An Introduction to Treatment of Steam Boiler Water

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1. STEAM BOILER SYSTEMS

1.1 STEAM BOILER SYSTEM DEFINED. A steam boiler is an enclosed vessel that holds water and is heated by an external source that converts the water to steam. All steam boilers contain tubes that separate the water from the heat source. Steam boilers are described in this publication.

1.1.1 TYPES OF STEAM BOILERS. Boilers are classified by two criteria*:* 1) operating pressure (i.e., the amount of internal pressure generated by the steam that is produced); and 2) the operational design (i.e., whether the water [water tube boiler] or the heat source [fire tube boiler]) passes through the inside of the tubes of the boiler vessel.

1.1.1.1 PRESSURE CLASSIFICATION. A boiler that operates at pressures below 103 kilopascals (15 pounds per square inch gauge) is defined as a low-pressure boiler. A boiler operating pressure greater than 103 kilopascals (15 pounds per square inch gauge) is defined as high pressure. High-pressure boilers can operate at pressures reaching thousands of kilopascals (thousands of pounds per square inch gauge).

1.1.1.2 FIRE TUBE BOILERS. Fire tube boilers pass fire and hot combustion gas through the interior of the boiler tubes to heat the water that surrounds the tubes (see Figure 1.1). This type of boiler design is commonly used for factory-assembled (package) boilers, which are low pressure.

1.1.1.3 WATER TUBE BOILERS. Water tube boilers pass water through the boiler tubes, with the fire and hot combustion gases contacting the exterior of the tubes (see Figure 1.2). Water tube boilers are used in high-pressure and very-high-pressure applications. Most military installations have a central boiler plant containing water tube boilers in addition to fire tube boilers that are located in, and serve, individual buildings.
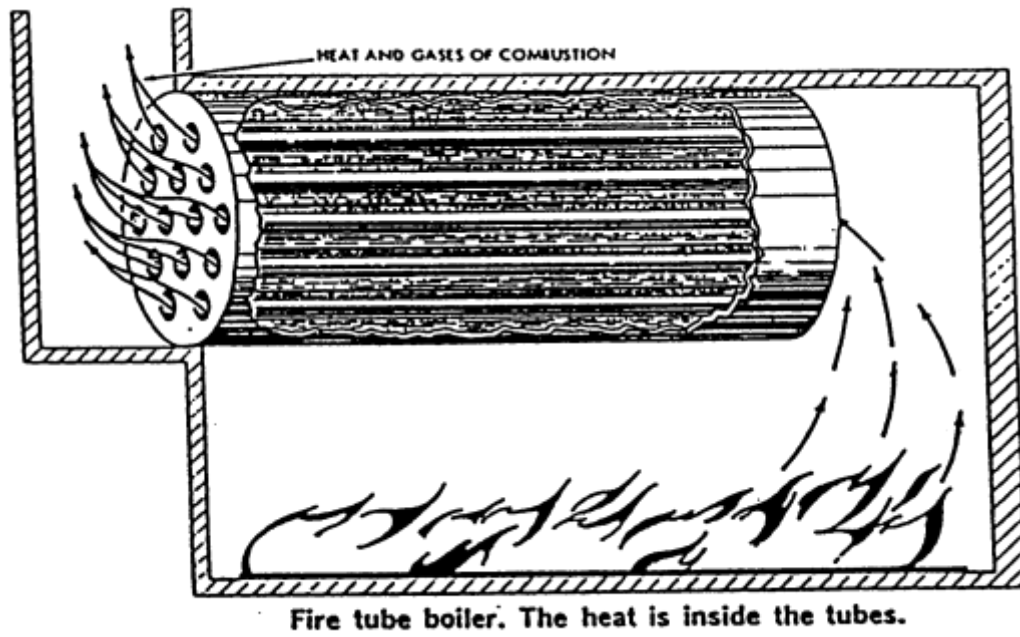
Fire tube boiler. The heat is inside the tubes.

Figure 1.1

Fire Tube Boiler
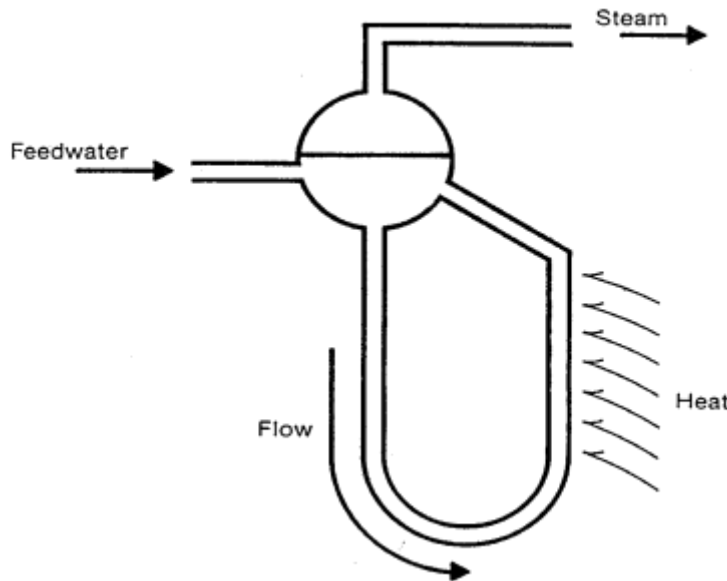
Figure 1.2. Water Tube Boiler

Figure 1.2

Water Tube Boiler

1.1.1.4 BOILER CAPACITY RATING. Boiler capacity rating is given as units of either boiler horsepower, kilograms of steam per second (pounds per hour), or kilowatts (British thermal units [BTU] per hour), specifically: 1) one boiler horsepower unit reflects the energy to convert 15.7 kilograms (34.5 pounds) of water to steam from (and at) 100 ^{o}C at sea level, which is equivalent to 9.812 kilowatts (33,479 BTU per hour); 2) kilogram of steam produced per second (pound of steam produced per hour) represents the number of kilograms of water used each second (pound per hour) to produce the steam; and 3) kilowatts (3,413 BTUs per hour) reflect the energy needed to evaporate the water (produce steam) each hour. The actual quantity of steam produced will vary depending on the boiler efficiency, boiler operating pressure, and altitude with respect to sea level.

1.1.2 COMPONENTS OF A STEAM BOILER SYSTEM. The functional components of steam boiler systems vary from one system to another based on a variety of design,

engineering and service requirements. The typical components that may be included in a specific unit are illustrated in Figure 1.3 and are briefly described in paragraphs 1.1.2.1 through 1.1.2.5.

Figure 1.3

Components of a Simple Steam Boiler System

1.1.2.1 PRE-BOILER. The pre-boiler section of a steam boiler encompasses the boiler system's structural components that hold, move, and treat the water before the water enters the boiler. These pre-boiler system components include the integrated or supplementary water pre-treatment equipment used to process the boiler makeup water, the deaerator used to remove oxygen and other non-condensable gases, and

the feedwater heaters and pumps. The pre-boiler section may include a storage tank for the treated makeup water. The boiler feedwater is usually composed of the makeup water combined with the condensed steam (condensate) that is returned from the distribution system (called the condensate return). The feedwater, pre-heated or not, then enters the deaerator, which is used to remove (deaerate) oxygen and other volatile gases.

1.1.2.2 AFTER-BOILER. The after-boiler, or post-boiler, section of the boiler system encompasses all structural components of the boiler system that hold, move, and process the steam and water downstream from the actual boiler. The after-boiler includes steam piping, heat exchangers, steam traps, condensate piping, turbines, process equipment, and superheaters.

1.1.2.3 BOILER COMPONENTS. A fire tube boiler passes the hot combustion gases through the tubes, which are surrounded by the water to be converted to steam. A water tube boiler passes the hot combustion gases around the tubes, which contain the water to be converted to steam. In either type of boiler, the steam passes into a steam drum and then into the steam lines. The circulation of water in the water tube boiler may be accomplished by heating only, through a process of "natural circulation," which requires no external force or pumping. Alternatively, the water can be pumped through the heating circuit of the boiler by a process referred to as "forced circulation." Usually, a mud drum is provided at the lowest point in the water circulation section to allow the removal of any water-formed sludge. There will be at least two locations for the removal of boiler water blowdown: 1) for surface blowdown, sometimes referred to as a skimmer, located just below the operating water level of the steam drum; and 2) one or more bottom blowdown locations at the mud drum.

1.1.2.4 STEAM DRUM. The feedwater is added to the steam drum, where a mixture of steam and water is produced and where the steam is separated from the water. This separation process usually includes using mechanical devices to assist in removing any entrained boiler water from the steam. Chemicals used for internal

boiler water treatment may be added (fed) to the water in the steam drum. A process of either continuous or intermittent surface blowdown is used to maintain the TDS of the boiler water and achieve the optimal operating conditions in the boiler. In some boiler systems, the blowdown water will be discharged to a flash tank, where a lower pressure steam is produced (possibly for use in the deaerator). Also, water from continuous blowdown may be used to preheat the makeup water by means of a heat exchanger. Steam from the drum may be discharged directly to the steam header or, in some boilers, heated further in a superheater to generate superheated steam.

1.1.2.5 STEAM HEADER. The steam generated by the boiler is discharged from the steam drum to a header. The steam header feeds the steam to the steam distribution system. The steam is consumed by process equipment, lost through leaks, lost from valves, fittings, or steam traps, or condensed for return to the deaerator and subsequently reused for additional steam production.

1.1.3 MEASURING EQUIPMENT. To develop an appropriate water treatment program for a steam boiler system, as well as to monitor the effectiveness of the ongoing program, measure the quantities of steam, feedwater, blowdown, makeup, and condensate into and from the system. As a minimum, install a flow meter in the makeup water line. Installing flow meters on the feedwater line and in the steam header is also advisable, but due to cost considerations this practice is usually limited to large steam boilers. The rates and volumes for production of condensate and blowdown water can be calculated using the method described below.

1.1.4 COMMON BOILER PROBLEMS. Common water-related problems inside the entire boiler system are corrosion, deposition, and carryover.

1.1.4.1 CORROSION PROBLEMS. Corrosion problems are the result of the action of oxygen and the effect of low or high pH on metal components, including the boiler tubes and drum, which are constructed of carbon steel. Corrosion can also occur from excessive alkalinity of excessive pH of the boiler water. This caustic attack is most

likely to occur under scale or deposits, where very high local concentrations of hydroxide can build or in zones where insufficient cooling flows fails to sufficiently remove the heat input, leading to boiling, and thus steam blanketing occurs." Corrosion can occur in the boiler, as well as in the pre-boiler and after-boiler sections, which can also be constructed of carbon steel. Corrosion can result in loss of metal volume or in a reduction of the integrity of the metal, situations that can lead to structural failure, particularly when metal loss is localized (see Figure 1.4). Corrosion is therefore also a safety concern. Corrosion in the steam lines, condensate lines located in the after-boiler section, and in the carbon steel piping can result in the production of system leaks leading to the loss of condensate, a situation which increases demands for energy, water, and chemicals.
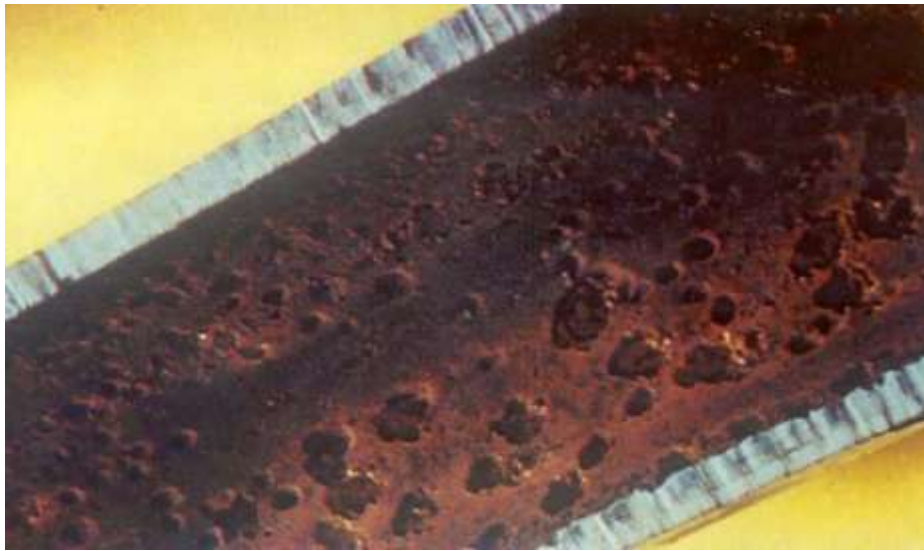

Figure 1.4

Boiler Tube Oxygen Pitting

1.1.4.2 DEPOSITION PROBLEMS. Deposition problems result from the precipitation of minerals dissolved in the feedwater, causing the formation of one or more types of scale on boiler system components. Deposition can occur by other mechanisms when corrosion products (rust) enter the boiler after being created in either the after-boiler or pre-boiler sections. These corrosion products can form iron-based scales. Using

certain water treatment chemicals can also result in the formation of scale when the chemicals are not properly applied. All scales provide insulation to the transfer of heat between the water and the heated metal tubes. Scale can occur in any section of the boiler system, resulting in a reduced capacity for heat transfer. Due to the resulting reduced heat transfer from the fireside of the tube to the water, the metal tubes operate at a higher temperature than if the scale were not providing insulation. Consequently, steam is produced inefficiently due to greater fuel demands, and fuel costs are increased. The greater the thickness of scale, the greater the insulating effect, and the higher the temperature of the tubes (see Figure 1.6). At sufficiently high metal temperatures, the tube can lose its tensile strength and rupture.
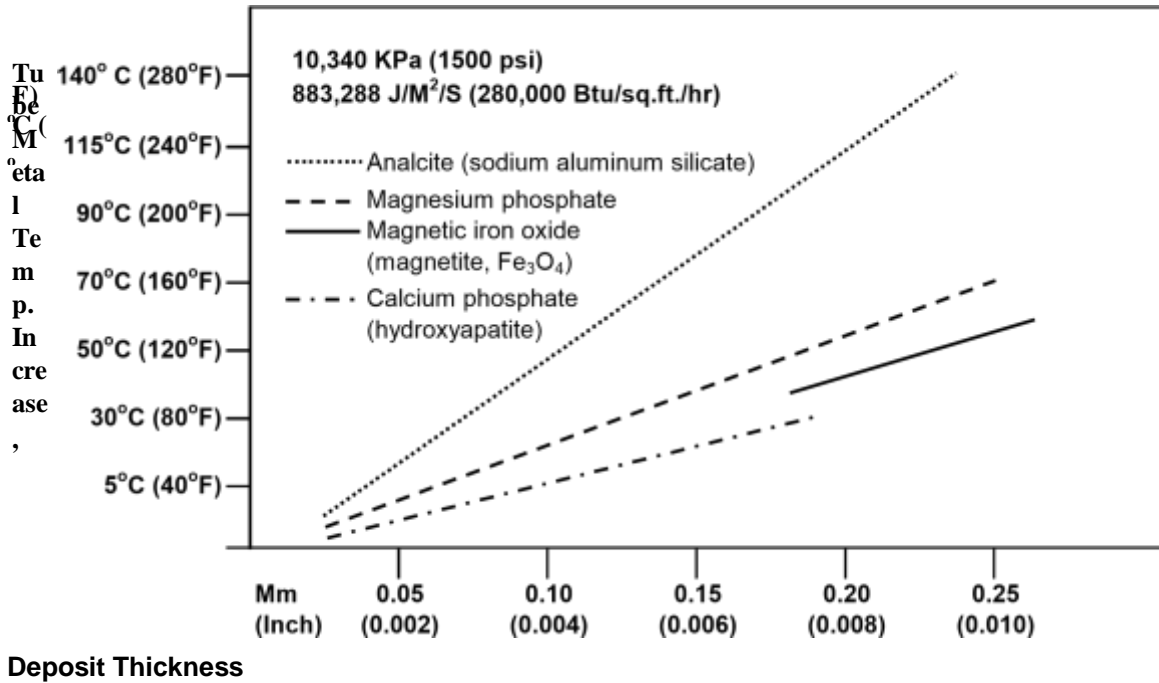

Figure 1.5
Scaled Boiler Tube

Tube Metal Temp. Increase, °C (°F)

10,340 KPa (1500 psi)
883,288 J/M^2/S (280,000 Btu/sq.ft./hr)

.... Analcite (sodium aluminum silicate)
− − − Magnesium phosphate
——— Magnetic iron oxide
(magnetite, Fe$_3$O$_4$)
−·−·− Calcium phosphate
(hydroxyapatite)

140° C (280°F)
115°C (240°F)
90°C (200°F)
70°C (160°F)
50°C (120°F)
30°C (80°F)
5°C (40°F)

| Mm (Inch) | 0.05 (0.002) | 0.10 (0.004) | 0.15 (0.006) | 0.20 (0.008) | 0.25 (0.010) |

Deposit Thickness

Figure 1.6

Impact of Scale on Heat Transfer

Figure 1.7

Metal Fatigue on Boiler Tube

Figure 1.8
Failed Boiler Tube

1.1.4.3 CARRYOVER PROBLEMS. Carryover problems are caused by misting, foaming, priming, and silica carryover. Carryover is a process that results in impure steam quality. Dissolved solids contained in the carryover material can contribute to corrosion and deposition problems.

