (5\text{-}4)$$

$$\text{Makeup, gal per day} = \text{evaporation, gal per day} \times \text{makeup, \% of feed water}$$

If there are no condensate returns, the boiler makeup will equal the amount of water evaporated. However, when the water is preheated with exhaust steam in an open heater, about 12 to 16 per cent of this steam condenses and returns to the boiler. Then the per cent makeup to the boiler is in the range of 84 to 88 per cent.

EXAMPLE 10. A 250-hp boiler operates at 150 per cent rating for eight hours per day. During the summer months, none of the condensate is returned. In the winter, part of the steam is used for heating and is returned to the boiler. How much is the makeup in gallons per day during the summer and the winter? The per cent makeup during the winter months is estimated from a chemical analysis of the chlorides in both the feed water and the makeup.

During the summer months the total number of gallons evaporated in eight hours is equal to the total makeup per day. Using Eq. (5-4) we get

$$\text{Water evaporation, gal per day} = 250 \times 4 \times \frac{150}{100} \times 8 = 12{,}000$$

During the winter months the chloride content of the makeup water is 6 ppm. The chloride in the feed water is 3 ppm.

$$\%\ \text{makeup} = 3/6 \times 100 = 50\%$$

The total amount of water evaporated per day equals 12,000 gal and the per cent makeup is 50 per cent. Therefore the amount of makeup for the winter is 6,000 gal per day.

5-12. Determining Boiler Makeup from Blowdown. In Chap. 4 the chemical-balance equations show that the chloride concentration and volume of water going into a continuous process equal the chloride concentration and volume of water leaving the process. This assumes that the volume of water in the process remains constant [see Eqs. (4-7) and (4-8)]. The relationship is expressed as follows:

$$\underset{\text{Input}}{C_m \times V_m} = \underset{\text{Output}}{C_b \times V_b}$$

where C_m = concentration of Cl in the makeup
V_m = vol of makeup, gal
C_b = concentration of Cl in blowdown
V_b = vol of blowdown, gal

This equation can be rearranged and solved for V_m, the amount of makeup.

$$V_m = \frac{C_b}{C_m} \times V_b \tag{5-5}$$

The ratio C_b/C_m in Eq. (5-5) is called the concentration factor. It indicates the number of times that the mineral content of the incoming water is concentrated in the process. The concentration factor C_b/C_m can also be determined without a chemical analysis of the chlorides in the raw water. If the vessel has a gauge glass, note the level changes when water is added and removed from the vessel. This ratio then equals

$$\frac{C_b}{C_m} = \frac{\text{makeup water added per day, in.}}{\text{blowdown per day, in.}}$$

EXAMPLE 11. In example 6 the number of gallons of water lost by blowdown is calculated by the tracer method. How many gallons of makeup per day are used in this boiler? In the previous example we also calculated the following information:

1. The boiler holds 1,000 gal of water.
2. The blowdown loss is about 100 gal per day.
3. Average chloride content of the boiler water is 20 ppm.
4. Blowdown loss is 3 in. per day on the gauge glass.

The number of gallons of water lost by blowdown is known. Only the concentration factor C_b/C_m is needed to make use of Eq. (5-5). The raw-water analysis reveals a chloride content of 2 ppm in the makeup. The gauge glass level reveals that 30 in. of makeup water is added every day.

$$\frac{C_b}{C_m} = \frac{\text{20 ppm chloride}}{\text{2 ppm chloride}} = \text{10 concentrations}$$

or

$$\frac{C_b}{C_m} = \frac{\text{30 in.}}{\text{3 in.}} = \text{10 concentrations}$$

On this basis the volume of makeup required per day equals 100 gal multiplied by 10, or a total of 1,000 gal.

6

Simple Chemical Feeds for Small and Moderate-sized Plants

Every plant must have some method of feeding boiler compounds and other water-treating chemicals. Many types of feeding apparatus are available for this purpose. Some of them deliver a measured quantity of chemical at a set rate for a given interval. Others are simple devices that just provide a convenient way of storing and feeding a prepared chemical dose. The feed systems discussed in this chapter include devices that are basically both simple and economical. This kind of equipment is most commonly used in small or moderate-sized plants. There are also many costly and more complex feed systems available, but these are usually employed in larger plants. Detailed design and application data for the larger feeds are readily available from manufacturers of this equipment.

The vast majority of simple feeding devices are designed to handle chemical compounds in liquid form. The dry chemicals are usually dissolved in hot water and then thoroughly stirred until all of the chemical is in solution. Sometimes the dry chemical is suspended in a basket at the surface of a tank full of hot or cold water. It then will dissolve in the water without the aid of any mechanical stirring. There are also a number of simple feeding devices designed to handle dry chemicals in the form of briquettes or large solid crystals. The briquette or crystal slowly dissolves within the feeder. The dilute chemical solution that forms is then periodically fed to the system as needed for treatment. As additional fresh water enters the feeder, it dissolves a little more of the solid material. The resulting dilute chemical solution is continuously fed into the system. This feeding process continues until all of the solid material in the feeder is dissolved and washed out as treatment. Briquette feeders are very practical for slowly adding small amounts of chemicals over an extended period of time.

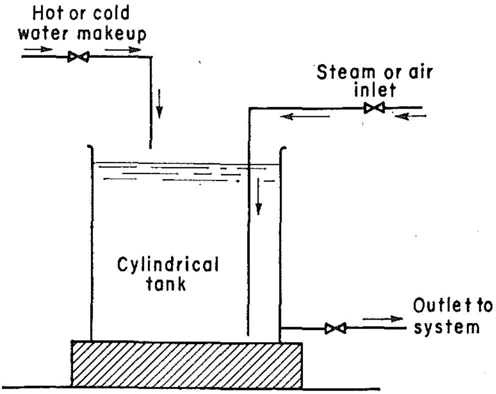


FIG. 6-1. Open-type gravity feeder.

6-1. Open-type Gravity Feeder. The open-type gravity feeder is best suited for feeding large volumes of prepared chemical solutions at frequent intervals. Essentially it consists of an open tank with an outlet at the bottom. The chemical solution is fed by gravity from this tank into the system needing treatment. Figure 6-1 shows a typical installation. The chemical tanks are usually cylindrical in shape and can be made of either wood or metal. Sizes vary from 1 to 300 gal. The entire contents of the tank can be fed manually in small shots from the main bulk of the solution. Or the valve on the outlet line can be throttled to deliver the entire amount in the tank within a prescribed time interval in accordance with plant needs.

In addition to serving as a feeder, the tank is useful for making and storing the chemical solution. For this kind of service the tank is usually equipped with one or more of the following:

1. A pipeline or a hose connection to a water source. A convenient water supply is necessary in order to prepare the desired strength of chemical solution.
2. A steam line either for heating the water to speed up solution of the dry chemical or to provide positive agitation of the mixture of solids and water.
3. A compressed-air line since this is also a good way to obtain positive agitation and mixing of the chemical solids with the water.
4. A hand paddle to ensure proper mixing of the solution. In many cases this is all that is needed. Actually any flat stick will serve.
5. An electrically driven mechanical stirrer. When heavy chemical solutions are needed which require long-term mixing, the chemical tank should be equipped with a motor-driven mechanical stirrer.
6. A wire basket. As mentioned before, some dry chemicals are best dissolved by immersing them in a wire basket placed at the surface of a tank full of water. The dry chemical will then go into solution in a few hours without further agitation or attention.

Before using any tank for chemicals, it is best to have it calibrated. In other words, 1 in. of tank depth will equal some equivalent number of gallons. The calibration is handled most simply by using one of the methods outlined in Chap. 5 for calculating the capacity of a cylindrical tank at various water levels. It can also be done by adding known amounts of water to the tank and then measuring the resulting depth.

EXAMPLE 1. Calibrate a cylindrical tank for use as a chemical feeder. A small vessel with a capacity of 25 gal is available. First, fill the cylindrical tank with water using the small vessel. After each 25-gal fill, measure the depth of water and prepare the following table:

Total water added, gal	Water height, in.	Calibration, gal per in.
25	5	5
50	10	5
75	15	5
100	20	5

From these data it is easy to conclude that each inch of tank depth is equivalent to 5 gal of solution.

With a calibrated tank it is a simple matter to prepare a known solution of desired strength and feed any amount in accordance with plant needs.

EXAMPLE 2. Assume that a boiler requires 5 lb of disodium phosphate per day. There is a 100-gal calibrated open-type gravity tank available for service as a chemical feed tank. One inch of depth in this tank equals 5 gal of water. Prepare 100 gal of solution containing 50 lb of disodium phosphate. How many inches of this solution must be fed to the boiler per day to satisfy its phosphate requirement?

First weigh out 50 lb of disodium phosphate. Then dissolve 5 to 10 batches of this powder in a 3-gal pail full of hot water. Constantly stir each pail until a clear solution forms. Then pour this into the 100-gal tank which has been partly filled with water. When all the disodium phosphate solution is added to the tank, pour in enough water to bring the level up to the 20-in. or 100-gal mark. Stir the entire contents with a hand paddle or other built-in mixing gadget until the chemical solution is uniform. Since the 100 gal or 20 in. of solution contains 50 lb of disodium phosphate, 10 gal or 2 in. of the solution will contain 5 lb of disodium phosphate. On this basis the required amount for the boiler is 2 in. of phosphate solution per day.

6-2. Closed-type Feeder. All the various designs of drip feeders and bypass feeding devices fall into this classification. These feeders are designed to operate in a closed system under full pressure. In general the chemical tanks are cylindrical and much smaller in capacity than the open-type feeders. The tank sizes range from 1 pt to 40 gal. The feed equipment can be installed on the suction side of the feed-water pump or put directly on the feed line. Figure 6-2 shows a typical simple closed-system feeder. It consists essentially of a small cylindrical tank with a capacity ranging from 1 pt to 1 gal. Threaded openings are located at both top and bottom so that the unit can be installed directly on the feed line or on a bypass. It is possible to make a homemade

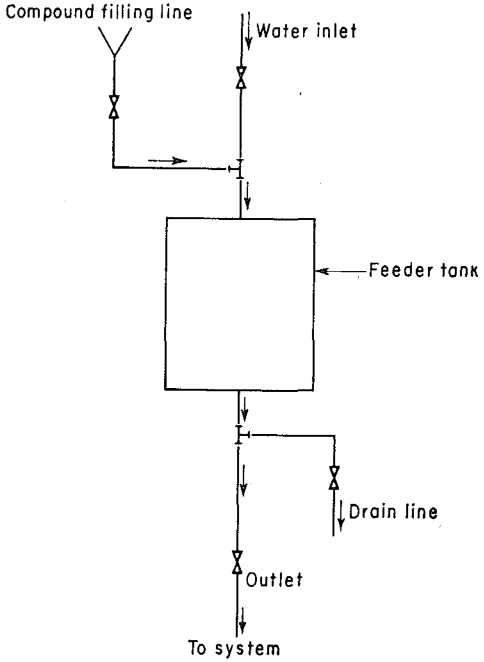


FIG. 6-2. Essential parts of closed-system feeder.

feeder of this type with either nipples of large diameter or standard pipe and the proper fittings to reduce the openings to regular pipe size. Table 6-1 provides a rough guide to the length of pipe needed. All nipples in this table are 1 ft long. The holding capacity can be increased or decreased by varying the length of the nipple.

Table 6-1. Capacity of Homemade Feeders

Pipe diameter, in.	Length of pipe, ft	Capacity
2	1	1 pt
2½	1	1 qt
3	1	3 pt
3½	1	2 qt
4	1	2½ qt

EXAMPLE 3. What size pipe can be used to construct a homemade boiler compound feeder having a capacity of 1 qt? Referring to Table 6-1, a nipple 2½ in. in diameter by 1 ft long is entirely satisfactory. Alternate selections include a 2-in.-diameter pipe 2 ft long or a 3½-in.-diameter nipple ½ ft long. Both these sections have the same 1 qt capacity. Typical arrangements for this type of feeder are given in Figs. 6-3 to 6-6. Figure 6-3 shows the feeder installed directly on the water line. Figure 6-4 shows a typical bypass hookup. Both these feed systems are very useful for putting in a small charge of chemical solution on a regular basis. The entire chemical charge goes immediately into the system needing treatment. The feeder shown in Fig. 6-3 is operated in the following manner:

1. First, disconnect the feeder from the water lines. This is done by closing valve A on the makeup-water line and valve B on the feed-outlet line to the system being treated.

2. Empty the feeder by opening drain valve D and valve C on the funnel. Be sure to open drain valve D first in order to release the pressure within the feeder.

3. When the feeder is empty, close drain valve D and charge the tank with chemical solution through the funnel.
4. When the feeder is fully charged, force all the solution into the boiler by closing valve C and opening valves A and B.

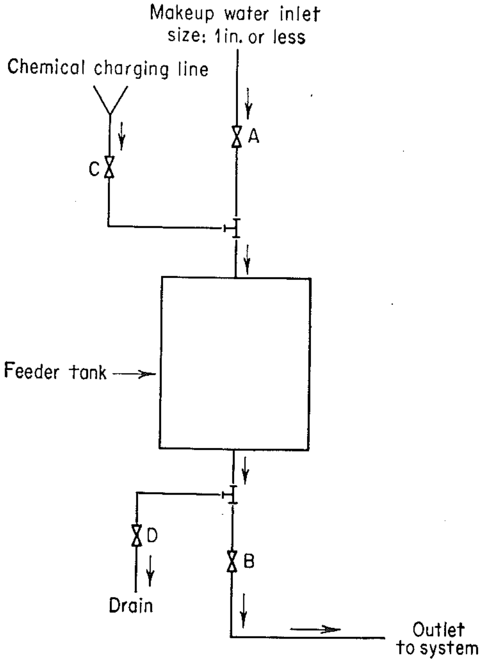


FIG. 6-3. Direct chemical feed.

5. Finally, stop the flow of water into the system by closing valve A or B.

The chemical feeder shown in Fig. 6-4 is similar to that shown in Fig. 6-3 except that it is located on a bypass connection. To operate this feeder some modifications in procedure are necessary.

1. Disconnect the feeder from the main water line to the system by closing valves E and F on the bypass.
2. Drain the feeder by opening valves D and C.

3. When the feeder is empty, close drain valve D and use the funnel to charge the feed tank with chemical solution.

4. When the feeder is fully charged, put it back on the main line by closing valve C and opening both valves E and F on the bypass line.

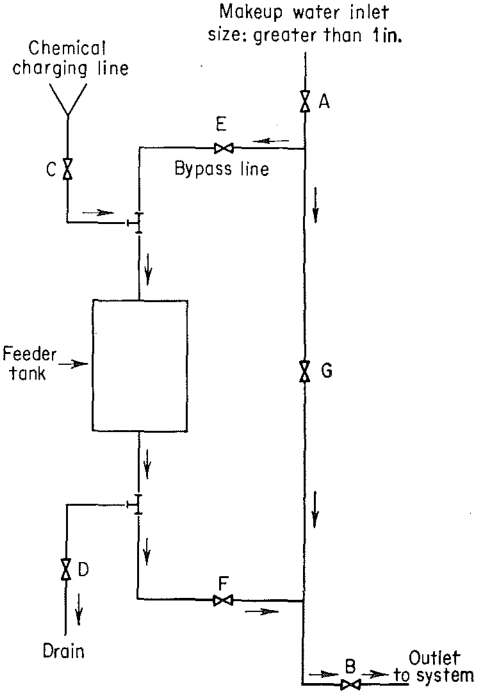


Fig. 6-4. Bypass chemical feed hookup.

5. Empty the feeder quickly by first closing valve G on the main line and then opening valve A on the makeup line and valve B on the outlet line to the system.

6. Finally, stop the flow of water into the system by closing either valve A or B.

Gravity feeding devices are shown in Figs. 6-5 and 6-6. These hookups differ from that shown in Fig. 6-4 in that the entire chemical charge is not immediately put into the system in one dose. The chemical solution slowly drips by gravity into the pipeline and gradually washes into the system. The simplest arrangement is given in Fig. 6-5. If the water-line pressure is too high to feed the chemical charge into the system by gravity, install an equalizing line like the one shown in Fig. 6-6. Many attempts have been made, with varying degrees of success, to make these and similar devices deliver a definite amount of chemical solution over a given interval of time. They all fall short of achieving the goal of a true proportioning system that discharges a specified amount of chemical solution for each 1,000 gal of water treated. The chemical feeders shown in Figs. 6-5 and 6-6 are operated as follows:

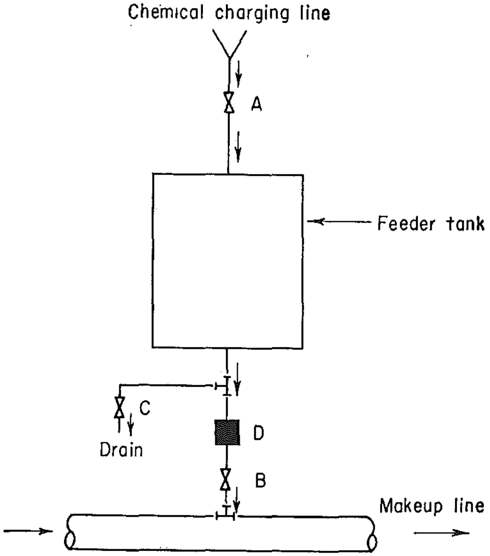


FIG. 6-5. Gravity-drip chemical feed.

1. Disconnect feeder from main line by closing valves B and E.

2. Drain the feeder by opening drain valve C and valve A. Make sure that drain valve C is opened first to relieve the pressure in the unit.

3. When the feeder is empty, close drain valve C and add the chemical charge through the funnel.

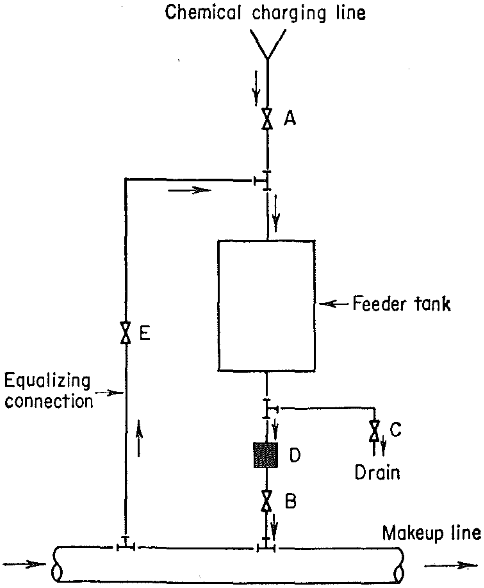


FIG. 6-6. Gravity-drip chemical feed with pressure-equalizing line.

4. When the feeder is fully charged, close valve A and open valves B and E. Now the chemical feeder is ready to operate.

In order to lengthen the discharge time of chemical solution from the drip feeder, valve B is throttled. However, it is much better to do this with another separate device on the feeder. Once set, this device does not have to be touched again; it is indicated as item D in both Figs. 6-5 and 6-6. Item D might be another gate valve throttled to a set position. It can be a needle valve or a machined nipple with a fixed bore as small as $1/32$ in. in diameter.

In Fig. 6-6, the pressure in the feeder is equalized with the makeup line when valve E is opened. With valve E closed the arrangements of Figs. 6-5 and 6-6 are identical.

6-3. Pot-type Proportional Feeder. As pointed out before, numerous attempts have been made to devise a closed-type feeder that delivers a definite amount of chemical over a specified time. Probably the simplest type of feed system considered a proportional design is the "pot-type" feed. Figure 6-7 shows a typical hookup of such a unit.

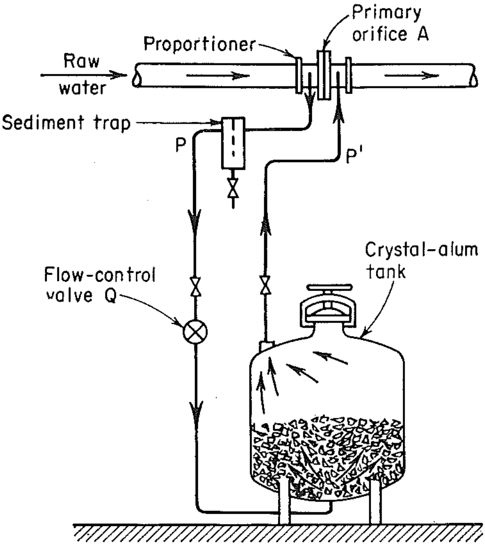


FIG. 6-7. Pot-type proportional feeder.

This type of feed can use only chemicals that are available in lump, large crystals, or brick form, and they must dissolve slowly when in continuous contact with water. Even then this feed gives results that are only roughly proportional. The pot-type feeder is commonly used to add alum and alkali to water for coagulation and clarification and to feed water for oil removal. Alum used for this type of feeder must be either potash or ammonium alum in lump form. If alkali is used it must be sal soda in similar form.

The installation includes an orifice plate in the main raw-water line to be treated. It also includes a line from the "high" or upstream side of the orifice to the underside of the dissolving pot. This connecting line is equipped with a sediment trap and a flow-control valve. To complete the system the discharge line from the top of the pot is connected to the main water line just after the orifice. Shut-off valves in both these lines permit recharging the

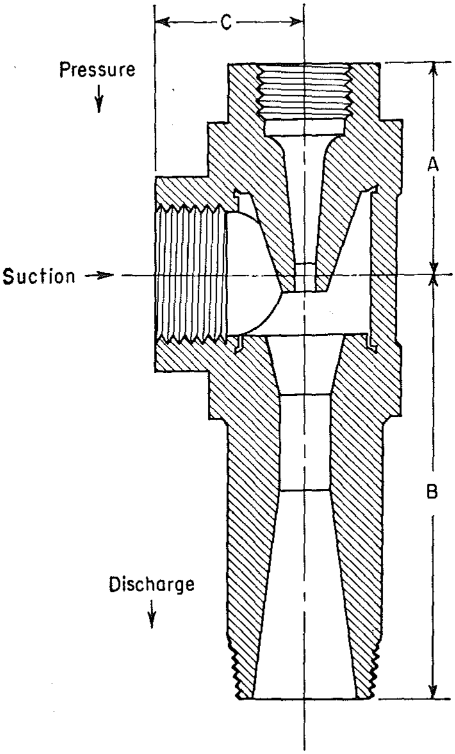


FIG. 6-8. Jet-type feeder. (*Courtesy of Schutte and Koerting Co.*)

pot with chemical. The main-line orifice is a thin disk or plate secured between two flanges. The plate has an opening a little smaller than the inside diameter of the main pipe. It diverts part of the main stream through the pot feeder. As water flows through the main raw-water line, there is a pressure loss across the orifice plate. This pressure differential causes a small stream of water to flow from the high-pressure side of the orifice through the chemical pot to the low-pressure side. This forces an equivalent stream of heavy chemical solution from the pot into the main line. The

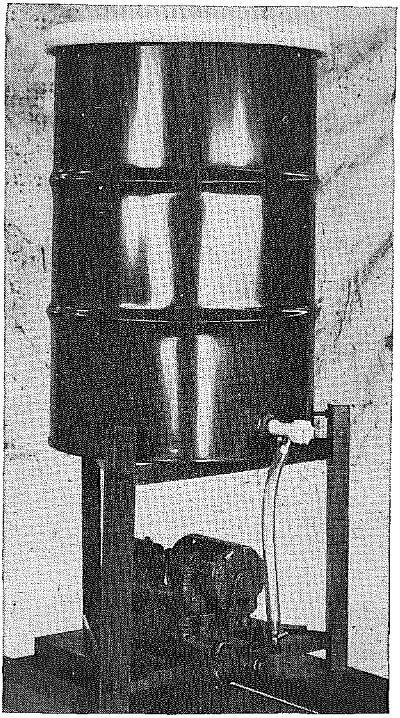


FIG. 6-9. Package chemical feed complete with chemical feed tank, cover, and positive-displacement chemical feed pump. (*Courtesy of Milton Roy Co.*)

flow-control valve is available to accurately regulate the amount of chemical solution coming from the pot-feed unit.

6-4. Jet-type Feeders. Another common method of moving water or feeding a chemical solution without using moving parts is by means of jet-type feeders. These are also commonly known as *ejectors* or injectors. Other names include *syphons*, *exhausters*, and *eductors*.

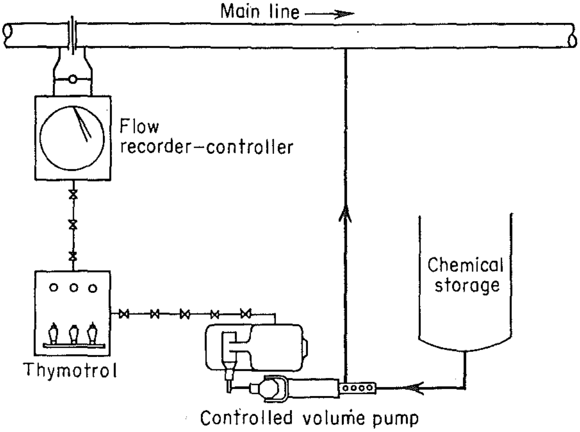


FIG. 6-10. Automatic chemical feed. Recording flow controller varies pump speed in proportion to flow through a thymotrol unit. (*Courtesy of Milton Roy Co.*)

A simple-design jet feeder of the ejector type is shown in Fig. 6-8. The pumping fluid (water or high-pressure steam) enters the nozzle at the top (pressure side) and passes through the venturi nozzle at the center. From there it goes out the discharge. As pumping fluid passes through the venturi nozzle, a high-velocity jet is created. This develops a suction at that point which induces a flow of water or chemical solution from the suction line up into the ejector or injector. The mixture of pumping liquid and suction-line liquid is delivered through the discharge line to the system requiring treatment.

The ejector is very useful in cases where the system (discharge) pressure is low. This head must be less than the head of the pumping fluid. The ejector also has the disadvantages of mechanical inefficiency and of diluting the chemical as it is transferred.

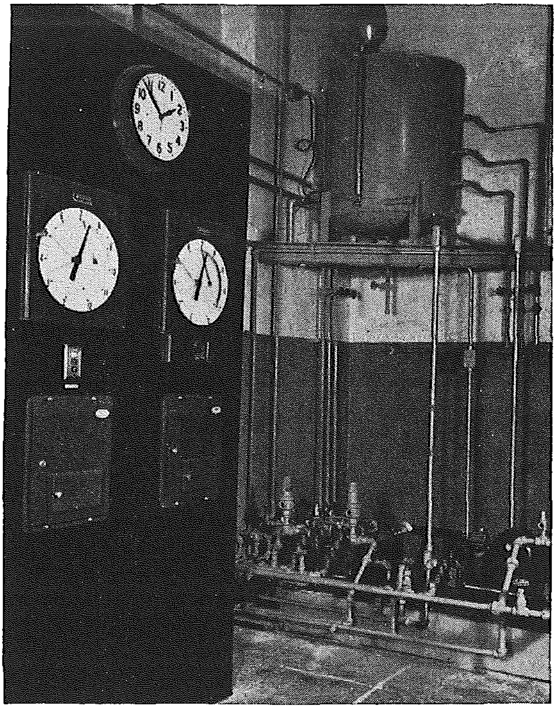


FIG. 6-11. Caustic-feed equipment includes chemical feed tank with agitator at top of photograph. Positive-displacement chemical pumps are located below. Panel, left, has two indicating and recording pH instruments monitoring the amount of caustic fed. (*Courtesy of Minneapolis-Honeywell Regulator Company.*)

The steam type of ejector has been developed to the point where it is very efficient mechanically, so much so that the ejector can pump a fluid into a space under the same pressure as the pumping fluid. In this form it is called an injector. The best example of this type of injector is that used for feeding boilers. In steam injectors for boiler feed and similar services, where the heat of the steam is recovered, the efficiency is close to 100 per cent. The mechanical efficiency of the usual ejector is around 1 or 2 per cent.

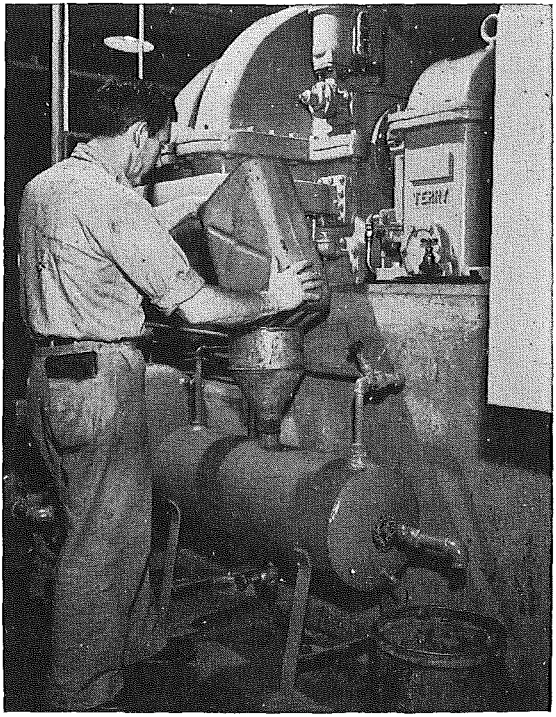


Fig. 6-12. Chemical feed for closed air-conditioning circulating-water system is charged with chemicals by the operator. (*Courtesy of Water Service Laboratories.*)

Feed systems with positive displacement chemical pumps are also used in many plants. A package feed unit including chemical pump, solution tank, and pressure-relief valve is shown in Fig. 6-9. The pump stroke is adjustable and is set so that the pump will deliver the required amount of chemical over the day at a constant rate. This system can be modified to deliver the chemical solution in rough proportion to flow by adding a totalizing meter on the water line and a pump control timer. The feed pump is then controlled by the water meter and operates intermittently for a time interval after a given preset volume of water passes through the meter. Therefore, as the rate of water flow increases, the pump will operate more frequently and in this way deliver the required additional chemical solution. Still another arrangement is shown on the flow diagram in Fig. 6-10. Since the chemical solution is delivered in slugs, a mixing tee or chamber is needed to properly mix the chemical solution with the main flow. A Thymotrol is employed to vary the speed of the pump motor in proportion to flow.

Figure 6-11 shows a caustic-feed system where pH controls the amount of caustic added. A special feeder in a closed air-conditioning circulating-water system is shown in Fig. 6-12. This feeder has an internal dissolving basket and is designed to handle solid caustic and chromate.

7

Boiler Water Troubles

The modern boiler must be considered more than just an ordinary vessel producing steam. It is a highly complicated pressure chamber where the various substances dissolved in the feed water undergo many complicated chemical changes. Harmful elements dissolved in the water may react, causing scale to deposit on heating surfaces. Other harmful elements promote active corrosion, foaming, priming, carryover, and even caustic embrittlement. None of these potential troubles can be neglected under normal operating conditions.

7-1. Scale Deposits. When water evaporates in the boiler, the calcium and magnesium salts dissolved in the water deposit on the tube surfaces as scale. These deposits are highly objectionable because they are poor conductors of heat, actually reduce efficiency, and are frequently responsible for tube failures. Tube replacements are always expensive, and the shutdowns caused by such failures are even more costly. Scale formation on heating surfaces can be avoided by removing all the calcium and magnesium salts before the water enters the boiler. This is known as *external treatment.* Chemicals can also be added to the boiler water which will react with the calcium and magnesium to form a soft sludge. The sludge is readily removed from the boiler by blowdown. This method is called *internal treatment.*

7-2. Corrosion. Corrosion is the eating away of boiler metal. If allowed to progress, it causes deterioration and equipment failure. This eventually calls for major repairs or expensive shutdowns.

Corrosion of boilers, economizers, feed-water heaters, piping, etc., is caused by an acid or low pH in addition to the presence of dissolved oxygen in the boiler feed water. It can be minimized by adding alkali salts to neutralize acids in the water and raise the pH. Use of mechanical deaeration followed by scavenger chemicals to remove the last traces of oxygen from the water is also very effective.

7-3. Carryover, Foaming, Priming. Foaming, priming, and carryover are very closely associated terms. Each describes conditions that cause boiler water and its dissolved solids to leave the boiler. The water is carried off in the form of tiny droplets of moisture entrained in the steam.

Foaming is the production of froth on the surface of the water. The resulting foam may stand slightly above the water surface, or it may fill the entire steam space. In either case foaming contaminates the steam with appreciable amounts of boiler water.

Priming is a more violent and spasmodic discharge of water with steam from the boiler. It can be compared to the bumping of water that frequently accompanies rapid heating in an open vessel. In a priming boiler the water level undergoes relatively great changes. There are violent discharges of bursting bubbles high into the steam space. "Slugs" of boiler water are thrown over with the steam.

Boiler water solids are also carried over in the moisture mixed with steam even when there is no noticeable indication of foaming or priming. This is known as *carryover.*

When a boiler is foaming or priming, it is difficult and often impossible to read the true level of the boiler water on the gauge glass. The slugs of boiler water can wreck engines or turbines. The carryover of boiler water solids usually caused by foaming and priming disrupts operation of the equipment coming in contact with the steam. Deposits form in steam piping, valves, superheaters, engines, or turbines. These solids erode the turbine blades or seriously interfere with the lubrication of reciprocating engines. They often clog pipe and any apparatus following the boiler. If live steam is used for process or cooking, the solids present may seriously damage the final product. And also, any moisture carried over with the steam corresponds to additional blowdown and heat loss through the steam line.

