

7.0 Chemical Treatment

7.1 OVERVIEW

This section deals with specific chemical treatments. Type, purpose, and application are all discussed. The treatments are divided along the lines of preboiler and condensate systems, and the boiler itself. The preboiler system is usually treated with pH adjustment chemicals, amines, and oxygen control chemicals, called scavengers. The condensate system is treated with pH adjustment and corrosion control chemicals, volatile amines and filming amines. The boiler is treated with chemicals to control deposition of salts and corrosion products, buffering of pH, and dispersants.

The main objective in every case is to permit the safe and efficient operation of the boiler and steam handling system. Corrosion control aids in boiler cleanliness and prevention of equipment failures. Deposit control aids in the maintenance of good heat transfer, which translates into better efficiency and prevention of tube failures. In the condensate system, corrosion and deposit control are essential for recovery of condensate for re-use.

In discussing chemical treatment in boiler systems, the following terminology will be used:

- Pretreatment or external treatment: Chemical and physical treatment of makeup water to prepare a consistent, satisfactory quality boiler feedwater.
- Internal treatment: Chemical treatment of the boiler water to control mineral scaling, corrosion and general deposition in the boiler drums and boiler tubes.
- Condensate treatment: Chemical treatment of steam condensate, applied either in the steam lines or in the boiler, to control carbonic acid and dissolved oxygen corrosion in the condensate lines.

As a general rule, the higher the boiler pressure, the higher the quality of feedwater required. Therefore, the higher the pressure, the more chemical treatment is concentrated outside the boiler in water preparation (chapter 2), and the less internal boiler water treatment and condensate treatment is required.

Boilers are often classified by operating (throttle) pressure. These groupings are arbitrary, and there is much overlapping between groups, but for purposes of discussing chemical treatment the following groupings are convenient:

- Low pressure steaming boilers, operating below about 300 psig, that use untreated, or at best zeolite softened feedwater to make steam primarily for HVAC and humidification use. Feedwater may or may not be mechanically deaerated. These boilers require substantial internal treatment to maintain clean surfaces and prevent corrosion. Systems are simple, and precise control of chemical dosages and boiler operations is generally not required.

- Medium pressure boilers, between about 300 and 900 psig, are the workhorses of industry. These boilers are designed in many different ways, either packaged or field-erected (section 3.0) They provide steam for heating, power generation, transportation and process uses in a wide variety of commercial, institutional and industrial facilities. Feedwater is at least softened, and is normally demineralized and mechanically deaerated. Internal chemical treatment is required for alkalinity control to prevent boiler and condensate corrosion, and to prevent residual solids deposition. Dosages are lower than in low pressure boilers, but since many of these boilers are quite large, usage can be substantial. Chemical reactions are complex and careful control is required. Many of these boilers are controlled by manual testing, but automatic control is preferred, especially in higher pressure systems.
- High pressure boilers, between about 900 and 1200 psig, are used primarily for electric power generation, in large industrial plants and power stations. Feedwater is always demineralized and mechanically deaerated. Chemical dosages are low, primarily for alkalinity and corrosion control. Dosages are critical and control is almost always automated.
- Very high pressure boilers, from above 1200 psig to supercritical pressures (section 5.3.4) are found in large power generation stations. They require the highest possible purity feedwater but only very small amounts of chemical treatment.

Although not part of the above classification, hot water heating boilers are also an important segment of boiler water treatment. These units are similar to closed cooling systems. Chemical treatment of hot water heating boilers is discussed in this section and also in chapter 4 (cooling water).

This chapter is organized by chemical treatment (oxygen scavengers, internal treatments, condensate treatment, etc.). Then the treatments are classified by application to boilers in the pressure groupings above.

7.2 DISSOLVED OXYGEN CONTROL

Dissolved oxygen can lead to severe corrosion in the economizer section and in the boiler. In the feedwater system, it will contribute to metals transport into the boiler, where deposition can lead to under-deposit corrosion and long term overheating. Dissolved oxygen enters the system via makeup water, which is often air saturated, or leaks into condensers or through pump seals.

The most common effect of dissolved oxygen is to increase the corrosion of the feedwater heaters. Copper and iron oxides are formed which break loose and travel to the boiler. These metal oxides deposit on the hottest part of the boiler tubes and create insulating deposits. From the heat transfer discussion in section 5.1, such insulating deposits increase the temperature gradient needed to provide a constant heat flux. The temperature rises on the tube wall, and overheating may result. Over a long time, such overheating can lead to metal fatigue and failure. Copper deposits can also lead to galvanic corrosion of steel.

Oxygen problems are especially severe where ammonia is present in significant quantities. In the presence of oxygen, ammonia is very corrosive to copper. Ammonia is used for feedwater pH adjustment. It can also be formed from the thermal breakdown of hydrazine:



or from hydrothermal breakdown of organic amines:



Where R is a general organic group like (HO)CH₂-CH₂- (ethanolamine).

Ammonia cannot attack copper metal itself. It reacts only with copper ions in the +2 oxidation state (cupric). In the feedwater loop, these will be in the form of cupric oxide (CuO) and hydroxide (Cu(OH)₂). The cupric state can only form if oxygen is present. So it is the combination of ammonia AND oxygen that is aggressive to copper alloys. If oxygen is kept low by mechanical and chemical means then ammonia will not be a problem for copper.

However, maintaining low oxygen levels can be a difficult task. Oxygen enters the system from makeup water, cooling water leaks, condensate storage tank equilibration with the atmosphere, and pump seal leaks. Systems that are frequently laid up or which fluctuate widely in load may be more susceptible to air leakage.

The economizer section is very susceptible to oxygen corrosion. It is the first predominantly steel surface where dissolved oxygen can directly attack the metal. The high flow rates through this section preclude deposit buildup. Instead, deep hemispherical pits form in the tubes. These tubes are thinner than boiler tubes, and so can fail faster.

In the boiler itself, excessive oxygen levels can lead to oxygen pitting and tube failure. Pits are hemispherical, with sharp edges, and often have caps of corrosion products.

7.2.1 Methods for Dissolved Oxygen Removal

Two methods are available for removing dissolved oxygen from boiler water and steam systems: mechanical stripping, or deaeration (section 4.3); and chemical oxygen scavengers. Oxygen scavengers are reducing agents that react with even the very low levels of oxygen left in water by good deaeration. They are normally added to the storage section of the deaerator, to allow time for reaction before the feedwater reaches the boiler.