1.1.5 CALCULATIONS. To understand and produce efficient boiler operations, boiler calculations are performed and the results applied correctly. Boiler calculations are the means for providing information used to determine optimal blowdown rates and to assess condensate return. The greatest efficiency of boiler operations can be achieved by optimizing the COC by adjusting the amount of blowdown to give the proper volume of water. Efficient boiler operations recover and return as much condensate as possible. The material balance or mass balance of an operating boiler system can be calculated from the results of water tests and the known (measured)

value of a single boiler operational parameter such as steam production, makeup water usage, feedwater usage, or blowdown. Steam table data can be used with mass balance information to calculate energy input and energy output for the boiler system. Chemical feed rates can be used with mass balance information to develop an estimation tool for the annual consumption of water treatment chemicals. Familiarity with these calculation procedures and their application to boiler system operations assessment is required of any base or facility engineer or section supervisor. This knowledge is also useful for boiler operators.

1.1.5.1 CYCLES OF CONCENTRATION (COC). COC in a steam boiler is a term that refers to the number of times the minerals in the feedwater have been concentrated in the boiler by its operation. As boiler water is evaporated and steam is produced, minerals that were dissolved in the boiler water remain behind, increasing the mineral content of the remaining water. As steam is produced, additional mineral-laden feedwater enters the boiler, resulting in additional minerals being introduced into the boiler and increasing the amount present in the boiler. Mineral content in an operating boiler water system can be limited only by blowdown.

1.1.5.2 BLOWDOWN. Blowdown consists of draining some of the boiler water with its accumulated solids, and replacing it with treated feedwater before harmful levels of solids are reached. Dissolved solids tend to concentrate near the water surface in the steam drum. Therefore, surface blowdown is most effective in reducing the concentration of dissolved solids. Bottom blowdown is used to remove precipitated sludge from the boiler mud drum. However, blowdown results in the loss of heated water and treatment chemicals. Economical operation requires careful control of blowdown to maintain sage solids levels, while minimizing both heat and chemical additive losses.

1.1.5.3 WATER BALANCE FOR FEEDWATER, EVAPORATION, AND BLOWDOWN. The total volume of the water (feedwater) that is added to the boiler must equal the total volume of the water (steam plus boiler water blowdown) that is

removed from the boiler. By convention, these water quantities are commonly expressed in kilograms per second (pounds per hour) in this equation for water balance:

$$F = E + B$$

where

F = feedwater, kg/s (lb/hr)
E = steam generated, kg/s (lb/hr)
B = blowdown, kg/s (lb/hr)

1.1.5.4 CALCULATION OF FEEDWATER AND BLOWDOWN WATER. The feedwater or blowdown water (or both) can be calculated in relation to the COC using these equations:

EQUATION $\quad\left|\quad\begin{array}{l} COC = F \div B, \text{ or } F = B \times COC \\ or \\ B = F \div COC \end{array}\right.$

where

COC= cycles of concentration, no units
F= feedwater, kg/s (lb/hr)
B= blowdown, kg/s (lb/hr)

It is common to express blowdown as a percentage:

EQUATION $\quad\left|\quad \% B = 100/COC\right.$

1.1.5.5 RELATIONSHIP BETWEEN FEEDWATER, BLOWDOWN, STEAM GENERATION, AND COC. Using the terms defined above, the relationship between feedwater, blowdown, steam generation, and COC is represented as:

a) F = B x COC, from COC, Equation (2) above
b) F = E + B, from COC, Equation (1) above
c) B x COC = E + B, replacing F in Equation (2) with Equation (1)
d) B x COC - B = E, rearranging Equation c) above
e) B x (COC-1) = E, rearranging Equation d) above
f) B = E ÷ (COC-1), rearranging Equation a) above

1.1.5.6 CALCULATING BLOWDOWN RATES. The blowdown water volume is rarely measured by a meter. As shown below, it can be calculated if any two of the following parameters are known: 1) feedwater; 2) COC; or 3) steam generation (E). Steam volume is usually measured in units of meters on large boilers. The COC can be calculated by measuring the conductivity or TDS in both the boiler water and the feedwater. Note that the conductivity and quantity of TDS is the same for the boiler water and the blowdown water.

$$COC = B_{TDS} / F_{TDS}$$
or
$$B_{\mu mhos} / F_{\mu mhos} 3$$

where

COC = cycles of concentration, no units
B_{TDS} = blowdown TDS, ppm
F_{TD} = feedwater TDS, ppm
$B_{\mu mhos}$ = blowdown conductivity, micromhos
$F_{\mu mhos}$ = feedwater conductivity, micromhos

1.1.5.7 DETERMINING FEEDWATER AND BLOWDOWN RATES. The blowdown calculations in paragraph 1.1.5.6 can be used to determine the feedwater rate in units of kilograms per hour (pounds per hour). Note that the term "feedwater" refers to water that is fed to the boiler and includes the makeup water plus the condensate return and steam from the deaerator.

EXAMPLE:

a) A 1720-kilopascal (250-pound-per-square-inch-gauge) boiler operates at a conductivity level of 5000 μmhos. The boiler feedwater has a conductivity of 250 μmhos. The COC calculation is:

$$COC = B_{\mu mhos} / F_{\mu mhos}$$
or
$$5000 \ \mu mhos / 250 \ \mu mhos = 20 \ COC$$

b) The percent blowdown is:

$$\%B = 100/COC$$
or
$$100/20 = 5\%$$

c) If the boiler is producing 5 kilograms per second of steam (40,000 pounds per hour), the blowdown must be:

$$B = E \div (COC - 1)$$
$$= 5.0 \div (20 - 1) = 0.26 \ kg/s \ (2105 \ lb/hr)$$

d) The feedwater is calculated to be:

$$F = E + B = 5.0 + 0.26 = 5.26 \ kg/s \ (42,105 \ lb/hr)$$

This is equivalent to 5.3 liters per second (5054 gallons per hour at 8.33 pounds per gallon). This example is illustrated in Figure 1.9.
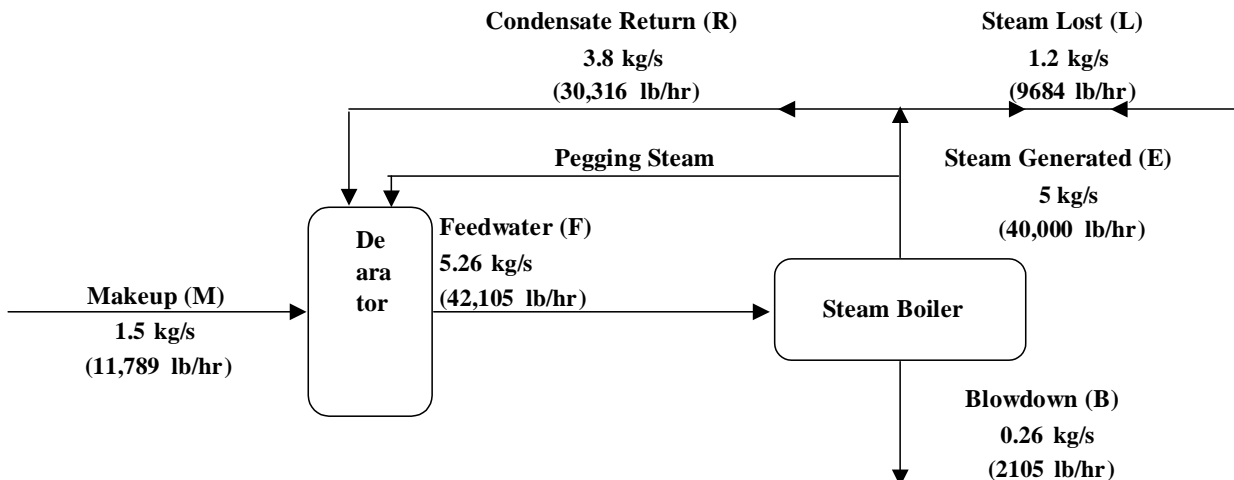
Condensate Return (R)
3.8 kg/s
(30,316 lb/hr)

Steam Lost (L)
1.2 kg/s
(9684 lb/hr)

Pegging Steam

Steam Generated (E)
5 kg/s
(40,000 lb/hr)

De
ara
tor

Feedwater (F)
5.26 kg/s
(42,105 lb/hr)

Makeup (M)
1.5 kg/s
(11,789 lb/hr)

Steam Boiler

Blowdown (B)
0.26 kg/s
(2105 lb/hr)

Figure 1.9

Simplified Boiler System Water Balance

1.1.6 DETERMINING MAKEUP WATER AND CONDENSATE RETURN RATES.
Makeup is the water from the external water treatment system added to the boiler
system upstream of the deaerator. The amount, expressed as either volume or
percentage, of makeup water required in a boiler is affected by blowdown, steam
leaks, consumption of steam in process equipment, and loss of condensate by boiler
system leakage. In a "tight" boiler system, where steam is not lost in process
equipment, about 5 to 10% makeup is expected. Water balance is affected by
condensate return; however, boilers that lose considerable condensate due to losses
of steam or condensate can approach a requirement for 100% makeup, which is a
very inefficient and costly condition. The calculations below can be used for
determining makeup water needs and condensate return rates.

1.1.6.1 MAKEUP WATER RATE. Makeup is the difference between the volume of
condensate return and the volume of feedwater.

$$M = F - R$$

where

M = makeup, kg/s (lb/hr)
F = feedwater, kg/s (lb/hr)
R = condensate return, kg/s (lb/hr)

1.1.6.2 CONDENSATE RETURN RATE. Since the returned condensate usually does
not contain any appreciable level of dissolved solids or conductivity, determination of
percent makeup is calculated using the equation:

$$\%M = (1 - F_{\mu mho} / M_{\mu mho}) \times 100\%$$

where

$\%M$ = % makeup
$F_{\mu mho}$ = feedwater conductivity, micromhos
$M_{\mu mho}$ = makeup conductivity, micromhos

EXAMPLE

a) Makeup water conductivity is 900 μmhos for the boiler water in this example. The percent makeup is calculated:

$$\%M = (1 - F_{\mu mho} / M_{\mu mho}) \times 100\%$$
$$\text{or } (1 - 250 / 900) \times 100\%$$
$$\%M = 72\%$$

b) This means that the makeup water is 28% of the feedwater. The condensate return percent is calculated:

$$\%R = 100 - \%M = 100 - 28 = 72\%$$

c) The quantity of makeup water is calculated:

$$M = (\%M/100) \times F$$
$$\text{or } (28/100) \times 5.3 \text{ kg/s } (42{,}105 \text{ lb/hr})$$
$$M = 1.5 \text{ kg/s } (11{,}789 \text{ lb/hr})$$

d) The quantity of condensate return is calculated:

$$R = F - M = 5.3 - 1.5 = 3.8 \text{ kg/s } (30{,}316 \text{ lb/hr})$$

1.1.6.3 DIFFERENCE BETWEEN AMOUNT OF STEAM PRODUCED AND AMOUNT OF CONDENSATE. The difference between amount of steam produced and the amount of condensate returned represents the combined loss from the system of both steam and condensate. These losses may result from leakage of steam, consumption of steam by the process equipment, leakage of condensate, or

deliberate discharge of contaminated condensate. The total water loss can be calculated:

$$L = E - R$$

where

L = total steam and condensate losses, kg/s (lb/hr)
E = steam generated, kg/s (lb/hr)
R = condensate return, kg/s (lb/hr)

EXAMPLE

a) The steam losses from the boiler

$$L = E - R = 5.0 - 3.8 = 1.2 \text{ kg/s (9684 lb/hr)}$$

1.1.6.4 BASIS FOR EVALUATING BOILER SYSTEM EFFICIENCY. A good basis for evaluating boiler system efficiency can be developed by monitoring the system's water conductivity values, measuring the quantity of steam generated, and performing the required calculations after a regularly scheduled interval of time. An increase in steam loss may indicate a new leak, a size increase in existing leaks, a new consumption of steam, or condensate losses. Additionally, calculations of boiler system efficiency can provide a good basis for estimating savings in steam cost resulting from maintenance efforts to reduce steam and condensate losses.

2. BOILER WATER TREATMENT AND CONTROL. References to boiler water treatment in the late nineteenth century relate that the process of removing the scale from a boiler required much less effort and time if the boiler operator had forgotten to remove cooked potatoes from the boiler water. It was determined that the starch in potatoes causes a soft sludge, rather than a hard scale, to be formed, and this sludge was easier to remove than hard scale. Other natural organics, including lignin and tannins from wood, plant matter, plant extracts, and even manure and coffee grounds, produced similar results. It was determined that addition of phosphate by itself produces a manageable sludge, although starch, lignins, and tannins have been used to supplement the phosphate. Phosphate is still very commonly combined with other water treatment chemicals. Early use of alkaline materials included lime, soda ash, and caustic soda. Oxygen scavengers, such as sodium sulfite, were found to be effective for preventing oxygen corrosion. Many of these materials are still used today. The wide range of water treatment chemicals that is currently available allows for development of a comprehensive approach to industrial boiler water treatment, including using specialty chemicals such as chelants, polymers, and amines.