7-4. Caustic Embrittlement. Caustic embrittlement or the intercrystalline cracking of boiler steel may be defined as the destructive action of highly concentrated caustic boiler water on metal below the water line. Irregular cracks appear where the metal is under strain. These cracks are visible under a microscope and follow the boundaries of the metal crystals.

The metal becomes brittle and weak, which causes eventual failure and boiler shutdown.

The general indications of an embrittled metal are:

1. Cracks in the metal located below the water line
2. Metal failure along drum seams, under rivets, at tube ends, and near metal areas that are under stress in the boiler
3. Irregular cracking

The problem of caustic embrittlement is not as common as many other boiler water troubles. However, it must be considered in every water treatment plan and measures must be taken to prevent it.

Embrittlement control calls for maintaining low-hydroxide alkalinity in the boiler water, avoiding leaks at stressed metal areas, and adding special chemical-inhibiting agents.

Boiler water troubles are often interrelated. There is no general rule saying that corrosion, scale, carryover, and caustic embrittlement cannot take place at the same time. Therefore, in any complete system of water treatment all of these must be considered potential operating difficulties.

7-5. Scale—Cause and Prevention. Chapter 1 explains that water traveling through the earth picks up and dissolves both mineral salts and gases. The amount picked up depends on the kind of minerals present and their solubility in water. Other important factors include the length of time the water remains in contact with the mineral bed and the water temperature.

The various salts dissolved in the water are in chemical balance with one another. A change in any of the conditions putting these salts into solution may actually bring about their precipitation.

Water, heated in the boiler under pressure, evaporates to form steam. This upsets the natural chemical balance of salts in the water. The heat destroys the bicarbonates of calcium and magnesium usually present in the raw water. Less-soluble calcium and magnesium carbonates and carbon dioxide are formed. Some of these less-soluble salts such as calcium carbonate precipitate and settle in the boiler. The equation for this reaction is

$$\underset{\substack{\text{Calcium}\\ \text{bicarbonate}}}{Ca(HCO_3)_2} + \text{heat} = \underset{\substack{\text{Calcium}\\ \text{carbonate}\\ \text{precipitate}}}{\underline{CaCO_3}} + \underset{\substack{\text{Carbon}\\ \text{dioxide}\\ \text{gas}}}{CO_2} + \underset{\text{Water}}{H_2O} \qquad (7\text{-}1)$$

The carbon dioxide formed flows out of the boiler with the steam. The rest of the salts stay in the boiler water and concentrate as new feed water is added.

A given amount of water can hold only a definite quantity of any particular mineral salt in solution at a given temperature and pressure. When the allowable concentration is exceeded, solid particles form in the water. At boiler water temperatures and pressures the limiting concentration of both calcium and magnesium salts is quickly reached with the formation of insoluble precipitates. The resulting sludge is harmless as long as the salts settle as solid particles that flow easily with the water. Generally the sludge is controlled within practical limits by regulating the blowdown. But if the precipitates adhere or cement themselves to metal surfaces, the resulting scale seriously interferes with normal operation of the boiler.

In addition to the natural minerals, organic matter such as oil, grease, or vegetation finds its way into the boiler. This material acts as a binder and cements together particles that might otherwise form a free-flowing sludge.

The salts of calcium and magnesium are the major source of scale formation in the boiler primarily because of their low solubility. The solubility of these compounds at the high temperature of boiler water determines whether they will form scale or sludge. It is generally accepted that the scale-forming salts are those that become less soluble as water temperature increases.

The thin film of water next to the boiler-heating surfaces is necessarily hotter than the main body of water. Under these operating conditions, the salts which are less soluble at higher temperatures will deposit directly on the heating surface from the hotter thin film of water. This also explains why scale often forms on the heating surface even though the limit of solubility of scale-forming salts in the cooler main body of water has not been reached.

7-6. Internal Boiler Water Treatment for Scale Prevention. Some compounds of calcium and magnesium precipitate and form a sludge or mud that is easily controlled by boiler blowdown. Other salts of calcium and magnesium cement themselves directly on the boiler metal as scale. The problem of scale prevention is

Table 7-1. Internal Treatment for Scale Prevention

Compounds in raw water	Treating chemicals	Sludge formed
Calcium bicarbonate	1. Caustic soda or soda ash	1. Calcium carbonate
	2. Phosphates	2. Tricalcium phosphate
Calcium sulfate	1. Caustic soda or soda ash	1. Calcium carbonate
	2. Phosphates	2. Tricalcium phosphate
Magnesium sulfate	1. Caustic soda	1. Magnesium hydroxide

then simply one of getting sludge to form in the boiler instead of scale. This is accomplished by adding treating chemicals that precipitate the calcium and magnesium salts in the main body of the water as sludge. This keeps the soluble calcium and magnesium scale-forming salts out of the thin film of water next to the boiler-heating surfaces. Table 7-1 lists the various sludges that can form from the compounds of calcium and magnesium originally present in the incoming water.

In general it is best to precipitate the calcium salts as carbonate or phosphate and all the magnesium salts as the hydroxide. These are the least soluble forms.

The two chemicals most frequently used for the internal treatment of boiler water to prevent scale formation are sodium carbonate and phosphate. Of these two, the phosphate compounds are far more generally used. But no matter which chemicals are added, the boiler water must show the following characteristics to ensure precipitation of the proper kind of sludge:

1. *Alkalinity.* The boiler water should be alkaline at all times. Table 3-1 gives the suggested minimum and maximum total alkalinity for boilers at various operating pressures. This value ranges from a minimum of 120 ppm at 900 psi to a maximum of 700 ppm at pressures below 300 psi. As alkalinity goes up, the total dissolved-solids content of the boiler water also increases. Higher alkalinity, therefore, increases the tendency for carryover of boiler water. If the alkalinity is too low, the addition of sodium carbonate does not assure effective precipitation of the calcium as calcium carbonate. When phosphates are used as the main treating chemical, the alkalinity must be high enough to form tricalcium phosphate. The hydroxyl alkalinity or free caustic should be in the range of 100 to 350 ppm expressed as calcium carbonate. This is accomplished by keeping the phenolphthalein alkalinity at 60 to 80 per cent of the total alkalinity. Higher hydroxyl alkalinity increases the danger of boiler metal cracking by caustic embrittlement. Lower hydroxyl alkalinities do not assure precipitation of the incoming magnesium in the hydroxide form.

2. *Hardness.* The hardness in the boiler water should be zero.

3. *Amounts of Treating Chemical.* There should be a free excess of treatment chemical in the boiler water at all times. Sodium carbonate is often the main treatment chemical for boilers under 150 psi. Enough should be added to maintain the recommended total and hydroxyl alkalinities. This assures the presence of a sufficient excess of either carbonate alkalinity or undecomposed carbonate. When phosphates are the main conditioning chemical, a free-phosphate residual should be maintained in the range of 30 to 60 ppm expressed as PO_4.

7-7. Sodium Carbonate Treatment. Sodium carbonate reacts with the sulfates of calcium and magnesium in the boiler water to form calcium and magnesium carbonates. Both compounds will form sludge under these operating conditions. But at higher boiler temperatures the sodium carbonate will become unstable. It partially hydrolyzes (reacts with the water) to form some free caustic soda. The caustic soda in turn reacts with the soluble magnesium salts to form the very desirable insoluble magnesium hydroxide sludge. In the following chemical equations for these reactions the underlined components are those which form sludge.

$$CaSO_4 + Na_2CO_3 = \underline{CaCO_3} + Na_2SO_4 \tag{7-2}$$

$$Na_2CO_3 + 2HOH + \text{heat} = 2NaOH + H_2O + CO_2 \tag{7-3}$$

$$MgSO_4 + 2NaOH = \underline{Mg(OH)_2} + Na_2SO_4 \tag{7-4}$$

These chemical equations show that proper amounts of sodium carbonate with favorable temperature and pressure conditions will

1. Destroy sulfate hardness
2. Favor the precipitation of calcium carbonate and magnesium hydroxides sludges, which are easy to control by blowdown

Even with sodium carbonate treatment some scale still forms on the heating surfaces of the boiler. But it is very thin, soft, and eggshell-like. Calcium carbonate intermixed with small amounts of silicate and sulfate is the main ingredient.

7-8. Phosphate Treatment. As temperature and pressure of the boiler water increase, the rate of decomposition of sodium carbonate to caustic soda also increases. Free caustic alkalinity then forms so rapidly in boilers operating above 150 psi that it is impractical to maintain the required alkalinity needed to ensure calcium carbonate precipitation. Under these conditions a more stable chemical treatment is desirable. The required degree of stability is obtained with treatment by phosphate compounds. The phosphates give good results at all operating pressures. Their use is essential at higher boiler pressures. The phosphate ions are not destroyed like the carbonate ion. When they are used properly, a sludge of tricalcium phosphate is formed in preference to one of calcium carbonate.

There are many phosphate compounds readily available for use in boiler water treatment. They differ mainly in their degree of alkalinity or acidity. Table 7-2 lists some of these compounds and their properties.

Table 7-2. Characteristics of Common Phosphate Compounds

Common name	Formula	Degree of alkalinity
Trisodium phosphate...........	$Na_3PO_4{\cdot}12H_2O$ Na_3PO_4	Highly alkaline
Disodium phosphate...........	$Na_2HPO_4{\cdot}12H_2O$ $Na_2HPO_4{\cdot}2H_2O$ Na_2HPO_4	Moderately alkaline
Monosodium phosphate........	NaH_2PO_4	Slightly acid
Sodium hexametaphosphate.....	$(NaPO_3)_6$	Slightly acid

When a boiler is low in alkalinity, trisodium phosphate is the most desirable choice for treatment since it is the most alkaline phosphate. But additional alkali may still be needed. Either soda ash or caustic soda can be used.

If the boiler water alkalinity is sufficient, the preferred compound is disodium phosphate. But it may be that the alkalinity in the boiler water is too high and must be reduced. In that case either monosodium phosphate, sodium hexametaphosphate, or possibly phosphoric acid should be used.

7-9. Colloidal Treatment. There is still another kind of internal boiler water treatment for scale prevention which is physical in nature. It involves the use of colloidal materials of organic origin. This treatment is used to best advantage in combination with sodium carbonate or phosphate. The physical characteristics of sludge precipitated in a boiler water are not very predictable. Sometimes the sludge is not carried along with the water satisfactorily. In that event blowdown does not do an effective job of removal. But proper colloidal materials added to the boiler water will condition the sludge so that it can be more easily removed by blowdown. The colloidal materials have excellent absorbing and coagulating properties. They do not go into a true solution when added to water but are broken up into particles so finely divided that they are almost molecular in size. These finely divided colloidal particles do not tend to settle. Unstable and quick to react with other salts, the finely divided inorganic sludges are readily absorbed onto the surface of the colloid. The entire mass forms a fluid sludge that is easily removed by blowdown.

One of the earliest schemes for scale prevention involved the use of potato peelings in a boiler. Apparently this treatment was of some value. The potato peelings and the bits of potato left on the peelings contain starch, an active colloidal ingredient. The U.S. Navy has for many years advocated an internal boiler water treatment formula containing cornstarch, soda ash, and disodium phosphate. Vegetable products known as *tannins* are also used a great deal. The principal sources are chestnut and quebracho tannin. These materials are available at fairly reasonable prices. Since quebracho is marketed in several grades with different tannin content, it should be ordered to specification. Colloids extracted from seaweeds such as agar-agar are also used to some extent. The number of reactive colloids used for boiler water conditioning is on the increase.

The main disadvantage of colloidal materials is that there is no simple chemical-control method for determining how much is actually in the boiler water. The required amount is arrived at largely by trial and error. This involves making a careful study of sludge characteristics with various colloid dosages. Finally, the type and quantity of colloid that produce the best sludge is selected. If the colloid is tannin, enough should be fed to the boiler water to produce a color that closely approximates that of moderately strong tea.

The use of phosphates should be avoided in waters containing appreciable hardness. The sludge produced is heavy and tends to aggravate carryover conditions in the boiler. The harder the water, the more likelihood of such an unfavorable condition occurring. One solution is to reduce the hardness with external treatment. Another is to use sodium carbonate treatment in combination with proper colloidal materials to improve the properties of the resulting sludge.

7-10. Corrosion—Cause and Prevention. Corrosion is the term used to describe the deterioration of metal by chemical reaction. It can be looked upon as nature's way of trying to revert refined metals to their original natural state. Take iron, for example. Rust is formed when this metal corrodes. Chemically speaking, this rust is iron oxide. Iron ore is also iron oxide.

Each year industry pays a tremendous toll in repairs, replacements, and preventive measures to combat the evils of corrosion. The factors influencing corrosion of metallic substances are numerous and, for this reason, very difficult to control. Water and its dissolved gases, particularly oxygen, are two of the most important factors in internal boiler corrosion. For example, oxygen dissolved in boiler feed water is released by the increase in temperature and may attack boiler metal locally in the form of pitting. Other dissolved gases, such as carbon dioxide, lower the pH of the boiler water and also promote attack of the boiler metal. When the pH is less than 7 (the acidic range), corrosion is general in nature over the entire surface rather than localized pitting.

7-11. The Electrochemical Theory. Many theories have been advanced to explain the mechanics of boiler corrosion. The electrochemical theory is the one most generally accepted. It provides a good explanation of the fundamental reactions responsible for corrosion in the greatest number of cases.

There are many substances that dissolve in water to a certain extent. For example, if a small amount of sugar is added to a cup of water, coffee, or tea, usually all of the sugar will go into solution. However, if too much is added, particles of undissolved sugar will be found on the bottom of the cup. Under these conditions no more sugar is dissolved by stirring the solution. At this point it is completely saturated with sugar. This simply illustrates that only a limited amount of any given substance will dissolve in water, no matter how much of the substance is added.

According to the electrochemical theory, all metals tend to dissolve in water to a certain extent. This tendency is very slight and almost disappears in the presence of just a small quantity of dissolved metal in the water. For example, water in contact with iron puts a very small quantity of iron into solution. The water quickly becomes saturated with iron, which tends to stop further dissolving. However, the dissolved iron is in a different condition from that in the solid metallic state. Every iron particle going into solution takes on an electric charge and is then called a ferrous (Fe^{++}) ion.

$$\underset{\text{Metallic state}}{\mathrm{Fe}} = \underset{\text{Ferrous ion}}{\mathrm{Fe}^{++}} \tag{7-5}$$

Even water will ionize to a very small extent. It tends to form positive hydrogen ions and negative hydroxyl ions.

$$\underset{\text{Water}}{\mathrm{H_2O}} = \underset{\substack{\text{Positive}\\ \text{hydrogen ion}}}{\mathrm{H}^{+}} + \underset{\substack{\text{Negative}\\ \text{hydroxyl ion}}}{\mathrm{OH}^{-}} \tag{7-6}$$

The ferrous ions tend to unite with the negatively charged hydroxyl ions forming the chemical substance known as ferrous hydroxide.

$$\underset{\text{Ferrous ion}}{\mathrm{Fe}^{++}} + \underset{\text{Hydroxyl ion}}{2\mathrm{OH}^{-}} = \underset{\text{Ferrous hydroxide}}{\mathrm{Fe(OH)_2}} \tag{7-7}$$

At this point the amount of dissolved oxygen in the water is an important factor in the rate of corrosion. The oxygen acts in two ways. First, it oxidizes any ferrous hydroxide to ferric hydroxide. The ferric hydroxide is much less soluble than the first form and tends to precipitate from the solution. This in turn allows more iron to go into solution.

$$\underset{\substack{\text{Soluble}\\\text{ferrous hydroxide}}}{4Fe(OH)_2} + \underset{\substack{\text{Dissolved}\\\text{oxygen}}}{O_2} + \underset{\text{Water}}{2H_2O} = \underset{\substack{\text{Insoluble}\\\text{ferric}\\\text{hydroxide}}}{4Fe(OH)_3} \qquad (7\text{-}8)$$

The second and more important effect comes from the excess hydrogen ions that form on the surface of the metal. Hydroxyl ions from the water unite with the ferrous ions, and hydrogen ions are left over.

$$\underset{\text{Ferrous ion}}{Fe^{++}} + \underset{\text{Water}}{2HOH} = \underset{\substack{\text{Ferrous}\\\text{hydroxide}}}{Fe(OH)_2} + \underset{\substack{\text{Hydrogen}\\\text{ions}}}{2H^+} \qquad (7\text{-}9)$$

These excess hydrogen ions form a protective coating on the surface of the metal that tends to prevent further solution of metallic iron. But any dissolved oxygen in the water also tends to combine with this layer of hydrogen to form more water. This removes the protective hydrogen and allows more iron to dissolve in the water.

$$\underset{\substack{\text{Protective}\\\text{coating of}\\\text{hydrogen ions}}}{4H^+} + \underset{\substack{\text{Dissolved}\\\text{oxygen}}}{O_2} = \underset{\text{Water}}{2H_2O} \qquad (7\text{-}10)$$

7-12. The Effect of Acidity and Alkalinity. The amount of acidity and alkalinity is also an important factor in corrosion. Increased acidity means an increase in the hydrogen-ion content of the water. Under these conditions dissolved oxygen is not required for corrosion. The hydrogen coating on the surface of the metal becomes a gas, leaving the metal surface open to further corrosive attack. The actual rate of corrosion is proportional to the hydrogen-ion concentration.

In extremely alkaline waters the hydrogen-ion concentration is low. In such cases there is usually plenty of dissolved oxygen available. This oxygen removes the protective hydrogen film as fast as it forms. But excessive acidity or alkalinity is rare in boiler feed water. Therefore, in the majority of cases, the rate of corrosion is proportional to the concentration of dissolved oxygen in the water.

7-13. The Role of pH. The role of pH in the corrosion of metals is extremely important. The corrosion rate of iron in the absence of oxygen is proportional to pH up to a value of 9.6. At this point hydrogen-gas formation and the dissolving of iron practically stop. This is the same pH produced by a saturated solution of ferrous hydroxide. At this pH the formation of more ferrous ions is prevented by an effect similar to back pressure.

However, the oxygen present simultaneously unites with the ferrous hydroxide to form ferric hydroxide. This reaction lowers the pH of the solution and again tends to stimulate corrosion.

In all cases corrosion in water can be measured by a velocity or intensity factor and a quantity factor. The velocity factor is a function of pH because the rate at which the iron dissolves depends on pH. The quantity factor is a function of the available dissolved oxygen.

7-14. Film Formation. Protective films also control the amount of corrosion taking place in a boiler. The ferrous hydroxide initially formed serves to retard further corrosion by producing a partially protective film on the metal surface. The stability of the ferrous hydroxide film depends upon the degree of acidity of the water near the metal since a saturated solution of ferrous hydroxide is definitely alkaline.

The presence of strong alkalies in the water decreases the solubility of the film, making it stronger and more protective. The presence of acid increases the film solubility with loss of protective action. The chief natural process retarding corrosion is the formation of these protective films.

There are other protective films in addition to the simple ferrous hydroxide type. These are usually more complex in nature and may be produced either naturally or artificially. Silicates, chromates, phosphates, and carbonates of iron, calcium, and magnesium all produce films giving excellent protection. Some of these substances are found naturally in the water, and others are intentionally added to promote formation of protective films.

7-15. Other Causes of Corrosion. As far as corrosion is concerned, the most troublesome gas in boiler operation, next to oxygen, is carbon dioxide. Bicarbonates, present in most boiler feed waters, yield carbon dioxide when heated under pressure. The carbon dioxide combines with the water to form a weak acid known as *carbonic acid*. This acid slowly reacts with iron and other metals to form their bicarbonates. The bicarbonates are decomposed by heat once more, and carbon dioxide gas is liberated. This gas again unites with water to form carbonic acid, and the cycle is repeated.

$$\underset{\substack{\text{Metallic}\\ \text{iron}}}{\mathrm{Fe}} + \underset{\substack{\text{Carbonic}\\ \text{acid}}}{2\mathrm{H_2CO_3}} = \underset{\substack{\text{Ferrous}\\ \text{bicarbonate}}}{\mathrm{Fe(HCO_3)_2}} + \underset{\substack{\text{Hydrogen}\\ \text{gas}}}{\mathrm{H_2}} \tag{7-11}$$

$$\underset{\substack{\text{Ferrous}\\ \text{bicarbonate}}}{\mathrm{Fe(HCO_3)_2}} + \underset{\text{Water}}{2\mathrm{HOH}} + \text{heat} = \underset{\substack{\text{Ferrous}\\ \text{hydroxide}}}{\mathrm{Fe(OH)_2}} + 2\mathrm{H_2O} + \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{2\mathrm{CO_2}} \tag{7-12}$$

Corrosion is also caused by certain other gases such as hydrogen sulfide, sulfur dioxide, and ammonia. But damage from these substances is relatively unimportant compared with the corrosion damage brought about by oxygen and carbon dioxide.

Organic matter can enter the boiler through a condenser leak contaminated by sewage or other waste. At boiler operating pressures and temperatures this organic matter breaks down to form highly corrosive organic acids.

Oil and grease, animal and vegetable oils—all decompose under the right conditions to produce free acids and glycerine. The free organic acids attack iron in the same manner as carbon dioxide. In addition the attack is cyclic in nature. The merest trace of oil in the boiler can initiate what may become a very serious corrosion problem. Therefore, it is important to avoid using animal or vegetable oils if there is the slightest possibility of getting them into the boiler.

The class of oil known as *hydrocarbon* or *mineral* is preferred for boiler plant use. But under certain conditions even these oils can promote an acid attack on iron.

7-16. Preventing Corrosion. The prevention of corrosion in the boiler means regulating alkalinity of the water, producing protective films, and removing the dissolved oxygen.

Alkalinity adjustment and film formation are closely related and are accomplished in much the same manner. The pH value of the boiler water should be greater than 9.5, and a small amount of hydroxide alkalinity should be maintained.

The alkalinity should be adjusted with such chemicals as soda ash, caustic soda, and trisodium phosphate.

Film formation occurs when the alkalinity is kept in the desired range. The simplest film is composed of the iron hydroxide initially formed on the metal surface. As long as the alkalinity is high enough, the iron hydroxide remains insoluble and acts as a protective film.

Complex reactions between the alkaline chemicals added and the mineral constituents in the water also result in the formation of protective films. Small amounts of certain colloids form a protective coating that has a marked effect in reducing corrosion.

Operators of modern high-pressure boiler plants find it necessary to install deaerating equipment to remove the dissolved oxygen from the feed water. But this investment in equipment is usually unwarranted in a low-pressure plant, particularly if an open feed-water heater is used. As long as it is suitably vented, the open heater will drive off most of the oxygen and free CO_2.

It is desirable to increase the boiler feed temperature as much as possible using the heat from surplus exhaust steam. In doing this it is best to take advantage of the deaerating effect of an open feed-water heater. This unit is capable of heating the water to within a few degrees of saturation temperature corresponding to the operating pressure of the exhaust steam. If there is not enough exhaust steam, the deficiency can be made up by bleeding high-pressure steam into the heater. Enough should be added to maintain the feed-water temperature at a minimum of 210°F.

The second line of defense calls for chemical removal of the last traces of oxygen. Sodium sulfite, hydrazine, and various other organic reducing compounds, such as tannin, are recommended for this purpose.

7-17. Carryover, Foaming, and Priming. Carryover of boiler water solids is partly a mechanical and partly a chemical problem. The mechanical causes include deficiency in boiler design, high water level, improper method of firing, overloading, and sudden load changes. A poorly designed boiler may have insufficient steam disengaging space. It is fairly obvious that the faster steam is produced in a given vessel, such as a boiler, the more violent is the boiling effect. There is also increased opportunity for carryover or foaming and priming. But if the steam space above the water level is large enough, the steam leaving the vessel will not show any evidence of carryover. When the steam storage space above the water level is too small, carryover of solids will take place. The size of the steam header and the velocity of steam leaving the boiler are therefore important elements in boiler design. The more obstructions within a boiler such as stay bolts, braces, and baffles, the greater is the tendency to carryover.

Operating with the water level too high reduces the size of the steam space above the water and therefore promotes carryover. As the rate of steam production goes up, so does the tendency to steam contamination from carryover. Therefore, deliberate overloading of the boiler beyond the original design rate or other unavoidable incidents of operation will probably increase steam contamination. The sudden opening of a steam valve or the cutting in of a boiler too quickly speeds up the production of steam, which may cause violent bubbling and carryover.

The primary chemical causes of carryover are high total dissolved and suspended solids in the boiler water, excessive alkalinity, and the presence of oil. When distilled or pure water is boiled, large-sized, unstable steam bubbles are formed. These rapidly reach the surface of the water and instantaneously burst through. As the concentration of solids in the water increases or as the water becomes contaminated with oil, numerous small-sized steam bubbles are formed. These smaller bubbles are much more stable and do not instantaneously burst through the surface of the water. Instead a thick layer of small-sized bubbles accumulates on the surface. This ultimately produces carryover or violent foaming.

7-18. Preventing Carryover, Foaming, and Priming. Since the cause of solids carryover is partly mechanical and partly chemical, control of this problem must be along the same lines. Boiler design is a most important factor. Production of dry steam is aided by boiler designs that provide maximum water and steam space. This means the largest possible drum diameter. The plant operator can help by following some simple rules. Keep the boiler water level from getting too high. Operate the boiler at an even rating. Wherever possible, arrange the distribution of load so that the rate of steam flow is held as uniform as is practical. The difficulties from carryover can also be overcome by a secondary approach involving mechanical design. Mechanical separators, steam purifiers, special baffles, etc., can be incorporated into the boiler design. These features provide for a change in the direction of steam flow. Their purpose is to separate entrained water and solids from the steam before these solids can damage the equipment that follows.

The chemical approach to the problem of carryover depends greatly upon the operating personnel. Control of the nature and amount of total solids in the boiler water is the most important factor. Another effective control measure is the addition of antifoam compounds directly to the boiler.

Table 7-3 shows the maximum boiler water concentrations allowed by the American Boiler Manufacturers Association in their standard guarantee on steam purity.

The limits on total solids in Table 7-3 are only a guide and do not tell the complete story. The amount of suspended solids and alkalinity in the boiler water is also very important. Table 3-1 is a guide to the maximum total alkalinity allowed at various operating pressures. Small amounts of organic matter and oil are also undesirable. These will form soap in the boiler and must not be allowed to enter.

Table 7-3. Maximum Allowable Total Solids in Boiler Water

Boiler pressure, psi	*Total solids in boiler water, ppm*
0–300	3,500
301–450	3,000
451–600	2,500
601–750	2,000
751–900	1,500

The most practical way to fix control limits for any given boiler plant is to make sure first that oil and organic matter are kept out of the boiler. Then allow the boiler water to concentrate with treating chemical present until trouble with carryover starts. This limiting concentration marks the danger zone. The concentration can then be determined by making chloride tests on both the boiler water and the raw water. After this is completed, establish a blowdown schedule to keep the level of solids in the boiler reasonably well below the upper limit.

Truly remarkable strides have been made in developing antifoam treatment chemicals. As a result boilers can be operated at higher concentrations than the limits mentioned in the literature. This means it is entirely possible to operate boilers in areas where the water supply is extremely high in total solids. With antifoam chemical, 30,000 ppm total solids can be maintained in a boiler without development of carryover. It is also possible to control many bad cases of foaming and priming caused by organic contamination of the feed water. Another beneficial effect of antifoam chemicals is reduced rate of blowdown. This saves heat normally lost with the blowdown.

In general antifoam chemicals are complicated organic materials. Among the most effective compounds are the polymerized esters, alcohols, and amides. All these chemicals are readily available.

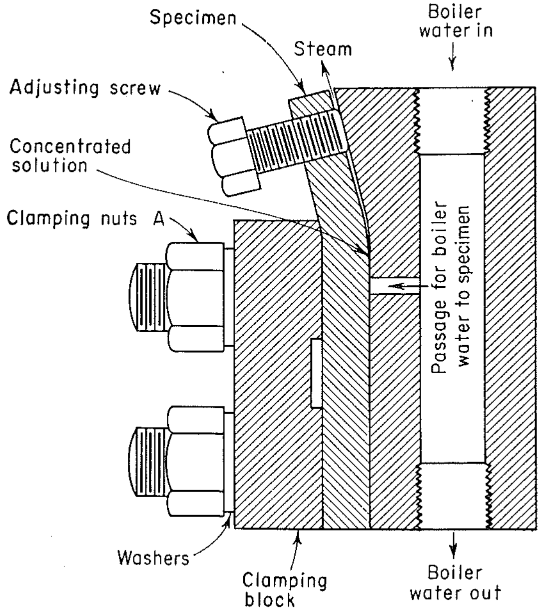
7-19. Caustic Embrittlement. The three conditions needed to produce metal failure from embrittlement are:

1. Boiler metal subject to stress, either internal from cold working or external due to expansion or contraction.
2. Boiler water leakage in the stress area. As a result, steam escapes and the boiler water solids concentrate at the point of leakage.
3. Free sodium hydroxide in the boiler water which concentrates at the point of leakage and chemically attacks the metal.

All these conditions must exist simultaneously for embrittlement to take place. Unfortunately, a simple analysis of the boiler water does not reveal whether or not the metal will become embrittled.

7-20. Preventing Caustic Embrittlement. Once the boiler is erected, stress characteristics are inherited which cannot be changed. Whether or not these stresses will make the metal subject to caustic embrittlement is unpredictable. But if there is free caustic in the boiler water and any leaks are present, embrittlement can take place. Fortunately, the use of welded boiler drums has eliminated riveted seams where leaks may occur. The most practical method of preventing caustic embrittlement is to regulate the chemical composition of the boiler water. Since there is no chemical test that directly indicates whether or not a boiler water will cause embrittlement, a special device and testing method was developed. This device, called the embrittlement detector (Fig. 7-1), was developed by the U.S. Bureau of Mines. It consists of a steel specimen placed in the circulating boiler water to duplicate the high stress and concentrations needed for embrittlement. If there is embrittlement under these conditions and tests on the boiler water show embrittling characteristics, chemical treatment is called for. The effectiveness of treatment can also be tested with the embrittlement detector. However, the problem is not simple, and there are numerous complicating testing factors. Therefore, all embrittlement studies should be conducted under the supervision of a qualified laboratory experienced in this kind of work.

The most obvious chemical solution to embrittlement is to eliminate all free sodium hydroxide from the boiler water. But this is not always possible. One method of this type has been developed using phosphates. The pH of the boiler water is controlled so that any solid material deposited at the point of concentration is trisodium phosphate and not free sodium hydroxide. Figure 7-2 gives the approximate pH values of trisodium phosphate solutions of various concentrations. If the pH of the boiler water is kept just slightly below the value indicated on the curve,



Patent applied for

FIG. 7-1. Embrittlement detector. (*From Bureau of Mines Bulletin* 443.)

the boiler water will not have any free sodium hydroxide. This chemical method requires close supervision and control to prevent caustic embrittlement.

A simpler chemical approach is to keep the free sodium hydroxide alkalinity as low as possible. Then chemicals that are capable of preventing this type of failure should be added.

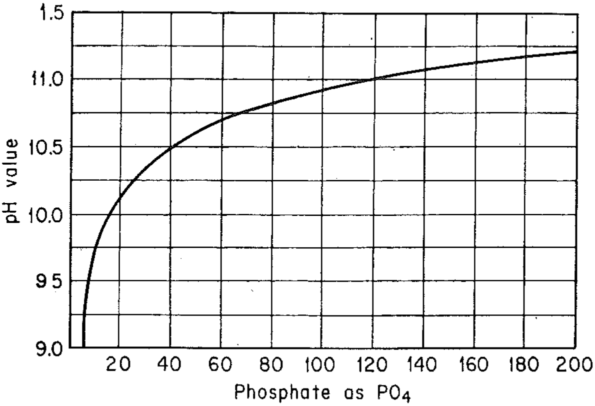


FIG. 7-2. Approximate pH values of various concentrations of trisodium phosphate solutions.

Chemicals offering protection against embrittlement include mainly lignin-containing materials such as waste sulfite liquor; certain tannins, particularly quebracho tannin; and sodium nitrate. The results of considerable research indicate that protection from embrittlement is obtained from quebracho tannin or sodium nitrate if the ratio of these chemicals to total alkalinity is not less than 0.4.

Sodium nitrate lends itself more easily to simple routine control analysis than quebracho tannin. Where this feature is important, sodium nitrate should be used. But the quebracho tannin does have other beneficial effects including the ability to absorb oxygen. In addition it helps form a more fluid sludge in the boiler. The embrittlement detector is very useful in selecting the type and amount of chemicals needed for a given boiler water.

8

Water Treatment for Low-pressure Heating Boilers

The low-pressure heating boiler is one that usually operates at 10 psig or less. It is mainly used for the generation of steam for heating a plant or a building. Practically all of the condensate returns to the boiler. In addition a small amount of the generated steam is often used for such services as heating the steam tables in a restaurant. Treating the water for a low-pressure boiler does not present any major problem. But there are certain special factors that do affect the treatment. These must be thoroughly understood before attempting to treat the boiler water chemically.