Low pressure boilers sometimes do not include mechanical deaerators. In these systems, oxygen scavengers are required to do the whole job of dissolved oxygen removal. Obviously, much larger dosages are required in this case.

Oxygen scavengers fall into several classes. These include sulfites and ascorbates (non-volatile), and hydrazines, hydroquinones, hydroxylamines, and ketoximes (volatile). Each of these is discussed in the following sections.

7.2.2 Sulfite

Sulfites are used in lower pressure boilers. They are non-volatile, and so add dissolved solids to the boiler. Sulfites are very reactive, and reduce oxygen to very low levels, less than 5 ppb if used correctly.

The reaction of sulfite with oxygen can be written as:



Above 430°F (350 psia) sulfite reacts with iron oxide:



Fe_3O_4 is magnetite, an intermediate valence form of iron oxide that forms good protective oxide films (passive films) under boiler conditions (low or zero oxygen levels). However, sulfite is not considered to be a good passivating agent because it does not passivate low pressure boilers, where sulfite is most often used. Passivation can be accomplished in high pressure boilers, but high dosages of sulfite are needed.

Sulfite is commonly supplied as sodium sulfite, Na_2SO_3 ; sodium bisulfite, NaHSO_3 ; ammonium sulfite, $(\text{NH}_4)_2\text{SO}_3$; or sodium metabisulfite, $\text{Na}_2\text{S}_2\text{O}_5$.

Sodium sulfite can decompose to sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) in the boiler. For this reason, the use of sulfites is limited to boilers under 900 psig. Up to 600 psig, residuals of 30-50 mg/L can be used; above 600 psig, 10-20 mg/L is the safe limit. Avoid large overfeeds.

Table 3-5
Sulfite Feed Requirements

Chemical	mg/L SO_3 per mg/L O_2
Na_2SO_3	7.88
NaHSO_3	6.5
$(\text{NH}_4)_2\text{SO}_3$	7.25
$\text{Na}_2\text{S}_2\text{O}_5$	5.94

A sulfite residual should be maintained in the boiler of about 5 to 20 mg/L as SO_3 . The feed rate should be that shown in Table 3-5 plus 5 to 20 mg/L as sulfite divided by the boiler cycles.

Although sulfite reacts slowly with oxygen at room temperature, it reacts very quickly at elevated temperatures. Also, the presence of minute quantities of oxidizable metal ions like ferrous iron (Fe^{+2}) or cobalt (Co^{+2}) will greatly accelerate the rate of reaction with oxygen. The presence of Fe^{+2} ions in boiler feedwater is usually sufficient to promote rapid oxygen scavenging by sulfites.

Many water treatment suppliers supply catalyzed sulfite products, usually containing cobalt.

As discussed above, sulfite does not passivate metal surfaces as well as other common oxygen scavengers, and is rarely used for this purpose.

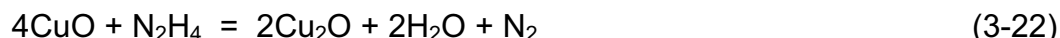
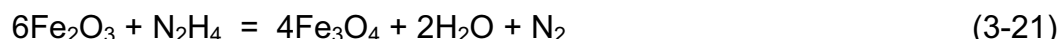
7.2.3 Hydrazine

Hydrazine is a very common oxygen scavenger. It is an inorganic reducing agent of great power. However, the reaction rate of hydrazine with dissolved oxygen is slower than the sulfite reaction. For this reason, plus difficulties in handling, hydrazine is not often used in low pressure boilers.

The reaction of hydrazine with oxygen is:



At temperatures greater than 250°F, hydrazine reacts with metal oxides:



Ferric oxide is reduced to the familiar black, protective magnetite film (equation 3-21), and cupric oxide is reduced to red cuprous oxide (3-22). These reactions passivate, or protect the metal surfaces in the boiler, and hydrazine is used as a passivating agent as well as an oxygen scavenger.

Hydrazine decomposes in the boiler water at 400-600°F (250-1500 psia):

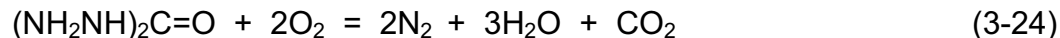


Feed rates of about 5 times stoichiometric are required for good oxygen scavenging. For every 1 mg/L of oxygen feed about 5 mg/L of hydrazine. The excess will break down to ammonia in the boiler (equation 3-23) and may cause problems in copper condensate systems unless they are air free. Hydrazine is typically supplied as a 35% solution in water.

Hydrazine is listed as a carcinogenic compound and must be handled with proper precautions.

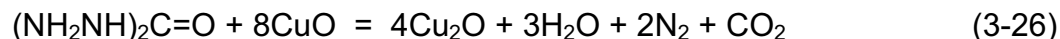
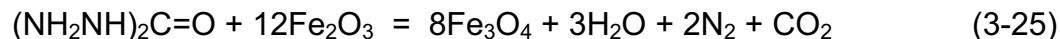
7.2.4 Carbohydrazide

Carbohydrazide is a derivative of hydrazine. It reacts readily with oxygen:



Decomposition: carbohydrazide first breaks down to hydrazine and carbon dioxide, and then decomposes to ammonia and nitrogen.

Reduction of metal oxides:



Thus, the passivating properties of carbohydrazide are similar to hydrazine. However, the produced carbon dioxide adds to the potential for acidic condensate, and must be taken into account.

The feed rate is the same as for hydrazine: about 2.5 times stoichiometric, or about 5.6 mg/L per mg/L of oxygen.

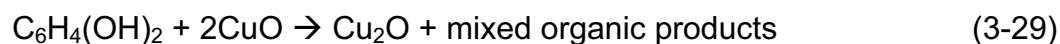
7.2.5 Hydroquinone

Hydroquinone is a powerful reducing agent (scavenger). Hydroquinone is dangerous to handle, and may cause copper transport problems.

Reaction with oxygen:



Metal oxide reduction (passivation):



The feed rate of hydroquinone for oxygen scavenging is approximately 3 to 7 mg/L per 1 mg/L oxygen.

The oxidation product of hydroquinone, benzoquinone (equation 3-27) can also scavenge oxygen. Thus the stoichiometric relation does not fully apply.

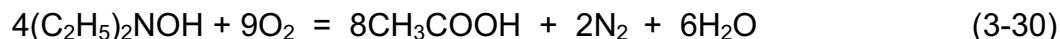
Hydroquinone is more reactive than other oxygen scavengers, and scavenges at temperatures below 180°F.