2.1 BOILER DEPOSIT FORMATION. Dissolved solids in boiler feed water become more concentrated in the boiler water as steam is generated. Some of the dissolved solids can come out of solution (precipitate) and form scale in the boiler tubes. Some dissolved solids can form sludge (mud) in the boiler and form adherent deposits on boiler tubes. These deposits reduce heat transfer.

2.1.1 SCALE. Scale can occur in isolated spots due to water evaporation. When a steam bubble forms on a heated surface, a thin film of water situated between the bubble and the tube wall becomes more concentrated with the dissolved materials. This thin layer can be as much as 17 ^{o}C (30 ^{o}F) hotter than the average boiler water temperature. These local conditions can cause precipitation of the dissolved solids and local formation of scale.
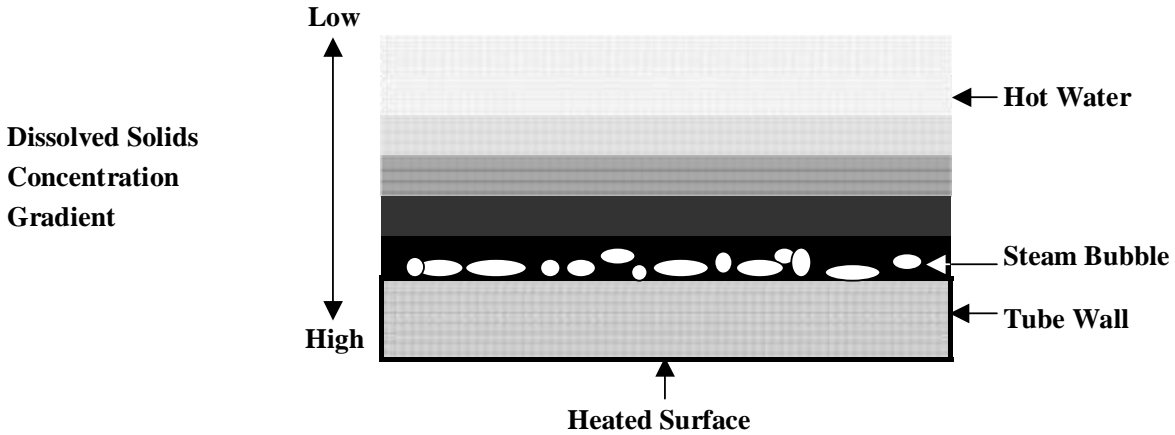
Figure 2.1

Localized Scale Formation Process

2.1.1.1 Sludge Deposits. Sludge deposits can form when the precipitated materials in the boiler water stick to the boiler tubes due to their hot surfaces as a result of the same phenomenon described in paragraph 2.1.1. Scale and sludge often form together.

2.1.1.2 Dissolved Solid Materials. Some dissolved solid materials become less soluble as the water temperature increases. This situation occurs with most of the salts that constitute calcium and magnesium hardness ($CaCO_3$, $CaSO_4$, $MgCO_3$, $Mg[OH]_2$). As a result of this property, these materials tend to form scale in the hotter areas of the boiler because they remain soluble in the cooler areas of the boiler. By using an appropriate form of water treatment, these scaling agents can be removed from the boiler system water either before they enter the boiler (external treatment) or after (internal treatment), although it is often best to remove the dissolved magnesium and calcium minerals (hardness) before they enter the boiler (see paragraph 2-2). With the proper chemical treatment, they can be effectively controlled and treated internally in the boiler.

2.2 COMMON SCALE FOUND IN BOILERS. The most common scale materials consist of calcium and magnesium salts and iron oxide. Calcium and magnesium salt

deposits are white or off-white. Iron oxide scales are red or black deposits. The type of scale can be identified accurately by deposit analysis. It is common to have more than one type of scale in boiler deposits.

2.2.1 CALCIUM CARBONATE. Calcium carbonate scale is white or off-white in color and is formed by the breakdown of calcium bicarbonate with heat. Calcium carbonate scale is formed in both untreated boilers and improperly treated boilers. A drop of a dilute acid solution on the deposit will cause bubbling on the calcium carbonate scale area as a result of the release of carbon dioxide. This procedure can be used to identify this type of scale. Calcium carbonate scale can result when there is calcium hardness in the boiler feedwater due to improper softener operation and when there is an inadequate level of sludge or scale conditioner or dispersant.

2.2.2 CALCIUM SULFATE. Calcium sulfate (gypsum) is off-white or tan in color and is formed in boilers that are using water of high hardness and low alkalinity without proper treatment. Addition of a strong acid will dissolve the calcium sulfate scale with no gas bubble formation or release of carbon dioxide. Calcium sulfate is much less common than calcium carbonate, but it can form when there is calcium hardness in the boiler feedwater due to improper softener operation and when there is an inadequate level of sludge or scale conditioner or dispersant.

2.2.3 CALCIUM PHOSPHATE. Calcium phosphate is formed when the dissolved calcium in the feedwater reacts with phosphate treatment chemicals added to the boiler water. With proper treatment controls, calcium phosphate forms a sludge that will be removed in the blowdown. However, calcium phosphate can deposit as scale if the pH of the boiler water is below 11.0 and if a sludge conditioner is not used. Addition of a strong acid will dissolve this scale fairly easily with no gas bubble formation.

2.2.4 MAGNESIUM PHOSPHATE. Magnesium phosphate scale is an off-white deposit formed by the reaction of magnesium salts from the feedwater with the

phosphate used in the boiler water treatment. It will form only if both the hydroxide content and silica content of the boiler water are low. Addition of a strong acid will dissolve this scale fairly readily with no gas bubble formation.

2.2.5 MAGNESIUM SILICATE. Magnesium silicate scale, an off-white deposit, is formed from the magnesium and silica in the feedwater when the pH is above 11.0 and the silica level is more than half that of the phosphate level in the boiler water. Normally, it forms as a sludge that will be removed in the blowdown, but it may form scale deposits on tubes if a sludge conditioner is not present. Most acids will not remove this deposit. Caustic or special chemicals are needed to remove the magnesium sulfate scale.

2.2.6 IRON OXIDE AND IRON HYDROXIDE. Iron oxide scales and iron hydroxide scales are red/black deposits that are formed when the iron salts dissolved in the feedwater react with hydroxide found in the boiler water. Usually, the dissolved iron is introduced into the system from the condensate return due to corrosion. Iron oxide can be deposited as a scale on the boiler tubes if the proper type of sludge conditioner is not present. With proper water treatment, this deposit should form as sludge, rather than scale, and can be removed by blowdown. The presence of iron oxide on the internal boiler surfaces can be caused by oxygen corrosion of the boiler metal.

2.3 EXTERNAL BOILER WATER TREATMENT. The strategy for external treatment is to remove unwanted impurities in the makeup water before they can enter the boiler. Proper external treatment can eliminate, or at least minimize, scale- and corrosion-forming conditions and minimize the internal water treatment required to protect the boiler system components.

2.3.1 External Water Treatment for High-Pressure Boilers. The higher the pressure of the boiler, the greater the need for high-purity feedwater. A 5-kilogram-persecond (40,000-pound-per-hour) water tube boiler operating at 6205 kilopascals

(900 pounds per square inch gauge) requires deionized feedwater. External treatment options include RO followed by demineralization.

2.3.2 External Treatment for Low-Pressure Boilers. Low-pressure boilers can operate with simple external treatment or sometimes no external treatment at all. A 0.44-kilogram-per-second (3450-pound-per-hour) (100 horsepower) fire tube boiler operating at less than 103 kilopascals (15 pounds per square inch gauge) may require using only a sodium zeolite softener for water treatment. A small heating boiler that is returning over 99% of the condensate may not require any external treatment, particularly if the makeup water is low in hardness and the condensate is not contaminated.

2.4 INTERNAL TREATMENT OF BOILER WATER. Internal treatment of boiler water is a process of adding chemicals to the boiler to control deposition and corrosion. Internal water treatment, together with proper blowdown control, controls the water impurities that have not been removed or reduced through external treatment.

2.4.1 PREVENTING SCALE FORMATION. Internal boiler water treatment for scale prevention can be performed using either a solubilizing chemical treatment program or a precipitating chemical treatment program. The solubilizing treatment program uses chemicals designed to keep scale-causing materials with hardness (mineral ions) in solution, whereas the precipitating treatment program uses chemicals designed to react with hardness-causing materials and precipitate them as a sludge that will not adhere to tube surfaces. Both the solubilizing approach and the precipitating approach require good blowdown control to keep hardness and sludge levels within chemical performance capabilities.

2.4.1.1 LOW-PRESSURE BOILERS. Low-pressure steam boiler systems (103 kilopascals [15 pounds per square inch gauge] and less) that use little or no makeup or blowdown are usually not chemically treated for scale control because, due to low makeup water demands, there is no continuous addition of scaling agents (present in

the makeup water) to the boiler. If there are high makeup requirements (over 1% per month) or if the makeup water is over 300 ppm total hardness, a treatment program is required to protect the boiler system.

2.4.1.2 HIGH-PRESSURE BOILERS. High-pressure boilers (103 to 6205 kilopascals [15 to 900 pounds per square inch gauge]) must use either a precipitating-type water treatment chemical program or a solubilizing-type chemical treatment program.

2.4.1.2.1 PRECIPITATING WATER TREATMENT PROGRAMS. A precipitating program often uses phosphate, which will react with calcium to form a calcium phosphate sludge called "hydroxyapatite" ($3Ca_3[PO4]_2 \cdot Ca[OH]_2$), and act as both as a sludge conditioner or dispersant. Magnesium reacts with hydroxide and silica to form a magnesium silicate sludge called "serpentine" ($2MgSiO_3 \cdot Mg[OH]_2 \cdot H_20$). Sufficient hydroxyl alkalinity (causticity) is required to allow the formation of the proper types of sludge. Sludge that is properly formed and conditioned is fluid enough to be removed through bottom blowdown of the boiler. Sodium hydroxide may be required to maintain the appropriate hydroxyl alkalinity (causticity). Phosphate precipitating agents are prepared as either orthophosphate ("ortho" means single phosphate) or as one of several forms of polyphosphate ("poly" means multiple phosphate molecules bonded together). Sodium hexametaphosphate, sodium tripolyphosphate, and sodium pyrophosphate are examples of polyphosphates. In the boiler, polyphosphate breaks down to the orthophosphate form due to the higher temperature. Polyphosphates can be added either to the feedwater or directly to the steam drum. Orthophosphate should only be fed into the steam drum, not to the feedwater, since it can react with the hardness (mineral ions) to form scale in the feedwater lines.

2.4.1.2.2 SOLUBILIZING WATER TREATMENT PROGRAMS. A solubilizing program uses one or more of the following chemicals to keep scale-forming materials in solution: phosphonates (also known as organic phosphate), chelants, or polymers. Solubilizing agents, such as phosphonates (not to be confused with phosphate), chelants, and polymers are common chemicals used in boiler water treatment

formulations. Chelants, such as ethylene diamine tetra-acetic acid (EDTA) or nitrilo-triacetic acid (NTA), bind (chelate) calcium, magnesium, and iron. Using phosphonates and chelants requires special injection systems and excellent feed control. Excess (free) phosphonate or chelant can attack metal surfaces, causing corrosion, although phosphonates are less aggressive than chelants. Water-treating polymers are long-chain, water-soluble compounds containing electrochemically active side branches that perform various functions such as solubilization, dispersion, agglomeration, and crystal distortion to prevent boiler deposits. Polymers do not attack metal surfaces and can be fed into the feedwater line or directly into the boiler steam drum with proper injection equipment.

2.4.1.2.3 BOILER-SPECIFIC TREATMENT PROGRAMS. High-pressure boilers over 6205 kilopascals (900 pounds per square inch gauge) use high-quality feedwater that is produced by extensive external treatment; thus, scale-forming materials are not normally present in the water and cannot form scale in the boiler. These boilers often use water treatment programs designed specifically for that particular boiler. These programs require excellent control of water chemistry and involve applying coordinated phosphate, congruent phosphate, equilibrium phosphate, and all volatile treatment. Boiler pressures of this level are usually found in operations used to drive turbines for the generation of electrical power.

2.4.2 DETERMINING CHEMICAL TREATMENT FEED RATES. Development of a chemical treatment program involves selecting the type of chemical to be used, selecting appropriate concentration levels for each chemical (when used in combination with other chemicals), and selecting the required chemical treatment (addition) scheme to ensure proper water treatment. Blowdown discharge rates can be used to calculate the rate of chemical addition and the amount of chemical required to replace that lost in the blowdown and to meet the treatment objectives. In practice, chemical feed equipment is set up to deliver the chemicals on a "proportional-feed-on-demand" basis. The operator must keep treatment levels within prescribed control ranges by adjusting pumps and timers while controlling COC within the system.

Selection of the type and quantity of required chemical treatment is an issue that involves both technical concerns and ancillary issues pertaining to institutional concerns in the areas of procurement, contracts, and budgets. The Example below illustrates phosphate demand. Similar approaches could be used for other treatment technologies. In the case of sulfite, the treatment requirement must first satisfy the demand due to oxygen in the feedwater. Additional sulfite is fed to attain a residual or excess amount in the boiler water to ensure adequate protection. The second part of the Example takes into account that the treatment chemical formulation is not composed of 100% active ingredients. Formulations are most often less than 50% active and can be as little as 10% active chemical, with the balance of the formulation usually being water.

EXAMPLE:

a)   The boiler will be operated with a phosphate level of 60 ppm (as PO_4) in the boiler water. The blowdown has been determined to be 0.26 kilogram per second (2105 pounds per hour). The required phosphate addition on a daily basis must equal the phosphate that is discharged with the blowdown water, plus that used up in precipitating calcium phosphate. The amount of phosphate required to replace that lost in blowdown is calculated by this method:

Phosphate loss = (B)(treatment ppm residual)/1,000,000
          = 0.26 kg/s x (60 ppm)/1,000,000
          = 0.000016 kg/s (0.13 lb/hr) or 1.38 kg/day

b)   The treatment chemical selected is sodium hexametaphosphate (HMP) containing 90.5% phosphate as PO_4. This means there is 0.905 kilogram (0.905 pound) of phosphate (PO_4) per kilogram (pound) of chemical:

Chemical required = phosphate loss ÷ 0.905
          = 1.38 ÷ 0.905
          = 1.52 kg/day (3.35 lb/day)

NOTE: This calculation does not incorporate any phosphate reaction and precipitation with hardness, so the practical amount of HMP needed would be slightly higher.