8-1. Water Troubles. Corrosion is the major problem in low-pressure heating systems. Its presence within the boiler can generally be recognized by the uneven eating away of boiler metal surface. As previously discussed, corrosion of this type is appropriately called *pitting*.

Corrosion and pitting are commonly caused by the dissolved gases oxygen and carbon dioxide. Of these two gases, oxygen is the primary offender. The carbon dioxide acts like the accelerator in a car by speeding up the rate of corrosion.

The damage caused by these dissolved gases can be controlled by adding alkali to the boiler water. The aim is to neutralize all the carbon dioxide and produce about 100 to 350 ppm hydroxyl alkalinity expressed as $CaCO_3$. This is simply accomplished by using enough alkali chemical to produce and maintain a total boiler water alkalinity of 300 to 500 ppm expressed as $CaCO_3$. Under these conditions the phenolphthalein alkalinity will be 60 to 80 per cent of the total alkalinity.

Chromate chemicals are also very effective inhibitors of boiler corrosion caused by oxygen and carbon dioxide. For maximum protection, keep 500 to 1,000 ppm as sodium chromate in the boiler at all times. Maintain the pH in the range above 7.5.

Scale formation can be a major problem when steam or condensate losses are heavy, particularly in hard-water areas. The steam leaving the boiler is practically the equivalent of pure distilled water. The mineral salts originally in the water remain behind when the steam is produced. If the resulting condensate is not returned to the boiler, fresh-water makeup must be added in its place. As the makeup is added, more and more mineral salts are brought into the boiler water. These salts in the boiler water eventually concentrate to the point where the hardness salts exceed their solubility and come out of solution to form scale. The greater the amount of hardness in the original makeup water, the quicker the boiler water reaches the point of scale formation.

When steam or condensate losses are heavy, first concentrate on eliminating any water waste. Make regular checks of the over-all system for leakage in radiators, return lines, or any auxiliary equipment on either the steam or the condensate return system. If the leakage still persists, then formulate a plan of chemical treatment that will prevent scale. In addition, make sure that provision is made for regular boiler blowdown to keep the concentration of boiler water mineral salts at a reasonable level.

8-2. Makeup and Blowdown. The raw-water makeup and the blowdown are normally just a minor part of the over-all job of treating the boiler water in a low-pressure heating system. Usually all the steam is condensed and returned to the boiler. The only exception is some small steam loss through the radiator valve-packing gland or the air vent. Therefore, very little makeup water is needed, and for this reason, heavy blowdown is not a planned part of the water treatment program.

Blowdown is necessary and included in the treatment plan only when the boiler water analyses indicate that the concentration of mineral salts is high enough to possibly form scale. Use the following rough guide to help determine the limiting chloride concentration for a given boiler water. First analyze the makeup water for both total hardness and chlorides. Then substitute these figures in Eq. (8-1) based on maintaining boiler water total hardness under 1,000 ppm at all times.

$$\mathrm{Cl}_{bw} = \frac{\mathrm{Cl}_m \times 1{,}000}{TH_m} \tag{8-1}$$

where Cl_{bw} = maximum allowable boiler water chlorides, ppm
Cl_m = chlorides present in the makeup, ppm
TH_m = total hardness present in the makeup, ppm

Just enough blowdown is needed to keep the chloride concentration in the boiler water safely below the maximum allowable chloride level. Table 8-1 gives the amount of blowdown required for typical soft and hard waters. This is calculated from Eq. (8-1). The per cent of blowdown is obtained by dividing the amount of chlorides in the makeup by the quantity of chlorides in the boiler water and then multiplying by 100. Very little makeup or blowdown is normally required for a low-pressure heating boiler. Therefore, base the initial chemical dose on the amount of water normally contained in the boiler. Any treatment given later will be small in amount by comparison and needed only infrequently.

If a large amount of makeup is needed along with frequent chemical doses, carefully check the boiler water chlorides. If they are not much higher than the chlorides in the makeup water, look for excessive water losses from the boiler. These losses should be tracked down and eliminated as soon as possible. When the boiler water chlorides are higher than the maximum allowed and a large amount of makeup water is needed, the system is probably losing excessive steam or condensate. These losses must be found and eliminated. Blowdown is called for only when it is actually needed to hold the chloride concentration in the boiler below the maximum allowable level.

Table 8-1. Per Cent of Blowdown Required for Typical Hard and Soft Waters

Type of water	Makeup analysis		Boiler water chlorides, maximum ppm	Blowdown, per cent of makeup
	Total hardness ppm	Chlorides, ppm		
Soft	25	2	80	2.5
Hard	200	20	100	20

NOTE: The 2.5 per cent blowdown equals 1 in. of boiler blowdown for every 40 in. of makeup water added. The 20 per cent blowdown equals 1 in. of boiler blowdown for every 5 in. of makeup water added.

8-3. Water Losses. Excessive loss of water from a boiler aggravates boiler water troubles. When the boiler water is treated, the loss of water means the loss of a sizable amount of treatment chemicals. This increases the cost of treatment and the equipment may still not be fully protected. The major sources of heavy water loss from a heating-type boiler are:

1. Miscellaneous losses from leaky tubes or blowdown valves.

2. Excessive blowdown primarily because the operator is given wrong information.

3. Auxiliary equipment failure. For example, if an automatic makeup valve sticks open, fresh water pours into the boiler. Blowdown then has to be heavy to keep the boiler from flooding.

4. Condensate trapped in the return lines. This may happen when making steam before the boiler is brought up to full operating pressure. The first steam coming from the boiler con-

denses or "hangs up" in the system. The cause may be faulty trap action or perhaps poorly pitched condensate-return lines. But in the meantime water enters the boiler to maintain the boiler water level. Later, when the boiler is under full pressure, the trapped condensate finally flows back. As a result, blowdown is called for in order to prevent flooding and to maintain the proper water level in the boiler.

5. Leaks in a hot-water coil often admit fresh water directly into the boiler. Then heavy amounts of blowdown are needed to maintain the desired boiler water level.

6. Return-line leakage, in faulty equipment or fittings or possibly from active return-line corrosion.

8-4. Treatment Chemicals. One of the most widely used chemicals for treating low-pressure heating boilers is sodium silicate or chemical mixtures containing sodium silicate and other alkalies. Chemicals of this type are available in both liquid and solid form. A mixture of soda ash and trisodium phosphate with sodium bichromate or sodium chromate is also frequently used. Table 8-2 lists the important properties of these treatment chemicals.

Table 8-2. Common Alkali and Chromate Chemicals for Water Treatment

Common name	Formula	Na_2O, %	SiO_2, %	Amounts needed per 1,000 gal—	
				To increase alkalinity 500 ppm as $CaCO_3$	To increase chromate 1,000 ppm as Na_2CrO_4, lb
Water glass	$(Na_2O)(3.22SiO_2)$	8.9	29	9 qt	
Sodium metasilicate	$Na_2SiO_3 \cdot 5H_2O$	29.2	28.3	8.8 lb	
Soda ash	Na_2CO_3	58.0	....	4.5 lb	
Trisodium phosphate	$Na_3PO_4 \cdot 12H_2O$	16.3	....	16.0 lb	
	or Na_3PO_4	37.8	....	6.9 lb	
Sodium bichromate	$Na_2Cr_2O_7 \cdot 2H_2O$	....	....	....	7.7
Sodium chromate	Na_2CrO_4 or	....	....	....	8.4
	$Na_2CrO_4 \cdot 4H_2O$	....	....	....	12.1

When alkali salts are the main treatment chemical, the ideal boiler water analysis is the one containing 100 to 350 ppm hydroxide alkalinity with 300 to 500 ppm total alkalinity, expressed as $CaCO_3$. Actually an alkalinity as high as 1,000 ppm will not harm a low-pressure heating boiler. Finally, it is necessary to make sure that the boiler water chlorides never exceed the maximum allowable limits calculated from Eq. (8-1).

Sodium silicates not only help reach the desired alkalinity level, but also combat corrosion by producing a uniform chemical film over the boiler metal surfaces.

When chromates are the main treatment chemical, the ideal boiler water analysis is one containing 500 to 1,000 ppm of chromates expressed as Na_2CrO_4 with the pH above 7.5. As long as the pH of the treated boiler water is higher than 7.5, sodium bichromate can be used, even though this chemical is slightly acid. If the pH is less than 7.5, any alkali may be used in combination with the sodium bichromate to raise the pH. Since sodium chromate is slightly alkaline, it will not lower the boiler water pH below 7.5. All of these chemicals do an excellent job when used properly. Therefore, each particular plant should use those that are most readily available.

8-5. A Blueprint for Low-pressure Boiler Water Treatment. Now that the conditions affecting the treatment of low-pressure heating systems are understood, a plan of attack can be prepared in accordance with the principles outlined in Chap. 4, A Blueprint for Efficient Water Treatment. The first step in this plan is to make a survey. Table 8-3 is a typical boiler room survey sheet. This form will help collect the necessary background data including boiler capacity, blowdown, makeup, and possible sources of water losses from the system. Several methods of obtaining these kinds of data are fully discussed in Chap. 5.

The second step in the plan is to prepare three simple line sketches similar to the flow-sheet diagrams shown in Chap. 4. These flow diagrams should be as simple as possible with only the most important streams identified.

Table 8-3. Typical Boiler Room Survey Form

Company..

Survey made by..Date..............................

DESCRIPTION OF BOILER PLANT

1. Boiler designation..
2. Type of boiler:....................Fire tube..........Water tube..........Cast iron
   ....Package type
3. Manufacturer..
4. Manufacturer's type designation..........................Catalog No...............
5. Year boiler installed..........................
6. Any tube replacements? (Year and No.)..
   Any plugged tubes?..............................Any leaking tubes?................
   Any other major repairs?..
7. Last insurance or other inspection report...
   Year........................By whom?..
   Condition reported..
8. Any scale or corrosion in boilers?...
9. Makeup ....Automatic...............Manual makeup........................
10. Condensate return ....Gravity...............Vacuum
11. Fuel: No...............Oil...............Coal...............Gas
12. Which boiler(s) is (are) used for domestic hot water? ....
13. Is boiler water or steam used to preheat oil?....................................
14. Data for determining gallons water boiler holds:
    Steel fire-tube boilers
        Diameter of door on shell (hinge to hinge).................................
        Length of shell..
        Volume of water boiler holds...
    Cast-iron boilers or water tube
        Length of boiler................................Width.................................
        Height of boiler to water line in gauge glass...............................
        Volume of water boiler holds...
15. Description of chemical-feeding equipment.......................................

FACTORS AFFECTING STEAM BOILER MAKEUP

1. How much water is blown down?........................Inches per........................
2. Any condensate losses known?...
3. Any steam usage where condensate is not returned?..........................
4. Does condensate ever "hang up" in system?....................................
5. Any boiler water losses?...

Table 8-3. Typical Boiler Room Survey Form (Continued)

WATER TREATMENT FACTORS

1. Source of water supply..
2. Samples taken:....................Raw water....................Boiler water
3. Treatment chemical selected..
4. Reason:....................Corrosion prevention....................Scale prevention
   ....Other
5. Concentration of treatment chemical desired in boiler water....................
6. Maximum allowable Cl concentration..

8-6. Material Balance in Gallons of Water. The most important fact in Fig. 8-1 is the number of gallons of water contained in the heating boiler. Condensate returns are normally close to 100 per cent of the total feed water. Therefore, the amount of makeup and blowdown is negligible if there are no extraordinary water or steam losses from the system. If water or steam losses cannot be eliminated, then it is very important to note the amounts of makeup and blowdown on this flow diagram.

8-7. Chemical Balance of Raw-water Changes (see Fig. 8-2). If there is no appreciable loss of boiler water, steam, or condensate from the heating system, the chemical balance is relatively unimportant and often is not needed. But when these losses are heavy, the chemical analysis of the raw-water makeup and the untreated boiler water is very important. The total hardness and chlorides are particularly critical. Calculate the maximum allowable boiler water chlorides that can be carried without scale formation and include these data on the chemical balance diagram.

Compare the chlorides in the makeup water with those in the boiler water. This comparison shows just how fast salts are building up in the boiler water. It helps to better judge the effect of boiler water losses and determine the need for blowdown.

Suppose a certain boiler water normally has a concentration factor of 10. In other words, there is 10 times as much chloride in the boiler water as in the makeup water. Calculations for this system show that the maximum allowable number of boiler water concentrations is 20. If at any time the concentration factor exceeds 20, there is a need for blowdown. This means a blowdown schedule must be started or the amount of blowdown increased if a blowdown schedule is already followed. When the boiler water concentration falls below the normal value of 10, either the amount of blowdown is too great or boiler water leaks have developed.

A comparison of alkalinity in the raw and untreated boiler water shows whether or not chemical treatment is required. It is possible for the makeup water to bring enough alkalinity into the boiler without additional chemical treatment.

8-8. Chemical Balance of Treatment Chemicals. Before the flow diagram in Fig. 8-3 can be completed, the desired chemical treatment must be selected. Silicates, alkali chemicals, or chromates can be used. If scale formation is the major problem, because of steam and condensate losses or hard makeup water, silicates or the alkali salts are indicated. When pitting and corrosion are the main problems and the makeup water is soft, silicates or chromates should be used. The advice of a competent water treatment specialist is very helpful in selecting the proper combination of treatment chemicals.

Corrosion is kept well under control with silicates or alkali salts by holding the boiler water alkalinity in the range of 100 to 350 ppm hydroxide and 300 to 500 ppm total alkalinity, both expressed as $CaCO_3$. Any one or any mixture of the alkali chemicals in Table 8-2 will produce the desired results. If water losses are small and the noncarbonate hardness (total hardness minus total alkalinity) is low, the initial chemical dose to attain 500 ppm total alkalinity is readily obtained from Table 8-2. This tabulation is based on the volume of water normally held by the boiler.

EXAMPLE 1. A boiler holds 2,000 gal of water. The analysis of the boiler water shows total hardness of 100 ppm and total alkalinity of 85 ppm. Treat the boiler water with sodium metasilicate and maintain about 500 ppm total alkalinity. Table 8-2 shows that 8.8 lb of sodium metasilicate is needed per thousand gallons of water in the boiler. The total amount of chemical needed is then 8.8 multiplied by 2, or 17.6 lb of sodium metasilicate.

When the noncarbonate hardness is high, the alkali salts react with the hardness to form sludge in the boiler before they raise the alkalinity. Table 8-4 gives the amount of alkali salt needed to react with the noncarbonate hardness to form sludge in the boiler. The alkali needed for this purpose must be added before using Table 8-2. The procedure for making calculations of this type is fully covered in Chap. 4, Sec. 4-6, The Batch Method of Treatment.

EXAMPLE 2. A boiler holds 2,000 gal of water. An analysis of the boiler water reveals total hardness of 500 ppm, total alkalinity of 100 ppm, and noncarbonate hardness of 400 ppm. Treat this boiler water with sodium metasilicate to maintain about 500 ppm total alkalinity. Table 8-4 shows that 0.018 lb of metasilicate is needed per thousand gallons for each part per million of noncarbonate hardness. The total amount required is then 0.018 × 2 × 400, or 14.4 lb of metasilicate.

Table 8-4. Amount of Alkali Needed to React with Noncarbonate Hardness

Common name	Formula	Amount needed per 1,000 gal to react with each ppm of noncarbonate hardness as $CaCO_3$
Water glass	$(Na_2O)(3.22SiO_2)$	0.02 qt
Sodium metasilicate	$Na_2SiO_3 \cdot 5H_2O$	0.018 lb
Soda ash	Na_2CO_3	0.0089 lb
Trisodium phosphate	$Na_3PO_4 \cdot 12H_2O$ or	0.022 lb
	Na_3PO_4	0.0096 lb

In addition, Table 8-2 reveals that 17.6 lb of metasilicate will raise the alkalinity of the boiler water to 500 ppm. Therefore, a total of 32.0 lb of metasilicate is needed to achieve the required level of 500 ppm alkalinity.

When the amount of makeup water needed is considerable because o heavy system losses, the fixed volume of water in the boiler is no longer important. This means that alkali must be added continuously to the incoming makeup water to maintain the 500 ppm total-alkalinity level in the boiler. The calculations for this are fully covered in Chap. 4, Sec. 4-7, The Continuous Method of Treatment.

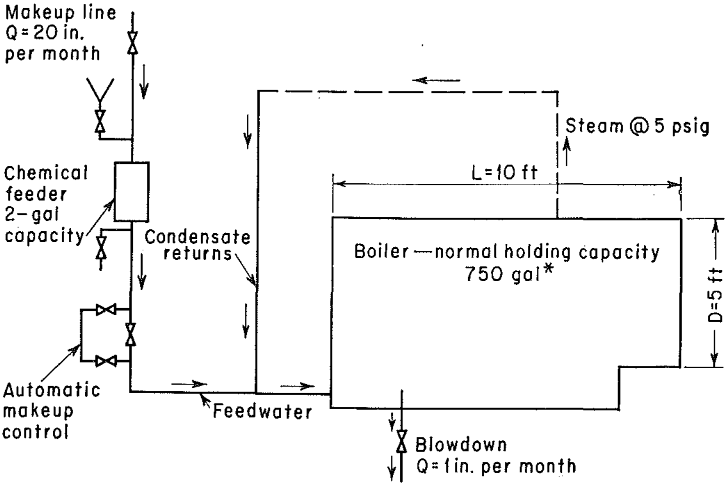


FIG. 8-1. Material balance in gallons of water.
NOTE: Boiler volume is computed from the empirical formula for a steel fire-tube boiler, 3 D^2L.

Chromates can be used to keep corrosion well under control if the chromate concentration is maintained in the range of 500 to 1,000 ppm as Na_2CrO_4 with pH values above 7.5. Actually, there is no danger if the chromates are higher than 1,000 ppm. The amount of chromate needed is given in Table 8-2. It is good practice to add 1,000 ppm as the initial dose. But do not add any more chemical until the chromate concentration first falls below 500 ppm. The chromates do not react with hardness to form a sludge like the alkali chemicals. Therefore, any heavy loss of chromate indicates a loss of boiler water through leaks or blowdown.

Set up a treatment program to maintain the desired alkalinity.

chromate, or chloride in the boiler. For full protection, maintain these boiler water conditions continuously. This means keeping a complete set of records such as those shown in Fig. 8-4. Make periodic tests for chlorides and alkalinity when alkali salts are used for the treatment. Test for chlorides, pH, and chromate when chromate is added.

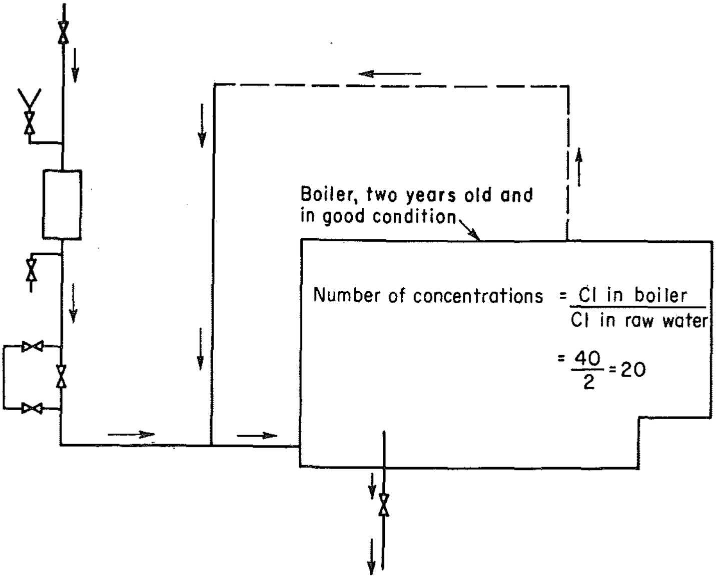


FIG. 8-2. Chemical balance of raw-water changes.

Raw-water analysis:	
Total hardness	35 ppm
Alkalinity	30 ppm
Noncarbonate hardness	5 ppm
Chlorides	2 ppm
Boiler water analysis (untreated):	
Total hardness	200 ppm
Phenolphthalein alkalinity	60 ppm
Total alkalinity	100 ppm
Noncarbonate hardness	100 ppm
Chlorides	40 ppm
Chlorides, *maximum allowable* [see Eq. (8-1)]	57 ppm

Under normal conditions any change in alkalinity or chromate will be gradual. To counteract a gradual decrease, just add a proportionate amount of a full charge. For example, if 500 ppm alkalinity is the desired level for the boiler water, add a full chemical charge when the alkalinity falls below 200 ppm. If the alkalinity is more than 200 ppm but less than 500 ppm, just add half a charge.

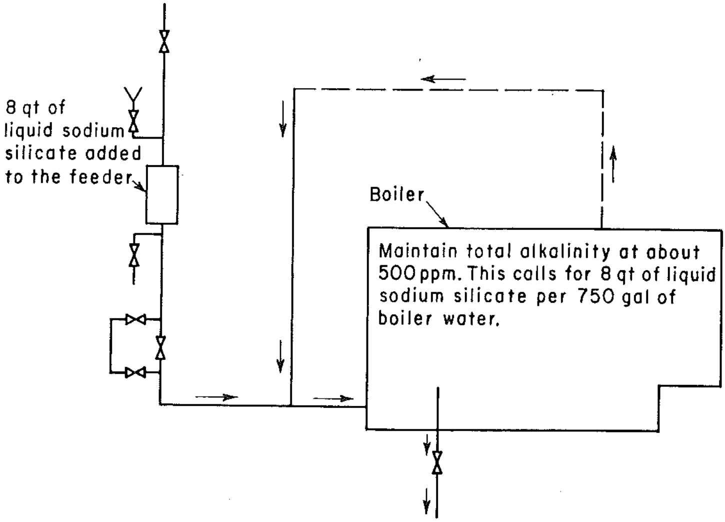


Fig. 8-3. Chemical balance of treating chemicals.

Treated boiler water analysis:

Total hardness	0 ppm
Phenolphthalein alkalinity	470 ppm
Total alkalinity	550 ppm
Chlorides	40 ppm

If the chlorides rise above the maximum allowable chloride limit, then by all means check for steam or condensate losses. If the chlorides fall sharply within a short time period and at the same time the alkalinity or chromate also decreases, look for boiler water losses.

Boiler Water Treatment Control Record

Name of Co.: *John Wilson Co.* Date: *5/1*

Boiler No.: *1* Type: *Fitzgibbons Steel Fire Tube*

Boiler dimensions: *D = 5 ft, L = 10 ft* Boiler volume: *750 gal*

NORMAL OPERATING DATA

Makeup: *20 in. per month* Blowdown: *1 in. per month*

Type treatment: *Liquid sodium silicate*

DOSAGE SCHEDULE

Total alkalinity found (M.O.), ppm	*−200*	*200–500*	*500+*
Liquid silicate charge, qt	*8*	*4*	*0*

Maximum allowable Cl.: *57*

Remarks: *Chloride in city water, 2 ppm, 4/28*

Total hardness in city water, 35 ppm

Date	Boiler		Blow-down, in.	Make-up, in.	Alk P.T.	Alk M.O.	Cl	Dose, qt	Remarks
	On	Off							
4/1	X				0	100	40	8	Before treatment
4/2	X			5	470	550	40		
4/7	X			5	400	510	40		
4/12	X			5	410	510	38		
5/1	X		1	5	400	480	42		
5/15	X			10	400	450	40		
6/1	X		1	10	310	420	40		
6/15	X			10	300	380	38	4	
6/16	X				500	600	40		
7/1	X		1	10	470	590	42		
7/10		X							Opened for inspection
7/15	X				0	30	2	8	Fresh water added
8/1	X		1	10	450	560	5		
8/15	X			10	400	510	10		
9/1	X		1	10	400	480	15		
9/15	X			10	370	450	20		
10/1	X		1	10	320	420	25		
10/15	X			10	300	380	30		
11/1	X		1	10	220	320	35	4	
11/2	X				500	580	40		
11/15	X			10	460	570	40		
12/1	X		1	10	450	560	40		

FIG. 8-4. Typical form of boiler water treatment control record.

EXAMPLE 3. A low-pressure steel fire-tube boiler must be treated to prevent pitting of the tubes. Use liquid sodium silicate as the treating chemical. The results of the survey are shown in Figs. 8-1 to 8-3. These diagrams contain all of the important data.

Figure 8-1 shows that the boiler holds 750 gal of water. In addition, the makeup and blowdown requirements of this system are not very high.

Figure 8-2 shows that the boiler concentration factor is 20. Over a 3-month period of continuous operation the water has concentrated 20 times in the boiler. Even though the chlorides in the boiler have concentrated 20 times, the maximum allowable chloride limit has not been exceeded. The blowdown and makeup are not excessive. Therefore, it can be concluded that the boiler is tight. In addition, boiler water steam or condensate losses are not excessive. But the total alkalinity of 100 ppm in the boiler water means that treatment is needed.

Figure 8-3 shows that about 8 qt of liquid sodium silicate is needed to produce 500 ppm total alkalinity in the boiler. The noncarbonate hardness present calls for 1½ qt, or about 18 per cent of the full chemical dosage. Actually the 1½ qt of liquid sodium silicate needed to react with the noncarbonate hardness is not too important in this case. Even if it is completely neglected, the resulting total alkalinity is about 410 ppm instead of 500 ppm. The 410 ppm alkalinity is well within the acceptable range for this type of low-pressure boiler. With the data outlined in this chapter, it is a simple matter to maintain the desired alkalinity in the boiler water. The control record (Fig. 8-4) illustrates how this has been done over a period of 8 months.

9

Internal Treatment for High-pressure Boilers

9-1. High-pressure Range. High-pressure boilers generate steam for power, process, and heat in all kinds of plants. The operating pressure ranges from 10 to 2,300 psi and higher. Boiler operation at supercritical pressures is a reality. Developments in these extremely high ranges are continually moving ahead. The very smallest boilers operate at pressures between 100 and 450 psi. In the larger industrial power plants the trend is to higher pressures considerably in excess of 450 psi. In public-utility central-station plants designed to deliver power to the community, the long-range trend is definitely toward even higher pressures with the supercritical range above 3,200 psi as the ultimate goal.

9-2. Types of American Steam Generators. The steam boilers employed in American power-plant practice fall into two general classes: fire tube and water tube. The fire-tube design is usually found in small and medium-sized installations operating at pressures up to 150 psi. In a fire-tube boiler the hot gas passes inside tubes surrounded by water. The most common unit of this type is the horizontal-return tubular or HRT boiler. Both the

Scotch marine and locomotive-type units fall into this classification. Vertical fire-tube boilers are also encountered. Figure 9-1 shows a package fire-tube boiler of four-pass design. The total cross-sectional area of each successive pass is decreased to maintain an efficiently high flue-gas velocity.

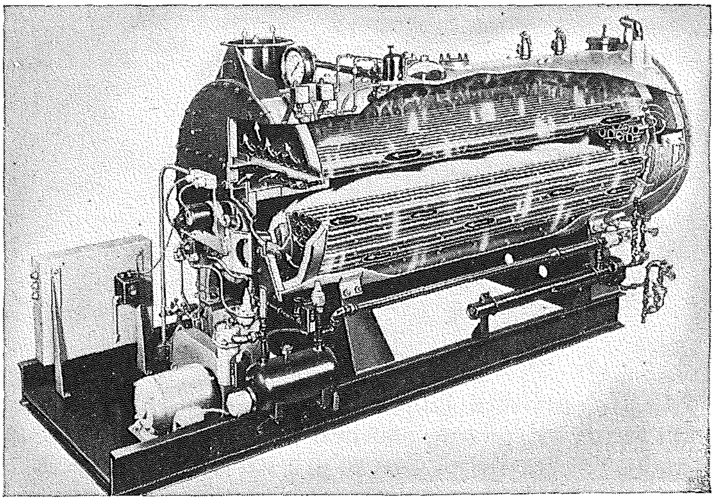


FIG. 9-1. Package fire-tube boiler. (*Courtesy of Cleaver-Brooks.*)

In the water-tube design, water circulates inside the tubes. Heating is accomplished by passing hot gases over the tubes. The water-tube design is available for both low and high pressures. It is particularly adaptable for pressures over 150 psi and is much quicker-steaming. Water-tube boilers include the following types: (1) straight, inclined tubes with longitudinal or cross drums, (2) bent tubes with single or multiple steel drums, (3) vertical and semivertical tubes with vertical or cross drums, and (4) various combinations of these arrangements. The boiler may also have partly fire-tube and partly water-tube construction. Figure 9-2 shows a package water-tube boiler. Water cooling on four sides, roof, and floor gives a high ratio of furnace cooling to furnace volume and produces rapid heat absorption. Figure 9-3 shows a package boiler installation with compact, self-contained oil-gas combustion equipment and controls.

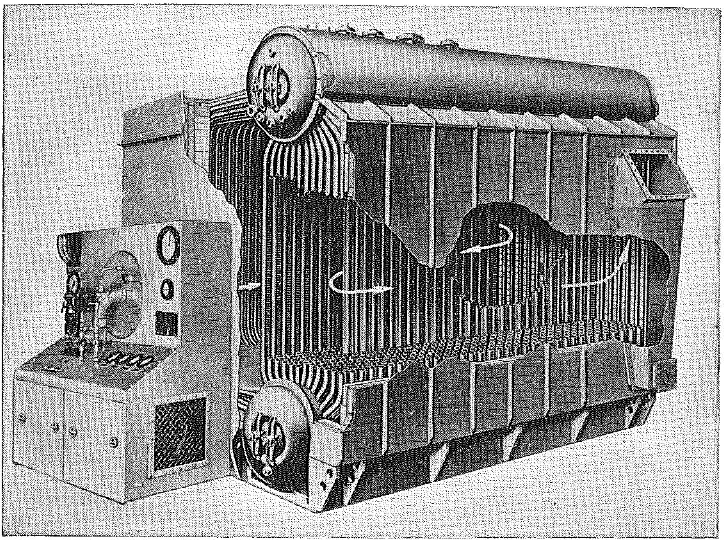


FIG. 9-2. Package water-tube boiler. (*Courtesy of Combustion Engineering, Inc.*)

9-3. Chemical Feed-water Treatment. Regardless of the type of boiler or the temperature and pressure at which it operates, one or more of the common boiler water troubles can develop. These include scale, corrosion, pitting, priming, and caustic embrittlement. All these troubles have already been defined and described in detail. In general, they come from two main sources: first, from substances found in the feed water and, second, from the incorrect application of water-conditioning chemicals.

If the makeup water is hard and contains large amounts of calcium and magnesium, the major problem will be scale formation. This is particularly true when the amount of makeup needed for the boiler is also high. When the makeup water is soft or acid in nature, corrosion or pitting is the troublesome factor. If the feed water is contaminated with oil or organic matter, the result is often priming, foaming, or carryover. However, all these troubles can be prevented by using the right chemical treatment. Broadly speaking, the required treatment can be classified as either internal or external.

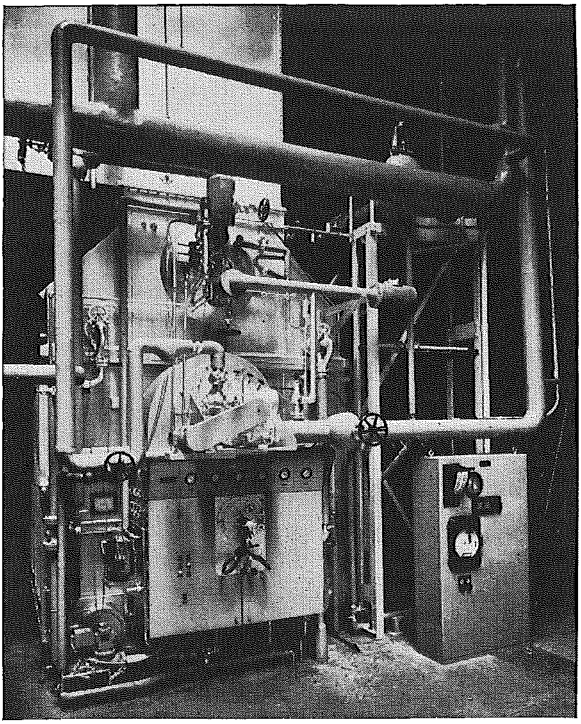


Fig. 9-3. Package boiler installation. (*Courtesy of Power magazine.*)

In internal treatment the chemicals are fed directly into the boiler with the feed water. The major chemical reactions take place at boiler operating temperature and pressure. However, the end products of the reactions remain in the boiler. This increases the level of total dissolved solids and the amount of sludge.

Higher total dissolved solids and more sludge increase the possibility of boiler priming, foaming, and carryover. Usually the concentration of solids can be held within safe limits by regulating the blowdown from the boiler. But it is possible for the resulting blowdown heat losses to become excessive for efficient boiler operation. In many cases blowdown alone cannot hold the dissolved solids and sludge concentration within safe operating limits. In both these situations external treatment of the feed water is also advisable. Internal treatment alone is satisfactory in small and medium-sized plants where operating conditions are not severe. But generally in the larger plants it is used to supplement external treatment.