Hydroquinone is very toxic, and must be handled in a well ventilated area.

7.2.6 Diethylhydroxylamine (DEHA)

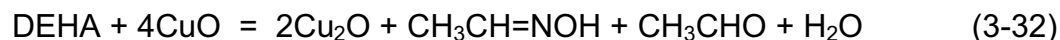
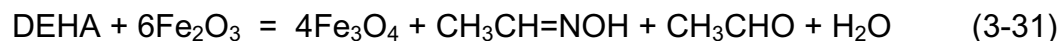
The hydroxylamines, mainly diethylhydroxylamine, DEHA, are also used effectively for oxygen control.

Reaction with oxygen:



The reaction product, acetic acid, is neutralized to form acetate ions with hydroxide in the boiler, and is removed with blowdown.

Reactions with metal oxides:



DEHA has passivating properties, as shown by (3-31) and (3-32), but it is less effective and slower reacting than hydrazine and hydroquinone.

DEHA breaks down above 300 psig to form a small amount of ammonia plus organic acids and carbon dioxide.

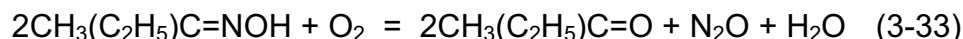
The feed rate is 6 mg/L per mg/L O₂ (a 5:1 stoichiometric excess).

DEHA is an amine, and is sometimes used to neutralize carbon dioxide (carbonic acid) in condensate, as well as to scavenge oxygen (section 7.4).

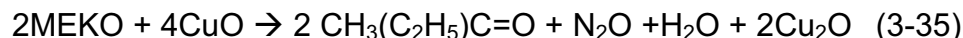
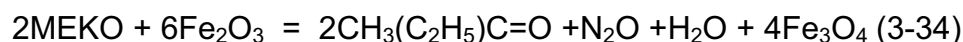
7.2.7 Methylethylketoxime (MEKO)

Methylethylketoxime (MEKO) is another scavenger, not as widely used.

Reaction with oxygen:



Reaction with metal oxides:



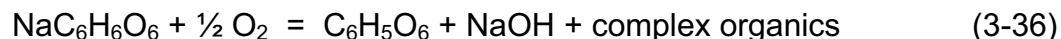
MEKO also breaks down to ammonia and organic acids above 1800 psig.

Feed rate: the stoichiometric rate is 4.7 mg/L per mg/L O₂; feed normally at 5 times stoichiometric.

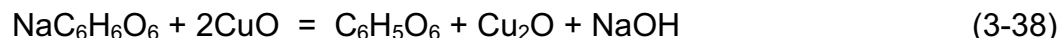
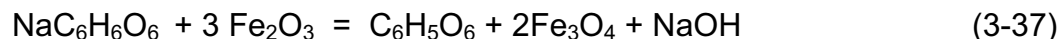
7.2.8 Ascorbate/Erythorbate

Ascorbic acid (vitamin C) and erythorbic acid, an isomer of ascorbic acid, are organic, non-volatile, non-toxic oxygen scavengers useful up to about 1500 psig.

Reaction with oxygen:



Reduction of metal oxides:



Feed rate: the stoichiometric rate is 12 mg/L active acid per mg/L O₂; feed at 5 times stoichiometric.

7.2.9 Handling of oxygen scavengers

Oxygen scavengers are fed to the downcomer or storage section of the deaerator. A stoichiometric amount based on feedwater is added, plus enough to give the required stoichiometric residual at the economizer inlet. Table 3-6 summarizes feed rates for the various scavengers.

Table 3-6
Oxygen Scavenger Feedrates

Oxygen Scavenger	Operating Pressure, psig	mg/L Active / mg/L Oxygen
Sulfite	0-600	6-8 + 5-50 mg/L residual (see Table 3-4)
Sulfite	601-900	6-8 + 5-20 mg/L residual (see Table 3-4)
Hydrazine	>2500	5
Carbohydrazide	>2500	5-6
Hydroquinone	>2500	3-7
DEHA	>2500	6
MEKO	<1800	25
Ascorbate/erythorbate	<1500	30

For lay-up, oxygen scavengers are fed to the boiler water as it is being filled, to provide 100 to 500 mg/L active scavenger. Amines are also added for pH adjustment.

7.3 INTERNAL CHEMICAL TREATMENT: HARDNESS CONTROL PROGRAMS

Boiler internal treatments are designed to prevent deposition of sparingly soluble salts of hardness and silica that may be in the feedwater. The recommended limits of these substances for various pressure ranges are discussed in section 7-3.

Internal treatments are also designed to prevent corrosion by a variety of means. Ordinarily, the hydrothermal reaction of iron with water will produce a stable, protective (passive) film of magnetite, Fe_3O_4 , if the pH is controlled in the 9 to 11 range. Corrosion inhibiting programs are designed to maintain this pH by a buffering effect, or by the control of alkalinity breakdown in the boiler.



It is still vital to control oxygen levels with good deaeration and oxygen scavenging practice. Internal treatments cannot prevent unacceptable levels of corrosion in a boiler if oxygen levels are above 5 to 10 ppb in the boiler on a regular basis.

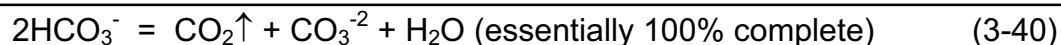
7.3.1 Carbonate Cycle

Unless the feedwater is demineralized and polished (demineralizer train, mixed bed polisher, or reverse osmosis/mixed bed polisher, chapter 2) it will contain alkalinity. Alkalinity is defined as the capacity to neutralize hydrogen ion, H^+ . Alkalinity should not be confused with “alkaline”, which is a water condition where the pH is on the basic side of neutral (chapter 1, section 6).

Although the definition of alkalinity is general, and can apply to any proton (hydrogen ion) acceptor, in boiler systems alkalinity is concerned mainly with carbonate.

Carbonate salts exist in water due to the dissolution of limestone by acidic waters. The carbonic acid so formed reacts with alkaline metals like sodium or potassium, to form carbonate salts. Carbonic acid, H_2CO_3 , exists in three forms: free carbon dioxide (carbonic acid/water), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). Carbonic acid equilibrium, alkalinity and P and M alkalinity relationships are discussed in chapter 1, section 6 of this manual.