2.4.3 PREVENTING SLUDGE DEPOSITS. In either low-pressure or high-pressure boilers, the feedwater hardness (dissolved minerals) can precipitate in the boiler. To prevent the formation of adherent sludge deposits, natural or synthetic (or both) watersoluble organic chemicals are added to the boiler water. Organic chemicals help to create sludge by distorting the crystal structure of scale-forming compounds and preventing the formation of scale. Properly formed and conditioned sludge is fluid enough to be removed through bottom blowdown of the boiler mud drum. A typical natural organic compound, quebracho tannin, has been used traditionally with satisfactory results in military boilers, but its use is diminishing in favor of the new synthetic, water-soluble polymers. Tannin is effective for the control and minimization of sludge and contributes to corrosion control since it absorbs a small amount of dissolved oxygen and helps to form a protective film on mild steel surfaces. To be effective, tannin levels should be maintained at several hundred ppm (of active component) in the boiler water. Polymer materials are typically maintained between 5 to 20 ppm (of active component). The most recently developed synthetic water-soluble polymers have been shown to be more cost-effective than tannins. For example, polyacrylates or copolymers of methacrylate and sulfonated styrene are dispersants, sludge and scale inhibitors commonly used for minimizing the formation of deposits in boilers. Polymer treatments are commonly found in water treatment formulations available from vendors.

2.5 CORROSION IN THE BOILER. Corrosion within the boiler results from an improper pH level (below 10.3), a situation that contributes to general (overall) corrosion, and from oxygen not being removed from the feedwater, a situation that causes pitting of the mild steel tubes and drums.

2.5.1 GENERAL CORROSION. "General corrosion" is a term that refers to an overall uniform corrosion of metal surfaces. Adequate prevention of general corrosion is achieved by maintaining a proper pH, thus allowing the formation of a protective iron oxide coating known as magnetite. Magnetite is a self-limiting form of corrosion that forms in the outermost surface layers of, and that adheres to, the mild steel tube surfaces. Magnetite is composed of an iron oxide complex of $Fe_3O_{4 +} FeO + Fe_2O_3$.

2.5.1.1 PROPER PH FOR BOILERS UP TO 6205 KILOPASCALS. The proper pH range for boilers up to 6205 kilopascals (900 pounds per square inch gauge) is between 10.3 and 12.0. Adjustment of the boiler water to within this pH range is achieved through cycling up the natural alkalinity contained in the feedwater and, if necessary, adding a chemical alkalinity agent such as sodium hydroxide (caustic soda), sodium carbonate (soda ash), or an alkaline phosphate treatment.

2.5.1.2 PROPER PH FOR BOILERS OVER 6205 KILOPASCALS. Proper pH adjustment for boilers over 6205 kilopascals (900 pounds per square inch gauge) is achieved by using water treatment chemicals, which are added because the demineralized feedwater is essentially unbuffered. The chemical treatment programs include coordinated phosphate, congruent phosphate, equilibrium phosphate, and all volatile treatment. Phosphate programs of this type are not used as conventional precipitating agents for hardness-causing materials but instead are used as buffering agents for pH control (see Table 2.1).

Program	PO_4	OH	Na:PO_4 Ratio	pH
Conventional	30-60	20-350	N/A	11-12
Coordinated	5-25	trace	2.85:1 to 3:1	9-10.5
Congruent	2-5	zero	2.3 to 2.6:1	8.8-9.4
Equilibrium	<2.4	<1.0	N/A	9.9.6

Table 2.1

Summary of Phosphate Treatment Programs

2.5.2 PITTING CORROSION. Pitting corrosion is a term that refers to a deep, localized corrosion usually caused by oxygen molecules on the metal surfaces in the boiler water. This process results in the formation of corrosion pits that can extend into the interior metal layers of metal boiler components. Corrosion pitting can be severe enough to lead to perforations of tube surfaces.

2.5.3 OTHER TYPES OF CORROSION. Other types of corrosion can occur in high-pressure boilers over 6205 kilopascals (900 pounds per square inch gauge) for which the water treatment program includes coordinated, congruent, or equilibrium phosphate type chemical treatment (not to be confused with standard phosphate precipitating programs). These other corrosion mechanisms include caustic attack, hydrogen embrittlement, and phosphate hideout.

2.6 REMOVING OXYGEN FROM FEEDWATER. A very corrosive liquid results when oxygen is dissolved in water. Oxygenated water is particularly corrosive to mild steel, which is almost always used to construct the main components of the boiler system. The corrosivity rate of oxygenated water doubles with every 10 ^{o}C (18 ^{o}F) increase in temperature. Oxygen corrosion can be recognized by the presence of pits found typically in the top of, or at the waterline of, the steam drum. Oxygen can be removed from feedwater by mechanical or chemical methods, or both; a combination of these methods is used commonly.

2.6.1 MECHANICAL OXYGEN REMOVAL. Mechanical removal of oxygen from feedwater requires a deaerating heater in which both the makeup water and condensate return are in contact with live steam and mixed using trays, sprays, or both. This heating process literally strips most of the oxygen and other non-condensable gases out of the feedwater. The oxygen and other gases, along with a small amount of steam, are vented from the deaerator to the atmosphere.

2.6.1.1 DEAERATOR OPERATION. Two key parameters associated with deaerator operation are controlled to maintain maximum oxygen removal. First, the deaerator vent is checked to verify that a plume of steam is always flowing out of the vent. Second, both the pressure within the deaerator and the temperature of the outlet water are controlled. Deaerators should operate at a pressure of 20.68 kilopascals (3 pounds per square inch gauge) or more. At any given pressure, the deaerator water outlet temperature should be within 1 ^{o}C (2 ^{o}F) of the water temperatures shown in Table 2.2, adjusted for the altitude of the installation. If the deaerator is operating with low or no steam flow or at a low water temperature, the deaerator is not being operated efficiently and is not removing the maximum amount of oxygen.

Deaerator Pressure kPa (psig)	Deaerator Water Outlet Temperature °C (°F)	Deaerator Pressure kPa (psig)	Deaerator Water Outlet Temperature °C (°F)
0.00 (0)	100 (212.0)	75.84 (11)	116.4 (241.6)
6.89 (1)	101.8 (215.3)	82.74 (12)	118 (244.4)
13.79 (2)	103.6 (218.5)	89.63 (13)	119.1 (246.4)
20.68 (3)	105.3 (221.5)	96.53 (14)	120.2 (248.4)
27.58 (4)	106.9 (224.4)	103.42 (15)	121.3 (250.3)
34.47 (5)	108.4 (227.1)	110.32 (16)	122.3 (252.2)
41.37 (6)	109.9 (229.8)	117.21 (17)	123.4 (254.1)
48.26 (7)	111.2 (232.2)	124.11 (18)	124.1 (255.3)
55.16 (8)	112.7 (234.8)	131 (19)	125 (257.0)
62.05 (9)	113.9 (237.1)	137.90 (20)	126 (258.8)
68.95 (10)	115.2 (239.4)	--	--

NOTE: For every 152 meters (500 feet) in elevation from sea level, subtract 0.5 °C (1 °F) from the listed temperature. A mechanical deaerator that is operating efficiently can reduce the oxygen content of feedwater from the saturation level to a fraction of a ppm. However, even a trace amount of oxygen can cause corrosion pitting in the boiler. The complete removal of oxygen requires the addition of a chemical agent called an "oxygen scavenger."

Table 2.2

Deaerator Water Outlet Temperature for Boiler Systems at Various Sea Level Pressures
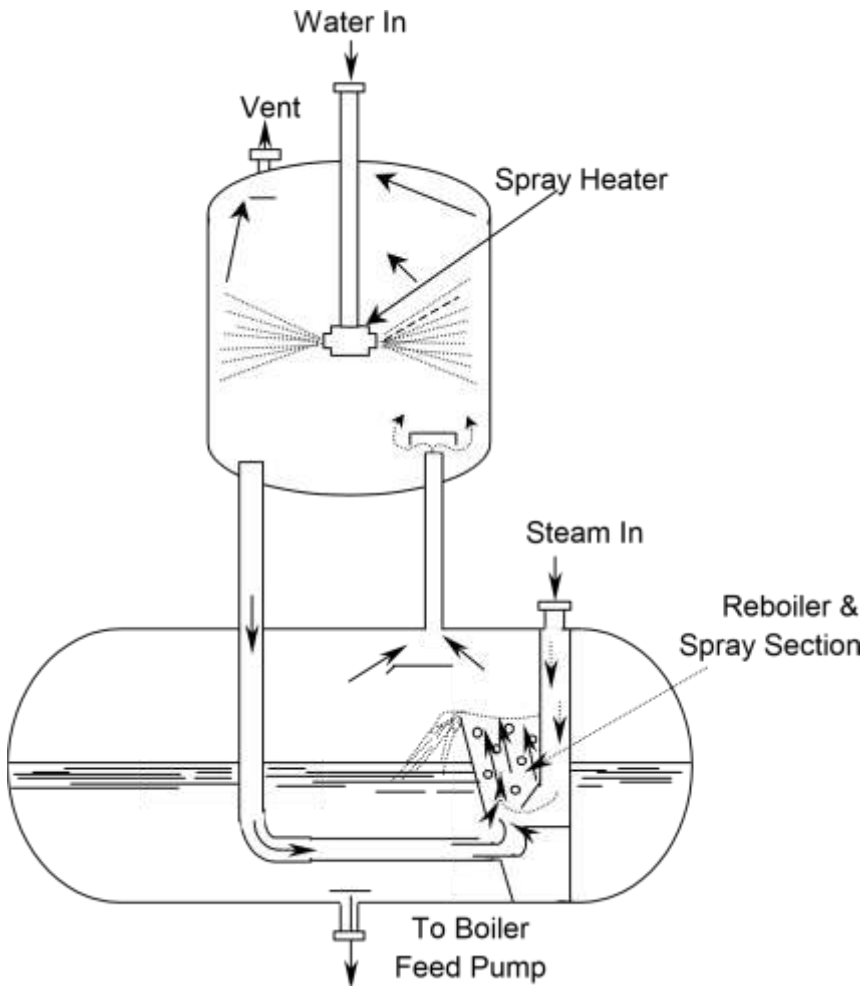
Figure 2.2

Mechanical Deaerator Schematic (Spray Type)

Figure 2.3
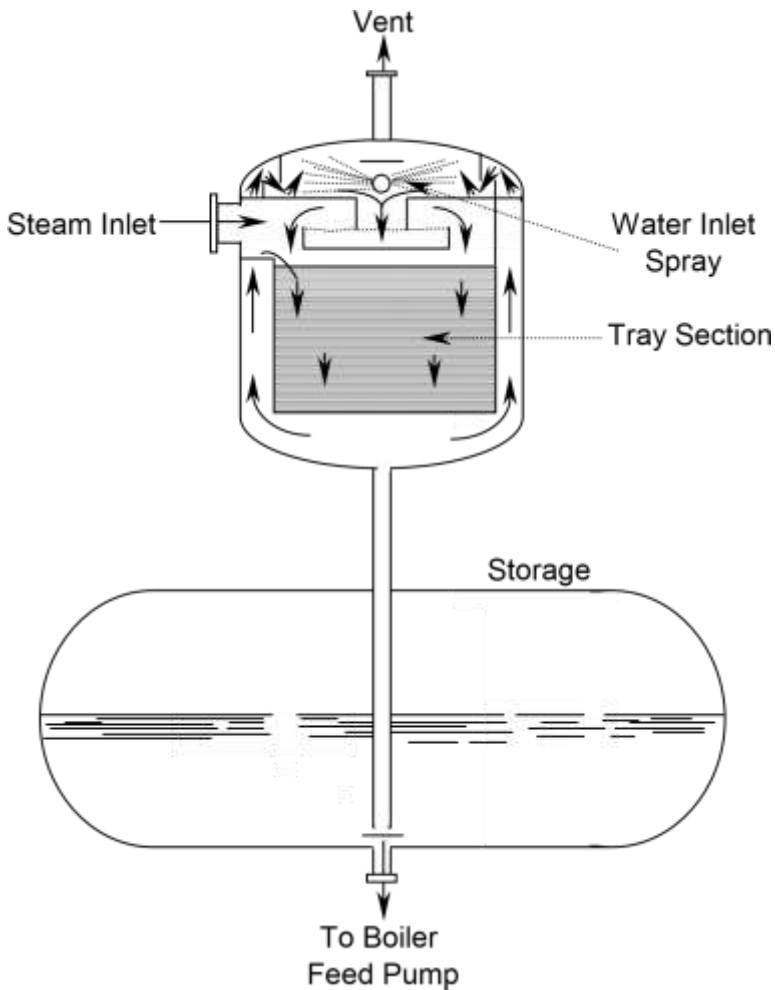
Mechanical Deaerator Schematic (Tray Type)

2.6.2 CHEMICAL REMOVAL OF FREE OXYGEN. Oxygen scavengers are chemicals that react with oxygen. Oxygen scavengers remove the oxygen from the boiler feedwater so it will not cause pitting corrosion.

2.6.2.1 OXYGEN SCAVENGERS FOR BOILERS UP TO 6205 KILOPASCALS.
Oxygen scavengers for boilers up to 6205 kilopascals (900 pounds per square inch

gauge) include catalyzed sodium sulfite and uncatalyzed sodium sulfite, both of which are oxygen scavengers and sources of sulfite. When a deaerator is used, any uncatalyzed oxygen scavenger will suffice and can be fed into the storage area of the deaerator. Use catalyzed sodium sulfite in systems without a deaerator. A cobalt sulfate salt, which is present in the catalyzed sodium sulfite material, is used as the catalyst. Catalyzed sulfite reacts more quickly with oxygen than does uncatalyzed sulfite. Both the sodium sulfite and the catalyst must be fed into the feedwater upstream from the boiler so oxygen can be scavenged before the feedwater enters the boiler. This addition scheme also serves to protect feedwater piping from corrosion. A sufficient amount of the oxygen scavenger must be fed to meet the demand for the oxygen initially present and provide an excess residual (reserve amount) for occasions when the oxygen level may increase unexpectedly, so that water testing will always indicate that an excess amount is present. (See Table 2.3 for typical sulfite levels in the boiler water.)

Boiler Pressure KPa (psig)	Sulfite Residual (as ppm SO_3)
0-103 (0-15)	20-40
110-1020 (16-149)	20-40
1030-2060 (150-299)	20-40
2070-3100 (300-449)	20-40
3100-4130 (450-599)	20-40
4140-5160 (600-749)	15-30
> 5170 (> 750)	15-30

Table 2.3

Levels of Sulfite to be Carried in Boiler Water

2.6.2.2 OXYGEN SCAVENGERS FOR BOILERS OVER 6205 KILOPASCALS. For boilers over 6205 kilopascals (900 pounds per square inch gauge), the list of oxygen

scavengers includes specialty volatile treatments such as hydroxylamine, hydroquinone, carbohydrazide, hydrazine sulfate, and erythorbic   acid. Hydrazine can no longer be used because it is a suspected carcinogen. Like hydrazine, these specialty volatile treatments not only scavenge oxygen but also passivate metal surfaces. These chemicals are normally maintained in the boiler water in the parts-per-billion (ppb) range. Sulfite-type oxygen scavengers are not used in boilers over 6205 kilopascals (900 pounds per square inch gauge) because of the potential for thermal decomposition producing sulfur dioxide and hydrogen sulfide, both of which can cause corrosion. The thermal decomposition reactions are:

$Na_2SO_3 + H_2O + Heat \rightarrow 2NaOH + SO_2\uparrow$

$4Na_2SO_3 + 2H_2O + Heat \rightarrow 3Na_2SO_4 + 2NaOH + H_2S\uparrow$
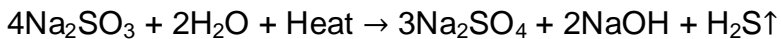
These reactions have been shown to occur at boiler pressures as low as 4140 kilopascals (600 pounds per square inch gauge), although they do not usually create a serious problem until pressures exceed 6205 kilopascals (900 pounds per square inch gauge).