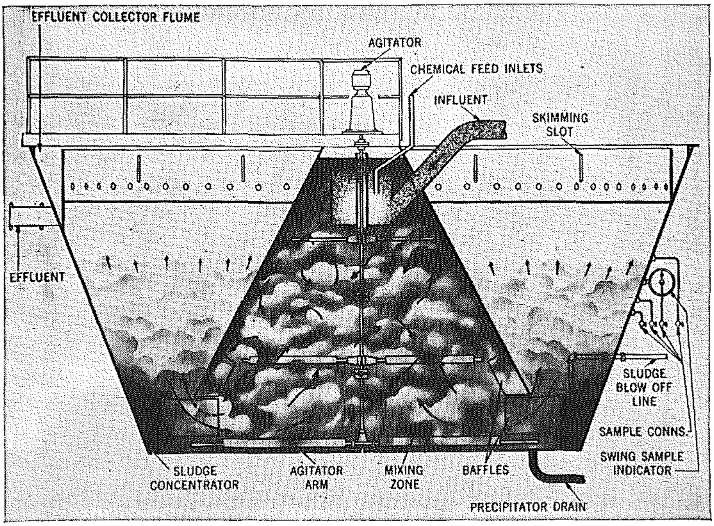


FIG. 9-4. Cross-sectional view of a precipitator employed for coagulation and settling of water. (*Courtesy of The Permutit Company.*)

External treatment means that the feed water is treated before it enters the boiler. Harmful dissolved solids, gases, and suspended matter are removed by a variety of elaborate water-treating equipment. The equipment available for this purpose includes coagulating tanks, filters, lime and soda-ash softeners, zeolite softeners, demineralizers, evaporators, and deaerators. The aim of external treatment is to produce a uniform boiler feed water low in harmful impurities. Therefore, the quantity of water that must be removed from the boiler to keep the impurity concentrations within safe operating limits is kept to a minimum. This type of water-treating equipment is illustrated in Figs. 9-4 to 9-8. In addition, the job of supplementary internal treatment is simplified. Every boiler requires either straight internal treatment or a combination of external and internal treatment. In the final analysis the success or failure of any treatment program depends upon the final condition of the water contained in the boiler.

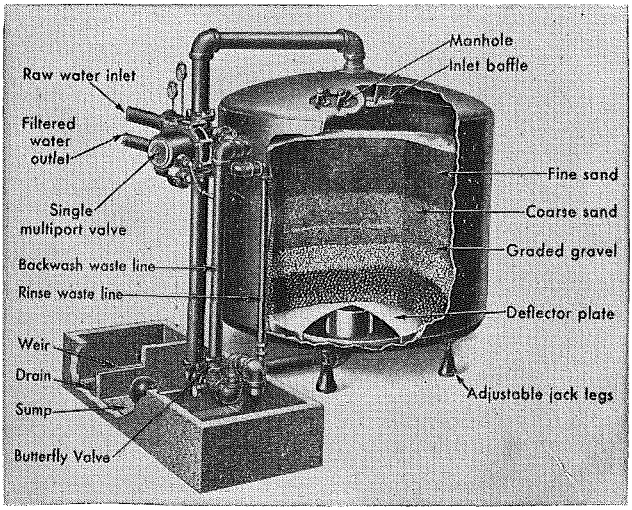


Fig. 9-5. Pressure filter using graded layers of sand and gravel. (*Courtesy of The Permutit Company.*)

9-4. Judging Ideal Water Composition for a Given Boiler.

The ideal water composition for any given boiler cannot be

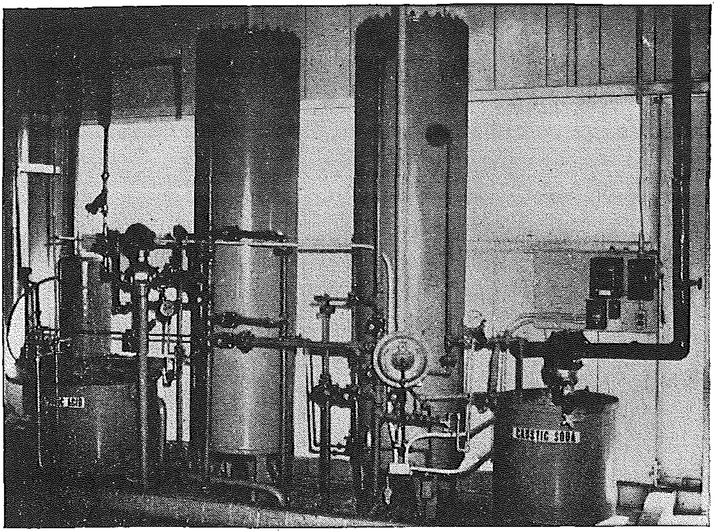


Fig. 9-6. Two-step demineralizing equipment. (*Courtesy of The Permutit Company.*)

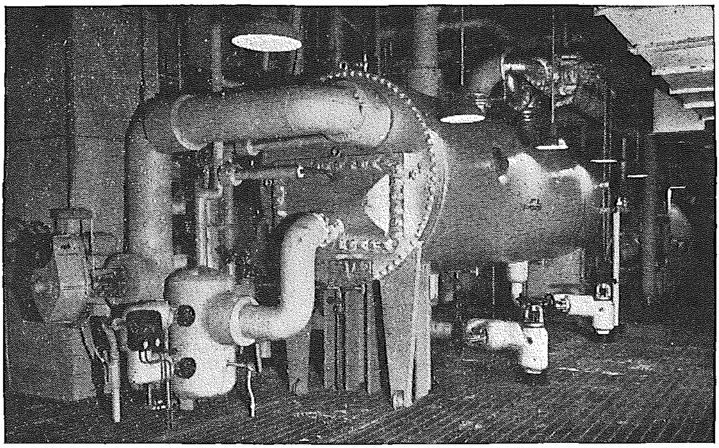


Fig. 9-7. Evaporator employed to produce pure makeup for high-pressure boilers. (*Courtesy of The Griscom-Russell Company.*)

simply calculated from any single formula. It should be determined with the help of a water treatment consultant. The following guide, therefore, is general in nature.

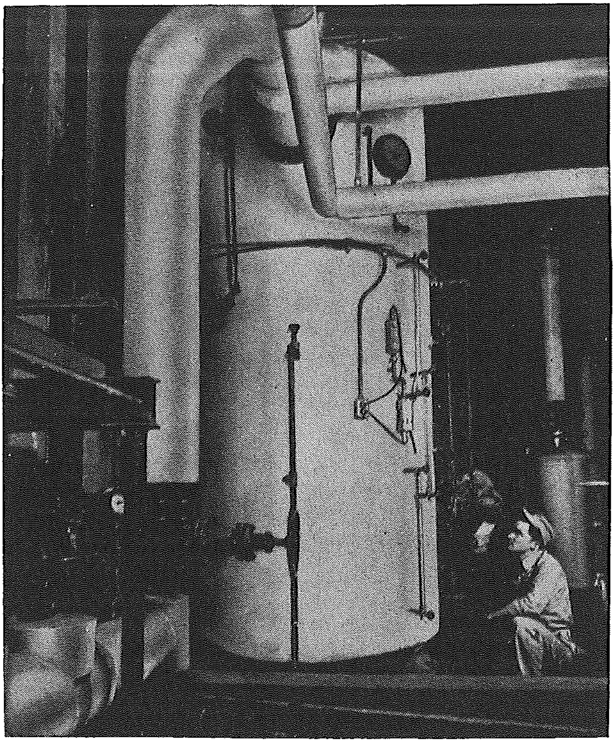


FIG. 9-8. Deaerator used to heat and deaerate boiler feed. Steam enters near top of unit. Heated, deaerated feed water discharges to the boiler feed pump. (*Courtesy of Worthington Corporation.*)

1. *Total Solids.* Establish a minimum blowdown schedule that will prevent any boiler water solids from leaving the boiler with the steam. The amount of blowdown needed will depend upon the rate at which the solids concentrate in the boiler water. Total dissolved solids, suspended solids, alkalinity, and oil must be controlled and kept below maximum allowable limits in order to

prevent carryover. Satisfactory boiler water concentrations range from 1,500 to 3,500 ppm total solids, depending upon the boiler operating pressure (Chap. 7, Sec. 7-18 and Table 7-3). In addition, if antifoam chemicals are used, the total solids in the boiler water can be allowed to go as high as 30,000 ppm without developing carryover. There is one practical way to set up limits for total dissolved solids at any given boiler installation. Merely omit any blowdown and allow the boiler water concentration to build up until carryover or priming starts. This concentration marks the danger zone. Take a sample of the boiler water and analyze it for chlorides and alkalinity. Then, to prevent carryover, keep the boiler water chlorides well below this danger zone. Also make sure that the boiler water alkalinity is not too high.

2. *Alkalinity.* Boiler water alkalinity must be high enough to prevent acidic corrosion. It must be low enough to prevent carryover of solids with steam and caustic embrittlement of the boiler metal. The suggested alkalinity range for various boiler operating pressures is given in Chap. 3 (Sec. 3-7 and Table 3-1). As already suggested, maintain the phenolphthalein alkalinity at 60 to 80 per cent of the total alkalinity.

The various phosphate compounds, caustic soda, and soda ash are all extremely helpful in adjusting the alkalinity in the boiler. The chemical composition of the feed water, the boiler water concentration, and the total alkalinity desired in the boiler—all affect the choice of treatment chemical. Generally speaking, if the boiler water is low in alkalinity, trisodium phosphate is needed. If the alkalinity is still low after the necessary phosphate is added, use caustic soda or soda ash for further adjustments. If the boiler water contains too much alkalinity, then an acid phosphate is needed to reduce the level. With alkalinity already in the correct range, use disodium phosphate. When the boiler alkalinity is at the proper level, the phosphate compounds will react with all the calcium hardness and form an insoluble tricalcium-phosphate sludge. All the magnesium hardness forms an insoluble magnesium-hydroxide sludge. Both these sludges are removed easily by blowdown. If the alkalinity in the boiler water is too low, an acid phosphate salt may form that often produces scale on the boiler metal.

3. *Phosphates.* Establish an excess PO_4 content in the boiler water when phosphates are used for treatment. A satisfactory range is between 30 and 60 ppm as PO_4. The phosphate must first react with all the calcium hardness in the water before there is any excess PO_4. Add enough phosphate to react with all the calcium hardness and produce a phosphate excess in the boiler water ranging from 30 to 60 ppm.

4. *Hardness.* No matter what method of treatment is used, it is desirable to reduce the hardness in the boiler water to zero. Table 9-1 shows the quantities of the various chemical compounds needed to produce zero ppm hardness in the boiler water. To make sure that the reaction goes to completion, use at least 10 per cent more than the amounts called for in this table. This explains why an excess of 30 to 60 ppm phosphate is needed with the phosphate treatment.

9-5. Common Internal-treatment Chemicals. The chemicals commonly used for internal treatment of high-pressure boilers include:

1. *Soda Ash* (Na_2CO_3). Soda ash is an alkaline salt. As such it will neutralize any corrosive salts or gases and increase the alkalinity of boiler water. In addition, soda ash reacts with the scale-forming sulfates of calcium and magnesium to form a carbonate sludge that is removed by blowdown. The chemical reaction is

$$\underset{\text{Soda ash}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\ \text{sulfate}\\ \text{(scale-forming)}}}{CaSO_4} = \underset{\substack{\text{Calcium}\\ \text{carbonate}\\ \text{(sludge)}}}{\underline{CaCO_3}} + \underset{\substack{\text{Sodium}\\ \text{sulfate}}}{Na_2SO_4} \tag{9-1}$$

Magnesium carbonate is fairly soluble in boiler water. Therefore, a large percentage of magnesium compounds will remain in the boiler water as hardness. Since magnesium hydroxide, also a sludge-forming salt, is very insoluble, it is much more desirable to favor its formation. At boiler temperatures soda ash partially decomposes into caustic soda and carbon dioxide. The resulting caustic reacts with the magnesium salts to form magnesium hydroxide sludge. The reactions are

$$\underset{\text{Soda ash}}{Na_2CO_3} + \underset{\substack{\text{Boiling}\\ \text{water}}}{H_2O} + \text{Heat} = \underset{\substack{\text{Caustic}\\ \text{soda}}}{2NaOH} + \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{CO_2} \tag{9-2}$$

$$\underset{\substack{\text{Caustic}\\ \text{soda}}}{2NaOH} + \underset{\substack{\text{Magnesium}\\ \text{sulfate}\\ \text{(scale-forming)}}}{MgSO_4} = \underset{\substack{\text{Magnesium}\\ \text{hydroxide}\\ \text{(sludge)}}}{\underline{Mg(OH)_2}} + \underset{\substack{\text{Sodium}\\ \text{sulfate}}}{Na_2SO_4} \tag{9-3}$$

One disadvantage of soda ash is that the decomposition to caustic soda may take place too rapidly at the elevated temperature and pressure of the boiler water. When this happens, there is not enough sodium carbonate to react with the calcium hardness. There is also an excess of caustic soda that helps to promote caustic embrittlement. In addition, the carbon dioxide formed in Eq. (9-2) passes off with the steam. When the steam condenses, the carbon dioxide redissolves in the condensate and greatly increases its corrosiveness. Another disadvantage of soda ash is that the resulting calcium carbonate forms a thick and troublesome deposit. This is particularly true in a fire-tube boiler where the boiler water circulation is often sluggish.

Soda ash is not widely used as a main water-treating chemical because of these disadvantages. But in certain specific cases, in combination with organic colloids such as tannin, lignin, starch, and seaweed derivatives, soda ash gives better results than phosphate. In high-hardness waters the phosphate produces a heavy sludge that may call for excessive blowdown. In that kind of situation treatment with soda ash and an organic compound leads to formation of a sludge that is more fluid and can be handled with less boiler blowdown.

2. *Caustic Soda* (NaOH). Since caustic soda is an alkali, it will neutralize any corrosive acid salts or gases and increase the alkalinity of the boiler water. But caustic soda is rarely used as the main treating chemical for high-pressure boiler waters. As already pointed out, caustic soda excess may lead to caustic

embrittlement. However, it is very useful in removing the magnesium hardness. The chemical reaction forms insoluble magnesium hydroxide sludge. Caustic soda is also frequently used to advantage in conjunction with the acid or mildly alkaline phosphate salts.

3. *The Phosphates of Sodium.* In general the phosphates of sodium have assumed the role of the main conditioning chemical for internal high-pressure boiler water treatment. The phosphate ion is very stable. It is not destroyed in the boiler like the carbonate ions. Phosphates also produce a calcium-phosphate sludge instead of the calcium-carbonate sludge formed with soda ash. The amount of excess phosphate customarily is maintained at a level of about 50 ppm expressed as PO_4. This concentration is high enough to be measured easily.

There are many phosphate compounds capable of producing the desired treatment results. Table 9-1 is a partial listing of the phosphates and their main characteristics. Some of these compounds contain water of crystallization. This fact should be kept in mind when buying and using phosphates in this form. Each pound of chemical then contains a fixed percentage of water.

Phosphates also differ in their degree of alkalinity. Trisodium phosphate is the most alkaline. The disodium and tetrasodium pyrophosphates are mildly alkaline. Monosodium and hexametaphosphates are mildly acid. The relative strength of phosphate compounds is obtained by comparing the actual amount of PO_4 each contains. This value is usually expressed as per cent PO_4. Table 9-1 is useful in calculating the amount of phosphate compound needed to supply the required amount of PO_4. The equation for this is

$$PO_4\text{, ppm} = \text{phosphate compound, ppm} \times \%\ PO_4 \times 0.01 \qquad (9\text{-}4)$$

The natural alkalinity of the boiler water actually determines the most expedient phosphate combination. To ensure formation of tricalcium phosphate, $Ca_3(PO_4)_2$, the treated boiler water must be alkaline. If acid phosphate salts are permitted and not all the hardness is precipitated as sludge, more phosphate is required for

Table 9-1. Common Chemicals Used in Boiler Water Treatment

Common name	Formula	Molecular weight	Equivalent weight	Alkalinity as $CaCO_3$, %	Commercial-grade PO_4, %	Chemically pure PO_4, %	Commercial-grade chemical			
							To react with each ppm hardness as $CaCO_3$		To establish 50 ppm excess in zero-hardness water	
							ppm	lb per M gal	ppm	lb per M gal
Trisodium phosphate	$Na_3PO_4 \cdot 12H_2O$	380	126.7	26.4	23.75	25	2.66	0.022	211	1.76
	Na_3PO_4	164	54.7	61	55	58	1.15	0.0096	91	0.76
Disodium phosphate	$Na_2HPO_4 \cdot 12H_2O$	358	119.4	14	25.2	26.5	2.52	0.021	198	1.65
	$Na_2HPO_4 \cdot 2H_2O$	178	59.3	28	50.5	53.3	1.25	0.014	99	0.83
	Na_2HPO_4	142	47.3	35.2	63.5	66.9	1.00	0.0083	79	0.66
Tetrasodium pyrophosphate	$Na_4P_2O_7$	266	88.7	37.6	67.6	71.4	0.93	0.00775	74	0.62
Sodium hexametaphosphate	$(NaPO_3)_6$	102	34	.....	88.6	93.4	0.716	0.006	56	0.47
Sodium tetraphosphate	$Na_6P_4O_{13}$	310	103.3	9.6	80.8	80.8	0.517	0.0043	62	0.515
Monosodium phosphate	$NaH_2PO_4 \cdot H_2O$	138.1	46	.....	65.5	69	0.97	0.008	76	0.63
	NaH_2PO_4	120	40	.....	75.3	79.3	0.84	0.007	67	0.56
Caustic soda 76% Na_2O	NaOH	40	40	122.5	.....	....	0.82	0.0066		
Soda ash 58% Na_2O	Na_2CO_3	106	53	93.5	.....	....	1.07	0.0089		

the same amount of calcium hardness. And also, acid phosphate salts can produce an adherent scale. Table 9-1 also shows the per cent alkalinity in each phosphate compound. With this figure the increase in alkalinity for each part per million of phosphate excess can be calculated. The same data are also given for soda ash and caustic.

$$\text{Alkalinity increase, ppm} = \text{phosphate or alkaline chemical, ppm} \times \%\ \text{alkalinity} \times 0.01 \qquad (9\text{-}5)$$

9-6. Effect of Makeup, Blowdown, and Water-holding Capacity. The amount of raw-water makeup and the quantity of blowdown required are major considerations in the internal treatment of a high-pressure boiler. With a low-pressure heating boiler, over a month may pass before the boiler water concentrates 20 times. But in a high-pressure boiler, 20 concentrations can be reached in a day or two.

In a boiler that evaporates 20 boiler volumes of water per day, the feed-water solids concentrate 20 times. After a week's operation, the concentration of solids in the boiler will be 140 times that in the feed water. This assumes that none of the solids pass out with the steam or leave by blowdown. Concentrations higher than normal aggravate practically all boiler water troubles. The simplest way to reduce concentration is to blow down the boiler. By regulation of the amount of blowdown, the concentration of solids can be held within prescribed limits. The blowdown needed varies directly with the amount of makeup and the level of total dissolved solids in the makeup. After enough time is allowed to reach steady boiler operating conditions, the following is the relationship between makeup and blowdown:

$$\text{Concentrations in boiler} = \frac{\text{rate of makeup}}{\text{rate of blowdown}} \qquad (9\text{-}6)$$

In Chap. 8, Examples 1 and 2, the batch method is used to calculate chemical treatment needed for a low-pressure heating boiler with very little makeup. The procedure for this is explained in Chap. 4, Sec. 4-4. These batch-treatment calculations are based on the volume of water held in the boiler. The amount of chemicals needed for treatment is easily determined.

However, in high-pressure boilers the daily makeup is often greatly in excess of the water volume normally held in the boiler. In addition, boiler blowdown is employed on a regular schedule to control the concentration of solids in the boiler water. Under these conditions the fixed volume of water contained in the boiler is not important. But the amount of chemical treatment is readily obtained by following the calculations for the continuous method of treatment. These calculations are based on the amount of makeup and blowdown (Chap. 4, Sec. 4-7).

The following example illustrates the basic difference between the batch and the continuous methods of treatment.

EXAMPLE 1. A boiler contains 500 gal of water. Using trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, as the treating chemical, maintain 400 ppm total alkalinity in the boiler water. To simplify the problem, assume there are no other minerals in the water. In other words, the feed water will be mineral-free. We know that 13 lb of trisodium phosphate per thousand gallons will raise the alkalinity of the boiler water to 400 ppm. Therefore, 6.5 lb of trisodium phosphate will also raise the alkalinity in 500 gal of boiler water to 400 ppm.

If the boiler water losses are infrequent and small compared with the volume of water contained in the boiler, the batch method is most desirable. Assume that 50 gal of water is blown out every day. This is 10 per cent of the volume of water contained in the boiler. With this 10 per cent loss of boiler water there is a corresponding 10 per cent loss of chemical. This amounts to 0.65 lb of the original trisodium phosphate added to the boiler. As more mineral-free water enters the boiler to replace the blowdown, the alkalinity is diluted by 10 per cent. It becomes 360 ppm since 40 ppm leaves with the blowdown. In order to maintain 400 ppm alkalinity, 0.65 lb of trisodium phosphate must be added to the incoming water every day. This is enough to replenish the phosphate lost with the blowdown from the boiler and will maintain the total alkalinity at 400 ppm.

If the boiler water losses are frequent and very large compared with the volume of water contained in the boiler, the continuous-treatment method is recommended. If the boiler blowdown is continuous at 50 gal per hour or 1,200 gal a day, adding 6.5 lb of trisodium phosphate to the boiler will raise the alkalinity to 400 ppm. But the trisodium phosphate must be added continuously at the rate of 0.65 lb per hour to maintain the alkalinity level. Every 24 hr about 15.6 lb of trisodium phosphate is added. This is an extremely rapid turnover of water and chemicals. Therefore, it is safe to ignore the first 6.5 lb of trisodium phosphate added to the original untreated boiler water. In other words, the calculations can be based only on the turnover of water. In 10 days 156 lb of trisodium phosphate is added. The original 6.5 lb of trisodium phosphate is about 4 per cent of the total, a very small percentage of the total chemical used.

Continuous chemical treatment gradually builds the alkalinity in the boiler during the first day toward the desired 400 ppm level. This is a definite advantage when first starting chemical treatment of a boiler. Any sudden chemical changes should be avoided. It pays to be cautious. There may be scale or oil in the boiler. If hardness is present in the water, this means more sludge deposits, increased alkalinity, and higher total dissolved solids. As boiler water alkalinity builds up, troubles such as carryover, foaming, and priming may develop. Therefore, it may be necessary to stop chemical treatment temporarily until the boiler water reaches equilibrium. Alternately, the blowdown rate can be varied to accommodate changes in boiler water analysis.

9-7. Phosphate Treatment of Boiler Water. No matter which phosphate is selected for boiler water treatment, the basic chemical principles are the same. The phosphates react with all the calcium hardness in the boiler water. This converts the calcium hardness to tricalcium-phosphate [$Ca_3(PO_4)_2$] sludge. In addition there must be enough alkalinity in the water to react with all the magnesium hardness. This forms magnesium hydroxide [$Mg(OH)_2$] sludge. Alternately, caustic soda or soda ash will do the same job. When using phosphate treatment, excess alkalinity in the boiler water is very important. It ensures the formation of tricalcium phosphate and magnesium hydroxide sludge.

The alkalinity in water includes soluble carbonate, bicarbonate, hydroxide, and phosphate ions. (See Chap. 3.) The alkalinity in a natural water supply normally includes calcium and magnesium bicarbonate and occasionally some sodium bicarbonate. In a steaming boiler under pressure, the bicarbonates form carbonates and carbon dioxide. Under high boiler water pressures and temperatures, the formation of hydroxide alkalinity is also a possibility. These reactions in the boiler water will precipitate part of the carbonates as an insoluble deposit. As long as the carbonates remain insoluble, they represent alkalinity removed from the original boiler water. The remainder of the soluble carbonates and hydroxides is the natural alkalinity of the boiler water. When one or more phosphates, carbonates, or hydroxide chemicals are added, the natural alkalinity balance of the boiler water is raised or lowered. The following two equations show how phosphate-treating chemicals affect the boiler water alkalinity.

1. $3CaCO_3 + 2Na_3PO_4 = \underline{Ca_3(PO_4)_2} + 3Na_2CO_3$

Initial alkalinity in boiler water	Added alkaline trisodium phosphate	Insoluble sludge, tricalcium phosphate	Final alkalinity in boiler water

2. $3CaCO_3 + 2NaH_2PO_4 = \underline{Ca_3(PO_4)_2} + Na_2CO_3 + 2H_2O + 2CO_2$

Initial alkalinity in boiler water	Added slightly acid monosodium phosphate	Insoluble sludge, tricalcium phosphate	Final alkalinity in boiler water

In both these equations $3CaCO_3$ on the left side of the equation stands for three units of alkalinity initially in the boiler water. The $Ca_3(PO_4)_2$ on the right side of the equation represents the formation of an insoluble sludge of tricalcium phosphate. The sludge no longer contributes to boiler water alkalinity. The $3Na_2CO_3$ on the right side of the first equation means that three units of sodium carbonate alkalinity form when trisodium phosphate is added to the boiler water. The Na_2CO_3 on the right side of the second equation means that one unit of sodium carbonate alkalinity forms when slightly acid monosodium phosphate is added to the boiler water. The one unit of sodium carbonate alkalinity formed in the second equation is a net loss of two alkalinity units compared with the alkalinity formed in the first equation.

These equations show that the addition of trisodium phosphate will keep the alkalinity in essentially the same range. Therefore, if the initial alkalinity is about right, use trisodium phosphate for treatment. But if the alkalinity is too high, a chemical such as monosodium phosphate should be used since it also reduces the alkalinity.

The various ion groups affecting the boiler water alkalinity are listed in Table 9-2. A relative numerical alkalinity value is assigned to each ion group. This information is very useful in predicting the ultimate effect these ions will have on the final alkalinity of the boiler water.

Table 9-2. Relative Numerical Alkalinity of Various Ion Groups

Ion group	Chemical name	Relative numerical alkalinity
$CO_3^=$	Carbonate	2
$PO_4^≡$	Phosphate (tribasic)	3
OH^-	Hydroxide	1
$HPO_4^=$	Phosphate (dibasic)	2
$H_2PO_4^-$	Phosphate (monobasic)	1

The relative numerical alkalinity from Table 9-2 is used to calculate the net gain or loss in boiler water alkalinity when treating with phosphate, carbonate, or hydroxide. Here are the steps to follow:

1. First, write a balanced chemical equation of the desired chemical reaction. Represent the initial alkalinity of the boiler water by the chemical formula $CaCO_3$.

2. Next, note the relative numerical alkalinity from Table 9-2 of each ion group in the reaction.

3. Multiply the value for each ion group by the number of units of this group contained in the equation. Then compile a table showing the sum of all the numerical values on the right and left sides of the equation. The sum of these numerical values will be equal.

4. The insoluble ion group that precipitates in the boiler no longer contributes to the alkalinity. Final alkalinity is composed of the soluble ion group only.

5. The net change in boiler water alkalinity is the difference between the total initial relative numerical value and the total final value of the water.

The use of Table 9-2 is best illustrated by studying a typical chemical reaction in a boiler water. The equation for one typical reaction is given in the following example.

EXAMPLE 2. What is the change in alkalinity when disodium phosphate (Na_2HPO_4) is added to the boiler water and forms tricalcium-phosphate sludge? The equation for this reaction is

$$3CaCO_3 + 2Na_2HPO_4 = \underline{Ca_3(PO_4)_2} + 2Na_2CO_3 + H_2O + CO_2 \quad (9\text{-}7)$$

1. In this equation, $3CaCO_3$ stands for the three $CO_3^{=}$ units of natural alkalinity initially present in the boiler water.

2. The $2Na_2HPO_4$ represents the two $HPO_4^{=}$ units added to the boiler water.

3. The $\underline{(Ca_3PO_4)_2}$ stands for the two $PO_4^{\equiv}$ units of sludge that are formed and no longer contribute to the alkalinity.

4. The $2Na_2CO_3$ means that there are finally two $CO_3^{=}$ units of soluble alkalinity remaining in the boiler water.

The numerical alkalinity values on both sides of the equation are summarized in Table 9-3.

1. The three $CO_3^{=}$ ion groups on the left side of the equation stand for the six units of alkalinity present initially before the phosphates are added.

2. The two $PO_4^{\equiv}$ ion groups on the right side mean that six alkalinity units have been lost because of sludge formation.

3. The two $CO_3^=$ ion groups on the right side are the four soluble alkalinity units remaining in the boiler water.

The original boiler water before treatment contained six alkalinity units. After treatment, the boiler water ends up with four soluble alkalinity units in the boiler water. The net reduction in alkalinity is two units or one-third of the original alkalinity present. The equation showing the alkalinity units is as follows:

Table 9-3. Numerical Alkalinity Balance

Left side of equation		Right side of equation	
Ion group	Numerical value	Ion group	Numerical value
$3CO_3^=$ $2HPO_4^=$	$3 \times 2 = 6$ $2 \times 2 = 4$	$2CO_3^=$ $2PO_4^{\equiv}$	$2 \times 2 = 4$ $2 \times 3 = 6$
TOTAL......	= 10	TOTAL....	= 10

$$3CaCO_3 + 2Na_2HPO_4 = \underline{Ca_3(PO_4)_2} + 2Na_2CO_3 + H_2O + CO_2$$

$$\underline{6 \text{ units}} + 4 \text{ units} = 6 \text{ units} + \underline{4 \text{ units}}$$

Original alkalinity Final alkalinity

9-8. Typical Phosphate Reactions. The various phosphate compounds used for boiler water treatment all act differently. The following equations show some of the typical chemical reactions. The $Ca_3(PO_4)_2$ stands for the insoluble sludge formed in the boiler.

TRISODIUM PHOSPHATE. Trisodium phosphate has no effect on the alkalinity originally present in the boiler.

$$3CaSO_4 + 2Na_3PO_4 = \underline{Ca_3(PO_4)_2} + 3Na_2SO_4$$

$$3CaCO_3 + 2Na_3PO_4 = \underline{Ca_3(PO_4)_2} + 3Na_2CO_3$$

DISODIUM PHOSPHATE. Disodium phosphate effectively reduces the alkalinity in the boiler water by about one-third.

The first reaction with disodium phosphate results in the formation of $CaHPO_4$. This compound can be scale-forming and is produced when no alkalinity is present in the boiler water.

$$CaSO_4 + Na_2HPO_4 = CaHPO_4 + Na_2SO_4$$

$$3CaCO_3 + 2NaOH + 2Na_2HPO_4 = \underline{Ca_3(PO_4)_2} + 3Na_2CO_3 + 2H_2O$$

$$3CaSO_4 + Na_2CO_3 + 2Na_2HPO_4 = \underline{Ca_3(PO_4)_2} + 3Na_2SO_4 + H_2O + CO_2$$

$$3CaCO_3 + 2Na_2HPO_4 = \underline{Ca_3(PO_4)_2} + 2Na_2CO_3 + H_2O + CO_2$$

TETRASODIUM PYROPHOSPHATE. Tetrasodium pyrophosphate effectively reduces the alkalinity in the boiler by one-third. The boiler water heat hydrolyzes the tetrasodium pyrophosphate, converting it into disodium phosphate.

$$Na_4P_2O_7 + H_2O + \text{heat} = 2Na_2HPO_4$$

$$2CaSO_4 + Na_4P_2O_7 + H_2O = 2CaHPO_4 + 2Na_2SO_4$$

$$3CaCO_3 + Na_4P_2O_7 + H_2O = \underline{Ca_3(PO_4)_2} + 2Na_2CO_3 + H_2O + CO_2$$

$$3CaSO_4 + Na_4P_2O_7 + 2NaOH = \underline{Ca_3(PO_4)_2} + 3Na_2SO_4 + H_2O$$

$$3CaSO_4 + Na_4P_2O_7 + Na_2CO_3 = \underline{Ca_3(PO_4)_2} + 3Na_2SO_4 + CO_2$$

MONOSODIUM PHOSPHATE. This phosphate effectively reduces the alkalinity in the boiler water by two-thirds.

$$CaSO_4 + 2NaH_2PO_4 = Ca(H_2PO_4)_2 + Na_2SO_4$$

$$3CaCO_3 + 2NaH_2PO_4 = \underline{Ca_3(PO_4)_2} + Na_2CO_3 + 2H_2O + 2CO_2$$

$$3CaSO_4 + 4NaOH + 2NaH_2PO_4 = \underline{Ca_3(PO_4)_2} + 3Na_2SO_4 + 4H_2O$$

$$3CaSO_4 + 2Na_2CO_3 + 2NaH_2PO_4 = \underline{Ca_3(PO_4)_2} + 3Na_2SO_4 + 2H_2O + 2CO_2$$

SODIUM HEXAMETAPHOSPHATE. This compound effectively reduces the alkalinity of the boiler water by two-thirds. The heat of the boiler water hydrolyzes the hexametaphosphate and converts it to monosodium phosphate.

$$(NaPO_3)_6 + 6H_2O + \text{heat} = 6NaH_2PO_4$$

$$3CaSO_4 + (NaPO_3)_6 + 6H_2O = 3Ca(H_2PO_4)_2 + 3Na_2SO_4$$

$$9CaCO_3 + (NaPO_3)_6 + 6H_2O = \underline{3Ca_3(PO_4)_2} + 3Na_2CO_3 + 6H_2O + 6CO_2$$

$$9CaSO_4 + (NaPO_3)_6 + 12NaOH = \underline{3Ca_3(PO_4)_2} + 9Na_2SO_4 + 6H_2O$$

$$9CaSO_4 + (NaPO_3)_6 + 6Na_2CO_3 = \underline{3Ca_3(PO_4)_2} + 9Na_2SO_4 + 6CO_2$$

These equations show how soda ash or caustic soda is generally used to adjust the alkalinity of boiler water with phosphate treatment.