If either softened or raw water is used for makeup, alkalinity will be in the feedwater. For most feed waters, the alkalinity is almost completely in the form of bicarbonate. The bicarbonate breaks down in the boiler in a two stage reaction:



Taken together, two moles of bicarbonate will produce about 1.8 moles of carbon dioxide, or about 0.649 mg/L of CO_2 per mg/L of HCO_3^- . Converting bicarbonate to M alkalinity, about 0.79 mg/L of CO_2 are produced for every 1 mg/L of M alkalinity (as CaCO_3) in the boiler feedwater (chapter 1).

The carbon dioxide passes completely into the steam, and dissolves in the condensed steam to form carbonic acid. This makes the condensate very acidic. Treatment with neutralizing amines is therefore needed to prevent acidic attack in condensate lines (section 7.4).

Left behind in the boiler is hydroxide ion (equation 3-41), making the boiler alkaline. This is desirable, since the pH range for optimum magnetite formation is about 9.5 to 12. High pH is also needed for effective formation of calcium phosphate precipitates, preventing scaling of the boiler by hardness. Also, precipitation of magnesium hydroxide and control of silica are dependent on maintaining the proper pH range.

For every mole of bicarbonate, about 0.8 moles of hydroxide are formed, or about 0.22 mg/L hydroxide for every 1 mg/L of bicarbonate. Put in terms of alkalinity expressed as mg/L CaCO_3 , every one mg/L of M alkalinity in the feedwater will produce about 0.79 mg/L of P alkalinity expressed as CaCO_3 .

Early treatments for low pressure boilers made use of the carbonate cycle. Breakdown of alkalinity to form hydroxide (equation 3-40) forms the basis for this program. However, this same reaction forms carbonate ions (equation 3-41), which can react rapidly with calcium ion to form a hard scale of calcium carbonate on the boiler tube walls. Because calcium carbonate has inverse solubility (chapter 1), it will precipitate on the hottest parts of the system first. The scale is hard, tenacious, and very insulating. Boiler efficiency is severely decreased, and tube overheating and failure can ensue.

To help overcome this problem, scaling was controlled first by the addition of natural dispersant polymers obtained from seaweed, lignin from trees, etc. Current technology involves the addition of synthetic polymers for scale control.

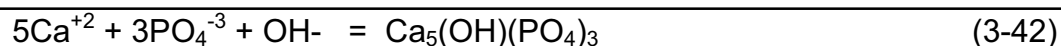
Carbonate cycle treatments are still in use today in very low pressure boilers. However, these programs have mostly been replaced by phosphate precipitation programs (section 7.2.2, below) that are more effective in controlling calcium carbonate scaling.

7.3.2 Phosphate Precipitation Programs

Phosphate precipitation programs are based on two important phenomena:

- The solubility of calcium phosphate is substantially less than calcium carbonate, so that phosphate added to boiler water will precipitate calcium hardness as calcium phosphate, thus preventing formation of calcium carbonate scale.
- The form of calcium phosphate that precipitates under boiler water conditions is hydroxyapatite, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$. Hydroxyapatite forms a loose, fluffy precipitate that can be dispersed in the water with the aid of either natural or synthetic polymers, and removed with blowdown. This effectively prevents mineral scale deposits from forming in the boiler.

Phosphate is added to the boiler to precipitate calcium hardness entering from the feedwater. Phosphate precipitation treatments are typically used in low and medium pressure boilers. Even with softened or demineralized feedwater, these boilers may contain hardness levels as high as 3 to 5 mg/L as CaCO_3 due to breakthrough from the water preparation train. Phosphate converts the hardness to hydroxyapatite:



For every one mg/L of calcium as CaCO_3 in the feedwater, one mg/L of disodium phosphate (DSP, Na_2HPO_4) is needed to react with all the calcium. Some additional DSP should be added to produce a phosphate residual in the boiler. A typical residual would be from 5 to 30 mg/L as PO_4^{-3} . Since 1.49 mg/L of DSP contributes 1.0 mg/L PO_4^{-3} , the amount of DSP needed will be about 1.49 times the desired phosphate residual in the boiler. Taking boiler cycles into account, DSP fed to the feed water will be:

$$\text{FW DSP} = \text{FW Ca} + 1.5 \times \text{desired residual } \text{PO}_4^{-3}/\text{boiler cycles} \quad (3-43)$$

Or, if fed directly to the boiler based on blowdown:

$$\text{DSP} = \text{FW Ca/cycles} + 1.5 \times \text{desired } \text{PO}_4^{-3} \text{ residual} \quad (3-44)$$

If trisodium phosphate (TSP, Na_3PO_4) is used instead of DSP, then the corresponding TSP fed to the feed water will be:

$$\text{FW TSP} = \text{FW Ca} \times 1.15 + 1.7 \times \text{desired residual } \text{PO}_4^{-3}/\text{cycles} \quad (3-45)$$

Or, if fed directly to the boiler based on blowdown:

$$\text{TSP} = \text{FW Ca} \times 1.15/\text{cycles} + 1.7 \times \text{desired PO}_4^{-3} \text{ residual} \quad (3-46)$$

The values above are calculated based on the anhydrous forms of the phosphate salts. However, most of the phosphate salts come as hydrates. Table 3-7 details the addition rates of the various phosphates and Table 3-8 contains operating parameters for phosphate precipitation programs vs. boiler pressure.

Table 3-7
Phosphate Salt Addition Parameters

PO ₄ Salt	Feedwater		Boiler (based on blowdown)	
	Ca	Residual	Ca	Residual
DSP	FW Ca	1.5 x target residual/cycles	FW Ca/cycles	1.5 x target
DSP•12H ₂ O	2.5 x FW Ca	3.8 x target residual/cycles	2.5 x FW Ca/cycles	3.8 x target residual
TSP	FW Ca x 1.15	1.7 x target residual/cycles	1.15 x FW Ca/cycles	1.7 x target residual
TSP•12H ₂ O	FW Ca x 2.7	3.95 x target residual/cycles	2.7 x FW Ca/cycles	3.95 x target residual

Table 3-8
Phosphate Treatment Guidelines

Parameter	Operating pressure psig		
	0-300	300-600	600-1000
PO ₄ ⁻³	30-60	30-60	20-40
P –alkalinity	300-600	300-500	200-400
SiO ₂	150	50	15
neutralized conductance	2500-3500	2000-2500	1000-1500

Polymer is also needed to disperse the calcium phosphate formed by the reaction of phosphate with hardness. A typical treatment polymer is a low molecular weight polyacrylic acid (PAA) or polymethacrylic acid (PMA).

Boiler conductivity will adversely affect polymer dispersancy capabilities. Polymer levels need to be augmented in higher conductivity waters. Typical polymer addition levels are given in Table 3-9.