2.7 CONDENSATE CORROSION AND CONTROL

2.7.1 CAUSES OF CONDENSATE CORROSION. Oxygen and carbon dioxide are common steam condensate impurities that promote condensate corrosion. Less common are process contaminants, each of which has corrosive properties dependent upon the nature of the contaminant and on the materials that may be corroded. The piping found in steam condensate systems is commonly constructed of mild steel, whereas heat exchangers are usually copper or mild steel.

2.7.1.1 AIR. Air is the source of oxygen in a condensate system. Condensate lines that are used intermittently are particularly susceptible to condensate corrosion because the cooling of a heated condensate line creates a vacuum that can draw air into the system piping through valve seals or condensate sumps. Additionally, any

dissolved oxygen in the feedwater that is not completely removed, either chemically or mechanically, can enter the boiler and pass with the steam into the condensate lines where it is consumed in a pitting corrosion attack on the metal surfaces. Oxygen corrosion in a condensate system is evidenced by pitting and by the presence of corrosion product deposits called "tubercles."

2.7.1.2 CARBON DIOXIDE. Carbon dioxide (CO_2) can enter the boiler system if it is dissolved in the feedwater. However, CO_2 can be removed effectively through the deaerator. The most common source of carbon dioxide in steam condensate is the carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions (alkalinity) in the feedwater. Under the influence of heat and pressure in the boiler, the carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions (alkalinity) break down into hydroxyl (OH^-) ions (alkalinity) and CO_2 gas. This free CO_2 is volatile and leaves the boiler with the steam. When the steam subsequently condenses, the CO_2 dissolves in the condensate and forms carbonic acid (H_2CO_3), which lowers the pH of the condensate and is corrosive to most metals, particularly to mild steel (see Figure 2.4). You can recognize carbon dioxide corrosion by the thinning of condensate line walls, particularly at the condensate liquid level within the pipe and at pipe threads where the condensate flows. Prevent corrosion in steam boiler systems by neutralizing the CO_2 with volatile amines.
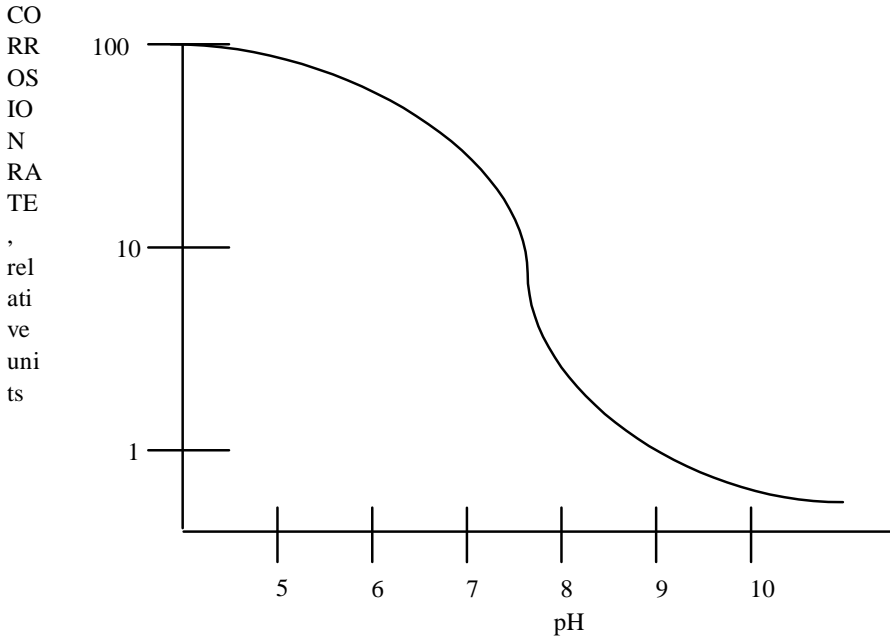
Figure 2.4

Effect of pH on Mild Steel and Copper Corrosion

2.7.2 ESTIMATING CARBON DIOXIDE IN STEAM. Corrosion engineers find it useful to know the amount of carbon dioxide (CO_2) in steam when assessing the return on investment (i.e., cost savings from removing the CO_2 versus the cost for use of internal chemical treatment to remove the CO_2). Engineers and water treatment service companies need to estimate the amount of CO_2 to properly estimate the amount of neutralizing amine water treatment chemical that must be used. Example 5 illustrates this estimation:

CO2 levels in the steam can be estimated from the amount of bicarbonate and the carbonate alkalinity present in the feedwater as follows, where the "P" and "M" alkalinity measure these compounds.

$$CO_2 = [\text{bicarbonate} \times 0.79] + [\text{carbonate} \times 0.35]$$
$$CO_2 = [(M - 2P) \times 0.79] + [2P \times 0.35]$$

where:

CO_2 = carbon dioxide estimate, ppm as CO_2

M = total (methyl orange) alkalinity, ppm as $CaCO_3$

P = phenolphthalein alkalinity, ppm as $CaCO_3$

EXAMPLE

a) Measured P = 2 ppm, M = 60 ppm

b) Bicarbonate CO_2 contribution $[60 - (2 \times 2)] \times 0.79 = 44.2$

c) **Carbonate CO_2 contribution $(2 \times 2) \times 0.35 = 1.4$**

d) **Carbon dioxide estimate $CO_2 = 44.2 + 1.4 = 45.6$ ppm CO_2 in the steam**

NOTE: This is a significant amount of CO_2 in steam due to the amounts of P and M alkalinity in the feedwater. There is some requirement to reduce alkalinity in this quality of feedwater.

2.7.3 CONTROL OF CARBON DIOXIDE BY NEUTRALIZING AMINES. Amines are organic compounds containing a nitrogen group similar to ammonia. They are referred to as "neutralizing amines" in boiler applications because they neutralize acidic (carbonic acid) conditions by raising the pH of the condensate. These amine compounds are volatile and escape the boiler with the steam and eventually dissolve in the steam condensate.

2.7.3.1 CONTROL LIMITS. Amines are added to maintain the pH between 7.5 to 9.0, ideally 7.5 to 8.5, in all parts of the condensate return system. The condensate pH level should not be allowed to fall below 7.5 anywhere within the entire condensate return system or corrosion will occur. For shore-to-ship steam, the Navy requires 8.0 to 9.5 pH (see Table 17). These amines are fed separately from other chemicals and are fed directly into the boiler steam drum where they vaporize and travel with the

steam into the steam lines. Use continuous amine feed to maintain a constant, effective pH in the steam condensate. See Table 2.4.

2.7.3.2 VAPOR-LIQUID DISTRIBUTION RATIOS. Morpholine, diethylamino-ethanol (DEAE), and cyclohexylamine are the three neutralizing amines approved for use in military boilers. When steam condenses in a condensate return system that services multiple heat exchangers in different locations along the steam distribution system, some amines tend to "fall out" into condensate in legs close to the boiler while some amines tend to stay in the steam and come out in condensate toward the end of the steam distribution system. The degree to which this occurs is called the "vapor-liquid distribution ratio" and is expressed:

Vapor-Liquid Distribution Ratio = Amine in steam phase/Amine in condensate phase

Property	Morpholine	DEAE	Cyclohexylamine
Boiling point (100% amine)	129 $^\circ$C (264 $^\circ$F)	163 $^\circ$C (325 $^\circ$F)	134 $^\circ$C (273 $^\circ$F)
Boiling point (amines/water azeotrope)	--	99 $^\circ$C (210 $^\circ$F)	96 $^\circ$C (205 $^\circ$F)
Decomposition temperature	340 $^\circ$C (644 $^\circ$F)	423 $^\circ$C (794 $^\circ$F)	330 $^\circ$C (626 $^\circ$F)
Vapor-liquid distribution ratio	0.4	1.7	4.7
Specific gravity (100% amine)	1.002	0.88	0.86
pH, 100 ppm solution	9.7	10.3	10.7
Amount of amine required to maintain pH of 8.0 in water containing 10 ppm CO_2	37 ppm	22 ppm	15 ppm

Table 2.4
Physical and Chemical Properties of Neutralizing Amines

Amines have different vapor-liquid distribution ratios and will not work equally well in all systems. Depending on the particular amine, it can be effective in short-, medium-, or long-distance condensate lines. In complex condensate return systems, optimum results are obtained by choosing the appropriate amine or combination of amines on a system-by-system basis. A neutralizing amine selection chart is provided in Table 2.5. Often blends of different amines are used.

Amine	Low Pressure (below 103 KPa [15 psig])	High-Pressure Systems (above 103 KPa [15 psig])		
		Short System < 243 m (< 800 ft)[2]	Medium System < 1.61 km (< 1 mile)[2]	Long System > 1.61 km (> 1 mile)[2]
Morpholine		X		
DEAE	X		X	X
Cyclohexylamine [1]	X			
Cyclohexylamine/ morpholine mixture			X	X

NOTES:
1. Cyclohexylamine is not for use in systems having a feedwater alkalinity more than 75 ppm.
2. These system lengths are for classification only and are not absolute. For example, a medium-length system may have more of the characteristics of a long system if lines are poorly insulated or because of poor design. The characteristics of a condensate return system are best determined by a condensate pH survey.

Table 2.5

Neutralizing Amine Selection Chart

2.7.3.3 MORPHOLINE. Morpholine has a low vapor-liquid distribution ratio and will drop out of steam quickly, making it suitable for protecting condensate return systems of short to moderate length. Morpholine is best suited for use in high-pressure systems (103 to 6205 kilopascals [15 to 900 pounds per square inch gauge]) because of its high boiling point. Very little morpholine is lost in deaerators from returning condensate.

2.7.3.4 DEAE. DEAE has a vapor-liquid distribution ratio between that of morpholine and cyclohexylamine. This makes DEAE a good choice for protecting systems of

moderate length where either morpholine or cyclohexylamine, if used separately, would not provide complete protection. The low boiling point of a mixture of DEAE and water makes DEAE suitable for use in both low-pressure boilers and highpressure boilers.

2.7.3.5 CYCLOHEXYLAMINE. Cyclohexylamine has a high vapor-liquid distribution ratio and consequently is best suited for protecting extremely long systems. Cyclohexylamine can also be used in low-pressure systems. Cyclohexylamine is not used in systems when the feedwater alkalinity exceeds 75 ppm because of the low solubility of cyclohexylamine bicarbonate, which can be produced and form deposits. The likely areas for formation of these deposits are low-flow areas at the far end of the condensate return system. This deposition problem can be avoided by reducing feedwater alkalinity or by using DEAE. It is also necessary to treat long systems with morpholine to protect the early part of the system where steam is first condensed.

2.7.3.6 AMINE BLENDS. A mixture of morpholine, DEAE, or cyclohexylamine can be used to provide full protection in medium and large systems. The optimum blend of these amines is determined by measuring the actual pH of the condensate at various locations in the condensate return system. If samples from far sections have a lower pH than other samples, the cyclohexylamine in the mixture can be increased and vice versa. Another pH survey should be done when the blending ratio is changed. An initial blend of 1 part cyclohexylamine and 3 parts morpholine is a good starting point.

2.7.4 CONTROL OF CARBON DIOXIDE AND OXYGEN BY FILMING AMINES.
Carbon dioxide corrosion can be controlled with 0.7 to 1.0 ppm of a filming amine such as octadecylamine. This chemical will coat the condensate pipe and prevent the carbon dioxide in the water from coming into contact with the pipe wall. Filming amines may also be appropriate for use if there is a high degree of air leakage (oxygen) because they coat the metal; however, you should not use them in condensate systems that have had corrosion problems in the past. Excess adsorption of the filming amine on the rust will occur and the amine can dislodge the rust and

cause it to be returned to the deaerator or to the boiler. Adding filming amines continuously during operation and directly into the steam header through a quill, instead of into the steam drum, is essential. Addition of inadequate dosages can result in accelerated pitting-type corrosion due to incomplete surface coverage. You may need written authorization from the appropriate source before using filming amines in military boilers.

2.7.5 CONTROL OF CARBON DIOXIDE AND OXYGEN BY SPECIALTY VOLATILE AMINES. Some of the specialty oxygen scavengers described for boilers over 6205 kilopascals (900 pounds per square inch gauge) can be used for the purpose of control of both carbon dioxide and oxygen. The specialty volatile amines include hydroxylamine, hydroquinone, carbohydrazide, hydrazine sulfate, and erythorbic acid. They work by both raising the pH of condensate and by scavenging oxygen. They also passivate metal surfaces. Their use may not be appropriate and is restricted by the Food and Drug Administration (FDA). Note that these chemicals may not be needed for good operation of military boiler plants.

2.7.6 AMINE LIMITATIONS AND INDOOR AIR AND STEAM QUALITY ISSUES. 21 CFR Part 173.310 restricts using common neutralizing amines and filming amines to the limitations summarized in Table 2.6. Note that the limits shown in Table 6 are maximum allowable concentrations. Using amines may not always be advisable. If amine addition is not continuous, or if the boiler operation is cyclic (e.g., shutting down the boiler for several hours each day), the maximum amine concentration may vary widely and exceed limits, even though the average concentration is within the limits.

Amine	Limitation
Cyclohexylamine	Not to exceed 10 ppm in steam, and excluding steam in contact with milk and milk products.
DEAE	Not to exceed 15 ppm in steam, and excluding steam in contact with milk and milk products
Hydrazine	Zero in steam.
Morpholine	Not to exceed 10 ppm in steam, and excluding steam in contact with milk and milk products.
Octadecylamine	Not to exceed 3 ppm in steam, and excluding steam in contact with milk and milk products.

Table 2.6
Amine Limits

2.7.6.1 STEAM USED FOR STERILIZATION. Some facilities, hospitals in particular, use steam in autoclaves for the purpose of sterilizing equipment such as surgical instruments. There is often concern that neutralizing amines may leave an amine contaminant on the equipment. Installing a dealkalizer to process the makeup water and thereby reduce the levels of bicarbonate and carbonate alkalinity is an alternative to using neutralizing amines. Using a dealkalizer effectively reduces, and may even eliminate, the need for neutralizing amines to reduce carbon dioxide corrosion. Steamto-steam heat exchangers may be used to raise sterile steam.

2.7.6.2 FOOD PREPARATION. The use of neutralizing amines or filming amines is prohibited if the steam contacts milk or milk products. In addition, to provide a margin of safety, the military prohibits any amines in steam used directly for cooking. This may be a sufficient reason to prevent using building steam in food preparation kitchens. In some cases, kitchens use steam to heat jacketed kettles in which food is heated. This application of steam as a heat source does not involve direct contact of

the steam with foodstuffs. In other cases, direct contact between the steam and the foodstuffs is the method used to provide heating. There may be concerns that the amines will impart an amine taste or odor to the food. To alleviate this concern, use package steam generators to provide a source of steam that is independent of the building steam system. Another alternative is to use a steam-to-steam heat exchanger.