Trisodium phosphate, disodium phosphate, and monosodium phosphate are all known as *normal phosphates*. They immediately yield the PO_4 ion when added to an alkaline boiler water. But sodium hexametaphosphate and tetrasodium pyrophosphate do not yield a normal PO_4 ion when dissolved in water. These two compounds belong to a class of complex inorganic salts commonly called *polyphosphates*. With prolonged boiling in water or at the high pressures and temperatures in a steaming boiler, they hydrolyze or convert from the complex polyphosphate to the normal PO_4 ion.

Normal phosphate fed continuously to a boiler may form calcium or magnesium phosphate deposits in boiler feed lines. This is particularly true when it is added to the boiler feed-pump suction line. However, this disadvantage can be overcome by adding the phosphate directly into the boiler drum.

However, the polyphosphates do not produce this type of feed-line deposit. These compounds can actually hold the calcium and magnesium ions in solution until the feed water enters the boiler.

This unique phenomenon of holding calcium and magnesium salts in solution is known as *sequestering*. Therefore, polyphosphates are often referred to as sequestering agents.

When the makeup water is extremely hard, the sodium phosphates produce a very large quantity of tricalcium-phosphate sludge. This has the disadvantage of promoting carryover from the boiler.

9-9. Computing the Amount of Chemicals Needed for Treatment. The basic theory and the chemical reactions needed to produce an ideal boiler water composition have already been presented. With this background a qualified operator can determine what chemicals are needed and what is the most desirable boiler water composition. However, this is still a laborious and almost impossible job for the average operating engineer. He must write the chemical equation for each reaction in full and

I. Chemicals needed	II. Raw water	III. Hardness reduced to zero	IV. Excess chemicals required	V. Boiler water analysis with one concentration	VI. Desired boiler water composition
1. Chemical A, ppm					
2. Chemical B, ppm					
3. Chemical C, ppm					
4. Total chemicals, ppm					
5. Total chemicals, lb per 1,000 gal					
Water analysis and analytical data, ppm					
6. Phosphate, PO_4					
7. Sulfate, SO_4					
8. Chlorides, Cl					
9. Calcium hardness					
10. Magnesium hardness					
11. Alkalinity of water					
12. Magnesium alkalinity change					
13. Calcium alkalinity change					
14. Net alkalinity of water					
15. Alkalinity from excess phosphate					
16. Alkalinity from sodium carbonate					
17. Alkalinity from sodium hydroxide					
18. Total resulting alkalinity					
19. Total dissolved solids					

20. Formula desired
    Chemical A, %
    Chemical B, %
    Chemical C, %
21. Amounts needed
    Chemical A, lb per 1,000 gal
    Chemical B, lb per 1,000 gal
    Chemical C, lb per 1,000 gal
22. BWC = ________

FIG. 9-9. Chart for calculating the chemicals needed for internal treatment.

then calculate how much of each chemical is needed for a given feed-water analysis.

Figure 9-9 summarizes the expected results of each chemical reaction in a phosphate-treated boiler. This form simplifies the calculations required to arrive at the quantity of each chemical needed to obtain the desired ideal boiler water composition. The following steps show how this kind of chart is used.

1. *Select the chemicals needed* to obtain the desired ideal water composition. List these chemicals in the first column. The minimum choice to start should include phosphate and an alkali. Special chemicals for special jobs can then be added to the list as needed. Call on a water treatment specialist if you have any doubts about which chemicals to use.
2. *Analyze the raw water.* List the analysis of the raw water in parts per million in column II, labeled "raw water," under analytical data.
3. *Reduce the hardness to zero* (*column III*).
   - *a.* Calculate the amount of phosphate needed in parts per million to react with all the calcium hardness shown in column II. Table 9-1 gives the parts per million of phosphate needed to react with each part per million of calcium hardness in the raw water. Multiply this figure by the amount of calcium hardness shown in column II. The result is the total parts per million of phosphate required to remove the hardness. Put this figure in column III next to the parts per million of chemical A, the phosphate compound selected.
   - *b.* Then determine the changes in raw-water analysis that take place when both the calcium and magnesium hardness are reduced to zero.
     - (1) Since the hardness is removed, insert zero in column III next to calcium and magnesium hardness. The amount of Cl, SO_4, and alkalinity remains the same.
     - (2) The natural alkalinity in the water will react with the magnesium hardness.

$$\begin{array}{lllll} \mathrm{2NaOH} + & \mathrm{MgSO_4} = & \underline{\mathrm{Mg(OH)_2}} & + \mathrm{Na_2SO_4} & \quad (9\text{-}8) \\ \text{2 alkalinity} + & \text{0 alkalinity} = & & \text{0 alkalinity} & \end{array}$$

The magnesium hydroxide formed in this reaction is an insoluble sludge. Therefore, magnesium hardness reduces the alkalinity in the water by an equivalent amount. This is called the magnesium alkalinity change, column I, item 12. Insert the parts per million of magnesium hardness in column III opposite item 12. Use the figure from column II, item 10 with a minus sign to indicate a reduction in alkalinity.

(3) The phosphate compound actually used may affect the alkalinity of the boiler water. Table 9-4 shows the changes in alkalinity when calcium hardness is reduced to zero. This change is entered in column III, opposite item 13, calcium alkalinity change.

Table 9-4. Effect of Phosphate on Calcium Alkalinity

Name of phosphate	*Change in calcium alkalinity*
Trisodium phosphate	0
Disodium phosphate	$-1/3$ calcium hardness
Tetrasodium pyrophosphate	$-1/3$ calcium hardness
Monosodium phosphate	$-2/3$ calcium hardness
Sodium hexametaphosphate	$-2/3$ calcium hardness
Sodium tetraphosphate	$-1/2$ calcium hardness

(4) The net alkalinity of the water, item 14, can now be computed. The alkalinity of the water, item 11, minus the sum of the changes in calcium and magnesium alkalinity equals the net alkalinity of the water.

4. *Determine the desired composition for the boiler water (column VI).* Select the excess PO_4, total dissolved solids, and alkalinity called for by boiler operating conditions. The required boiler water concentration (BWC), chlorides, and sulfates can then be calculated.

The following procedure is useful in calculating the approximate total dissolved solids contained in a boiler water when the chlorides, sulfates, phosphates, and alkalinity are known. Just follow these steps:

a. Add the parts per million of chloride, sulfates, and phosphates in the boiler water.
b. Multiply the sum of these items by 1.5.
c. Then add the parts per million of alkalinity in the boiler water.
d. Next add about 10 per cent of the total to cover any elements not analyzed.
e. The final sum gives the total dissolved solids present in the boiler water.

$$\text{TDS} = 1.5(\text{Cl} + \text{SO}_4 + \text{PO}_4) + \text{alkalinity} + 0.1[1.5(\text{Cl} + \text{SO}_4 + \text{PO}_4) + \text{alkalinity}]$$

When all the dissolved solids in the boiler water, above, are expressed in parts per million, the equation can be consolidated and simplified.

$$\begin{aligned} \text{TDS} &= 1.1[1.5(\text{Cl} + \text{SO}_4 + \text{PO}_4) + \text{alkalinity}] \\ \text{TDS} &= 1.65(\text{Cl} + \text{SO}_4 + \text{PO}_4) + 1.1 \text{ alkalinity} \end{aligned} \tag{9-9}$$

In this simplified equation the total dissolved solids, alkalinity, and phosphate of the boiler water are known. These are fixed by the desired boiler water composition. The chlorides and sulfates are still unknown. To find the chlorides, sulfates, and boiler water concentrations, substitute the known data in Eq. (9-9). Then rearrange terms and solve for the unknown quantities.

Solve for BWC knowing the total dissolved solids, phosphates, and total alkalinity of the boiler water.

1. Prepare the following equations:

$$\begin{aligned} \text{Cl}_{BW} &= \text{Cl}_{RW}(\text{BWC}) \\ \text{SO}_{4BW} &= \text{SO}_{4RW}(\text{BWC}) \end{aligned}$$

where BW = ppm present in the boiler water
RW = ppm present in the raw water

With these data, Eq. (9-9) can be rewritten:

$$\text{TDS} = 1.65[\text{Cl}_{RW}(\text{BWC}) + \text{SO}_{4RW}(\text{BWC}) + \text{PO}_{4BW}] + 1.1 \text{ alkalinity}_{BW}$$

$$\text{TDS} = 1.65(\text{Cl} + \text{SO}_4)_{RW}(\text{BWC}) + 1.65\text{PO}_{4BW} + 1.1 \text{ alkalinity}_{BW}$$

2. Next, rearrange the equation so that all the known values are on the right side.

$$\text{BWC} = \frac{\text{TDS} - 1.1 \text{ alkalinity}_{BW} - 1.65 \text{ PO}_{4BW}}{1.65 \ (\text{Cl} + \text{SO}_4)_{RW}} \qquad (9\text{-}10)$$

3. The ideal composition of boiler water is not fixed but rather depends upon individual boiler operating conditions and upon the judgment of the engineer responsible for treatment. For boilers operating under 300 psig, typical boiler water conditions include:
Excess phosphate: 50 ppm
Total alkalinity: 500 ppm
Total dissolved solids: 2,000 ppm

Substitute these values in the general formula [Eq. (9-10)]. This results in a further simplification of the equation.

$$\text{BWC} = \frac{2{,}000 - (1.1 \times 500) - (1.65 \times 50)}{1.65 \ (\text{Cl} + \text{SO}_4)_{RW}}$$

$$\text{BWC} = \frac{830}{\text{Cl}_{RW} + \text{SO}_{4RW}} \qquad (9\text{-}11)$$

4. Next, calculate the chlorides and sulfates in the boiler water. Once the BWC is known, it is a simple matter to compute the quantity of sulfates and chlorides in the boiler. This is entered in column VI opposite items 7 and 8.

$$\text{SO}_{4BW} = \text{BWC}(\text{SO}_{4RW})$$
$$\text{Cl}_{BW} = \text{BWC}(\text{Cl}_{RW})$$

5. Compute the amount of excess chemicals required. Use the following table to make these calculations and enter the results in column IV of Fig. 9-9.

Chart item number	*Formula for excess chemical*
(6) Phosphate, PO_4, ppm......	$\dfrac{PO_{4_{BW}} \text{ (column VI)}}{\text{BWC}}$
(1) Chemical A (phosphate)....	$\dfrac{(6)\ PO_4\text{, ppm (column IV)}}{\%\ PO_4 \text{ (Table 9-1)} \times 0.01}$
(18) Total resulting alkalinity....	$\dfrac{\text{Total resulting alkalinity (column VI)}}{\text{BWC}}$
(14) Net alkalinity.............	(11) alkalinity of the water, ppm − (12) magnesium alkalinity change, ppm − (13) calcium alkalinity change, ppm
(2) Chemical B (an alkali)	
a. Sodium hydroxide, NaOH	*a.* Alkalinity from NaOH(column IV) × 0.82
b. Sodium carbonate, Na_2CO_3	*b.* Alkalinity from Na_2CO_3(column IV) × 1.07
(3) Chemical C, special additives such as organics, sodium nitrate	$\dfrac{\text{Chemical C (column VI)}}{\text{BWC}}$

6. *Boiler water analysis with one concentration* (*column V*). Column V is used to transfer the totals of chemicals needed from both columns III and IV and consolidate the resulting data from column IV.

   a. Total the amounts of chemicals A, B, and C shown in columns III and IV. Insert the individual totals in column V. Then add items 1 to 3 in column V to obtain the total amount of chemical (item 4).

   b. Divide the parts per million of each chemical by 120 to obtain the amounts in pounds per thousand gallons. List this total in column V. Then tabulate the individual amounts of chemicals used in item 20 of Fig. 9-9.

   c. Calculate the percentage of each chemical in the total amount listed in column V.

$$\text{Chemical A, B, or C in } \% = \frac{\text{amount of chemical A, B, or C}}{\text{total amount of chemical}} \times 100$$

Example 1 illustrates the use of Fig. 9-9 in computing the amount of treatment chemicals required. The completed chart is shown in Fig. 9-10.

EXAMPLE 1. The raw-water feed to the boiler contains 3 ppm chlorides and 12 ppm sulfates. The calcium hardness is 14 ppm expressed as calcium carbonate. The magnesium hardness is 6 ppm and the total alkalinity is 9 ppm, both expressed as calcium carbonate. Treat this boiler internally by using the following chemicals:

1. Anhydrous disodium phosphate to obtain about 50 ppm PO_4 excess in the boiler
2. Soda ash to produce about 500 ppm total boiler water alkalinity
3. Quebracho (Q) tannin extract to produce a ratio of 0.4 Q per NaOH in the boiler water

1. Assume that the maximum allowable total dissolved solids is 2,000 ppm. What BWC must be maintained to stay within this limit?
2. How much of each chemical is needed in terms of pounds per thousand gallons of raw-water makeup?

Solution. Prepare a chart such as the one shown in Fig. 9-10 and fill in the data as follows:

1. *Select the chemicals needed.* Those chosen are listed in column I as anhydrous disodium phosphate, soda ash, and quebracho.
2. *Analyze the raw water.* The analysis of the raw water is shown in column II next to items 6 to 11.
3. *Reduce the hardness to zero (column III).*
    - *a.* The chloride (item 8), sulfates (item 7), and alkalinity (item 11) in the raw water remain at the values shown in column II.
    - *b.* The calcium and magnesium hardness will be removed and are entered as zero in column III.
    - *c.* Determine the amount of disodium phosphate, anhydrous, required to react with the 14 ppm calcium hardness shown in column II. Table 9-1 reveals that 1 ppm of

I. Chemicals needed	II. Raw water	III. Hardness reduced to zero	IV. Excess chemicals required	V. Boiler water analysis with one concentration	VI. Desired boiler water composition
1. Disodium phosphate (anhydrous), ppm	...	14	1.6	15.6	
2. Soda ash, ppm	...	....	10.9	10.9	
3. Quebracho (Q), ppm	...	....	2.9	2.9	
4. Total chemicals, ppm	...	....	....	29.4	
5. Total chemicals, lb per 1,000 gal	...	....	....	0.245	13.5
Water analysis and analytical data, ppm					
6. Phosphate, PO_4	0	0	1	1	55
7. Sulfate, SO_4	12	12	....	12	660
8. Chloride, Cl	3	3	....	3	165
9. Calcium hardness	14	0			
10. Magnesium hardness	6	0			
11. Alkalinity of water	9	9			
12. Magnesium alkalinity change	...	−6			
13. Calcium alkalinity change	...	−4.7			
14. Net alkalinity of water	...	−1.7	−1.7		
15. Alkalinity from excess phosphate	...	....	0.6		
16. Alkalinity from sodium carbonate	...	....	10.2		
17. Alkalinity from sodium hydroxide					
18. Total resulting alkalinity as $CaCO_3$	...	−1.7	9.1	9.1	500
19. Total resulting alkalinity as NaOH	...	....	7.3		
20. Desired ratio of Q to NaOH	...	....	0.4		
21. Total dissolved solids	...	....	....	......	2,000

22. Formula desired
Disodium phosphate = 53.1%
Soda ash = 37.1%
Quebracho = 9.8%
23. Amounts needed
Disodium phosphate = 0.13 lb per 1,000 gal
Soda ash = 0.091 lb per 1,000 gal
Quebracho = 0.024 lb per 1,000 gal
24. BWC = 55

FIG. 9-10. Completed chart for calculating the chemicals needed for internal treatment.

disodium phosphate, anhydrous, is needed to react with each part per million of calcium hardness. Therefore, the 14 ppm calcium hardness calls for 14 ppm of disodium phosphate. List the 14 ppm in column III, item 1.

d. Item 12, change in magnesium alkalinity, equals 6 ppm for column III. Since this is a reduction in alkalinity, show a minus sign before it.

e. Item 13, change in calcium alkalinity, equals 4.7 ppm. This equals one-third of the calcium hardness and carries a minus sign, since the alkalinity is reduced by this amount.

f. The net alkalinity of the water, item 14, at this point is −1.7 ppm. This equals the sum of items 11 to 13 in Fig. 9-10.

4. *Determine the ideal composition wanted for the boiler water (column VI).*

   a. Using Eq. (9-11), calculate the allowable BWC.

$$\text{BWC} = \frac{830}{3 + 12} = 55$$

   b. Item 8, chloride, then equals 3 × 55, or 165 ppm.
   c. Item 7, sulfate, equals 12 × 55, or 660 ppm.
   d. Item 6, phosphate; the desired excess is 55 ppm.
   e. Item 18, total resulting alkalinity as $CaCO_3$, equals 500 ppm.
   f. Item 21; the total dissolved solids is 2,000 ppm.

5. *Compute the amount of excess chemicals required (column IV).*

   a. Item 6, phosphate, PO_4, calls for an excess of 1 ppm in column IV. This equals the amount of phosphate carried in the boiler water divided by 55.
   b. Item 1, the disodium phosphate (anhydrous) required, is 1.6 ppm. (Refer to Table 9-1: 1.0 ppm divided by 0.635 equals the 1.6 ppm.)
   c. Item 15, the alkalinity from excess disodium phosphate, equals 0.6 ppm (obtain factor of 0.352 from Table 9-1 and multiply by 1.6 to get 0.6).

d. Item 18, the total resulting alkalinity, is 9.1 ppm. This is obtained by dividing the 500 ppm alkalinity in the boiler by the BWC of 55.

e. Item 16, the alkalinity due to Na_2CO_3, equals 10.2 ppm. This is obtained by adding +9.1, +1.7, and −0.6.

f. Item 2, the amount of soda ash needed, is 10.9 ppm. This equals 10.2 multiplied by the conversion factor of 1.07.

g. Item 19, the total resulting alkalinity as NaOH, amounts to 7.3 ppm. Multiply 9.1 by the conversion factor of 0.8 to get this amount. Equivalent alkalinity as calcium carbonate of 50 is equivalent to an alkalinity of 40 expressed as NaOH. ($50CaCO_3 \times 0.8 = 40NaOH$).

h. Item 20, the desired ratio of quebracho (Q) to NaOH, is 0.4.

i. Item 3, the quebracho needed, is 2.9 ppm. This equals 7.3 multiplied by 0.4.

6. *Boiler water analysis with one concentration (column V).*
   a. Item 1, the disodium phosphate anhydrous, is then 15.6 ppm. This is obtained by adding the 14 ppm in column III to the 1.6 ppm in column IV.
   b. Item 2, the Na_2CO_3 required, is 10.9 ppm.
   c. Item 3, the quebracho needed, is 2.9 ppm.
   d. Item 4, the total chemicals, equals 15.6 + 10.9 + 2.9, or 29.4 ppm.
   e. Item 5, the total chemicals, in pounds per thousand gallons, equals 29.4 divided by 120, or 0.245. The pounds per thousand gallons of each individual chemical in column V is calculated the same way and listed as item 23.
   f. Item 8, the chloride, equals 3 ppm. Item 17, the sulfate, equals 12 ppm.
   g. Item 6, the phosphate, is 1 ppm.
   h. Item 18, the total resulting alkalinity, equals 9.1 ppm.

The answers to the questions posed by this problem can now be summarized.

1. The BWC is 55.

Table 9-5. High-pressure Boiler Water Survey Sheet

Name of company..Date..
Address..
Reason for generating steam...

EQUIPMENT DATA

Number boilers..........................Boiler designations..
No. operating at once: In winter....................In summer..............................

Boiler data	No. 1	No. 2
1. Name of manufacturer		
2. Water tube or fire tube		
3. Rated horsepower		
4. Actual horsepower		
5. Operating pressure		
6. Age of boiler		
7. Daily hours of operation, summer		
8. Daily hours of operation, winter		
9. Hours of operation per week		
10. Gallons of water held in boiler, normal		
11. How measured		
* Total number of drums		
* Total number of tubes		
* Length of drum shell		
* Diameter of drum shell		

* These data are needed to compute roughly the gallons of water the boiler normally holds when this figure is not otherwise available.

FACTORS AFFECTING MAKEUP

1\. How often is makeup water fed and how much?..
2\. Is all the condensate returned to boiler?..
3\. If not, why?..
4\. How often are the boilers blown down?..
5\. How many inches?....................Gallons?..
6\. Amount of fresh water used daily..
7\. % condensate..
8\. Total amount of water evaporated daily..
9\. How measured?..
10\. *Fuel used..*Grade of fuel..
11\. *Fuel consumption: Winter..........................Summer..........................
12\. *Stoker or hand fired..

Table 9-5. High-pressure Boiler Water Survey Sheet (Continued)

13. How often is boiler washed out?..........Opened?..........
Cleaned?..........Turbined?..........

* These data are used to compute roughly the total amount of water evaporated daily.

AUXILIARY EQUIPMENT

1. Feed-water heater..........Temperature, °F..........
2. Closed or open type..........
3. Hot well..........Pump..........Injector..........Economizer..........
4. Settling tanks..........Filter system..........Water softener..........
5. Other boiler equipment..........
6. What equipment is used to feed treating chemicals?..........
7. Do treatment chemicals go into boiler gradually or at once?..........
8. If gradually, how long does it take to add a full charge?..........

BOILER CONDITION

1. Is boiler scaled?..........Corroded?..........Pitted?..........
2. Thickness of scale..........Hard or soft..........Color..........
3. How badly corroded or pitted?..........
4. Do boilers prime?..........Foam?..........Carry over?..........
5. If so, state cause..........
6. How often is boiler inspected?..........By whom?..........
7. Last inspected..........Report..........
8. Any oil in condensate?..........

BOILER WATER TREATMENT DATA

1. Treatment now used..........Daily amount..........
2. Cost per year..........
3. Source of water supply (city, well, lake, or river)..........

ANALYTICAL WORK NEEDED

( ) Scale analysis
( ) Softened water
( ) Return water
( ) Raw-water analysis
( ) Feed water
( ) Boiler water

Remarks

(Include any additional information about unusual operating conditions or troubles at the plant)

....

....

....

....

2. The amount of each chemical required in pounds or ounces per thousand gallons of makeup is:

   a. Anhydrous disodium phosphate, 0.13 lb (2 oz)
   b. Soda ash, 0.091 lb (1½ oz)
   c. Quebracho, 0.024 lb (⅓ oz)

The pounds per thousand gallons is determined by dividing the parts per million of each chemical by 120. Since these figures are but a small fraction of a pound, they are often expressed in ounces.

9-10. A Blueprint for High-pressure Boiler Water Treatment. Now that the underlying principles of internal boiler water treatment have been covered, the treatment plan can be set up as outlined in Chap. 4, A Blueprint for Efficient Water Treatment. The first step in this basic plan is making the survey. Collect as many facts as possible about the equipment. Table 9-5 is a typical form used to collect the necessary data such as boiler capacity, blowdown, makeup, total evaporation, and operating conditions and troubles.

The second step is to prepare simple line sketches similar to the flow diagrams shown in Chap. 4. Label these as simply as possible using the data collected in the survey. Indicate only the most important streams.

9-11. Material Balance in Gallons of Water. The two most important items to label on the flow diagram in Fig. 9-11 are the amount of makeup and the amount of blowdown. The volume of water that the boiler holds under normal operating conditions is relatively unimportant. This is true when the continuous-treatment method is employed. With this method the amount of makeup and blowdown determines the amount of chemicals needed for treatment. Other information often noted on this diagram includes rated horsepower, gauge pressure, and rate of evaporation.

9-12. Chemical Balance of Raw-water Changes. The most important changes taking place in the chemical characteristics of the raw water in the process are easily determined by chemical analysis. This analysis should include most of the following items:

pH, total hardness, calcium hardness, total alkalinity, chloride, sulfate, and total dissolved solids. These quantities are also shown on the flow diagram in Fig. 9-12.

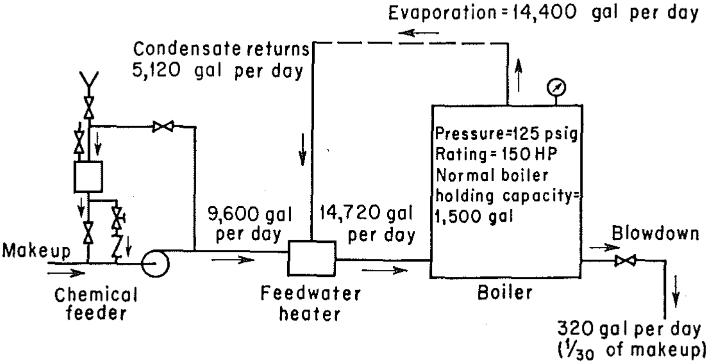


FIG. 9-11. Flow diagram with material balance in gallons of water. NOTE: Data from Fig. 9-10 indicate that blowdown can be reduced to 174 gal per day (one-fifty-fifth of makeup) if the raw-water makeup remains constant at 9,600 gal per day.

Now compare the chloride content of the raw and the boiler water to determine the extent to which the mineral salts concentrate in the boiler water. These data are helpful in regulating the amount of blowdown. For example, when the makeup concentrates 20 times (chloride in boiler water divided by chloride in raw water) and this concentration is desirable, any higher concentration indicates the need to increase the blowdown. Any lower concentrations indicate the need to reduce the amount of blowdown.

The number of concentrations multiplied by the total hardness in the raw water indicates the total concentration of calcium and magnesium in the boiler. Some of the calcium and magnesium remains dissolved in the boiler water. Some settles out as sludge, and if conditions warrant, some settles on the metal surfaces as scale. The amount of calcium and magnesium remaining dissolved in the boiler water is found by testing for hardness.

If the per cent of raw water or condensate in the feed water is unknown, it can be calculated. First determine the average amount of chlorides in the feed water by making several analyses.

Then divide this figure by the chlorides in the makeup water.

$$\text{Makeup in } \% = \frac{\text{Cl}_f}{\text{Cl}_m} \times 100 \tag{9-12}$$

$$\text{Condensate in } \% = 100 - \frac{\text{Cl}_f}{\text{Cl}_m} \times 100 \tag{9-13}$$

where Cl_f = average chlorides in feed water
Cl_m = chlorides in makeup water

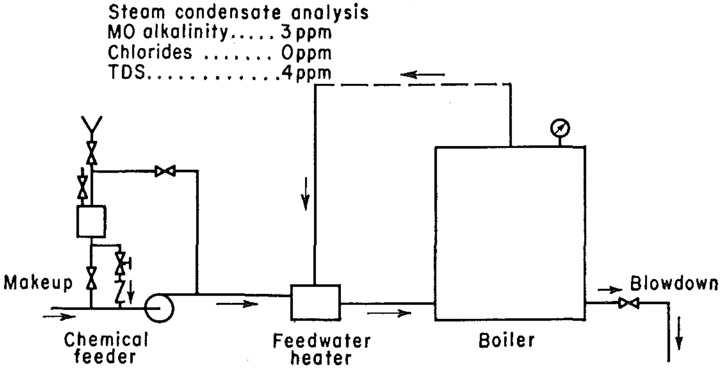


FIG. 9-12. Flow diagram with chemical balance of makeup-water changes.

Raw-water analysis:

pH	7.0
Total hardness	20 ppm
Calcium hardness	14 ppm
Methyl orange alkalinity	9 ppm
Chloride	3 ppm
Sulfate	12 ppm
T.D.S	35 ppm

Average feed-water analysis (untreated):

Chloride	2 ppm

Boiler water analysis (untreated):

pH	9.2 ppm
Total hardness	150 ppm
Phenolphthalein alkalinity	30 ppm
Methyl orange alkalinity	100 ppm
Chloride	90 ppm
Sulfate	200 ppm
T.D.S	589 ppm

NOTE: Data from Fig. 9-10 show that BWC is 55, not 30. Therefore boiler water chloride should be close to 165 ppm. This can be done by reducing blowdown to 174 gal per day.

9-13. Chemical Balance of Treatment Chemicals. Before the flow diagram in Fig. 9-13 can be labeled, the following questions must be answered:

1. What is the ideal water composition desired in this boiler?
2. What chemicals and auxiliary equipment are needed?
3. What is the cost of chemicals and the auxiliary equipment?
4. What is the most desirable blowdown rate?
5. What major troubles must be overcome or avoided (scale formation, corrosion, priming and foaming, carryover, and caustic embrittlement)?

For many of the answers to these questions the advice of a

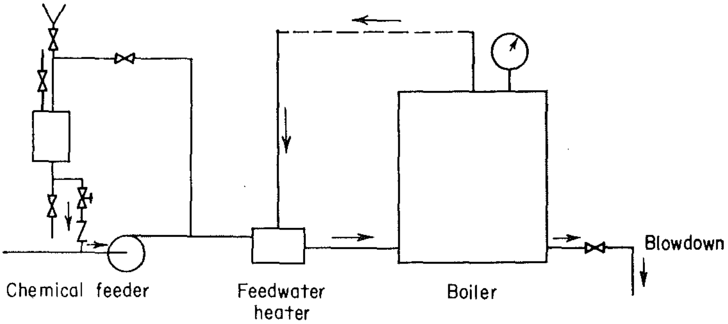


FIG. 9-13. Chemical balance of treating chemicals.

Daily amounts of chemical:

Disodium phosphate	1.25 lb
Soda ash	0.87 lb
Quebracho	0.23 lb
	2.35 lb total

Treated boiler water analysis:

pH	11.2
Total hardness	0
Phenolphthalein alkalinity	450 ppm
methyl orange alkalinity	500 ppm
Chloride	165 ppm
Sulfate	660 ppm
Phosphate	55 ppm
T.D.S.	2,000 ppm

competent water treatment specialist is very helpful. The charts of Fig. 9-9, Table 9-1, and Table 9-4 can then be used to calculate the desired boiler water composition and concentration, blowdown rate, and amount of chemicals required.

Once the chemical balance of treatment chemicals is determined these conditions must be maintained continuously. Keep a complete set of records to provide an accurate basis for adjusting the chemical treatment and the blowdown rates. Figure 9-14 is a typical example of such a control record. Example 2 shows how to set up a plan of treatment.

EXAMPLE 2. Treat a 150-hp high-pressure boiler internally using sodium phosphate as the main chemical. First make the survey and label the flow diagrams with all the important data. This is shown in Figs. 9-11 to 9-13.

The material balance in gallons of water (Fig. 9-11) reveals that the boiler holds 1,500 gal of water. About 9,600 gal of makeup is put in every day. The daily blowdown amounts to 320 gal. The calculations in Fig. 9-10 show that the desired boiler water concentration is 55. On this basis the blowdown can be reduced. If the makeup remains constant at 9,600 gal, the daily blowdown will be one-fifty-fifth of the makeup, or 174 gal.

Figure 9-12 shows that the raw water concentrates 30 times in the boiler. What proportion of raw water is contained in the feed water? This answer is obtained by using Eq. (9-12).

In this equation $Cl_f = 2$ ppm and $Cl_r = 3$ ppm. The per cent makeup in the boiler feed water then equals $\frac{2}{3} \times 100$, or $66\frac{2}{3}$ per cent.

The analysis of the untreated boiler water indicates that chemical treatment is needed to produce the desired ideal boiler water composition. All the important analytical data showing the changes that take place in the water as it enters and leaves the boiler are listed on the flow diagram.

Figure 9-13 tabulates the daily chemical charges for the boiler. These amounts are calculated as follows from Fig. 9-10 and are based on adding 9,600 gal of makeup per day.

Name of company *J. Jones Co.* Date *11/1*

Boiler No. *1* Rated hp *150* % rating *100*

Gauge pressure *125 lb.* Boiler holding capacity, gal *1,500*

NORMAL OPERATING DATA

Raw-water makeup *9600* gal per day: Blowdown *174* gal per day *5* in. per day.

Hours of operation *24* Type treatment *Sodium phosphate*

Chemical	Dosage schedule	
	lb per 1,000 gal of makeup	lb per day
A. Disodium phosphate	0.13	1.25
B. Soda ash	0.091	0.87
C. Quebracho	0.024	0.23
TOTAL	0.245	2.35

Remarks *Maintain concentration of 55, 165 ppm chloride, 50 ppm* PO_4*, 500 ppm total alkalinity, 2,000 ppm TDS*

FIG. 9-14. Typical form of boiler water treatment control record.