Table 3-9
Polymer Addition Parameters in Phosphate Programs

Boiler Hardness, mg/L as CaCO ₃	Polymer Actives, mg/L
<10	10-20
10-30	20-40
30-60	40-60
CONDUCTIVITY < 2200 µs/CM	ABOVE
2200-5000	1.5 x ABOVE
5000-9000	2 x ABOVE
9000-15000	3 x ABOVE
>15000	4 x ABOVE

7.3.3 Use of Polyphosphates and Organic Phosphates in Boiler Water

Inorganic phosphate chemistry is discussed in chapters 1 and 4. Briefly, phosphate compounds are available as a series of orthophosphates, discussed in section 7.2.2 above, and as polymerized forms known as polyphosphates. Typical commercial polyphosphates include potassium pyrophosphate, sodium tripolyphosphate, and sodium hexametaphosphate. These names are empirical and do not necessarily describe the chemical structures of these compounds. Structures vary with method of manufacture.

The important thing is that all of these complex phosphates are polymers of orthophosphate, and when dissolved in water, all will eventually hydrolyze (revert) to orthophosphate. The reaction rate is temperature sensitive. At boiler water temperatures, reversion is rapid, so that all forms of phosphate quickly become orthophosphate in the boiler.

However, this does not mean that polyphosphates should not be used. There are two good reasons for using polyphosphates in boiler water formulations:

- Ease of formulation: Trisodium phosphate is very alkaline and not very soluble in water. Phosphoric acid and dihydrogen phosphate are very soluble but also very acid. These factors create difficult problems in formulating complex boiler water products. Most of these problems can be avoided by using polyphosphates, which are quite soluble and more nearly neutral in pH.
- Avoiding calcium phosphate scale: Products containing orthophosphates should never be added to a boiler feedwater line, because of the possibility of precipitating calcium phosphate scale in the line. The consequence of doing this could be rapid plugging of the line, with disastrous effects on boiler operations. This problem also is easily avoided by using polyphosphates in formulations.

These same statements hold true for organic phosphates (phosphonates) such as HEDP. Papers have been published touting the value of using HEDP in low pressure boilers. The fact is, however, that the same results can be achieved by adding an equivalent amount of phosphate to the boiler as orthophosphate.

HEDP may well have important value in formulations, but it should be considered as a source of orthophosphate in the boiler water.

7.3.4 Chelant Programs

Another strategy for hardness control in boiler water is to complex the hardness and solubilize it. Chelants act to form complexes which are extremely stable because they form multiple attachment points to the hardness ions. They react stoichiometrically, like the phosphates. Unlike the phosphates, they do not form insoluble precipitates, but rather form soluble species.



$$K = [\text{complex}] / [\text{Ca}^{+}] [\text{chelant}] \quad (3-48)$$

The most common chelant is EDTA, ethylenediaminetetraacetic acid. Values for the complex ion formation constants are shown in Table 3-10. Equilibrium constants are explained in chapter 1.

Table 3-10
Complexation Constants for EDTA

Ion	K
Ca	3.9×10^{10}
Mg	4.9×10^8
Fe^{+2}	2.1×10^{14}
Fe^{+3}	1×10^{25}
Cu^{+2}	6.3×10^{18}

The EDTA complex effectively reduces the concentration of the available hardness, below its saturation value, so that calcium carbonate will not precipitate.

The stoichiometry is 1:1 on a molar basis. Since EDTA tetrasodium salt has a molecular weight of 380 and calcium carbonate has a molecular weight of 100, then 3.8 mg/L of EDTA will be needed for every 1 mg/L of hardness ion as CaCO_3 . Commercially, EDTA sodium salt comes as a 38% solution. Therefore, 10 mg/L of solution will be needed for every 1 mg/L of hardness. This is an easy relationship to use. However, when planning a chelant-based boiler water treatment program, the question of free chelant residual must be considered very carefully. See section 7.2.4, below, for a discussion of chelant corrosion and free chelant residuals.

Chelant programs need to be closely monitored, and controlled. Feedwater hardness is critical. The boiler hardness will be the feedwater hardness x boiler cycles. Iron and copper can also be treated with chelant. The feedwater should be analyzed for soluble or active iron and copper. This can be done by analyzing a micron filtered feedwater sample. For every one mg/L of iron, use 6.8 mg/L of chelant, or 17.9 mg/L of 38% chelant solution. For copper the corresponding values are 6 mg/L and 15.7 mg/L per mg/L of soluble feedwater copper.

The chelant demand for iron and copper must be added to the hardness demand before calculation the residual.

Overall, chelant programs have the ability to maintain very clean boilers, since they are based on soluble rather than precipitation chemistry. However, because they require careful control and monitoring, they are best-used in boilers that operate under stable conditions with few changes, and where experienced operators are available that have boiler monitoring as part of their assigned duties.

7.3.5 Chelant Corrosion and Free Chelant Residuals

In the complete absence of dissolved oxygen, EDTA and other chelants are not aggressive, and free residuals as high as 20 mg/L can easily be tolerated. However, dissolved oxygen, even in trace amounts, makes EDTA extremely corrosive. Chelant corrosion takes the form of deep, longitudinal gouges in the boiler tubes. The areas of attack are severely thinned, clean, and non-porous. The magnetite coating is removed, and bare metal is visible. Damage can occur very quickly if a substantial EDTA residual is present and dissolved oxygen should accidentally enter the boiler water.

The reason for this severe attack is that oxygen and chelant work cooperatively to attack steel. EDTA by itself is not corrosive. However, oxygen corrodes the steel surface and tries to form what would be a protective, passive layer of magnetite, Fe_3O_4 – except that the EDTA chelates the iron ions as they are formed, takes them out of circulation and prevents magnetite formation. No passive film is allowed to form, and the oxygen continues to attack bare steel.

The response to this situation must be twofold: (1) Never allow dissolved oxygen in the boiler. (2) Never use a chelant program in a boiler that may, even occasionally, show a measurable free oxygen residual. If a consistent level of residual oxygen scavenger can be maintained, this will normally solve this problem, except in unusual circumstances.

As insurance, do not use an unnecessarily large chelant residual. Any residual, even 1 mg/L above the expected calcium hardness level in the boiler water, will ensure that no calcium carbonate forms. Larger residuals are often used, to account for expected variability in calcium levels. This must be a site-specific judgment call. The best solution is to improve feedwater preparation and boiler operations so that hardness levels in the boiler water stay low and constant, and then use a low chelant residual.