2.7.6.3 HUMIDIFICATION. Steam is often used to humidify the air in buildings. The use of amines may raise a concern of contamination of the air in the building. To provide a margin of safety, the military prohibits using amines in steam that is used directly for humidification. Normally, the quantity of an amine in the air of a steamhumidified building is quite small, usually in the low ppb range; however, packaged steam generators can eliminate this concern.

2.8 WATER CARRYOVER IN STEAM. The steam that is produced from boiler water should not contain any liquid water. Common causes of water droplets or impurities being carried into the steam are misting, foaming, priming, and silica carryover.

2.8.1 MIST CARRYOVER. The term "misting" refers to a process in which a fine mist is produced as water boils. This stage process is illustrated in Figure 2.5. In stage 1, a bubble of steam vapor reaches the water surface. In stage 2, the bubble bursts, leaving a dent in the water. In stage 3, the water rises to fill the dent. The center of the dent fills at a faster rate than the edges resulting in a small droplet of boiler water that is thrown off as a fine mist. Most, if not all, of the mist is removed in the mist eliminator section of the steam drum; however, any mist that is not removed will be entrained in the steam. These fine droplets will have the same level of dissolved solids as the boiler water and will contaminate the steam and the condensate.
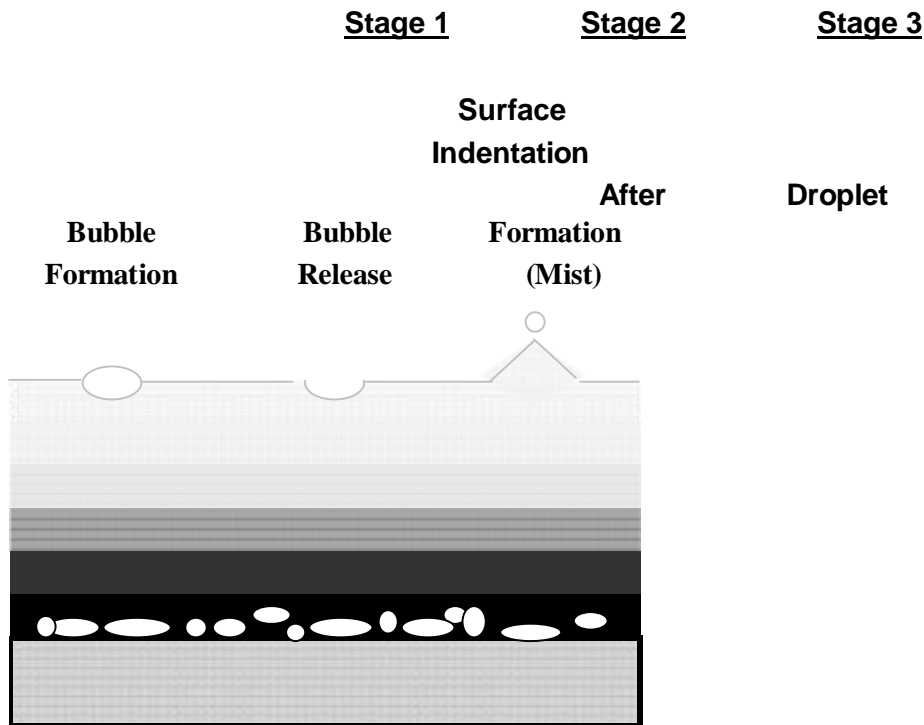
Stage 1   **Stage 2**   **Stage 3**

**Surface
Indentation**
                              After   **Droplet**
Bubble   **Bubble**   **Formation**
Formation   **Release**   **(Mist)**

Figure 2.5

Water Boiler Mist Formation

2.8.2 FOAMING CARRYOVER. The term "foaming carryover" refers to boiler water foam and the carryover of foam into the steam. A variety of conditions can cause foam. Excessive levels of alkalinity, TDS, SS, and at times water treatment chemicals can interact to create foam in the boiler. Normally, maintaining the total alkalinity at less than 20% of the TDS and the total suspended solids (TSS) at less than 8% of the TDS can control foaming to a reasonable level. In addition, adding antifoam agents to the boiler water can control foaming. Polyamides and polyglycols are examples of antifoam agents.

2.8.3 PRIMING CARRYOVER. The term "priming" refers to boiler water in the steam when, due to liquid level variations and surges in the steam drum, water is mixed with

the steam and is subsequently carried into the steam header. A mechanical problem or mechanical properties, such as oversensitive feedwater controls, large steam demands, or incorrect blowdown procedures, always cause priming. There is no chemical control method available, although the addition of antifoam chemicals may help reduce the extent of this occurrence. Boiler operations should be reviewed and modified if priming carryover is occurring.

2.8.4 SILICA CARRYOVER. The term "silica carryover" refers to a situation that occurs when silica in the boiler water volatilizes and enters the steam independently of water carryover. The silica can then form a deposit in the condensate lines and in process equipment when the silica condenses from the steam. When steam turbines are used, silica deposition can be very serious, resulting in unbalancing of the steam turbine blades. Maintaining a low silica level in the boiler water can control silica carryover. The acceptable level is dependent upon the boiler operating pressure; Table 2.7 shows suggested limits.

Boiler Pressure KPa (psig)	Allowable Silica ppm (as SiO_2)
0-103 (0-15)	150
110-1027 (16-149)	150
1034-2062 (150-299)	150
2068-3096 (300-449)	90
3104130 (450-599)	40
4137-5164 (600-749)	30
5171 (750)	20

Table 2.7

Silica Levels Allowed in Boiler Water

2.8.5 DETERMINING WATER CARRYOVER IN STEAM. The best way to determine if any water carryover is occurring is to measure the conductivity of the steam or of the steam condensate. If you detect less than 25 micromhos conductivity in the condensate, then carryover is probably insignificant. If conductivity is greater than 25 micromhos, you should investigate to identify the cause.

2.8.5.1 CONDUCTIVITY MEASUREMENT IMPLICATIONS. A conductivity measurement above 25 micromhos in the steam condensate indicates that there is either carryover or leakage into the steam or condensate system. Accordingly, a test for hardness in the condensate must also be performed. If you find hardness, contamination of the condensate is likely due to raw water or leakage into the condensate system rather than boiler water carryover. If boiler water is at a very low hardness, then raw water may be the cause.

2.8.5.2 DEPOSIT ANALYSIS. Any deposits found in the steam or condensate systems should be analyzed to determine the source. Deposits that are mostly magnetic iron oxide are due to corrosion of mild steel in the condensate system. Using neutralizing amines can control these deposits. If the deposits are mostly silica, increasing the blowdown or removing silica from the makeup water can reduce them. If the deposits are mostly sodium salts (sodium hydroxide, sodium carbonate, sodium chloride, sodium sulfate, and sodium phosphate), the cause is probably boiler water carryover from misting, priming, or foaming.

3. DEVELOPING A STEAM BOILER SYSTEM WATER TREATMENT PROGRAM. A complete boiler water treatment program takes into account industry developed guidelines for feedwater quality limits and boiler water quality limits. The water treatment industry recognizes the suggested water limits developed by the American Society of Mechanical Engineers (ASME), the American Boiler Manufacturers Association (ABMA), and USACE. The limits developed by these three organizations are not always identical; furthermore, the limits are actually only guidelines. In some cases these limits have been exceeded by boiler operations without unacceptable impacts; however, these limits should be considered as prudent, safe, and practical guidelines (see Tables 3.1 through 3.12).

3.1 ORGANIZING A TREATMENT PROGRAM. Once you have defined water treatment requirements, organize personnel to implement the program. The organization process consists of identifying a staff, training them to execute the program, and integrating the program into overall installation management.

3.2 OPERATOR TRAINING. Operator training is essential to a water treatment program. Operators should understand the operation of their specific plant and reasons for specified procedures, including requirements of CFR Title 29, Part 1910.1200, *Hazard Communication*. An understanding of reasons for, and results of, chemical treatment is essential. Knowledge of thermodynamic and mechanical interactions of plant equipment is important. The operator should be particularly aware of safe operating procedures. Since internal chemical treatment of boiler water is a significant factor in achieving reliable and efficient plant operation, operators should have an understanding of the subject. Training should include the specifics of water treatment and related costs.

3.2.1 PRETREATMENT TRAINING. Pretreatment is necessary to ensure the quality of the water to be treated for industrial use and to prevent or reduce associated problems such as deposits and corrosion. Training might address these methods of pretreatment (depending on the type of plant):

- Chemical addition.
- Ion exchange.
- RO.
- Distillation.

3.2.2 TREATMENT TRAINING. Steam boilers, high-temperature water systems, and cooling water systems all require treatment of feedwater to prevent or reduce deposits, scale, corrosion, and microorganisms.

3.2.2.1 BOILER WATER TREATMENT. The training related to boiler water treatment should address:

- Necessity for internal boiler water treatment.
- Deaeration and oxygen scavenging.
- Maintenance of concentration levels.
- Causes and effects of deposits, scale, and corrosion.
- Chemical treatment programs, such as phosphate, polymers, sulfite, hydrazine, and others.
- Where to feed chemicals.
- Effects of carryover and silica on steam purity.
- Prevailing ASME and internal standards.
- Corrosion in condensate returns from oxides of iron and copper.
- Effects of filming and neutralizing amines and hydrazine.
- Boiler layup procedures.

3.2.2.2 COOLING SYSTEMS TREATMENT. Training for treatment of cooling systems feedwater should address:

- Once-through cooling water systems.
- Recirculating cooling water systems.

• Need for and means of maintaining clean condensers.

  • Chemicals and methods of treatment.

  • COC.

3.2.2.3 BLOWDOWN. Blowdown is used in both cooling and steam systems to regulate COC of solids through dilution with makeup water. Training associated with blowdown procedures should include:

  • Surface versus bottom.

  • Internal provisions.

• Estimating blowdown.

  • Continuous and intermittent.

  • Controllers and COC.

  • Heat recovery through flash tanks and heat exchangers for boilers.

3.2.3 PROGRAM CONTENT. Training should be provided in steps that are geared to operators' capabilities. Weekly sessions, with handouts, periodic reviews, and testing should be planned to assess trainees' retention and understanding of material and effectiveness of teaching methods in subjects such as:

  • Basic water chemistry.

  • Chemistry concepts.

  • Water chemistry fundamentals.

  • Elementary water treatment.

  • Water chemistry applications.

  • Water treatment equipment.

• Boiler water treatment.

  • Raw water treatment.

  • Ion exchange.

  • Cooling water treatment.

3.3 FEEDWATER QUALITY LIMITS. Limits are specific for the type of boiler, operating pressure, and steam application. Since feedwater is the combination of makeup water and condensate return, recovering as much uncontaminated condensate as possible is advisable, considering the cost of boiler water treatment and the benefits derived from both energy and water conservation. The high purity of uncontaminated condensate minimizes the requirement for treatment of makeup water and boiler water. The feedwater parameters shown do not specify levels for alkalinity and silica because it is assumed that these levels in the boiler water will be limited through blowdown. In higher pressure boilers using demineralized makeup water, alkalinity and silica will be very low or even absent. Although not specified, it can make sense to reduce feedwater alkalinity and silica in boilers less than 6205 kilopascals (900 pounds per square inch gauge) to allow for an increase in COC and, consequently, to reduce chemical demand. The tables show limits for hardness, iron, and copper. Hardness and iron can be removed by softening the makeup water. Iron and copper may still be present in the feedwater if they are present in the condensate due to corrosion. In many instances, these limits cannot be met for small heating boilers (e.g., oxygen content in feedwater for boilers that lack a deaerator, or hardness levels in feedwater for boilers that lack softeners). The only alternative is to chemically treat boiler water and control COC, as required.

Feedwater Property	ASME	ABMA	USACE
Dissolved oxygen ppm O_2 before chemical oxygen scavenger addition	< 0.007	Note 6	NS
Total iron ppm Fe (as Fe)	< 0.1	Note 6	NS
Total copper ppm Cu (as Cu)	< 0.05	Note 6	NS
Total hardness ppm (as $CaCO_3$)	< 0.5	Note 6	softened
pH at 25 °C (77 °F)	8.10.5	Note 6	NS
Non-volatile TOC ppm (as O_2)	< 1	Note 6	NS
Oily matter ppm	< 1	Note 6	NS

NOTES:

1. Makeup water percentage: Up to 100% of feedwater.
2. Assumes existence of deaerator.
3. Conditions: no superheater, turbine drives, or process restriction on steam purity.
4. Steam purity: 1.0 ppm TDS maximum.
5. NS = not specified.
6. See ABMA Standard – Boiler 401

Table 3.1

Suggested Feedwater Limits for Industrial Water Tube Boiler

0–2068 KPa (0–300 psig)

Feedwater Property	ASME	ABMA	USACE
Dissolved oxygen ppm O_2 before chemical oxygen scavenger addition	< 0.007	Note 6	NS
Total iron ppm Fe (as Fe)	< 0.05	Note 6	NS
Total copper ppm Cu (as Cu)	< 0.025	Note 6	NS
Total Hardness ppm (as $CaCO_3$)	< 0.3	Note 6	NS
pH at 25 ℃ (77 °F)	8.10.5	Note 6	NS
Non-volatile TOC ppm (as O_2)	< 1	Note 6	NS
Oily matter ppm	< 1	Note 6	NS

NOTES:
1. Makeup water percentage: Up to 100% of feedwater.
2. Assumes existence of deaerator.
3. Conditions: no superheater, turbine drives, or process restriction on steam purity.
4. Steam purity: 1.0 ppm TDS maximum.
5. NS = not specified.
6. See ABMA Standard – Boiler 401

Table 3.2

Suggested Feedwater Limits for Industrial Water Tube Boiler

2075-4137 Kpa (301-600 psig)

Feedwater Property	Limit
Dissolved oxygen (ppm O_2) before chemical oxygen scavenger addition	< 0.007
Total iron ppm Fe (as Fe)	< 0.1
Total copper ppm Cu (as Cu)	< 0.05
Total Hardness ppm (as $CaCO_3$)	< 1.0
PH at 25 °C (77 °F)	8.10.5
Non-volatile TOC ppm (as O_2)	< 10
Oily matter ppm	< 1

NOTES:

    1.   Makeup water percentage: up to 100% of feedwater.

    2.   Assumes existence of deaerator.

    3.   Conditions: no superheater, turbine drives, or process restriction on steam purity.

    4.   Steam purity: 1.0 ppm TDS maximum.

Table 3.3 Suggested Feedwater Limits for Industrial Fire Tube Boiler

0-2068 Kpa (0–300 psig)

Feedwater Property	0 - 2068 KPa (0 - 300 psig)	2075-3103 KPa (301-450 psig)	3110 - 4137 KPa (451 - 600 psig)	4144 - 5171 KPa (601 - 750 psig)	5178 - 6205 KPa (751 - 900 psig)	6212 - 6895 KPa (901 - 1000 psig)	6902-10,342 KPa (1001 - 1500 psig)	10,349-13,790 KPa (1501 - 2000 psig)
Dissolved oxygen (ppm O_2) before adding chemical oxygen scavenger	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007
Total iron ppm Fe (as Fe)	≤ 0.1	≤ 0.05	≤ 0.03	≤ 0.025	≤ 0.02	≤ 0.02	≤ 0.01	≤ 0.01
Total copper ppm Cu (as Cu)	≤ 0.05	≤ 0.025	≤ 0.02	≤ 0.02	≤ 0.015	≤ 0.01	≤ 0.001	≤ 0.001
Total Hardness ppm (as $CaCO_3$)	≤ 0.03	≤ 0.03	≤ 0.02	≤ 0.02	≤ 0.1	≤ 0.05	ND	ND
pH at 25 °C (77 °F)	8.3-10.0	8.3-10.0	8.3-10.0	8.3-10.0	8.3-10.0	8.3-9.6	8.3-9.6	8.3-9.6
Chemicals for pre-boiler system	NS	NS	NS	NS	NS	VAM	VAM	VAM
Non-volatile TOC ppm (as O_2)	< 1	< 1	< 0.5	< 0.5	< 0.5	< 0.2	< 0.2	< 0.2
Oily matter ppm	< 1	< 1	< 0.5	< 0.5	< 0.5	< 0.2	< 0.2	< 0.2

NOTES:

1. Makeup water percentage: Up to 100% of feedwater.
2. Assumes existence of deaerator.
3. Conditions: Includes superheater, turbine drives, or process restriction on steam purity.
4. Saturated steam purity target as shown.
5. NS = not specified.
6. ND = not detectable.
7. VAM = Use only volatile alkaline materials upstream of a temporary water source.