Date	Time	Boiler		Blow-down, gal	Make-up, gal	Chemical charge, lb			Analytical data							
		On	Off			A	B	C	pH	T.H.	P alk.	M.O. alk.	Cl	SO_4	PO_4	TDS
11/1	9:00	✓		174	9,600	1.25	0.87	0.23	9.2	150	30	100	90	200	. . .	589
11/2	9:00	✓		174	9,600	1.25	0.87	0.23	9.5	140	50	120	100	250	. . .	709
11/3	9:00	✓		174	9,600	1.25	0.87	0.23	9.8	125	75	150	110	320	. . .	875
11/4	9:00	✓		174	9,600	1.25	0.87	0.23	10.2	110	120	210	125	370	. . .	1,048
11/5	9:00	✓		174	9,600	1.25	0.87	0.23	10.4	90	125	250	135	430	. . .	1,207
11/8	9:00	✓		174	9,600	1.25	0.87	0.23	10.6	65	270	300	140	490	. . .	1,384
11/9	9:00	✓		174	9,600	1.25	0.87	0.23	10.7	40	320	350	145	540	. . .	1,505
11/10	9:00	✓		174	9,600	1.25	0.87	0.23	10.8	0	375	400	150	580	25	1,686
11/11	9:00	✓		174	9,600	1.25	0.87	0.23	11.0	0	400	450	155	620	30	1,823
11/12	9:00	✓		174	9,600	1.25	0.87	0.23	11.0	0	425	475	160	650	45	1,933
11/15	9:00	✓		174	9,600	1.25	0.87	0.23	11.2	0	450	500	165	660	55	2,000

FIG. 9-14. Typical form of boiler water treatment control record (*Continued*).

Chemicals fed	Amount needed, lb per 1,000 gal	Amounts of makeup, gal per day	Amount needed, lb per day
Disodium phosphate	0.13	9,600	1.25
Soda ash	0.091	9,600	0.87
Quebracho	0.024	9,600	0.23
TOTAL	0.245	9,600	2.35

The continuous-treatment method should normally be used to calculate daily chemical dosages. However, there are times when the boiler is not in continuous use. Then it is desirable to change the 55 concentrations of untreated boiler water to its ideal composition as fast as possible. The amount of chemical needed for this is calculated in accordance with the batch-treatment plan. The accumulated charge of all the chemicals in Fig. 9-10 was obtained in this manner. The total chemical needed (Fig. 9-10, item 5, column V) is 0.245 lb per thousand gallons at one boiler water concentration. Column VI shows that 13.5 lb per thousand gallons is needed at a boiler water concentration of 55. Since the boiler holds 1,500 gal of water, a chemical charge of 20.5 lb is needed to produce the desired ideal boiler water conditions at once.

Keep a daily record of the number of gallons of makeup, amount of blowdown, and dosage of chemical, and analyze a sample of the boiler water daily. Figure 9-14 shows the first 11 entries on this record. The data illustrate the gradual build-up of all salts in the water toward the desired ideal boiler water composition with nothing unusual happening.

9-14. Control Record of Boiler Water Treatment. Once a plan of treatment is started, the continuous control record illustrated in Fig. 9-14 is very important. If nothing unusual happens, the data on makeup, blowdown, chemical charges, and chemical analysis will remain normal. But any sudden change in the data is a warning that something may be wrong and further checking is called for. For example, a sudden rise in chlorides and raw-water makeup may indicate that less condensate is coming back because of leaks or other wastage.

The ratio of raw-water sulfates to chlorides is normally the same as that in the treated boiler water when sulfite is not being used. If this ratio increases after chemical treatment is started, scale in the boiler is redissolving. If there is priming or carryover under these conditions, increase the blowdown temporarily to get rid of the excess dissolved solids. When the sulfate-to-chloride ratio decreases, scale may be forming in the boiler. If the ratio continues low with a specified chemical dosage, be sure to adjust the dosage. The data in Example 2 illustrate some of these points. The ratio of sulfates to chlorides in the raw water is 12 to 3, or 4 to 1. The first entry, dated 11/1, in Fig. 9-14 shows that the sulfate-to-chloride ratio for the treated boiler water is 200 to 90, or 2.2 to 1. This means that sulfate scale is probably forming in the boiler. The ratio of sulfates to chlorides for the last entry, dated 11/15, is 660 to 165, or 4 to 1. At this point the boiler is properly treated. Sulfate scale is no longer forming nor is any scale in the boiler going back into solution.

9-15. Special Conditions Affecting the Treatment Plan. Simple routine tests are the basis of controlling the harmful elements in the boiler water and the amounts of treating chemical used. Since this is not always possible, the simple material-balance calculations discussed in Chap. 4 do not always apply. Some harmful elements in the boiler water like dissolved oxygen and carbon dioxide are gaseous in nature. These elements cannot be readily measured by routine chemical testing. The test procedure for dissolved oxygen is very complicated. It calls for special precautions to avoid oxygen contamination of the sample during the test. Some chemicals used for treatment are complicated organic mixtures for which there are no simple routine control tests. Since the action of organic chemicals is mainly physical, dosage control depends greatly on experience and physical observations.

Chemicals that fall into the physical action group include those that promote formation of a fluid sludge with calcium and magnesium precipitates. These fluid sludges are less likely to form scale and are more easily blown out of the boiler. A list of the chemicals in this category includes such organic agents as tannin, lignin, starch, and seaweed derivatives. Highly effective organic antifoam agents are also examples of treating chemicals that are mainly physical in their action.

The amount of physical-action chemical needed in the boiler water is usually determined on a trial basis with the help of a water treatment specialist. The dosage is then prescribed in pounds per thousand gallons of raw-water makeup for use on a continuous basis along with the other treating chemicals. Since there are no simple tests for the presence of physical-action chemicals, all adjustments of the amount fed depend on visual observation of their effect on the boiler water.

Sodium sulfite removes the last traces of oxygen from boiler water. It is an example of a chemical which actually reacts with the harmful constituent. Because of this, routine testing for dissolved oxygen can be avoided by substituting a much simpler test for excess sodium sulfite. The chemical reaction and formula weights are shown in Eq. (9-14) and Table 9-6.

$$\underset{252}{2Na_2SO_3} + \underset{32}{O_2} = \underset{284}{2Na_2SO_4} \qquad (9\text{-}14)$$

Table 9-6. Amount of Sodium Sulfite Needed to React with Dissolved Oxygen in Water

Amount of oxygen present, formula weight of 32	*Sodium sulfite needed, formula weight of 252*
1 ppm	7.875 ppm pure sulfite 8.468 ppm 93% sulfite
1 lb	7.875 lb pure sulfite 8.468 lb 93% sulfite
1 ml per liter*	12.11 ppm 93% sulfite 0.101 lb/1,000 gal
0.05 ml per liter	0.606 ppm 93% sulfite 0.005 lb/1,000 gal

* NOTE: 1 ml per liter oxygen = 1.43 ppm = 0.012 lb per 1,000 gal.

An accurate determination of the dissolved oxygen in boiler feed water is difficult to make. The Winkler test gives an approximate value and is most commonly used for dissolved oxygen in the boiler room. But other methods of testing are more accurate. Boiler waters that show zero oxygen by the Winkler test often contain 0.02 to 0.05 ml of oxygen per liter. There are also cases on record where oxygen corrosion has taken place even though chemical tests consistently showed zero oxygen.

However, the presence of 30 ppm or more sodium sulfite in boiler water practically guarantees elimination of all dissolved oxygen in the feed water. For this reason routine tests for oxygen are not necessary with sulfite treatment. The following example shows how the normal water treatment plan is modified to accommodate the use of sodium sulfite.

EXAMPLE 3. The commercial sulfite used to treat a high-pressure boiler contains 93 per cent sodium sulfite. It is added continuously just after the deaerator in sufficient quantity to maintain 30 ppm excess sodium sulfite in the boiler water. No dissolved oxygen tests will be run. How much sulfite is needed for the initial charge? What amount must be added continuously?

Assume that the dissolved oxygen in the feed water is 0.05 ml per liter. The boiler holds 1,500 gal and the blowdown is 1,000 gal per day.

The initial charge of sulfite needed is calculated by the batch method. As shown in Table 9-6, the amount of 93 per cent sulfite needed to remove 0.05 ml per liter of dissolved oxygen from the boiler water is 0.005 lb per thousand gallons. For the 1,500 gal in the boiler this comes to 0.0075 lb of sulfite. To establish 30 ppm excess sulfite in the boiler requires 0.269 lb per thousand gallons. This amounts to 0.4035 lb of sulfite for the 1,500 gal in the boiler. The total initial charge of 93 per cent sulfite is then 0.274 lb per thousand gallons, or 0.411 lb, or 66 oz.

The initial charge of 0.411 lb gives 30 ppm excess sulfite in 1,500 gal of boiler water. But any loss of water such as boiler blowdown will reduce the level of sulfite present. Under normal operating conditions, the sodium sulfite can be maintained at

30 ppm concentration by simply replacing the amount lost with the blowdown. In the following equation let x equal the amount of sulfite that is added continuously to the boiler.

$$\frac{x}{0.411} = \frac{1{,}000 \text{ gal}}{1{,}500 \text{ gal}}$$
$$x = 0.274 \text{ lb}$$

Therefore, the continuous daily charge needed to maintain 30 ppm excess sulfite is 0.274 lb, or 44 oz.

Now that the initial and continuous chemical charge is set, test for sulfite excess in the boiler water at regular intervals. An eight-hour interval after the initial charge is satisfactory. If the boiler is blown down manually each day, take the test sample just before a regular manual blowdown. After eight hours of operation, the test shows that the sulfite excess in the boiler water is 25 ppm. Since 0.274 lb of commercial-grade sulfite gives a 25 ppm excess, a mathematical ratio can be used to determine how much is needed for 30 ppm excess. Let y equal the sulfite charge required.

$$\frac{y}{0.274 \text{ lb}} = \frac{30 \text{ ppm}}{25 \text{ ppm}}$$
$$y = 0.329 \text{ lb}$$

Therefore, the amount fed must be increased to 0.329 lb, or 53 oz per day to produce 30 ppm excess sulfite in the boiler water.

10

Water in Air-conditioning Systems

10-1. Refrigeration Basics. Two laws of nature must be clearly understood in order to know how a cooling system works. First, heat always flows from a hotter to a cooler body. Second, all gases cool on expansion and become warmer when compressed. One common illustration of this is the increase in automobile tire pressure on a hot day. Another, more dramatic example is obtained by suddenly releasing the pressure on a cylinder of carbon dioxide. Solid particles of very cold carbon dioxide (dry ice) immediately form around the outside of the valve on the cylinder.

Two elements are needed in every cooling system: they are the refrigerant, or working substance, and a cooling medium. The refrigerant is a fluid with the ability to extract heat from the space to be cooled. This heat is then discharged to another cooling medium. The great majority of modern refrigerating systems use a liquefiable vapor as the refrigerant. Two good examples are Freon and ammonia. Other commonly used refrigerants include gases like carbon dioxide and sulfur dioxide. The cooling medium is either air or water.

10-2. The Refrigeration Cycle. The refrigeration cycle is composed of a series of changes in state that restore the refrigerant to the physical condition in which it will extract heat from the space to be cooled. Figure 10-1 shows a typical basic cycle for a compression-type mechanical refrigeration system. The cycle is composed of two heat-transfer steps and two pressure-change processes.

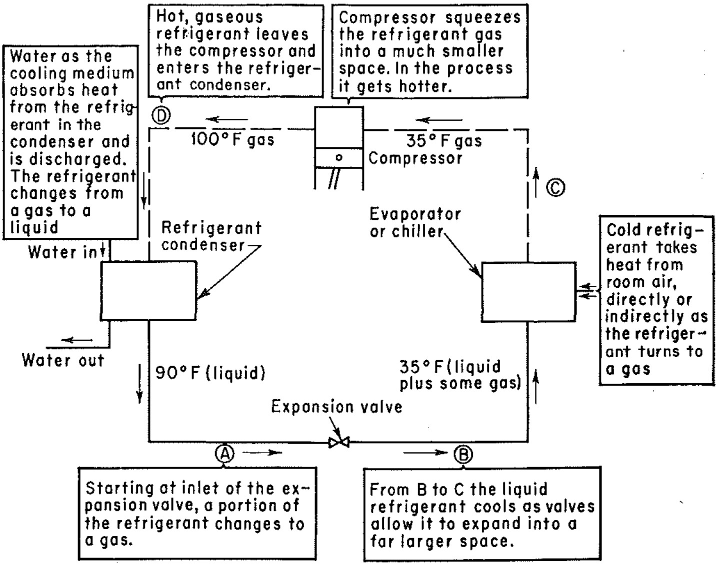


FIG. 10-1. The refrigeration cycle: Basic compression-type system.

In order to understand how the system works, start at A, the inlet of the expansion valve. After leaving the condenser, the liquid refrigerant flows through the *expansion valve* and is allowed to expand into a far larger space. This reduces the pressure. The refrigerant immediately cools, and in the process some of it changes to a gas. The cold refrigerant then enters the *chiller coils* (also called *cooling* or *evaporator coils*) where it removes heat from the warm room air. This can be done directly or through a chilled-water system. The refrigerant is now in the gaseous state. Next the compressor squeezes the refrigerant gas into a much smaller space. The pressure increases and the gas becomes hotter. Then the hot refrigerant from the *compressor* enters the condenser. Here another cooling medium of air or water going through the condenser absorbs heat from the refrigerant. As the refrigerant cools, it changes from gas to a liquid. Water, the cooling medium, discharges from the condenser. When the water leaves the condenser, the complete refrigeration cycle is repeated at A, the inlet of the expansion valve.

10-3. Water Use. Water is used in many ways in cooling system equipment. Some typical uses are illustrated in Figs. 10-1 and 10-2. Before planning any chemical water treatment program, you must have a basic knowledge of how the water is handled in each type of equipment. Be sure to understand and take into consideration any changes that take place in the cooling water

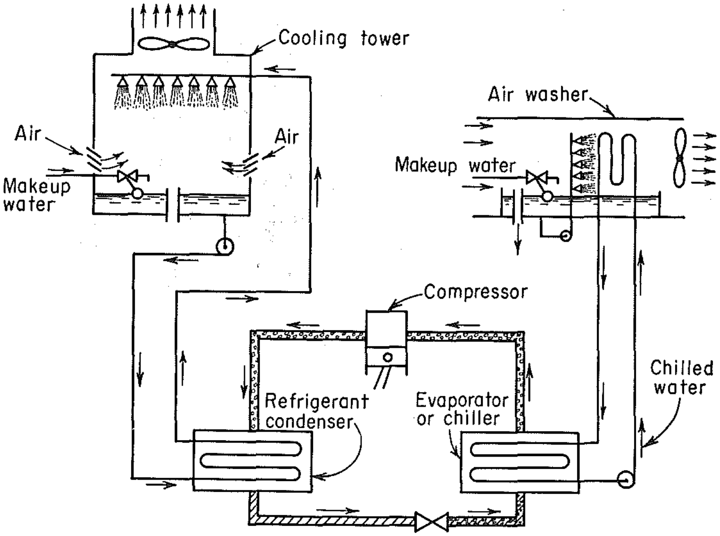


FIG. 10-2. Cooling system with cooling tower and air washer, showing chilled-water circuit.

because of the way it is used. The following paragraphs describe the equipment using water in the cooling system.

10-4. Once-through Cooling. If cooling water is available in abundance, at low cost, water can be put through the refrigerant condenser just once and then discharged to waste. This is by far the simplest way to cool the refrigerant. The big advantage is that there is no need for a lot of auxiliary cooling equipment. The main disadvantage is that relatively large quantities of cooling water are needed to do the job. Figure 10-1 shows a refrigerant condenser using cooling water on a once-through basis.

10-5. Cooling Towers. When the cooling water is not available in abundance or its use is restricted by law or the price is too high, the alternative is recirculating the cooling water used for the refrigerant condenser. This arrangement is shown in Fig. 10-2. The cooling tower is a water-saving device designed to do this job as efficiently as possible. Heated water leaving the refrigerant condenser is sprayed or dropped through a stream of air. This evaporates a small portion of the water and thereby reduces the temperature of the rest. The cooling effect of evaporation is best

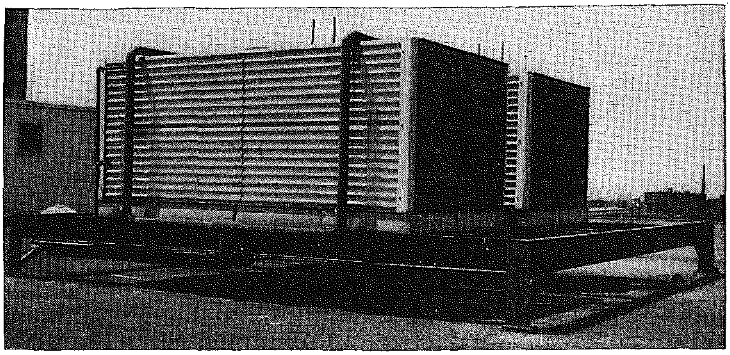


FIG. 10-3. Cooling towers like this design are used in air-conditioning systems with refrigeration capacity in the range of 60 to 1,100 tons. (*Courtesy of The Marley Company.*)

illustrated by pouring a small amount of alcohol over the hand. As the alcohol evaporates, the skin in contact with alcohol becomes colder. Based on this principle, the cooling tower permits reuse of the cooling water over and over again. Several cooling tower designs are shown in Figs. 10-3 to 10-5.

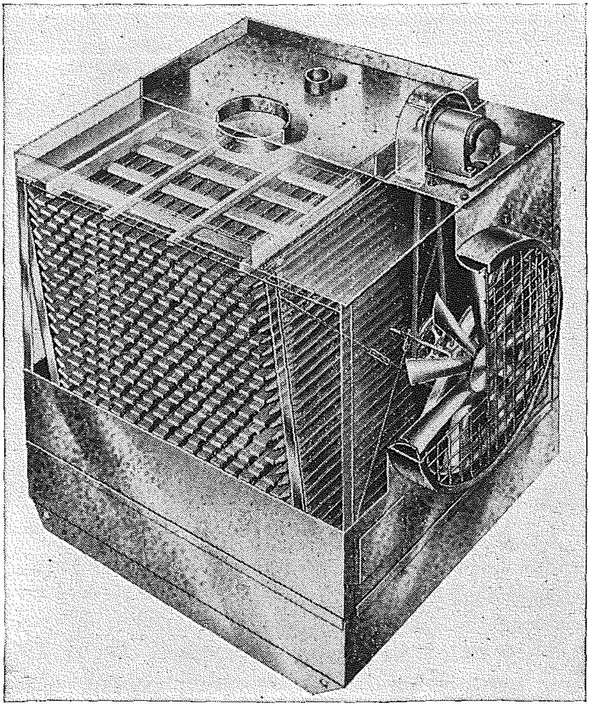


FIG. 10-4. Cutaway view of cooling tower designed for air-conditioning systems with refrigerating capacity in the range of 3 to 150 tons. (*Courtesy of The Marley Company.*)

Compared with the once-through cooling system, a cooling tower has the main advantage of saving large amounts of cooling water. Water is not always abundant and low in cost. But its cost in a once-through system must be compared with the added initial cost for the cooling tower. Operating and maintenance costs for the cooling tower system are also higher.

The cooling tower is designed to bring the hot water into intimate contact with the surrounding air. Although this produces efficient cooling, it also brings acidic gases from the air into solution, making the water more corrosive. In addition, the evaporation of water in the tower increases the total dissolved solids and hardness of the recirculating cooling water. This definitely increases the tendency of the water to form scale. Since the water comes in contact with dust and dirt, it also tends to pick up organic matter such as bacteria or algae.

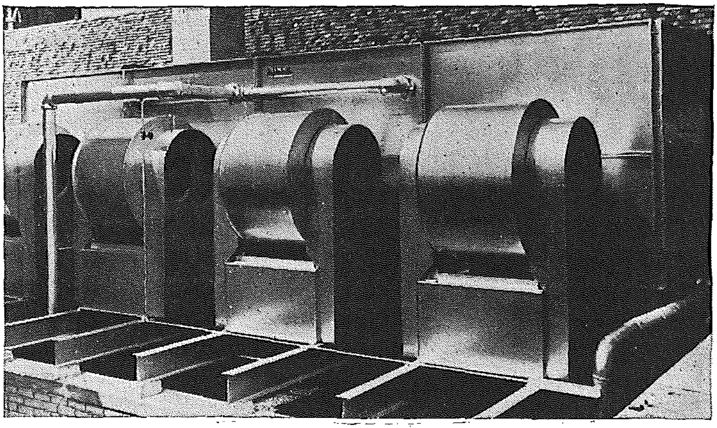


FIG. 10-5. Forced-draft cooling towers with a capacity of 480 gpm are part of the air-conditioning system at a large Southern university. (*Courtesy of Binks Manufacturing Company.*)

10-6. Spray Pond. This is the simplest type of equipment used to cool the recirculating water for the refrigerant condenser. As the name implies, the cooling water from the condenser goes to a large pond where the water is cooled by spraying it into the air. Enough water evaporates to produce the desired amount of cooling. Spray ponds call for a tremendous amount of space compared with a cooling tower. And, like the cooling tower, the water just as easily becomes corrosive and scale-forming and picks up organic matter from the atmosphere. Figure 10-6 shows spray ponds that effectively blend with the plant landscaping.

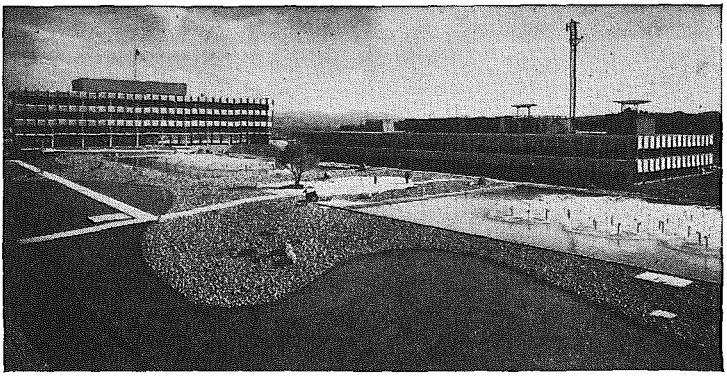


FIG. 10-6. These 330,000-gal spray ponds are located in scenic building mall. Heat rejected is vital to this plant's 2,500-ton air-conditioning system. (*Courtesy of The Recold Corp.*)

10-7. Evaporative Condenser. Illustrated in Fig. 10-7, the evaporator-condenser combines the action of the water-cooled condenser and the cooling tower. In this role it saves both water and space. However, the evaporative condenser is still subject to corrosion, scale formation, and slime in the recirculating-cooling-water circuit.

10-8. Chilled-water System. This is a closed recirculating system consisting mainly of pipes and coils. As shown in Fig. 10-2, the main purpose is to extract heat from the area being cooled. The evaporator coils chill water in the closed circulating system instead of directly cooling the air in the room. The chilled water in turn cools the room air. The cooling and dehumidifying effect of a chilled-water system is best illustrated by observing the cold-water piping in the basement of a building during summer months. The warm air coming into contact with the piping is cooled. Cooler air cannot hold as much water as warm air.

Therefore, the excess moisture in the air condenses on the pipes. This is commonly known as *pipe sweating*. As a result, the basement is much cooler and more comfortable than the rest of the building during the summer months.

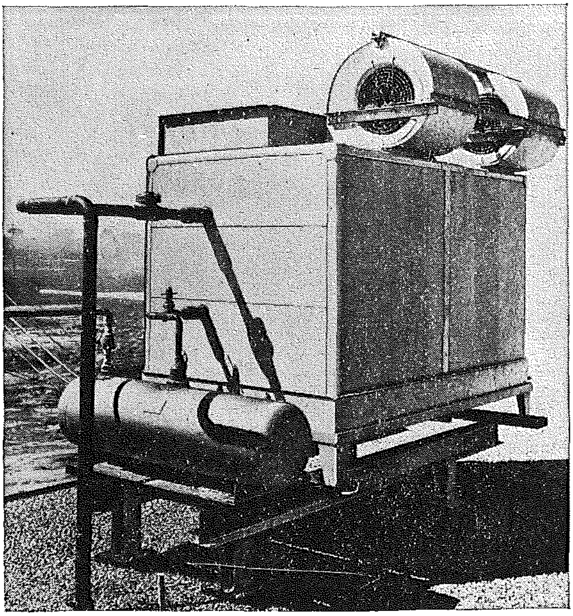


FIG. 10-7. Evaporative condenser. (*Courtesy of The Recold Corp.*)

The chilled-water system is subject to corrosion; however, scale or slime growths are usually not encountered. In any closed circulating system, total solids do not build up and there is no intimate contact with air. This also means that any corrosion encountered will not be as bad as that in an open-spray system.

10-9. Air Washer. This water-spray device cleans humidifies, dehumidifies, or cools the air. Figure 10-2 shows a typical air-washer installation containing coils from the chilled-water system. Essentially, the air washer uses a spray system to bring cold recirculated water into intimate contact with the conditioned air. The air washer is also subject to corrosion, scale formation, and slime growths from the recirculating water. Figures 10-8 and 10-9 show typical industrial air washers.

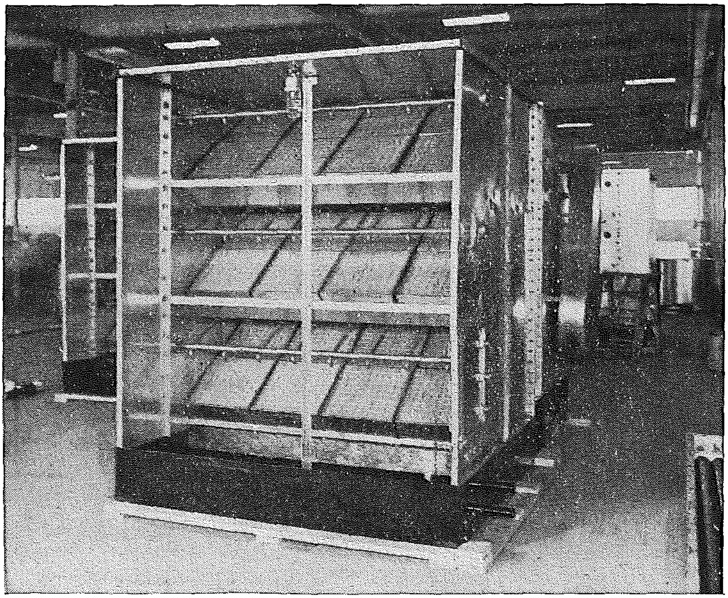


FIG. 10-8. Capillary air washer showing the capillary cells from the air inlet end. (*Courtesy of American-Standard.*)

10-10. Common Air-conditioning Terms—Ton of Refrigeration. A ton of refrigeration is equivalent to the amount of refrigeration produced when one ton of ice at 32°F melts and becomes water at 32°F. It is usually expressed as a rate per day, hour, or minute. One ton of refrigeration is also defined as the removal of heat at a rate of 200 Btu per minute. The Btu is the amount of heat needed to raise the temperature of one pound of water one degree Fahrenheit. But air-conditioning equipment is rated on the basis of its cooling effect. Therefore, an air-conditioning unit must draw 200 Btu per minute from a room for each rated ton of refrigeration. All the heat taken from the room plus heat friction in the machine, etc., is delivered to the cooling water. If machine efficiency is 80 per cent, then 250 Btu per minute is delivered to the cooling tower for each ton of refrigeration. In actual practice, for a compressor-refrigeration system, the heat delivered to the cooling tower is usually in the range of 250 Btu per minute for each ton of refrigeration. In a steam-absorption system, additional heat is brought into the equipment by the steam used to operate the machine. This heat must be taken into account since it is also dissipated in the cooling tower. In an air-conditioning plant of this type, the cooling tower must handle about 500 Btu per minute for each ton of refrigeration.

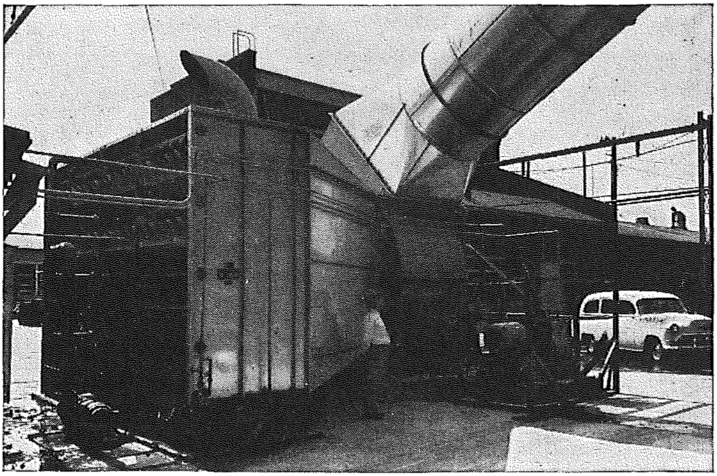


FIG. 10-9. Capillary air washer installed and in operation. (*Courtesy of American-Standard.*)

10-11. Circulation Rate of Cooling Tower Water. The pumping equipment circulates the water in a cooling tower at the rate of 3 gpm per ton in a compression-refrigeration system. For a steam-absorption system, the rate may vary from 3 to 4 gpm per ton. On this basis, the cooling tower in a 50-ton compression-refrigeration system must handle a circulating-water rate of 150 gpm.

10-12. Evaporation Loss. The evaporation loss is proportional to the tons of refrigeration produced. Therefore, it varies directly with the increase in temperature of the water cooling the refrigerant in the condenser. The cooling tower is usually designed to take care of a 10°F rise in water temperature. Under these conditions, the evaporation loss in the cooling tower is 1 per cent of the circulation rate for a 10°F change in temperature. Table 10-1 gives some typical data on evaporation loss in a 50-ton cooling tower.

Table 10-1. Evaporation Loss in a 50-ton Cooling Tower

Circulation rate, gpm	Evaporation loss, 1 % of circulating rate		
	gpm	gph	gal/24 hr
1. Per ton—3 gpm	0.03	1.8	43.2
2. Per 50 tons—150 gpm	1.5	90	2,160

NOTE: Water-holding capacity of tower is 300 gal.

As evaporation takes place in the cooling tower, only distilled water is lost. The mineral salts and solids remain in the water. This evaporation is comparable to the evaporation of pure steam in a boiler. The 50-ton cooling tower in Table 10-1 evaporates 2,160 gal of water per day. The tower itself holds only 300 gal of water. This means that if there is no windage or other water losses through leaks or blowdown, about seven times (2,160/300) the water-holding capacity of the cooling tower is evaporated. The water remaining in the pan still contains all the mineral salts present originally in the water. Therefore, the circulating water contains seven times more solids than the original water. Each day the solids will continue to concentrate as long as there is no windage or other water losses. The usual chemicals added to an air-conditioning system are not lost with the water that is evaporated. Therefore, the addition of a treatment chemical which does not react with the mineral salts, such as chromate, will continue to provide effective treatment.

The amount of evaporation from an evaporative condenser or air washer during winter operation (humidifying the air) depends on the tons of refrigeration produced. It amounts to about 0.03 gal per minute per ton. This is equivalent to 1.8 gal per hour per ton. This is usually expressed as gallons per ton-hour to indicate that the water lost by evaporation depends on both the system tonnage and the length of operation.

10-13. Windage Loss or Drift. This is the loss of entrained water droplets carried along with the water vapor. Naturally, these droplets contain a proportionate amount of dissolved solids in the water and any treatment chemicals added. Therefore, the amount of treatment needed to maintain the proper chemical concentrations in the cooling tower circulating water depends on both the windage loss and the amount of leakage. Tables 10-2 and 10-3 give some typical windage and mechanical water losses for open-type spray systems. Table 10-2 shows the average windage loss as a per cent of circulation rate. Table 10-3 gives

Table 10-2. Typical Windage Loss in Open-spray Systems

Equipment	*Windage or drift loss, % of circulation rate*
Spray ponds	1.0–5.0
Atmospheric towers	0.3–1.0
Mechanical draft towers	0.1–0.3

Table 10-3. Typical Windage Loss per Ton-hour of Operation

Equipment	*Water loss per ton-hour of operation (W/th), gal*
Spray pond	4.5
Atmospheric towers	0.9
Mechanical draft towers	0.27
Evaporative condenser or air washer (humidification)	0.165
Air washer (dehumidification)	0.5

the average expected windage or mechanical water losses in gallons per ton-hour of operation. This table is very helpful in calculating the monthly water loss that must be chemically treated. The water loss in gallons per ton-hour from Table 10-3 multiplied by the number of tons and the hours of operation per month gives the windage in gallons per month. The mathematical relationship is as follows:

$$Wm = \text{tons (hours/month)}(W/th) \tag{10-1}$$

where Wm = windage loss, gal per month
W/th = windage loss, gal per ton-hour

The equivalent tons of refrigeration for an air washer per thousand cfm of air flow can also be approximated. The following table gives these data in tons per thousand cfm based on the per cent of fresh air coming into the air washer:

Proportion of fresh air, %	*Tons per thousand cfm*
Up to 25	2.6
30	3.8
40	4.7
50	5.3
60	5.8
70	6.1
80	6.3
100	6.6

If the flow of air through the air washer is unknown, this can be computed by the following formula:

$$\text{Air flow, cfm} = H(W)650$$

where H = height, ft, from top of pan to top of air washer
W = width (dimension perpendicular to air flow), ft

10-14. Blowdown. This is the deliberate waste of a portion of the circulating water and is also known as *bleed-off*. It is usually done with the aid of a device or pipeline that continuously drains a small stream of water from the system. It can also be done at frequent intervals by partial draining of some of the recirculating water. However, continuous blowdown permits much better control of water conditions in the system. The purpose of blowdown is to control the level of dissolved solids in the circulating water and thus avoid the possibility of scale formation. Naturally, any treatment chemicals added to the system are also present in the blowdown.