7.3.6 All Polymer Programs

All polymer programs are used with waters containing sufficient natural alkalinity to raise the pH to 10 to 11. At that pH silica is rendered less volatile, magnesium will precipitate as the hydroxide, and calcium will form calcium carbonate.

Applications are generally limited to below about 1000 psig.

The treatment is based on dispersing the solids that will form in the boiler with polymers, and maintaining a high enough pH to passivate the metal surfaces and to minimize the volatility of silica. See Chapter 4 for an in-depth discussion of polymer dispersion and inhibition activity.

The main principle of all-polymer internal boiler water treatments is that polymers act in two ways in the boiler water:

- Like chelants, they complex with hardness ions so that the hardness does not precipitate. Polymers are not as powerful chelants as EDTA, so that the ratio of polymer to boiler water hardness must be carefully controlled. On the positive side, polymers do not prevent magnetite films from forming, so that the potential corrosion problem with EDTA does not exist with polymeric chelants.
- Polymers also act like threshold dispersants by adsorbing on micro-crystallites and distorting the crystal structure. This interferes with crystal growth and adsorption on walls. Polymeric dispersants, specifically selected to disperse iron oxides and calcium carbonate, keep deposits off the tube walls and maintain a loose sludge that can be removed with blowdown.

Polymers typically used are based on polyacrylic acid and polymaleic anhydride. Often copolymers of acrylic and maleic acids are used. For higher temperature applications, polymers incorporating polymethacrylic acid and sulfonated polymers are effective. Sulfonated styrene-maleic anhydride copolymers are common in these programs.

All-polymer programs can be used in boilers ranging from very low pressures up to about 1000 psig. Performance of specific polymers varies. Applications above 1200 psig are feasible, but should be used only if the specific polymers have been tested for stability and performance at higher pressures. Limitations on all-polymer programs arise because:

- The polymers begin to thermally degrade at higher temperatures.
- The polymer chelates, already less stable than the corresponding EDTA chelates, become even less stable with increasing temperature. At the same time, the solubility of calcium carbonate continues to decrease, so that above a specific temperature for each polymer, the chelation effect no longer prevents scale formation.

All-polymer programs are compatible with most oxygen scavengers and neutralizing amines. Caustic can be added to supplement the natural alkalinity in the feedwater. Because polymer programs do not intentionally add insoluble ions, as do phosphate precipitation programs, boilers tend to stay cleaner.

As the pressure increases, polymer levels should increase and allowable hardness levels decrease. Table 3-11 details general application guidelines. These are very general. Specific formulations will require a more conservative approach or allow for more relaxed guidelines. Polymer dosages should be based on total hardness plus iron demand in the system.

Table 3-11
All-Polymer Treatment Guidelines

Parameter	Pressure, psig		
	0-300	301-600	601-900
Polymer mg/L	15-30	30-60	60-90
P-alkalinity, mg/L CaCO ₃	200-500	200-400	1200-300
Silica (SiO ₂)	<200	<50	<15

7.3.7 Combination Programs

Chelants can be combined with phosphate to chelate some of the hardness, and precipitate the rest. In higher pressure boilers where hardness levels are low, one can add up to 1 mg/L of chelant (2.6 mg/L of 38% solution). The remainder of the hardness can be precipitated by phosphate according to the guidelines in section 7.2.2. In this system, it is not necessary to carry a chelant residual, with its associated problems.

Chelants, polymer and phosphate can all be combined. The use of chelant with phosphate decreases the overall amount of polymer needed. For every 10% reduction in hardness treated by chelant, the polymer can be reduced by from 5 to 10 %. This program optimizes dosages of all three components, and avoids the need for a free chelant residual.

These programs are attractive where precipitation programs are needed at the high end of the medium pressure range.

7.3.8 Comparison of Hardness-Control Programs

The four precipitation chemistry internal boiler water treatment programs discussed in this section overlap. In most cases, more than one program will be suitable. The choice must be made on a site-specific basis, involving feedwater quality, boiler operating modes, operator availability and skills, and economic factors.

The following summary in Table 3-12 highlights the advantages and disadvantages of each program, as an aid in program selection. It is important to remember, however, that site-specific factors and individual water treatment supplier technology may override the general recommendations in this section.

Table 3–12
Comparison of Precipitation Programs

Program	Advantages	Disadvantages
1. Carbonate cycle	• Simple and inexpensive. • No added boiler solids. • No special control or testing. • Dosages not critical. • Best in very low pressure boilers with little attention.	• Can not tolerate high heat loads. • Boilers will be considered dirty. • Not suitable for critical systems.
2. Phosphate precipitation	• Most forgiving program. • Tolerates variable feedwater, steam loads and cycles. • Best in low to medium pressure boilers with some hardness.	• Large amount of boiler sludge. • Boilers will show some deposits. • Not suitable in critical systems that must be kept clean.
3. Chelant	• Cleanest boilers. • No added boiler solids. • No boiler sludge. • Best for critical systems and long runs in stable systems.	• Requires monitoring & control by trained personnel. • Not best with variable loads or feedwater quality. • Danger of chelant corrosion if oxygen enters boiler.
4. All – polymer	• Clean boilers. • No added boiler solids. • Minimum sludge, no deposits. • Useful over wide pressure range, safe chemicals.	• Requires monitoring & control by trained personnel. • Will not tolerate variable loads or feedwater quality. • Polymers degrade at high temp.
5. Chelant – phosphate	• Advantages of phosphate program with less sludge, no chelant residual.	• Requires monitoring & control by trained personnel. • Not best with variable loads or feedwater quality.
6. Chelant–phosphate–polymer	• Optimized program – reduce phosphate & chelant dosage, no chelant residual.	• Requires monitoring & control by trained personnel. • Not best with variable loads or feedwater quality.

7.4 INTERNALCHEMICAL TREATMENT: ALKALINITY CONTROL

7.4.1 Coordinated Phosphate Programs

Boilers that use very high purity feedwater should have no need for precipitation-type internal treatment programs because there should be nothing to precipitate. Feedwater will be demineralized and mixed-bed quality, with conductivity approaching less than 0.5 $\mu\text{S}/\text{cm}$. This includes the high end of the medium pressure boiler range, and all high pressure and very high pressure boilers.

Chelant and all-polymer programs (section 7.2.3) may be the treatments of choice in these boilers if the feedwater contains soluble iron (often carried in with returned condensate). EDTA and polymeric chelants form complex ions with the iron so that iron oxide deposits can not form.