Table 3-4

ASME Feedwater Limits for Industrial Water Tube Boilers

Feedwater Property	3103-5861 KPa (450-850 psig)	5867-8618 KPa (851-1250 psig)
Dissolved oxygen (ppm O_2) before chemical oxygen scavenger addition	< 0.007	< 0.007
Total iron ppm Fe (as Fe)	< 0.02	< 0.01
Total copper ppm Cu (as Cu)	< 0.01	< 0.005
Total hardness ppm (as $CaCO_3$)	< 0.1	< 0.05
pH at 25 $^{\circ}$C (77 $^{\circ}$F)	8.3–9.0	8.3–9.0
Chemicals for pre-boiler system	VAM	VAM
Oily matter ppm	< 0.05	< 0.05

NOTES:
1. Makeup water percentage: Up to 5% of feedwater.
2. External treatment: at sea, evaporator condensate; in port, evaporator condensate or water from shore facilities meeting feedwater quality guidelines.
3. Assumes existence of deaerator.
4. Saturated steam purity: 30 ppb TDS maximum, 10 ppb Na maximum, 20 ppb SiO_2 maximum.
5. VAM = Use only volatile alkaline materials.

Table 3.5

ASME Suggested Feedwater Limits for Marine Propulsion Water Tube Boiler

3.4 BOILER WATER CHEMISTRY LIMITS. Tables 3.6 through 3.9 show boiler water chemistry limits. The limits are specific for the type of boiler, operating pressure, and steam application. There are two types of limits to recognize. The first comes from the presence of natural constituents in the feedwater (i.e., TDS or conductivity, silica, and alkalinity). These constituents can be the controlling factor for COC. Blowdown is ultimately required to keep their levels within limits. SS is the result of precipitation of minerals. These are kept within limits through bottom blowdown. The second type is treatment limits for chemicals added into the boiler (see Tables 3.10 and 3.11).

Boiler Water Property	0-2068 KPa (0-300 psig)	2075-4137 KPa (301-600 psig)
Silica (ppm SiO_2)	< 150	< 90
Total alkalinity	< 1000	< 850
Free OH alkalinity	NS	NS
Specific conductance (μmhos/cm) without neutralization	< 7000	< 5500

NOTES:
1. Makeup water percentage: Up to 100% of feedwater.
2. Assumes existence of deaerator.
3. Conditions: no superheater, turbine drives, or process restriction on steam purity.
4. Steam purity: 1.0 ppm TDS maximum.
5. NS = not specified.

Table 3.6

ASME Suggested Boiler Water Limits for

Industrial Water Tube Boiler

Boiler Water Property	0 - 2068 KPa (0 - 300 psig)	2075 - 3103 KPa (301-450 psig)	3110 - 4137 KPa (451 - 600 psig)	4144 - 5171 KPa (601 - 750 psig)	5178 - 6205 KPa (751 - 900 psig)	6212 - 6895 KPa (901 - 1000 psig)	6902 - 10342 KPa (1001 - 1500 psig)	10349 - 13790 KPa (1501 -2000 psig)
Silica (ppm SiO_2)	≤ 150	≤ 90	≤ 40	≤ 30	≤ 20	≤ 8	≤ 2	≤ 1
Total alkalinity	< 350	< 300	< 250	< 200	< 150	< 100	NS	NS
Free OH alkalinity	NS	NS	NS	NS	NS	NS	ND	ND
Specific conductance (μmhos/cm) without neutralization	5400-1100	4600-900	3800-800	1500-300	1200-200	1000-200	≤150	≤80
TDS (maximum) ppm	1.0-0.2	1.0-0.2	1.0-0.2	0.5-0.1	0.5-0.1	0.5-0.1	0.1	0.1

NOTES:
1. Makeup water percentage: Up to 100% of feedwater.
2. Assumes existence of deaerator.
3. Conditions: Includes superheater, turbine drives, or process restriction on steam purity.
4. Saturated steam purity target as shown.
5. NS = Not specified.
6. ND = Not detectable.

Table 3.7

ASME Boiler Water Limits for Industrial Water Tube Boilers

Boiler Water Property	Limit
Silica (ppm SiO_2)	< 150
Total alkalinity	< 700
Free OH alkalinity	NS
Specific conductance (μmhos/cm) without neutralization	< 7000

NOTES:
1. Makeup water percentage: Up to 100% of feedwater.
2. Assumes existence of deaerator.
3. Conditions: no superheater, turbine drives, or process restriction on steam purity.
4. Steam purity: 1.0 ppm TDS maximum.
5. NS = not specified.

Table 3.8

ASME Boiler Water Limits for Industrial Fire Tube Boilers

0-2068 Kpa (0–300 psig)

Boiler Water Property	3103-5861 KPa (450-850 psig)	5867-8618 KPa (851-1250 psig)
Silica (ppm SiO_2)	< 30	< 5
Total alkalinity	NS	NS
Free OH alkalinity	< 200	ND
Specific conductance (μmhos/cm) without neutralization	< 700	< 150

NOTES:
1. Makeup water percentage: Up to 5% of feedwater.
2. External treatment: at sea, evaporator condensate. In port, evaporator condensate or water from shore facilities meeting feedwater quality guidelines.
3. Assumes existence of deaerator.
4. Saturated steam purity: 30 ppb TDS maximum, 10 ppb Na maximum, 20 ppb SiO_2 maximum.
5. NS = not specified.
6. ND = non detectable.
7. VAM = Use only volatile alkaline materials.

Table 3.9

ASME Suggested Boiler Water Limits for Marine Propulsion Water Tube Boiler

3.5 TREATMENT GUIDELINES FOR LOW-PRESSURE STEAM. Treatment guidelines for boilers operating at less than 103 kilopascals (15 pounds per square inch gauge) are determined by size and type, as described in Table 3-18. Cast iron boilers and boilers less than 334 watts (10 horsepower) are not treated. Boilers with greater than 95% condensate return can either be treated the same as a closed hot water boiler, or treated the same as boilers with less than 95% condensate return. The latter uses external treatment, usually softening, and internal chemical treatment that includes a scale inhibitor (precipitating type – i.e., phosphate) or solubilizing type (i.e., phosphonates and polymers) sulfite to control pitting due to oxygen, and a neutralizing amine to control pH in the condensate system. Sometimes raising pH in the boiler water requires a supplemental source of alkalinity. Usually this supplemental source is caustic soda, but it can also be sodium carbonate (soda ash).

Boiler	Guidelines
Cast iron	Not treated
Less than 334 W (10 hp)	Not treated
Boiler with 95% condensate return	1. External treatment: softening. 2. Internal treatment: precipitating or solubilizing scale inhibitor, sulfite, tannin derivatives, filming surfactant, caustic supplement if necessary, neutralizing amine. 3. See Tables 3-19 through 3-20. Or 4. Treat same as closed hot water (see Chapter 5).
Boilers with less than 95% condensate return	1. External treatment: softening. 2. Internal treatment: precipitating or solubilizing scale inhibitor, sulfite, tannin derivatives, filming surfactant, caustic supplement if necessary, neutralizing amine. 3. See Tables 3-19 and 3-20.

Table 3.10

Treatment Guidelines for Low-Pressure Steam

3.6 TREATMENT GUIDELINES FOR MEDIUM- AND HIGH-PRESSURE STEAM.

Treatment of medium- (110 to 2062 kilopascals [16 to 299 pounds per square inch gauge]) and high-pressure (2068 to 6205 kilopascals [300 to 900 pounds per square inch gauge]) boilers is similar and is described in Table 3.11. Treatment can include either a precipitating (i.e., phosphate) or a solubilizing (i.e., phosphonate or polymers) approach to scale control. Sulfite is used to control pitting due to oxygen, and a neutralizing amine is used to control pH in the condensate system. Sometimes raising pH in the boiler water requires a supplemental source of alkalinity. Usually this source is caustic soda, but it can also be sodium carbonate (soda ash). Boilers operating between 4137 to 6205 kilopascals (600 to 900 pounds per square inch gauge) will sometimes use erythorbic acid or specialty volatile oxygen scavengers or amines (i.e., hydrazine, DEHA, carbohydrazide, hydroquinone or methylethylketoxime) as oxygen scavengers in boiler water. The volatile compounds can also scavenge oxygen in a condensate system.

Parameter	Boiler Water Treatment Control
COC	Maximum of 100, per ASME
General corrosion	Maximum total alkalinity, per ASME guidelines, pH of 10.3–12.0. May require alkalinity builder.
Pitting corrosion	20-40 ppm sulfite for boilers up to 6205 KPa (900 psig). Specialty volatile oxygen scavengers optional for boilers 4137-6205 KPa (600-900 psig). Also, tannin derivatives and other organic-based oxygen scavengers
Condensate corrosion	Maintain pH of 7.5-9.3 using neutralizing amines or follow guidelines for filming surfactant chemistry. Specialty volatile oxygen scavengers optional.
Deposition control	1. Precipitating program using phosphate or carbonate with a polymer sludge conditioner. Or 2. Solubilizing program using chelants, phosphonates, or polymers. Or 3. Tannin and lignin derivatives and phosphonates and/or polymers (including acrylate-styrenesulfonate co-polymers and polymethacrylates)
Carryover control due to foaming	Limit total alkalinity, per ASME guidelines, and treat with antifoam as required.

Table 3.11

Treatment Guidelines for Medium- and High-Pressure Steam

3.7 CONDENSATE CORROSION AND CONTROL. Oxygen and carbon dioxide are common steam condensate impurities that promote condensate corrosion. Less common are process contaminants, each of which has corrosive properties dependent upon the nature of the contaminant and the materials that may be corroded. The piping found in steam condensate systems is most commonly constructed of mild steel, whereas heat exchangers are usually copper or mild steel.

3.8 TREATMENT GUIDELINES FOR VERY-HIGH-PRESSURE STEAM. Treatment of very-high-pressure (greater than 6205 kilopascals [900 pounds per square inch gauge]) boilers is different than for those of lower pressure. Because temperatures and pressures are much more extreme, the boilers can tolerate little in the way of boiler water impurities. Table 3.12 provides treatment guidelines.

Parameter	Boiler Water Treatment Control
COC	Maximum of 100, per ASME.
General corrosion control	Maintain pH, per ASME guidelines, using coordinated, congruent, or equilibrium phosphate, or with all volatile treatment.
Pitting corrosion control	Volatile hydrazine substitutes: hydroxylamine, hydroquinone, carbohydrazide, hydrazine sulfate, tannin derivatives, or erythorbic acid.
Condensate corrosion control	Maintain pH of 7.5-9.3 using specialty volatile oxygen scavengers listed for pitting control above.
Deposition control	External treatment to remove scaling agents. Example: RO with demineralization
Carryover control due to foaming	External treatment to remove alkalinity and other minerals. Example: RO with demineralization

Table 3.12

Treatment Guidelines for Very-High-Pressure Steam

3.9 BOILER OPERATOR DUTIES. Operators should keep feedwater quality, COC, and treatment levels within program control limits at all times. Operators must perform recordkeeping and assess trends in the results of system performance tests routinely. When changes in feedwater quality, TDS, or chemical treatment levels occur, the operator must investigate and resolve the reasons for these changes. Boiler operators need to understand their equipment and how it operates. Does it operate seasonally? Does it operate intermittently? Does the amount of condensate return vary? These conditions may require adjustments in chemical treatment.

4. CHEMICAL REQUIREMENTS FOR BOILER START-UP. Start-up of a new or repaired boiler requires special water treatment procedures. The start-up of a boiler after a wet or dry layup period also requires special water treatment procedures.

4.1 COMMON PROBLEMS DURING START-UP OF NEW BOILERS. A common problem that can occur during start-up of new boilers is corrosion of the boiler tubes due to improper initial conditioning of the water and boiler metal. Carryover of boiler water due to improper start-up can also occur, particularly with new boilers.

4.2 START-UP OF NEW BOILERS AND CONDENSATE SYSTEMS OR REPAIRED BOILERS. As a result of the fabrication process, a new or repaired boiler that is erected in the field or shipped as a package unit will likely contain oils and greasy films, and perhaps rust, on the metal surfaces. The oils, grease, and rust can contribute to carryover and contaminate the steam and initiate corrosion of the boiler components. A pre-operational alkaline boil-out procedure is required to remove these materials. This pre-operational process is usually part of a new construction project and therefore may not be in the direct control of boiler operations personnel. Often, the contracting officer involved with the project can provide verification of the completion of this important step. The following example of an alkaline boil-out procedure consists of four steps:

- Inspect the inside of the boiler and remove all debris.
- Add an alkaline boil-out chemical formulation to the boiler water. This should be roughly equivalent to the following formulation: 10.4 kilograms (24 pounds) of caustic soda, 10.4 kilograms (24 pounds) of disodium phosphate, 3.5 kilograms (8 pounds) of sodium nitrate, 0.2 kilogram (0.5 pound) non-ionic wetting agent (a low-foaming detergent) per each 3785 liters (1000 gallons) of boiler capacity.
- Fill the boiler to the steam header and maintain at low fire for 1 to 2 days. For condensate systems, this formulation should be circulated for

3 to 4 days, drained completely, and the system dried completely by purging with dry air.

- Drain and flush. Proceed immediately to operational treatment levels or to a layup status. Untreated water should never be allowed to remain in the boiler.