10-15. Mechanical Losses. These are undesirable in any open-spray system. Both water and treatment chemicals are wasted. But, with proper maintenance, these losses can be kept to a minimum. Table 10-4 gives typical causes of mechanical water losses together with a suggested check list for keeping them under control.

Table 10-4. Causes of Mechanical Water Losses

Source of water loss	*Check list for minimizing loss*
1. Pump leaking excessively....	*a.* Tighten pump packing *b.* Repack pump *c.* Examine pump shaft for scoring
2. Pan water overflowing continuously (this does not apply to air washers in the summer, which must overflow continuously because of condensation)	*a.* Adjust arm of float valve so that it closes at a lower water level *b.* Replace washer in float valve so that it operates normally *c.* Replace float valve assembly *d.* Raise overflow level
3. Pan water overflows excessively on shutdown of unit because of large drainback from other parts of system	*a.* Adjust arm of float valve so that it closes at a lower level to accommodate extra water flowing into pan *b.* Raise overflow level *c.* Find and eliminate cause of large drainback (1) Examine perforated head pan for dirt and blockage; keep it clean (2) Refrigerant-condenser units higher than tower; install check valve on supply line only
4. Miscellaneous leaks in equipment	*a.* Repair all leaks promptly

10-16. Total Makeup. The total makeup to an open-spray system must equal the sum of the evaporation loss, windage loss, blowdown loss, and any leaks from the water portion of the system. This is expressed in the following equation

$$M = E + W + B + L \tag{10-2}$$

where M = total makeup
E = evaporation loss
W = windage loss or drift
B = blowdown loss
L = miscellaneous mechanical losses

The makeup can also be computed from the material balance formula:

$$M = C(W + B + L) \tag{10-3}$$

where C = the number of concentrations

10-17. Number of Concentrations. The circulating water in an open-spray system is much more concentrated with solids than the makeup water because of evaporation from the system. *Number* or *cycles of concentrations* is the term indicating the degree of concentration of the circulating water compared with the makeup water. For example, two concentrations means that the circulating water has twice the normal dissolved-solids content of the makeup water. One simple chemical control involves testing for a single element in the water which does not change composition or settle as water is evaporated. This element then acts as a tag or tracer element in checking the number of concentrations. Chlorides meet this specification for open-spray systems. However, if the treatment chemicals contain appreciable amounts of chloride the chloride analysis cannot be used as an indication of the number of concentrations. The mathematical expression for the number of concentrations is

$$\frac{\mathrm{Cl}_c}{\mathrm{Cl}_m} = \text{number of concentrations} \tag{10-4}$$

where Cl_c = chlorides in the circulating water
Cl_m = chlorides in the makeup water

Table 10-5 shows the relation between the number of concentrations and the amount of water lost in typical open-spray systems.

Table 10-5. Relation between Number of Concentrations and Water Loss

Number of concentrations	Water loss in open-spray systems, gal/t-hr			
	Cooling towers			Evaporative condenser
	Atmospheric	Mechanical draft		
		Compression refrigeration	Steam-absorption refrigeration	
1½	3.60	3.60	7.20	3.60
2	1.80	1.80	3.60	1.80
3	*0.933*	0.933	1.870	0.933
4		0.600	1.200	0.600
5		0.450	0.900	0.450
6		0.360	0.720	0.360
7		0.300	0.600	0.300
8		*0.270*	0.518	0.270
9			0.450	0.225
10			0.400	0.200
11			*0.360*	0.180
12				*0.165*

In this table the numbers in italics represent guaranteed maximum windage or drift loss with zero blowdown. When the blowdown is zero, the column on the left gives the resulting number of concentrations in the system.

Air washers in the winter give the same water loss as the evaporative condenser. But in the summer, because of dehumidification there is no relation between the number of concentrations and the water loss. The amount of this loss is estimated at 0.5 gal per ton-hour.

10-18. Judging whether Water Will Be Corrosive or Scale-forming. The changes that take place in the chemical composition of the cooling water often show whether it is corroding the equipment or whether there is a tendency for scale formation. For example, an analysis of the recirculating cooling water shows that copper is dissolved in the water. If the water circulates through equipment containing copper parts, this can only mean that the copper equipment is corroding.

The tendency to form scale may be indicated by testing for chloride and calcium hardness in both the makeup and the circulating cooling water. The number of concentrations equals the ratio of chlorides in the cooling water to chlorides in the makeup. If the ratio of calcium hardness in the cooling water to that of the makeup is less than the concentration factor, some calcium hardness may have come out of solution to form scale.

There are many factors that cause cooling water to become corrosive or scale-forming. These include pH, alkalinity, calcium hardness, total solids, and temperature of the water. Professor W. F. Langelier studied all these factors and developed the idea of a calculated saturation index to predict the scale-forming tendencies of water. The Langelier Saturation Index Chart is given in Fig. 10-10. The following example will show how this chart is used.

The saturation index I_s on the chart is $+0.68$. Here is how this is calculated. First locate the calcium hardness of 120 ppm on the parts-per-million scale. Extend this value vertically to the diagonal line marked calcium hardness as $CaCO_3$. Then read this value horizontally at the left on the pAlk and pCa scale. The value for pCa in this case is 2.92.

Now in the same way locate the M (total) alkalinity of 100 ppm on the parts-per-million scale. Then find its intersection with the diagonal line marked M Alk as $CaCO_3$. Then read the pAlk and pCa on the horizontal scale at the left. In this example the pAlk is 2.70.

The next step is to find C. Locate the total solids of 210 ppm on the parts-per-million scale. Extend this value vertically up

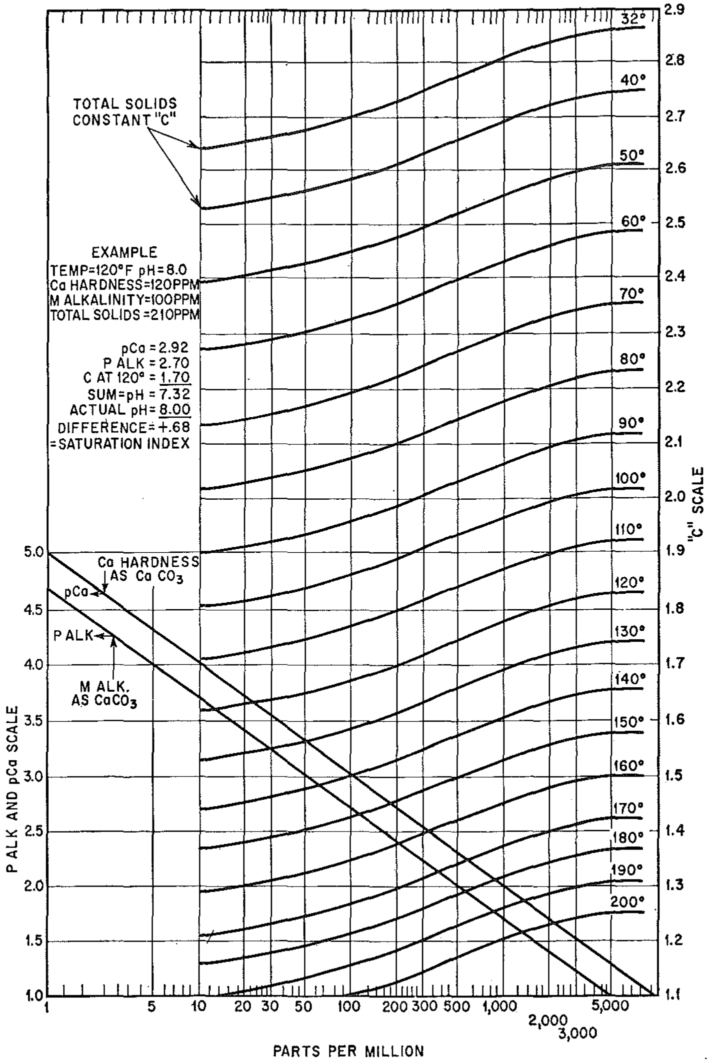


FIG. 10-10. Langelier Saturation Index Chart. (*Courtesy of Sheppard T. Powell, Water Conditioning for Industry, McGraw-Hill Book Company, Inc., New York, 1954.*)

to the line marked 120°F. At the intersection read horizontally to the right on the C scale. In this case C equals 1.70. The pH_s is the sum of the values for pCa, pAlk, and C. In the example pH_s is 7.32. The saturation index I_s is the algebraic difference between the actual pH of the water and the calculated pH_s. Since the actual pH is 8 and the pH_s is 7.32, the saturation index I_s is +0.68.

When I_s is zero, the tendency to form scale is at a minimum. When I_s is positive, there is a tendency to form scale in the cooling system. The actual pH is then greater than the pH_s.

When I_s is negative, the water will tend to be on the corrosive side. In this case the actual pH in the cooling water is less than the calculated pH_s. In practice, maintain a slightly positive saturation index varying from 0.6 to 1.0 or higher in order to minimize corrosion.

The saturation index can also be used as a guide to predict the maximum allowable concentrations in an open-spray system and still avoid scale. The method of doing this is shown in the following example.

EXAMPLE 1. The analysis of the makeup water to a cooling tower is:

Calcium hardness = 39 ppm
M alkalinity = 28 ppm
Chlorides = 8 ppm
Total solids = 103 ppm

The analysis of the cooling tower recirculation water is:

Calcium hardness = 500 ppm
M alkalinity = 450 ppm
Chlorides = 160 ppm
Total solids = 2,000 ppm
pH = 7.8
Temperature = 100°F

Is the cooling tower recirculating water corrosive or scale-forming? What is the maximum allowable concentration that is possible while still ensuring against possible scale formation? The maximum allowable saturation index I_s is 1.0.

Use Fig. 10-10 to obtain the following data from the analysis of the cooling tower water.

pCa = 2.3
pAlk = 2.05
C at 100°F = 2.0
pH$_s$ = −6.35
Actual pH = +7.8
I_s (difference) = +1.45

Therefore, the cooling tower water definitely has scale-forming tendencies with a positive saturation index I_s of 1.45.

Next a series of trial calculations is needed to determine the maximum allowable concentration of recirculating water without exceeding a saturation index of 1.0. In the example above, all the items except pH of the makeup water are multiplied by a trial concentration factor. Then the saturation index is determined. The largest concentration factor that does not give a saturation index above 1 is then the maximum allowable concentration. In our example the cooling system can tolerate eight concentrations. The calculations follow:

Analysis	Makeup water	Calculated circulating water	
		Concentrated 8 times	Saturation index data
Ca hardness	39	312	pCa = 2.5
M alkalinity	28	224	pAlk = 2.39
Cl	8	64	
Total solids	103	824	C at 100°F = 1.96
pH (actual)	7.2	7.8	pH$_s$ = 6.85
Temperature		100°F	I_s = +0.95

11

Water Treatment for Air-conditioning Systems

Water is a vital part of practically every air-conditioning system. But along with its use go the common water problems of corrosion, scale, slime, algae, and organic growths. Fortunately, these troubles can be controlled by proper operation and chemical treatment.

In both once-through and closed cooling water circulating systems, chemical treatment alone is often sufficient to prevent trouble. But in an open-spray system, chemical treatment plus regulation of total solids by blowdown is usually required to control the formation of scale. Algae and other organic growths need chemical treatment and regular cleaning to keep them under control.

There is at least one major difference between treating most waters and treating the water used for cooling in an open-spray system. In the open-spray system, the cooling water spray is continuously contaminated by the air through which it falls. This must be considered before setting up a plan of treatment. Acid gases like carbon dioxide and sulfur dioxide are scrubbed into the recirculating water. In addition, algae, slime, bacteria, dirt, sand, and dust are carried by the air into the recirculating water. These contaminants aggravate the cooling water problems in an open-spray system. For example, acid gas in the air surrounding a cooling tower, in large enough amounts, can lower the pH of the circulating water and thus eat holes through the condenser in a few months. As a further example, organic growths often block the coils in the refrigerant condenser. Figures 11-1 and 11-2 illustrate corrosion and scaling of piping in the cooling system.

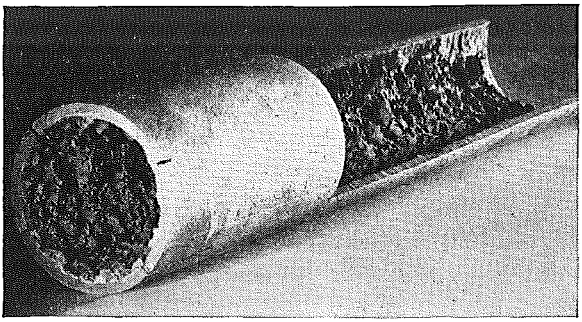


FIG. 11-1. Corroded and pitted section of pipe. (*Courtesy of The Permutit Company.*)

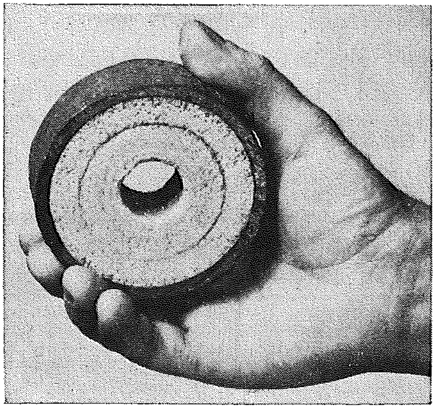


FIG. 11-2. Heavily scaled pipe section. (*Courtesy of The Permutit Company.*)

11-1. Common Treatment Chemicals. There are many chemicals commonly used to treat the water in air-conditioning systems. Each of these chemicals will be covered separately with an outline of its purpose, advantages, and disadvantages.

Chromates. Chromate compounds are most effective corrosion inhibitors. They are available in the following forms:

1. Sodium chromate, anhydrous, Na_2CrO_4
2. Sodium chromate crystals, $Na_2CrO_4 \cdot 4H_2O$
3. Sodium bichromate, $Na_2Cr_2O_7 \cdot 2H_2O$

Sodium bichromate is a slightly acid salt containing some water of crystallization. This compound is used when the pH of the water must be slightly lowered. Sodium chromate is a moderately alkaline salt available with and without water of crystallization. Table 11-1 summarizes these compounds and gives the conditions under which they are used. For example, cold water calls for a concentration of 200 ppm as Na_2CrO_4 to retard corrosion. If the water is hot, the dosage must be increased to about 500 ppm.

If a chilled calcium chloride brine solution is used, then the chromate concentration should be at least 1,800 ppm. For sodium chloride brine, increase the chromate to 3,500 ppm.

However, there are other considerations that may prevent the use of chromates. Since chromates are toxic, they can create a waste disposal problem. Some municipalities have actually passed laws that forbid the use of chromates in water that eventually discharges into the municipal waste disposal system. Cooling towers may be located so that windage sprays water on nearby objects such as cars on a parking lot. When the resulting deposit is white, it is hardly noticeable. But when chromates are used, the windage water is yellow. It then leaves a deposit that is also colored yellow. This frequently arouses strong complaints that may rule out the further use of chromates.

Caustic Soda. The chemical formula of this compound is NaOH. Since caustic soda is an alkali, it will neutralize acid salts and gases to increase the pH of the circulating water. If chromates

Table 11-1. Chemicals for Scale and Corrosion Control in Air-conditioning Systems

Chemical name	Formula	System	Problem	Concentration needed			pH range
				ppm	expressed as	lb/1,000 gal	
Sodium bichromate. .	$Na_2Cr_2O_7·2H_2O$	Chilled water	Corrosion	200	Na_2CrO_4	1.8	7.0 to 8.5
		Hot water		500	Na_2CrO_4	4.5	7.5 to 8.5
		Calcium chloride brine		1,800	Na_2CrO_4	16.1	7.5 to 8.5
		Sodium chloride brine		3,500	Na_2CrO_4	31.6	7.5 to 8.5
Sodium chromate (anhydrous)	Na_2CrO_4	Chilled water	Corrosion	200	Na_2CrO_4	1.7	7.0 to 8.5
		Hot water		500	Na_2CrO_4	4.2	7.5 to 8.5
Sodium chromate (crystal)	$Na_2CrO_4·4H_2O$	Chilled water	Corrosion	200	Na_2CrO_4	2.4	7.0 to 8.5
		Hot water		500	Na_2CrO_4	6.0	7.5 to 8.5
Sodium nitrite.	$NaNO_2$	Open spray	Corrosion	500	$NaNO_2$	4.2	7.5 to 8.5
Sodium sulfite.	Na_2SO_3	Hot closed	Corrosion	60	Na_2SO_3	0.5	7.5 to 8.5
Sodium hexametaphosphate	$(NaPO_3)_6$	Open- spray	Corrosion	20	PO_4	0.16	6.0 to 6.8
		Once-through	Corrosion†	5	PO_4	0.04	6.0 to 7.0
		All	Scale	5	PO_4	0.04	6.0 to 7.0
Sodium silicate (liquid)	$Na_2O/3·22SiO_2$	Open spray	Corrosion	30	SiO_2	*0.9	7.0 to 8.6
		Once-through		8	SiO_2	0.24	7.0 to 8.6
Sodium metasilicate. .	$Na_2SiO_3·5H_2O$	Open spray	Corrosion	30	SiO_2	0.9	7.0 to 8.6

* 0.9 lb liquid sodium silicate is about 0.3 qt; 0.24 lb, about 0.08 qt.

† Corrosion in so far as reducing iron oxide products, tuberculation, and red (rusty) water.

are added to inhibit corrosion, maintain the pH of cold circulating water at a minimum value of 6.5. If the circulating water is hot, the pH should be at least 7.5.

Sodium Nitrite. This compound, formula $NaNO_2$, is an effective corrosion inhibitor in open circulating systems. However, it is not as reliable or as effective as the various chromate compounds for this. Sodium nitrite is a white salt, colorless in water, that can be considered nontoxic for water purposes. Therefore, it is used whenever chromates are considered objectionable. For effective corrosion control, maintain at least 500 ppm of sodium nitrite with a pH of about 7.5. Table 11-1 includes the recommended quantities and conditions for sodium nitrite.

Polyphosphates. These are widely used for scale and corrosion control in practically all types of cooling water systems. The varieties include sodium hexametaphosphate, sodium tetraphosphate, sodium tripolyphosphate, and sodium decaphosphate.

Polyphosphates in the range of 2 to 5 ppm are particularly effective in reducing the amount of iron oxide–corrosion products that tend to clog distribution lines. They also help eliminate red (rusty)-water troubles in once-through cooling systems. In spite of these benefits the corrosion rate may not be appreciably reduced. To reduce the corrosion rate in open-spray systems, it is desirable to add polyphosphates to obtain 15 to 20 ppm at a controlled pH. Effective corrosion protection can also be obtained by using polyphosphates in conjunction with smaller-than-usual amounts of chromate at a controlled pH.

Scale is also controlled by the addition of polyphosphates. The chief scale-forming ingredient in cooling-water circuits is calcium carbonate. The polyphosphates belong to a class of surface-active materials that increase the apparent solubility of scale-forming salts. That is, they keep calcium carbonate crystals in solution and do not allow them to precipitate and form scale. This property of polyphosphates is very effective in scale prevention programs.

The chemical composition of the circulating cooling water is also extremely important in controlling scale. Not every problem can be solved by chemicals like the polyphosphates. If the hardness of the water is high, scale will form despite this chemical treatment. In once-through cooling systems, cost considerations make it uneconomical to change the composition of the cooling water. In open-spray cooling systems where recirculating water concentrates, the total solids must be kept under control to prevent scale. This is accomplished by controlling the amount of system blowdown in conjunction with the use of polyphosphates and other chemicals.

The amount of polyphosphate required for effective corrosion or scale control may be as little as 2 ppm. But this class of compound is somewhat unstable. In water, polyphosphates tend to change to the orthophosphates. The typical chemical reaction for this is

$$\underset{\text{Polyphosphate}}{(NaPO_3)_6} + \underset{\text{water}}{6H_2O} = \underset{\text{orthophosphate}}{6NaH_2PO_4} \qquad (11\text{-}1)$$

Table 11-1 shows the recommended amount of sodium hexametaphosphate. Start off by feeding from 5 to 10 ppm polyphosphate at a continuous rate. Then make regular tests for both the orthophosphate and the total phosphate in the treated water. The difference between these two figures is the polyphosphate. Finally, adjust the feed rate to keep a minimum of 2 ppm polyphosphate at all times. Bear in mind that many other factors also influence the results obtained with polyphosphate. Among these is the flow rate of treated water through the piping as well as the temperature and composition of the water. Sodium hexametaphosphate also requires a pH in the range of 6.0 to 7.0. If the circulating-water pH is lower than 6.0, add caustic soda. If the pH is more than 7.0, acid may be needed to drop the pH back into the desired range.

Sodium Sulfite. The chemical formula of this compound is Na_2SO_3. It will quickly remove dissolved oxygen from hot water. The reaction for this is

$$\underset{\text{Sodium sulfite}}{2Na_2SO_3} + \underset{\text{dissolved oxygen}}{O_2} = \underset{\text{sodium sulfate}}{2Na_2SO_4} \qquad (11\text{-}2)$$

Since dissolved oxygen is one of the main causes of corrosion, sodium sulfite is very effective in preventing corrosion in hot, closed circulating systems. An excess sodium sulfite of at least 60 ppm is necessary. Smaller residuals may be satisfactory but 60 ppm ensures removal of all the dissolved oxygen. If no oxygen is present, the metal equipment will not corrode. Sodium sulfite is a white compound, colorless in water, that can be considered nontoxic for water treatment. Therefore, it also has possibilities in systems where chromates are definitely objectionable. But, sodium sulfite and chromate cannot be fed in combination because they react with each other and nullify their individual usefulness in treatment.

One limitation of sodium sulfite is a very slow reaction time in cold water. Therefore, sulfite does not give effective protection in chilled-water systems. There is a grade of catalyzed sodium sulfite that will react better with dissolved oxygen in cold water. But this special chemical is relatively expensive and is not commonly used for closed chilled-water systems.

Silicates of Sodium. Many silicates provide corrosion control for once-through and open-spray cooling systems. Two typical compounds are listed in Table 11-1. The liquid sodium silicate consists of 1 part of Na_2O to every 3.22 parts of SiO_2. In solid form the sodium metasilicate formula is $Na_2SiO_3 \cdot 5H_2O$. Although sodium silicate is not as effective as chromate for corrosion control, it is much more economical, colorless in water, and nontoxic. Therefore, it is used where chromates may be too costly or where they are objectionable because of their yellow color or toxicity.

In open-spray systems, start treatment by feeding enough silicate to maintain about 70 ppm as SiO_2 in the circulating water. Continue feeding this amount for the first few weeks to establish a protective film. Then the concentration can be dropped to a minimum of 30 ppm as SiO_2. For maximum corrosion protection, maintain the pH between 7.0 and 8.6. The grade of liquid sodium silicate listed in Table 11-1 is less alkaline than sodium metasilicate. Therefore, if the pH is too high with sodium metasilicate crystals, switch to liquid sodium silicate. On the other hand, if the pH is too low with liquid sodium silicate, substitute sodium metasilicate. If the pH is still too low, use caustic soda or soda ash to reach the desired level.

The chemical composition of the circulating water is also very important. The magnesium hardness should not exceed 150 ppm as $CaCO_3$. Any higher amounts will reduce the protective action of the silicates. About 30 to 40 ppm SiO_2 gives good corrosion protection in waters containing up to 500 ppm chlorides. Keep the pH below the upper limit of 8.6 to avoid any damage to the protective silicate coating.

In once-through cooling water that is fairly soft, about 8 ppm of sodium silicate is generally sufficient for corrosion control. When the water is soft, the sodium silicate is preferred over the polyphosphate.

Slimicidal Chemicals. These are called for when slime or algae are a problem in open-spray-type cooling systems, which is frequently the case. Three common chemicals in this class are sodium hypochlorite, calcium hypochlorite, and sodium pentachloraphenate. The sodium hypochlorite is available in various strengths. Calcium hypochlorite comes in powder or tablet form. Sodium pentachloraphenate is prepared in both powder and pellet form. Table 11-2 gives the dosage required for shock treatment with these chemicals. Since both slime and algae can develop forms immune to continuous treatment, it is better to feed a killing

Table 11-2. Common Chemicals for Slime and Algae Control

Common chemical name	Chemical composition	Shock treatment dosage per 100 gal
Household bleach. .	5.25% NaOCl by weight	2 fl oz
Laundry bleach. . .	14.11% NaOCl by weight	0.6 fl oz
	16.8% NaOCl by weight	0.5 fl oz
HTH, granular	70% available Cl by weight of $Ca(OCl)_2$	0.135 oz
tablets		1 tablet
Dowicide G or Santobrite	Sodium pentachlorophenate in powder or pellet form	4 oz

dose at regular intervals. This method of feed is known as shock treatment. In addition, the chemicals should be varied from time to time.

Sodium hypochlorite or calcium hypochlorite cannot be used in air washers. Both chemicals impart a chlorine odor that is objectionable in the air-conditioned space. There is still much to be learned about slime and algae prevention in open-spray cooling water. Chemical treatment alone does not eliminate these growths, and regular cleaning is still necessary to keep the system clean.

11-2. Corrosion Control for Once-through Cooling Water. Before starting any chemical treatment for corrosion or scale control, collect all the data outlined in Chap. 4, A Blueprint for Efficient Water Treatment. The material balance in gallons of water flow sheet calls for the pumping rate through the condenser and the number of hours of operation. This gives the total water usage in gallons. On the flow diagram (chemical balance of the raw-water changes) show the temperature and chemical analysis of the untreated water entering and leaving the condenser. With this information the Langelier Saturation Index of the warm water can be calculated.

Then, using these data, prepare the final flow diagram showing the pounds of treating chemicals required on a daily basis or per thousand gallons of water. This diagram should show in detail the feeding equipment needed to add the chemical on a continuous basis. Once treatment is started, keep a control record and make regular check analyses on the treated water.

The main problem in corrosion or scale control in a once-through system is the cost of treatment because of the large amounts of water involved. For example, 200 to 500 ppm chromate will give excellent corrosion protection in a majority of cases. However, the cost of maintaining this dosage in a once-through cooling water is completely impractical. Another possibility is mechanical deaeration followed by sodium sulfite to remove the last traces of oxygen. But this usually means considerable investment in equipment.

From a cost standpoint, only those chemicals that give reasonable protection with small chemical dosages can be considered. Both the polyphosphates and sodium silicate meet this requirement. About 5 to 10 ppm polyphosphate is needed. If silicates are used, about 8 ppm as SiO_2 gives adequate protection. The silicate treatment is preferred when the water is very soft. If the water causes tuberculation and the pipelines clog with rust, polyphosphates are usually recommended. Example 1 shows how a typical corrosion problem can be handled.

EXAMPLE 1. The water in a once-through cooling system is causing extensive corrosion. A check of the water composition, temperature, and Langelier Saturation Index confirms the water's corrosive qualities.

The following data on the cooling water are available:

Ca hardness — 200 ppm	pCa	= 2.7
M alkalinity — 125 ppm	pAlk	= 2.6
Total solids — 300 ppm	C at 50°F	= 2.5
Temperature 50°F	pH_s	= 7.8
pH (actual) — 6.5	pH	= 6.5
	I_s	= −1.3 (corrosive)

What treatment is needed to minimize corrosion in the cooling-water circuit? Since the water can be classified as a hard water and the pH is in the proper range for polyphosphate treatment, use sodium hexametaphosphate. Add enough to maintain at least 2 ppm in the circulating water. Water is pumped through the condenser 10 hr a day at the rate of 300 gpm. A proportioning-type pump is available to feed liquid chemical solution from a 50-gal cylindrical tank.

The flow of water that must be treated is 300 gpm or 18,000 gal per hour. This amounts to a total of 180,000 gal every 10-hr day. Next, calculate the amount of polyphosphate in pounds needed to produce a concentration of 5 ppm. Since 120 ppm equals 1 lb per thousand gallons, 5 ppm polyphosphate is equal to 5 divided by 120, or 0.0417 lb per thousand gallons. The hourly phosphate dosage is then 18,000 multiplied by 0.0417 lb per thousand gallons, or 0.75 lb per hour. The amount of phosphate needed on a typical day is then 10 multiplied by 0.75, or 7.5 lb.

The 50-gal cylindrical tank is 21 in. in diameter and about 36 in. high. This tank has already been calibrated and contains 1.5 gal of water per inch. First, add 25 in. of water to the tank and then weigh out 7.5 lb of the hexametaphosphate in a wire basket. Put the basket into the tank just below the surface of the water and wait until all the chemical dissolves. Next, fill the tank with water to the 30-in. mark and stir the solution. Set the proportioning pump to deliver 3 in., or 4.5 gal, per hour. This flow of chemical solution will deliver 0.75 lb of hexametaphosphate per hour to the cooling water.

At the end of 10 hr, when the system is shut down, make up new chemical solution for the next day. After the pump has been running for about an hour, test the treated water every day for both total and orthophosphate concentration. Then calculate the concentration of polyphosphate. If the polyphosphate is too high (over 10 ppm), reset the proportioning pump to deliver less chemical. If the polyphosphate is too low (less than 2 ppm), increase the pump stroke to deliver more chemical. Make regular entries daily on the control record to show the amount of chemical used, gallons of water consumed, and the results of the tests for phosphate.

11-3. Scale Control for Once-through Cooling Water. The chief ingredient of scale in once-through cooling water systems is usually calcium carbonate. The main reason for this is that calcium carbonate is less soluble than the other minerals usually found in water. The formation of scale depends on the temperature increase of the cooling water passing through the condenser, the rate of heat transfer, and the chemical composition of the water. Calcium carbonate scale can be quickly identified by scraping off some of the deposit from the equipment and testing it with hydrochloric acid. Place a small amount of the scale in a test tube. Then add a few drops of concentrated hydrochloric acid. If there is a violent production of gas bubbles, calcium carbonate is probably the main ingredient of the scale deposit. The concentrated hydrochloric acid can also be used for this test when diluted with an equal amount of distilled or tap water.

Surface-active materials are most commonly used to prevent calcium carbonate scale formation. Among these compounds are the inorganic polyphosphates and such organic materials as starch, tannin, and lignin. When surface-active chemicals are added to the water, they increase the solubility of the scale-forming salts. This delays the production of calcium carbonate crystals and also prevents their growth.

In a moderately hard water, 2 to 5 ppm of polyphosphate often prevents scale formation completely. But if calcium carbonate scale still persists, the addition of more polyphosphate has little or no effect. It is then advisable to feed an organic material in combination with the polyphosphate. The organics actually extend the range of effective scale prevention beyond that of the polyphosphates. The amount of calcium and bicarbonate present and the temperature of water leaving the condenser—all affect the quantity of organic material needed to effectively prevent scale. Since cost is a major factor with materials of this type in a once-through system, the organic dosage is usually less than 50 ppm.

Some well waters contain appreciable amounts of ferrous (iron) bicarbonate. This impurity forms iron deposits in piping and in the condenser. Surface-active materials are also very useful in preventing this type of deposit. But the organic materials are usually superior for this purpose. Since iron problems are very tricky, be sure to consult with a water-treating specialist on this phase of the cooling water problem.

As usual, before starting treatment, collect all the operating and analytical data needed to solve the problem. The important information required for the once-through cooling system is outlined in Sec. 11-2. Example 2 illustrates the solution of a typical scale control problem.

EXAMPLE 2. A few months after starting polyphosphate treatment of the once-through cooling water in Example 1, a calcium carbonate scale was found on the water side of the condenser.

This scale formed even though 5 ppm of polyphosphate was maintained continuously in the cooling water. However, a check of the water composition, temperature leaving the condenser, and the Langelier Saturation Index showed considerable changes in these items. The new data indicate that the water is now scale-forming.

Ca hardness —300 ppm	pCa	= 2.5
M alkalinity —300 ppm	pAlk A	= 2.2
Total solids —500 ppm	C at 80°F	= 2.14
Temperature— 80°F	pH_s	= 6.84
pH (actual) — 7.9	pH	= 7.9
	I_s	= +1.06 (scale-forming)

Since 5 ppm polyphosphate is not enough to prevent the formation of scale, additional organic treatment is needed. About 10 ppm of tannin added to the 5 ppm polyphosphate should stop formation of the calcium carbonate scale. The 10 ppm of tannin is equivalent to 0.0833 lb per thousand gallons. On an hourly basis, the quantity of tannin needed equals 18,000 multiplied by 0.0833 lb per thousand gallons, or 1.50 lb. For a 10-hr day, this amounts to 15.0 lb.

Dissolve the 15.0 lb of tannin in a pail of hot water. Then pour this solution into the 50-gal tank containing the polyphosphates. Add enough water to the combined solution of polyphosphate and tannin to bring the level up to the 30-in. mark. Again set the proportionating pump to deliver 3 in., or 4.5 gal, per hour. This rate will deliver 5 ppm polyphosphate and 10 ppm tannin to the cooling water. Make regular control tests of the phosphate in the treated water. This should be sufficient to regulate the feed rate of both the phosphate and the tannin.