Another widely-used approach in high purity feedwater boilers is alkalinity control. The basis of these programs is to buffer the boiler water in the pH range of 9 to 11 so that a protective magnetite film can form, following the Schikorr reaction (equation 3-39). A secondary function of the program is to buffer the buildup of acid or caustic under any deposits that exist in the boiler. Chemical buffers for pH control are explained in chapter 1.

Phosphoric acid (H_3PO_4) is a weak acid. It ionizes in water in a manner very similar to carbonic acid (chapter 1), to form three ionized species: dihydrogen phosphate (H_2PO_4^-), monohydrogen phosphate (HPO_4^{2-}), and orthophosphate (PO_4^{3-}). These forms distribute according to pH, in a manner similar to the carbonate species. The phosphate ion distribution vs. pH is shown in Figure 3-17.

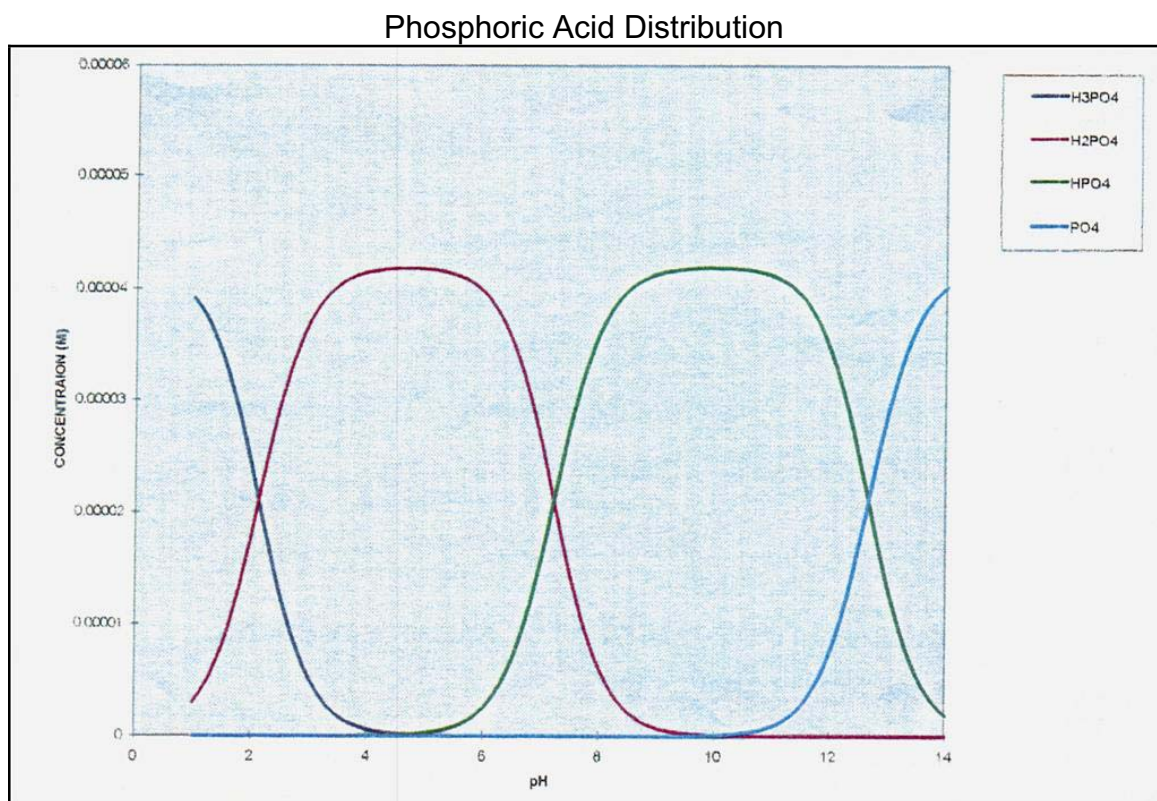


Figure 3-17. Distribution of phosphate species by pH

Note the similarity of Figure 3-17 to the carbonate species distribution graph in chapter 1, Figure 1-10.

In the critical pH region of 9 to 11.5 for magnetite formation, the predominant species are PO_4^{-3} , and HPO_4^{-2} (orthophosphate and monohydrogen phosphate). The sodium salts of these species are in the molar ratio of 3:1 and 2:1. In the pH 9 to 11.5 control range, then, the $\text{Na}/\text{PO}_4^{-3}$ molar ratio will be from about 2.3:1 to about 2.5:1.

Besides the molar ratio, the absolute concentration of orthophosphate must also be considered. At the tube walls, and under any deposits that form, deposits, boiling will increase the local concentration of sodium phosphate species by several thousand fold. The buffer system must remain soluble to work. The bulk concentrations of the phosphate species must be controlled so that at these high concentrations they will remain soluble. In general, as the pressure increases (higher heat flux) the bulk concentration of the phosphate ion must decrease.

Under deposits, acids and caustic can concentrate to serious levels. At high acid concentrations, the hydrogen ion will act as a cathodic species to promote high rates of corrosion. The hydrogen gas formed in the cathodic reaction will react with carbon in the grain boundaries of carbon steel to form methane gas. The decarburization weakens the grain structure, and brittle failures can occur.

Caustic, concentrated up to 10,000 fold or more under deposits can produce pH levels above 14. Iron is very soluble in this pH range, and large, hemispherical gouges will form on the tube surface. The rate of attack is very high, and a tube failure can occur in a short time. This phenomenon is called caustic gouging.

The phosphate buffer system reacts with excess acid or caustic as follows:



Figure 3-18 summarizes phosphate behavior in this program. This is the well known coordinated phosphate diagram. It has been published in many different forms, but program operating principles remain the same.