-

Problem	Recommended Solution/Possible Cause
Hardness in feedwater	1. Check softener 2. Possible leak into condensate system
Change in overall treatment levels	1. Change in amount of condensate return 2. Change in blowdown control 3. Change in overall chemical feed rate
Loss of alkalinity	1. Hardness incursion 2. Loss of caustic feed 3. Excessive blowdown
Loss of scale prohibitor	1. Hardness incursion 2. Loss of chemical feed 3. Excessive blowdown
Loss of sulfite	1. Loss of sulfite feed 2. Poor deaerator operation or influx of oxygen 3. Excessive makeup and loss of condensate
High conductivity (>25 μmhos) in steam	Carryover due to misting, foaming, or priming
Foaming carryover	Excessively high TDS, alkalinity, or chemical treatment
Priming carryover	Operational problem with excessive load demands, feedwater and level control problem, uneven firing patterns
Misting carryover	Defective mist eliminators

Table 3.13

Troubleshooting Boiler System Water

4.3 START-UP OF BOILER FROM WET LAYUP. Boilers that have been properly laid up wet will already have adequate excess levels of sulfite and alkalinity. Upon

adjusting the water level and firing up the boiler, feed all chemical treatments as normally added, except for sulfite and alkalinity supplement. There is no need to feed these treatments until blowdown results in reducing their levels. Then add chemicals in the amounts required to reach normal maintenance levels.

4.4 START-UP OF BOILER FROM DRY LAYUP. Boilers that have been properly laid up dry can be filled with feedwater to their normal operating boiler water level. The start-up dosage of sulfite and alkalinity supplement (caustic or soda ash) can be fed along with the standard chemical treatment feed rates to obtain normal levels of water treatment chemicals. It is necessary to achieve proper sulfite and alkalinity levels in the boiler water to control corrosion while the COC is increased to normal operating levels. The sulfite concentration should be at least 20 ppm (SO3), and the alkalinity level should result in a pH of about 11.0.

5. CHEMICAL REQUIREMENTS FOR BOILER LAYUP. Boiler layup also requires special water treatment. Boilers that will be out of service for more than 4 calendar days require special water treatment to prevent internal corrosion. Boiler layup can be either dry or wet. The advantages of wet layup are that it often provides better corrosion protection and the boiler can be brought on-line much faster than when dry layup procedures are used.

5.1 OPERATIONAL CONSIDERATIONS. Operational considerations are important to consider when determining the proper boiler status. The terms "lead" and "lag" are used commonly for boilers that need to meet varying load demands. The lead boiler satisfies the base steam load. The lag boiler meets any extra steam demand that might be needed during hours of the evening or mornings or when (additional) process loads are required. Lag status does not apply to a cold boiler that is not required for duty for a few days. Such a boiler should be considered in layup condition and should be prepared accordingly.

5.2 COMMON PROBLEMS THAT OCCUR DURING LAYUP. Common problems that occur during layup are: oxygen pitting of tubes and condensate piping, sometimes to the point of failure; general corrosion of tubes and condensate piping; and corrosion product contaminating feedwater via the condensate system.

5.3 DRY LAYUP OF BOILERS. Boilers with manholes may be laid up in one of two ways, depending on the length of storage and conditions in the boiler room: open dry layup, or quicklime or silica gel layup.

5.3.1 OPEN DRY LAYUP METHOD. The open dry layup method is recommended for short-term storage (30 to 150 days) where the boiler room is dry, has low humidity, and is well ventilated. It is important to keep the boiler dry. The recommended procedure consists of six basic steps:

1) Take the boiler out of service and drain it completely while still warm. Make sure the water walls and gauge columns are not overlooked.

2) Lock and tag out boiler in accordance with written procedures.

3) Break the feedwater and steam connections to the boiler and blank off connections if other boilers in the plant are operating.

4) The boiler may be opened and the inside washed of all loose scale and sediment by flushing with high-pressure water.

5) Use a stiff brush to clean all internal surfaces that can be reached.

6) Leave boiler open to the atmosphere. Should a humid atmosphere exist, the boiler must be closed up and the procedure specified used.

5.3.2 QUICKLIME OR SILICA GEL LAYUP METHOD. This procedure is recommended for storage over 150 days or for less than 150 days when the boiler room and atmosphere is quite humid and not well ventilated. The recommended procedure consists of eight basic steps:

1) Take the boiler out of service and drain completely while still warm. Make sure that water walls and gauge columns are not overlooked.

2) Lock and tag out the boiler in accordance with written procedures.

3) Break the feedwater and steam connections to the boiler and blank off connections if other boilers in the plant are operating.

4) The boiler may be opened and the water-contacted inside surface washed to remove all loose scale and sediment by flushing thoroughly with high-pressure water.

5) Use a stiff brush to clean all internal surfaces that can be reached.

6) Start a very light fire in the furnace to dry out the boiler water-contacted surfaces. Maintain this fire for at least 2 hours or until inspection shows no moisture on internal sections of the boiler.

7) Place quicklime (not hydrated lime) or new, unused silica gel in one or more metal or fiber trays in the boiler. Place the trays on wood blocks so air can circulate under them. The amount of lime or silica gel required is about 22 kilograms (50 pounds) per 0.36 kilogram of steam per second (3000 pounds per hour) boiler capacity.

8) Seal the boiler to prevent any moist air from entering the boiler.

9) Open and inspect the boiler every 2 months. Replace any moist quicklime or silica gel with new material.

10) Carefully reseal immediately after the inspection and after the addition of new chemicals.

5.3.3 WET LAYUP OF BOILERS. This method means that the boiler is kept completely full of treated water. This method is easier to check and the boiler can be put back in service more quickly. This method should not be used if the boiler is subject to freezing temperatures.

5.3.3.1 WET LAYUP WITHOUT DRAINING (OPERATIONAL BOILERS). This method is used most commonly when a boiler is to be shut down for 4 to 30 calendar days. Often the boiler must be maintained in a standby condition. Corrosion will most likely occur in the boiler unless both the water level in the steam drum and the chemicals in the boiler are increased. These procedures are recommended for wet layup of a boiler without draining or cleaning:

1) Approximately 4 hours before the boiler is to be shut down, add sufficient sodium hydroxide (caustic) to increase the hydroxyl alkalinity (causticity) to 10 to 20% higher than the upper limit given above for the pressure of the boiler to be laid up.

2) Add sufficient sodium sulfite to increase the sulfite residual to 200 ppm (as SO3).

3) Extinguish the fire to the boiler.

4) Add water to completely fill the entire boiler until the water runs out of the vent (safety) valve or air cock.

5) When the boiler is completely cool, add more water to ensure it is full.

6) Maintain a pressure of 35 to 69 kilopascals (5 to 10 pounds per square inch gauge) during layup and maintain the levels of alkalinity and sulfite.

7) Check the boiler frequently to make sure no water has leaked out.

8) Analyze the boiler water at least once per month to make sure the chemical residuals are being maintained.

5.3.3.2 WET LAYUP OF DRAINED BOILERS. These procedures are recommended for boilers that have been emptied for cleaning or repair before wet layup:

1) Drain the boiler completely and remove scale or deposits.

2) Remove connections to other active boilers, feedwater, and steam systems.

3) Fill the boiler with water (deaerated water if available) and add enough sodium hydroxide (caustic) to give a hydroxyl level of about 200 ppm (as OH).

4) Add sodium sulfite to give a sulfite residual of 200 ppm (as SO_3).

5) Circulate chemicals in the boiler by careful boiling for 2 hours. Be sure to fill the boiler to replace any losses during this treatment.

6) Extinguish the fire to the boiler.

7) Add water to completely fill the entire boiler until the water runs out of the vent (safety) valve or air cock.

8) When the boiler is completely cool, add more water to ensure it is full. Maintain a pressure of 35 to 69 kilopascals during layup and maintain the levels of alkalinity and sulfite.

9) Inspect the boiler on a regular basis and replace any water losses. To facilitate inspections, a small steel tank equipped with a gauge glass can be installed above the top of the boiler, as shown. Fill the tank with treated water and connect to a steam takeoff tap, vent, or safety valve connection. A glance at the water level in the small drum will quickly tell whether or not the boiler is completely filled.
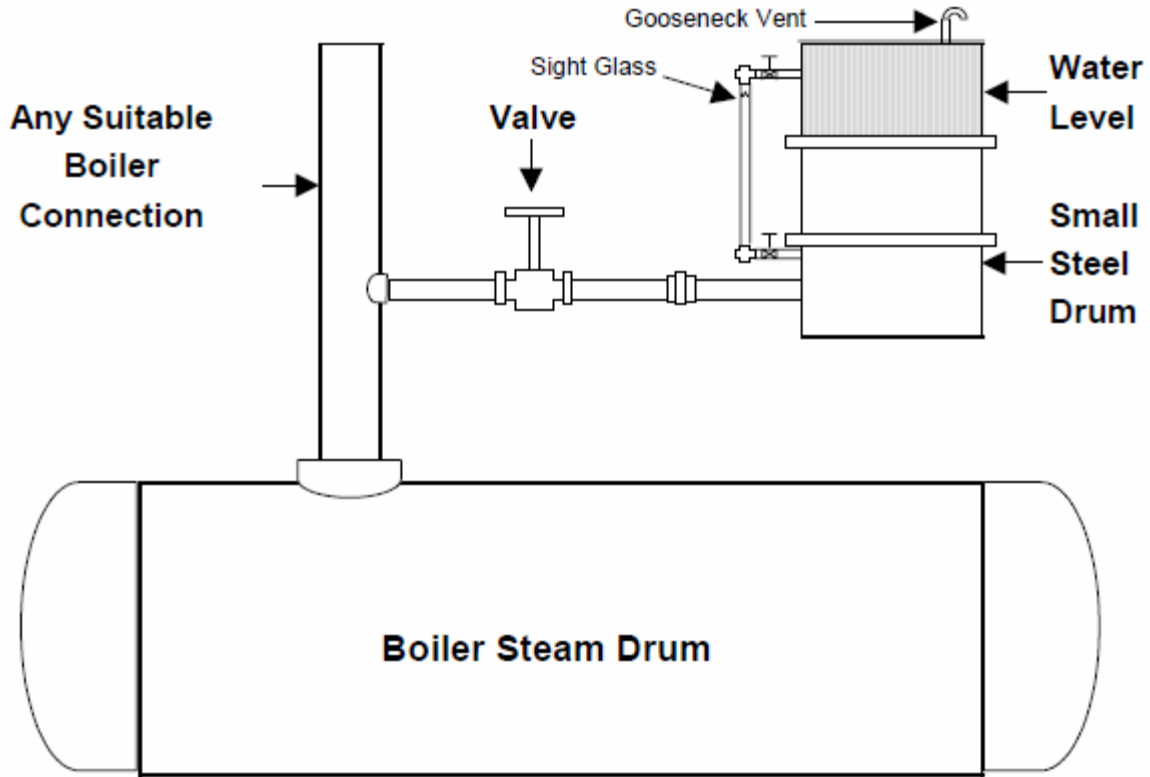
Figure 3.1

Inspection Gauge for Wet Boiler Layup

5.4 LAYUP OF CONDENSATE SYSTEMS. Layup of condensate systems is much more difficult than layup of boilers. As the system cools, oxygen will be drawn in, resulting in a situation that leads to corrosion. Purging the system with dry, inert gas can be effective, but the logistics can be nearly impossible and the hazards include the potential for suffocating people if the system is located in an unvented area. Application of a high dosage of a filming amine prior to shut down can be effective, but its use is restricted for many applications and is prohibited in military operations. Application of a high dosage of neutralizing amines or of a specialty volatile oxygen scavenger can be helpful. The application of any amine or specialty volatile oxygen scavenger can be limited where steam purity or FDA restrictions exist.

6. COMMONLY ASKED QUESTIONS AND ANSWERS ON BOILER WATER TREATMENT

Q1. What is meant by neutralized conductivity?

A1. Boiler water most often contains hydroxyl (OH-) alkalinity. The OH- contribution to conductivity is disproportionately large compared to other ion species. Furthermore, the OH- contribution towards conductivity is not used in calculating TDS. The OH-conductivity is therefore neutralized using an organic acid (i.e., gallic acid). Organic acids are used because they do not contribute to conductivity.

Q2. What is the relationship between conductivity and TDS?

A2. Conductivity is a measurement of electrical conductance of ionized species dissolved in water and is reported in units of micromhos or microsiemens per centimeter. TDS is the actual amount of mineral in solution measured in ppm. In boiler water, neutralized conductivity times 0.7 yields a good approximation to TDS. When tannin is used as a dispersant, the factor increases proportionally to the amount of tannin present.

Q3. Why are there different types of alkalinity to be concerned with?

A3. Alkalinity can exist as bicarbonate (HCO_3-), a carbonate

(CO_32-), or as hydroxyl (OH-). Natural waters usually contain bicarbonate or carbonate alkalinity. Hydroxyl alkalinity is required in steam boilers below 6205 kilopascals (900 pounds per square inch gauge) and is either provided by addition of caustic or by the breakdown of bicarbonate and carbonate alkalinity in the boiler. The breakdown of bicarbonate and carbonate alkalinity also produces carbon dioxide, which forms carbonic acid in the condensate system.

Q4. How often should bottom blowdown be done?

A4. There is no absolute rule for frequency of bottom blowdown. It can vary between once per shift to once or twice a week. The required frequency depends on the boiler, the feedwater quality and the type of chemical treatment program. A precipitating treatment program reacts with hardness in the feedwater to form a sludge that must be removed through bottom blowdown. A solubilizing treatment program keeps hardness in solution and creates little in the way of sludge.

Q5. Where is the best location to feed sulfite?

A5. Sulfite, like any oxygen scavenger, should be fed into the storage section of a deaerator. This ensures the removal of oxygen before the feedwater enters the boiler.

Q6. What is the difference between makeup water and feedwater?

A6. Makeup water is water that comes from a source outside of the boiler system. Feedwater is a combination of makeup water and condensate return.

Q7. How does one balance chemical treatment levels and COC?

A7. COC is controlled through blowdown. Blowdown is often measured by maintaining conductivity or TDS within a specific control range. Chemical treatment levels are controlled by the chemical feed rate into the boiler and by blowdown. It is best to maintain consistent control of COC first, followed by proper adjustment of chemical feed rates. If there is a sudden change in chemical treatment levels without any changes in blowdown or chemical feed rates, then there is likely to be a change in feedwater quality (e.g., change in condensate return rate, hardness excursion, poor deaerator operation).

Q8. Are boiler water treatment chemicals safe to work with?

A8. Yes, provided the directions on the MSDS sheets are followed. The highest hazard is due to chemical burns from highly caustic substances.

Q9. Why is it impossible to get all the parameters (e.g., alkalinity, TDS) in the control range?

A9. It is not impossible as long as the control ranges are proper for a given boiler operation. The first parameter to control is COC. Maximum cycles are limited by some parameter (i.e., alkalinity, TDS, silica, carryover). Any one of these can be the limiting factor for COC. Once proper cycles are established, chemical treatment feed rates should be adjusted to keep levels within control ranges.

Q10. The softeners need to be regenerated more often than before. What could be the problem?

A10. The problem could be one of many things. It usually is due to higher demands for makeup water. It could, however, be due to an increase in makeup water hardness levels or a deficiency in regeneration. Deficiencies in regeneration can be due to insufficient brine strength, insufficient brine time, inadequate backwash resulting in channeling, lost or cracked resin, and heavily fouled resin due to iron.