11-4. Water Treatment for Closed Recirculating Cooling Water. In a closed recirculating system, the cooling water is pumped through a chiller or heat exchanger to a series of pipes and coils and then back again to the chiller. The essential parts of a closed chilled-water recirculating system are shown in Fig. 10-2. Once a closed system has been filled with water, there is very little need for makeup. Fresh water is added only to compensate for pump gland leakage or other abnormal water losses. For example, there may be a leak in a coil or perhaps a continuous overflow from the expansion tank.

The water in a closed recirculating system does not evaporate. Therefore, the dissolved minerals do not concentrate. The recirculating water is kept within a series of pipes and coils and does not come into contact with the atmosphere. Therefore, acid gases are not absorbed from the air. When the water is chilled, as it circulates, hardness will not normally precipitate. If the water is heated hot enough, a very small quantity of scale may form. But, in general, the chemical composition of the water changes very little as it circulates through a closed system.

One of the main advantages of the closed recirculating cooling system from a treatment standpoint is that scale and corrosion problems are materially reduced. Also, there is no problem with slime or algae. The main problem in a closed system is usually corrosion from dissolved oxygen in the water. If the system is watertight and very little fresh water is added, the oxygen in the water is quickly used up and further corrosion will not take place. But closed recirculating systems, made up of pipes, coils, valves, and strainers, are very sensitive to clogging, and even a small amount of corrosion is objectionable. Furthermore, few closed systems are completely watertight. Therefore, some dissolved oxygen enters the system with the fresh-water makeup. In addition, if the closed system is heated, the rate of corrosion is increased. Thus, there is always need for corrosion control.

Chromates are practically the standard treatment for corrosion prevention in a closed recirculating system. The chromate compound called for varies with the composition of the water. For example, if the system is filled with distilled or very soft water, the slightly alkaline sodium chromate is preferred. When the water is hard and alkaline, use the slightly acid sodium bichromate to keep the hardness in solution.

Table 11-1 shows the quantity of chromate needed for different conditions. Although pH is not very critical when chromates are used in a closed system, this table does show the most beneficial ranges. When the pH is too low, the rate of corrosion is increased. If it is too high and the water is hard, scale formation is encouraged. High pH can be avoided by using sodium bichromate for corrosion control.

Sodium sulfite can be used as an alternative treatment since dissolved oxygen is the main cause of corrosion. This compound reacts very slowly with oxygen in a low-temperature chilled-water system. But it is much more efficient in hot closed-water systems. An excess sulfite of about 60 ppm is usually sufficient. Start with a dose that is twice the amount shown in Table 11-1. When the sulfite drops below 60 ppm, the amount listed in Table 11-1 is enough. Use sulfite in those areas where chromates may be objectionable. As already pointed out, sodium sulfite and the chromates react with each other and should never be used together.

Every closed recirculating system needs some fresh-water makeup. If the water is chilled in the system, there is very little danger of scale formation even when the makeup is fairly hard. But if the water is heated, there is a danger of gradual scale build-up. Since high pH favors scale formation, it should also be avoided.

Table 11-1 summarizes the conditions under which various chemicals are used in a closed recirculating system. Very little makeup is required. A closed system is not usually blown down. The initial chemical requirement is based on the gallons of water held in the system. If water losses are kept at a minimum by control of pump gland or other leaks, additional chemical will be infrequently needed and will be very small in amount. If the volume of water held by the system is not known, it can be calculated by any of the methods given in Chap. 5. The sodium chromate used for corrosion control usually does not react with any of the minerals already in the water. Thus it can also serve as a tracer chemical, with Table 11-1 being used to calculate the volume of water in the system. However, before using chromate as a tracer, be sure that the system is clean and does not contain organic matter like pipe dope. Chromate can be lost by reaction with organic matter of this general type.

EXAMPLE 3. Treat a chilled-water closed recirculating system with chromate to prevent corrosion. The exact volume of water held in the system is not known. However, rough calculations based on the size of the piping and the condenser indicate that the system contains about 1,000 gal of water. The makeup supply is soft, containing only 20 ppm total hardness with a pH of 6.5. Maintain at least 200 ppm of Na_2CrO_4 in the system. Crystal sodium chromate, $Na_2CrO_4 \cdot 4H_2O$, is available. Use about 600 ppm or more as the initial chemical dose. This gives enough excess chemical to allow for some water losses and considerably lengthens the time between charges.

Table 11-1 shows that 2.4 lb of $Na_2CrO_4 \cdot 4H_2O$ is needed per thousand gallons to maintain 200 ppm as Na_2CrO_4. Therefore, three times as much chemical is needed to produce 600 ppm as Na_2CrO_4. This equals 7.2 lb $Na_2CrO_4 \cdot 4H_2O$ per thousand gallons. Next, add this amount and analyze the water in the system for chromate. This analysis shows a chromate content of 1,200 ppm as Na_2CrO_4, or twice as much as expected. Therefore, the volume of water in the system is about 500 gal and not the 1,000 gal originally estimated. This relation can be expressed mathematically in the same manner shown in Chap. 4, Eq. (4-7).

$$C_1V_1 = C_2V_2 \tag{11-3}$$

where C_1 = concentration in ppm if system volume is 1,000 gal
V_1 = estimated vol of 1,000 gal
C_2 = concentration in ppm from an actual analysis
V_2 = calculated vol of water contained in the system

Once every week run an analysis to determine the loss of chromate. It took 5 months for the concentration to fall below 200 ppm. Then add 3.6 lb. of $Na_2CrO_4 \cdot 4H_2O$ to the 500 gal of water in the system. This increases the chemical concentration to 750 ppm as Na_2CrO_4.

11-5. The Open-spray Cooling System. The water spray comes into close contact with air in going through the system. Soluble gases in the air dissolve and concentrate in the recirculating spray water. In most large cities or industrial areas, the air may be highly polluted with acid gases. The result is highly acid spray water in the cooling tower, evaporative condenser, or air washer, that severely corrodes the metal sections of this equipment in a very short time.

In addition, air-borne dirt, debris, algae, or slime may clog condensers. These impurities may also cause the water to foam and interfere with proper water recirculation. Therefore, chemical treatment must take into account acid gases and other damaging impurities in the surrounding air. Both these factors definitely affect the composition of the water circulating in the system.

The air washer cools warm, humid air by passing it over chilled water coils. The cooled air in turn loses its moisture; the whole process is commonly referred to as *dehumidification* of the air. Droplets of distilled water are formed, which increase the total volume of water in the air washer. On a hot, humid day the water in the air-washer pan can rise quickly to the overflow pipe and go out to waste. Any chemicals in this water also go to waste. For this reason, the treatment plan must account for the moisture in the air that may be removed by dehumidification. Dehumidification can also take place in an air washer without chilled-water coils. The spray water may be chilled and in turn cool the warm, humid air, causing dehumidification and overflow to waste.

In any open-spray system, tonnage, evaporation, windage, blowdown, and other mechanical losses are all related to the number of concentrations in the circulating water. Evaporation and windage loss usually vary with the tonnage, hours of operation, and type of equipment. If the system is tight (no leaks), evaporation and windage loss determine the normal number of concentrations of the recirculating stream. If the normal concentration is too high, it can be reduced by blowdown. The relation between evaporation, windage, blowdown, and number of concentrations is shown in Eqs. (11-4) and (11-5). Example 4 shows how these equations are used.

$$B = \frac{E - W(C - 1)}{C - 1} \tag{11-4}$$

$$C = \frac{E + W + B}{W + B} = \frac{M}{W + B} \tag{11-5}$$

Where B = blowdown rate, gpm
E = evaporation rate, gpm
W = windage rate, gpm
C = number of concentrations
M = total makeup

EXAMPLE 4. A 50-ton mechanical-draft cooling tower operates under the following conditions:

Circulation rate = 150 gpm
Evaporation loss (E) = 1.5 gpm (1% of circulation rate)
Windage loss (W) = 0.225 gpm (0.15% of circulation rate)
Total makeup ($E + W$) = 1.725 gpm
Total makeup due to windage, % = 0.225/1.725 × 100 = 13%
Total makeup due to evaporation, % = 1.5/1.725 × 100 = 87%

The normal number of concentrations without blowdown is calculated from Eq. (11-5) by setting the value of B at zero.

$$C = \frac{1.5 + 0.225 + 0}{0.225 + 0} = \frac{1.725}{0.225} = 7.7$$

Therefore, the normal number of concentrations in this cooling tower is 7.7. This is the resulting concentration when blowdown and other mechanical losses are zero. But to avoid scale formation, the number of concentrations must not exceed four. This means that blowdown must be employed. The amount can be calculated from Eq. (11-4) using four concentrations as the value of C.

$$B = \frac{1.5 - (0.225 \times 3)}{3}$$

$$3B = 1.5 - 0.675 = 0.825$$

$$B = 0.275$$

Therefore, the blowdown required to produce just four cycles of concentration in the cooling tower is 0.275 gpm.

The chemical composition of the recirculating water under actual operating conditions determines whether or not it is corrosive or scale-forming. This can be predicted by calculating the Langelier Saturation Index of this water. An index of +0.6 or less indicates that the recirculating water has a tendency to be corrosive. A positive saturation index of 1.0 or higher indicates a tendency to scale formation. However, with correct chemical treatment and regulation of blowdown, the corrosive and scale-forming tendencies of the recirculating water can be changed. The Langelier Saturation Index can be used to determine the ideal chemical composition of the circulating water. This is explained in the following example.

EXAMPLE 5. The makeup and the untreated recirculating water in the cooling tower have the following analysis:

	Makeup	Untreated recirculating water
Ca hardness	39 ppm	750 ppm
M alkalinity	28 ppm	280 ppm
Total solids	100 ppm	2000 ppm
Cl	8 ppm	160 ppm
pH	6.5	5.5

The maximum temperature of the water leaving the refrigerant condenser is 110°F. The following information is needed:

1. Is the untreated recirculating water corrosive or scale-forming?
2. If the pH of the untreated recirculating water is adjusted with caustic to 7.5, will the water then be scale-forming or corrosive?
3. What is the most satisfactory composition of the water so that it will not be corrosive or scale-forming by Langelier Index calculations?

In general, the recirculating-water pH should be about 7.5. The index to avoid corrosion or scale should be in the range of +0.6 to +1.0.

Water analysis		*Langelier Index calculations, untreated recirculating water*	
Ca hardness	= 750	*p*Ca	= 2.12
M alkalinity	= 280	*p*Alk	= 2.23
Total solids	= 2,000	*C* at 110°F	= 1.9
Cl	= 160	pH_s	= 6.25
pH	= 5.5	pH	= 5.5
Number of concentrations	= 20	I_s	= −0.75 (corrosive)

At a pH of 5.5 the untreated recirculating water tends to be corrosive. But the pH can be adjusted with caustic. Increasing the pH to 7.5 also increases the *M* alkalinity and tends to make the pH_s less than 6.25. The result is a positive index greater than +1.25 (7.5 − 6.25), definitely indicating a tendency to form scale. From these facts it can be seen that the most satisfactory composition of recirculating water is obtained with less than 20 concentrations if scale formation is to be avoided. Trial calculations at 15, 10, 7, and 6 concentrations give the following results:

(1) *Makeup after 15 Concentrations*		*Langelier Index calculations*	
Ca hardness	= 585 ppm	*p*Ca	= 2.22
M alkalinity	= 420 ppm	*p*Alk	= 2.09
Total solids	= 1500 ppm	*C* at 110°F	= 1.89
Cl	= 120 ppm	pH_s	= 6.20
pH	= 7.5	pH	= 7.5
		I_s	= +1.3

(2) *Makeup after 10 Concentrations*		*Langelier Index calculations*	
Ca hardness	= 390 ppm	*p*Ca	= 2.40
M alkalinity	= 280 ppm	*p*Alk	= 2.24
Total solids	= 1000 ppm	*C* at 110°F	= 1.88
Cl	= 80 ppm	pH_s	= 6.52
pH	= 7.5	pH	= 7.5
		I_s	= +0.98

(3) *Makeup after 7 Concentrations*		*Langelier Index calculations*	
Ca hardness	= 273 ppm	*p*Ca	= 2.58
M alkalinity	= 196 ppm	*p*Alk	= 2.40
Total solids	= 700 ppm	*C* at 110°F	= 1.86
Cl	= 56 ppm	pH$_s$	= 6.84
pH	= 7.5	pH	= 7.5
		I_s	= +0.66

(4) *Makeup after 6 Concentrations*		*Langelier Index calculations*	
Ca hardness	= 234 ppm	*p*Ca	= 2.65
M alkalinity	= 168 ppm	*p*Alk	= 2.48
Total solids	= 600 ppm	*C* at 110°F	= 1.85
Cl	= 48 ppm	pH$_s$	= 6.98
pH	= 7.5	pH	= 7.5
		I_s	= +0.52

On the basis of these calculations, it appears that the best recirculating water composition has 7 to 10 concentrations with a pH of 7.5. In this range it is expected that the water will not be corrosive or scale-forming.

11-6. Treating Water in an Open-spray Cooling System. As in every water treatment problem, first make the survey and construct enough flow diagrams. Then select the treatment needed and finally set up a control system. The following steps show how to organize the data for treatment of an open-spray system.

STEP 1. Check the cooling system carefully to eliminate all mechanical water losses. Calculate the amount of makeup and the number of concentrations. Find the blowdown by direct measurement. Then use Eqs. (11-4) and (11-5) to calculate actual evaporation, windage, and other losses. Since evaporation varies directly with the load on the system, calculate all these variables for full load conditions. If the cooling tower is tested on a mild day when the compressors are not running, the evaporation loss is practically zero.

Be sure to check both evaporation and windage against the typical figures given for this type of equipment in Chap. 10. Look for differences in these data that are unusually large or small, to uncover any abnormalities in the system. For example, if the actual windage is unusually high, check carefully for abnormal water losses. A pump may be leaking excessively, or perhaps a badly adjusted float valve is causing overflow from the pan.

STEP 2. Chemically analyze both the makeup and the recirculating water. Then calculate the Langelier Saturation Index. Make sure that the water analysis includes pH, calcium hardness, total alkalinity, chlorides, sulfates, and total solids. Next, select the best composition for the recirculating water. As shown in Example 5, water with the right composition will not be corrosive or scale-forming. It will have a saturation index in the range of +0.6 to +1.0. If the pH of the recirculating water is 7.5, use this to calculate the index. If the pH is much below 7.5, add caustic soda to increase the alkalinity and pH of the recirculating water to bring the index into a better range that will avoid corrosion. Calculate the Langelier Saturation Index at the adjusted pH with the increased amount of alkalinity. If the recirculating water pH is higher than 7.5, use the actual pH to calculate the index.

STEP 3. Compare the actual composition of the recirculating water with the desired composition. If there is a difference, adjust the number of concentrations so that the actual analysis is close to the desired range. For example, if the number of concentrations is too high, increasing the blowdown will reduce the concentrations to the proper range. Then use Eq. 11-4 to calculate the revised amount of blowdown.

STEP 4. Select the treatment chemicals and the concentrations needed to minimize corrosion, scale formation, organic growths, and other problems. Calculate the amounts of chemical needed using the windage and blowdown losses given in Chap. 10 for typical cooling systems.

Choose feeding equipment that will add the chemicals continuously into the recirculating system. Fig. 11-3 shows a proportioning hydraulic feeder treating cooling tower recirculating water. The feeder is actuated by water taken from the cooling tower return line, and it feeds chemicals continuously at a controlled rate only when the circulating water pumps are in operation. Proportionating pumps complete with open chemical tanks are widely used. The chemical pumps start when

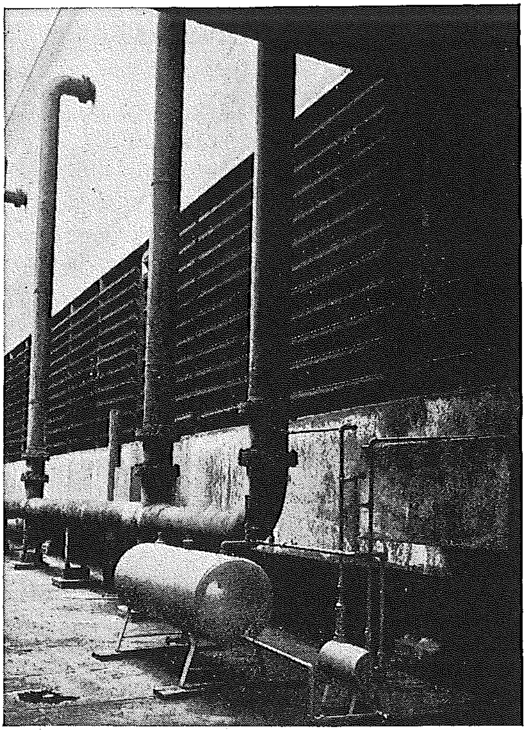


FIG. 11-3. Proportioning hydraulic feeder treating cooling tower recirculating water. (*Courtesy of Water Service Laboratories.*)

Air-conditioning Water Treatment Control Record

Name of Co. .... Date ....
Type of unit .... Location ....
Feeding equipment for chemical treatment ....
Circulation rate, gpm .... Tons ....
Hours of operation per month .... Per day ....
Windage loss, gpm .... Gallons per month ....
Blowdown loss, gpm ....
Satisfactory cycles of concentration range ....
Max. allowable chlorides (establish or increase blowdown if the chlorides are higher) ....
Reduce blowdown if chlorides are lower than ....

DOSAGE SCHEDULE

Chemicals needed	Maintain dosage, lb per month
Chemical A	
Chemical B	
Chemical C	

Remarks ....
....
....
....

Date	Blow-down, gpm	Feed settings	Lb chemical charged	Chemical analysis			Remarks
				pH	Cl	Chemical treatment	

Fig. 11-4. Typical form of air-conditioning water treatment control record.

the cooling tower sprays operate and stop when the sprays are off. Other types of specialized chemical-feeding equipment are also being used successfully.

STEP 5. Once it is decided to maintain a given pH and chemical concentration in an open-spray system, these operating conditions must be kept under continuous control for complete protection. This means keeping a complete set of records such as shown in Fig. 11-4. Periodic tests for pH, chlorides, and residual of treatment chemical are required. Record the results of these tests on the control record. In addition, note the amount of chemicals added, quantity of blowdown, and any adjustments made on the feeding equipment.

11-7. Corrosion Control for Open-spray Systems. Since the recirculating water in an open-spray system always has intimate contact with the surrounding air, acid gases and oxygen are washed into the water. As a result, corrosion is a major problem. If enough acid gases are in the air, the pH of the recirculating water rapidly drops to the range of 3 to 4. Such a low pH means a very corrosive water that can ruin iron and copper equipment in a short time. Therefore, carefully regulate the pH to avoid any acid conditions in the recirculating water. If no other chemical treatment is used, the desired pH varies from 7.5 to 8.5.

A control system for pH in an open-spray system has one major difference compared with a control system for other kinds of water treatment. The acid gases contained in the recirculating water were not originally present in the makeup. They find their way into the water from the surrounding air. For this reason, an analysis of the makeup water is not much help in predicting the acidity or alkalinity of the recirculating water. The amount of caustic or other alkali added is then determined by trial and error rather than by calculation. Analyze the untreated recirculating water for pH under operating conditions. If the pH is very low, caustic or alkali is needed. If the pH is already within the desired range, caustic or other alkali is *not* needed. If caustic is needed, estimate a trial quantity per thousand gallons of water loss. If the trial dosage does not increase the pH high enough, increase the amount of caustic. If the pH goes too high, cut the trial caustic dosage.

An open-spray system is continuously aerated. Therefore, it always contains plenty of dissolved oxygen. Since oxygen is usually the main cause of corrosion in an open-spray system, use chemical inhibitors to counteract the attack. Chromate is the most effective and most commonly used corrosion inhibitor for open-spray systems. The circulating water is usually not hot. Therefore, a minimum of 200 ppm of Na_2CrO_4 gives enough corrosion protection. With chromates a pH of 6.5 or higher is satisfactory for good corrosion protection.

Polyphosphates, silicates, and nitrites also inhibit corrosion. These compounds are described in some detail in Table 11-1. Although they are not as effective as the chromates, both polyphosphates and silicates are not as expensive. If cost is the major factor, they can be used in place of chromate. If cost is not a factor but chromates cannot be used because of their poisonous character or other objectionable features, nitrites are used. Various combinations of inhibitors are also added. One such dual treatment involves the feeding of metaphosphate and inorganic chromate. Chromates can be combined also with organic materials. However, do *not* use any of the substitutes for chromate without adequate advice from a water treatment specialist.

The following example shows how to solve a typical corrosion problem in an open-spray system.

EXAMPLE 6. A mechanical-draft cooling tower system must be protected against corrosion. First make a survey and construct the required flow diagrams. Then step by step assemble the information as outlined in Sec. 11-6:

STEP 1. Compile data on the system

Rating	= 50 tons
Operation time per month	= 600 hr

Ton—hours per month = 30,000
Total makeup from meter readings = 56,842 gal per month
Number of concentrations = 20
Actual windage loss ($W = M/C$—see Eq. 10-3) = 2,842 gal per month
Actual evaporation loss ($E = M - W$—see Eq. 10-2) = 54,000 gal per month
Expected normal number of concentrations = 7.7
Expected normal windage loss (see Table 10-3) = 8,100 gal per month
Expected normal evaporation loss (see Table 10-1) = 54,000 gal per month

These data show that the windage loss from the cooling tower is much less than originally expected.

STEP 2. The composition of the makeup and the recirculating water is the same as that shown in Example 5. Example 5 also shows that the best recirculating-water composition which will minimize scale formation and corrosion lies between 7 and 10 concentrations with a pH of 7.5.

STEP 3. With the actual windage loss of 2,842 gal per month, the number of concentrations is 20 and scale formation is indicated. With the expected normal windage loss of 8,100 gal per month, concentration is 7.7, which is in the desired range (7–10) to minimize scale and corrosion, if pH is 7.5. The difference between the desired water loss per month and the actual windage loss determines the amount of blowdown required. On this basis, the blowdown per month equals 8,100 minus 2,842, or 5,258 gal. This is 0.146 gpm. The blowdown is usually expressed in gallons per minute. It is set to run continuously to waste while the tower is operating.

STEP 4. Table 11-1 shows that 1.8 lb of sodium bichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) per thousand gallons is needed to obtain a minimum of 200 ppm as Na_2CrO_4 in the recirculating water. To maintain this level at all times, sodium bichromate is fed at the rate of 400 ppm, or 3.6 lb, $Na_2Cr_2O_7 \cdot 2H_2O$ per thousand gallons. Since the total water loss desired is 8,100 gal per month, the dosage of sodium bichromate equals 29.2 lb per month. By trial and error, we need 10 lb of caustic soda every month to maintain a pH close to 7.5.

Combine the 29.2 lb of sodium bichromate and the 10 lb of caustic soda. Dissolve both chemicals in the 50-gal tank hooked up to a proportionating pump. Set the pump to deliver about 50 gal over the 600-hr period that the cooling tower sprays operate.

STEP 5. Set up a control record similar to the one shown in Fig. 11-4. Then make regular tests of pH, chloride, and sodium chromate concentrations. Use the results to adjust the rate of feeding chemical as required by the control tests.

11-8. Scale Control for Open-spray Systems. In these systems the recirculating water is concentrated by evaporation increasing the total solids. This includes the calcium and magnesium hardness originally present in the makeup. These elements make the problem of scale formation much more troublesome in an open-spray system than in a once-through system. Many waters that are not scale-forming in a once-through system do form scale when the recirculating water concentrates in an open-spray system. Naturally, makeup water which is scale-forming originally gets much worse when it is concentrated. Calcium carbonate is the principal ingredient of most scale found in once-through cooling systems. This is primarily because of the very low solubility of calcium carbonate. This is also true in open-spray systems. Calcium sulfate, too, is often found in scale deposits because of the higher solids concentration in the tower water. By arbitrarily setting up a maximum limit of 1,000 ppm on the recirculating water sulfate, this ingredient is generally eliminated as a scale former. The limits that prevent calcium carbonate scale are usually sufficient to prevent the formation of sulfate scale.

Include blowdown and add caustic if necessary to get a satisfactory recirculating-water composition. As part of the water treatment control plan, maintain the saturation index in the range of +0.6 to +1.0. In addition, use polyphosphates and organic surface-active agents such as starches, lignins, and tannins. When phosphates are used, adjust the rate of feed to add 5 to 10 ppm. This maintains a minimum of at least 2 ppm polyphosphates in the recirculating water at all times.

If calcium carbonate scale still persists, adding more polyphosphates will have little or no effect. It is then advisable to lower the pH of the recirculating water or increase the quantity of blowdown to lower the saturation index. Another possibility is a mixture of polyphosphate with an organic material. Organic surface-active agents for scale prevention are usually added in amounts of 50 ppm or less. The following example shows how to handle a typical problem involving scale.

EXAMPLE 7. Add 5 ppm of sodium hexametaphosphate to the chemicals used in Example 6 to ensure against scale formation.

Table 11-1 shows that 0.04 lb of sodium hexametaphosphate is needed per thousand gallons of water loss. The total water loss (windage plus blowdown) is 8,100 gal per month. The dosage of sodium hexametaphosphate is then 0.324 lb (5 oz) per month. Dissolve the phosphate in water and add to the main batch of chemicals in the feeding tank.

After a few months of operation some calcium carbonate scale has started to form. This has happened even though there are substantial amounts of polyphosphate in the recirculating water at all times. At this point add 12 ppm of tannin in addition to the polyphosphate. This is equivalent to 0.1 lb per thousand gallons, or 0.81 lb of tannin per month to treat 8,100 gal of water. Dissolve the tannin in water and add to the other chemicals in the feeding tank. Further checks show that the scale formation is now under control.

11-9. Slime and Algae Control for Open-spray Systems. The recirculating water in an open-spray system is an excellent air scrubber. It will dissolve or suspend any number of harmful materials from the surrounding air. Included in this listing is air-borne dirt consisting of particles of sand, construction materials, soot, organic matter, bacteria, and algae.

Slimes are grayish or yellowish jellylike materials produced by the growth of bacteria. They also contain the mechanically entrapped particles of organic and inorganic air-borne dirt. Slime tends to cling to many parts of the air-conditioning system. If allowed to grow, it eventually blocks the flow of water through nozzles and causes high head pressure in refrigerant condensers, odors in air washers, and increased equipment corrosion.

Algae are colored organisms and are generally some shade of green. They are among the lowest and simplest forms of plant life. Their growth requires only sunlight. In open-spray systems algae are found mainly in the head pans of cooling towers that use perforated head pans for water distribution. Algae grow quite rapidly and form a thick mat of green organic material which may clog holes or nozzles in the head pan. In addition, pipelines and pumps are often clogged by large growths. Therefore, algae can interfere with normal operation of an open-spray system to the point where it no longer does an efficient job of cooling.

Both slime and algae are growths resulting from living organisms. For this reason, control is frequently more difficult than the control of scale and corrosion in open-spray systems. There are many types of bacteria and algae, and all react differently to various slimicides. In fact, a given bacteria often reacts differently to the same dose. However, they are no different from many human beings who react in various ways to a given dose of medicine. Slime and algae often build up resistance to the slimicide used. Therefore, it is not always possible to control slime and algae by simply adding a given slimicide along with the other chemicals used for scale and corrosion control.

The whole method of controlling slime and algae is essentially different from the method of controlling scale or corrosion. Continuous treatment with slimicides is not the rule. If slime growth is noted, "shock" treatment is very useful with one or more slimicides used at regular intervals. The dosage depends on the amount of water held in the open-spray system. This usually means that the volume of water normally held in the system must be calculated. This can be done by any of the methods outlined in Chap. 5. There is also a rule-of-thumb method for calculating the volume of water in an open-spray system. Multiply the tonnage of the cooling towers by 6 and all other spray systems by 4. Table 11-2 lists the "shock" treatment dosage for some of the common slimicides. The frequency of treatment can be determined only by trial and error and the rate of growth of the slime and algae.

Chemical treatment alone does not usually control slime and algae. Good housekeeping is also essential. The equipment must be thoroughly cleaned at regular intervals to avoid any excessive slime growths. The frequency of cleaning is determined by the rate of growth of slime and algae. The installation of a suitable cover over the circulating water pan to eliminate the effect of direct sunlight on algae growths may also be desirable.

11-10. Cleaning Program for a Badly Slimed Open-spray System

STEP 1. Drain the water from the unit.

STEP 2. Brush the unit, to remove as much dirt, debris, slime, or algae as possible. Hose thoroughly to remove loose material from the pan. Then clean all accessible areas such as head pans, fill, eliminators, side walls, pans.

STEP 3. Refill the unit with fresh water. Then add any of the following slime-killing chlorine chemicals.

Slimicide chemical	*Dosage per hundred gal water*
Household bleach (5.25% sodium hypochlorite Chlorox or equivalent)	36 fluid oz
Commercial bleach	12 fluid oz
Calcium hypochlorite (70% available chlorine, Pittchlor or equivalent)	2 oz

The cleaning process is aided by the use of a nonfoaming alkaline detergent or a low-foaming wetting agent. The amount of

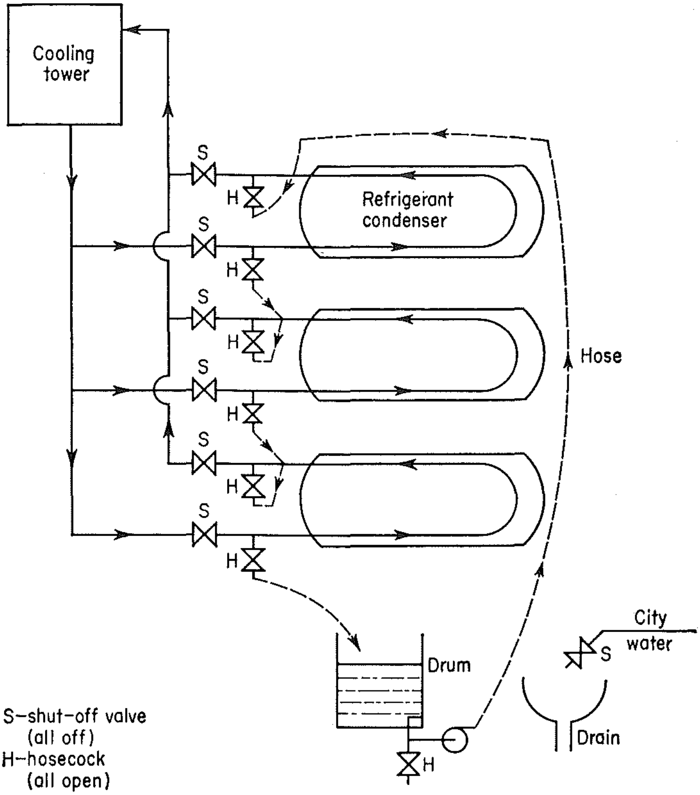


FIG. 11-5. Cleaning connections through multiple refrigerant condensers in series. (*Courtesy of Water Service Laboratories.*)

alkaline detergent depends upon the alkali and should be enough to raise the alkalinity in the fresh water 6,000 to 12,000 ppm. (Specific dosages for some common alkalies are given in Table 8-2.) The amount of wetting agent needed varies with the type of material used. Figure 11-5 shows a typical method of connecting the drum and chemical solution to clean out deposits in the water side of refrigerant condensers.

STEP 4. Circulate the chemically treated water for at least three hours. If any serious foaming develops in the pan, add an antifoam solution (Dow Corning antifoam A emulsion or equivalent). Add at the rate of one drop at a time until the foaming is reduced.

STEP 5. Drain the unit and repeat Step 2.

STEP 6. Refill the unit with fresh water. Then add the "shock" treatment dosage of slimicide indicated in Table 11-2. The unit is now ready to operate.

The following example shows how to handle a typical problem involving slime in an open-spray system.

EXAMPLE 8. A grayish slime has been growing rapidly in a 50-ton cooling tower. One result is high head pressure in the refrigerant condenser. The unit must be cleaned out in accordance with the usual cleaning program and then treated with a slimicide at regular intervals.

The volume of water in the 50-ton cooling tower is estimated at six times the tonnage, or 300 gal. Use commercial bleach as the slimicidal chemical for Step 3 of the cleaning program. The amount needed is 36 fl oz. From Table 11-2 choose calcium hypochlorite as the slimicidal chemical for the "shock" treatment. Add 3 tablets as described in Step 6 in the cleaning program. After this treatment the tower is inspected for slime growths and found clean.

Each day thereafter examine the tower for new growths. After 10 days a small amount of slime is noted and another 3 tablets are added. More calcium hypochlorite is added on the seventeenth, twenty-third, and twenty-ninth days after cleaning. But the amount of slime growth is gradually increasing, and the unit must be cleaned again after the twenty-eighth day. After this cleaning, 3 tablets of calcium hypochlorite are added once a week whether or not slime is noted. It is hoped that this will lengthen the time between shutdowns for cleaning. By addition of 3 tablets once a week, the cleaning period is actually extended to once every two months.

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Mr. Pincus brings 29 years of water treatment experience to this present work. The major portion of this experience has been with customer service, including planning, estimating, and supervising water treatment control of boilers, domestic water systems, hot water heating systems and air-conditioning systems.

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