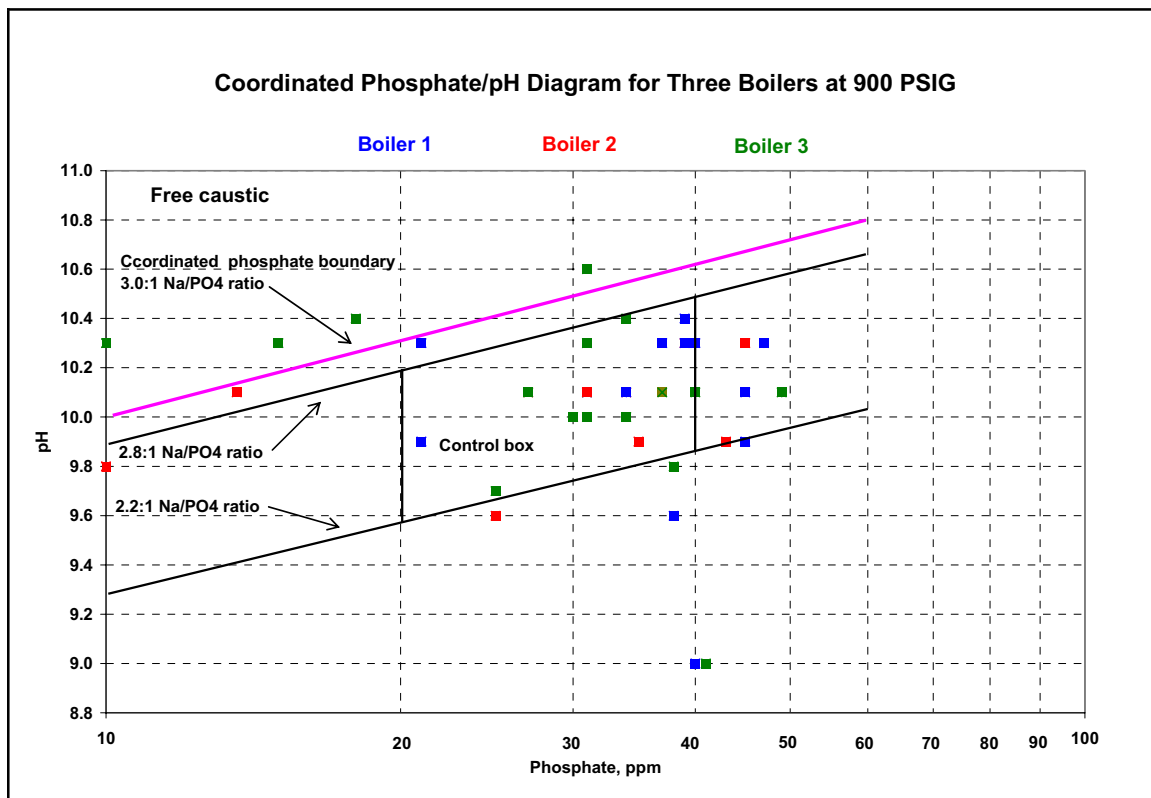


Figure 3-18. Coordinated Phosphate Control Diagram

The diagonal black and red lines in Figure 3-18 are lines of constant $\text{Na}/\text{PO}_4^{-3}$ mole ratio. This is the main parameter. A good program is controlled between 2.3:1 and 2.8:1 mole ratio.

The objective of coordinated phosphate treatment is to buffer the pH so that there can be no free caustic in the boiler water. Localized boiling sometimes causes precipitation of boiler solids on tube surfaces (hideout discussion in section 7.3.2). Water trapped beneath these deposits can become very concentrated. Avoiding free caustic in the water helps to ensure that caustic gouging of steel will not occur in these situations.

For this reason, the maximum boundary line in Figure 3-18 shows a $\text{Na}:\text{PO}_4$ mole ratio of 3.0. This is the ratio in trisodium phosphate, Na_3PO_4 . If the ratio is higher than 3, the excess sodium will come from caustic, NaOH . If the ratio is less than 3, there can be no free caustic because of the ionization equilibria in equations (3-49) and (3-50) and the phosphate ion distribution in Figure 3-3. See chapter 1 for more on ionization and chemical equilibria.

Figure 3-18 shows that as boiler pressure increases, the control region moves to lower phosphate levels. This is to reduce the danger of precipitation from localized boiling at increased temperatures and heat fluxes. However, it is not conversely true that lower pressures require higher phosphate levels.

It is just that more phosphate can be tolerated. The advantage to higher phosphate levels is that they buffer the pH better at higher levels of impurities.

Program control: A cooled sample of boiler water is analyzed for phosphate and pH. The coordinates of these two values are plotted on Figure 3-18. If the point lies within the correct shaded box for the operating pressure, then the program is under control.

If the point lies outside the control box, corrective action is taken. Excessive phosphate is removed by blowdown. Too low a ratio is corrected by the addition of caustic or trisodium phosphate. The latter will increase both phosphate and sodium levels. Too high a ratio is controlled by addition of disodium phosphate or monosodium phosphate to consume sodium, as shown in Figure 3-18. Monosodium phosphate is not recommended since overfeeds can depress the ratio to acidic pH's.

The boiler pH should not be allowed to fall below 8.8. Therefore, to avoid low phosphate levels, the mole ratio should be kept high to maintain adequate bulk water pH.

The data points in Figure 3-18 are from three boilers operating in parallel in a 900 psig cogeneration plant. Although most of the data points are within the control box, overall control of the coordinated phosphate program in this plant was poor. All three boilers operated at times below the minimum Na:PO₄ ratio, above the maximum phosphate level, and well into the free caustic range. This is not acceptable control, and over time, serious phosphate deposits, caustic gouging corrosion and boiler tube failures developed in this plant.

7.4.2 Hideout in Coordinated Phosphate Programs

Hideout is a phenomenon where phosphate levels decrease without apparent cause. The reverse process, hideout return, can also occur. Phosphate levels increase without apparent cause.

The reason for hideout or return is the precipitation of phosphate species at the boiler tube walls when the local concentration exceeds the solubility of sodium phosphate. Usually this is caused by hot spots or sudden increases in heat flux that raises the skin temperature sharply. Hideout return occurs when the precipitated deposits dissolve as temperatures drop.

In utility boilers, hideout occurs when unit load is increased, and return takes place when load is decreased. This is often associated with daily load cycles.

Hideout is a problem for coordinated phosphate programs because it makes program control difficult. Also, the phenomenon can result in mole ratios too high or too low for safe operation (>3.0:1 or < 2.2:1).

Hideout is generally incongruent. That is, the solid that forms does not have the same composition as the bulk solution. In that case, the solution chemistry will change. Not only phosphate levels, but mole ratios will change.

Attempts to prevent hideout by very closely controlling boiler water chemistry are usually fruitless and may make the problem worse. It is best to stay well within the control ranges in Figure 3-18, and to use as low a total phosphate level as possible while still maintaining good pH buffering in the water.

7.4.3 Congruent and Equilibrium Phosphate Programs

Generally, below a $\text{Na}/\text{PO}_4^{-3}$ mole ratio of 2.8:1, the precipitate that forms will have a mole ratio that is greater than the bulk solution mole ratio. The phosphate level will decrease, but the mole ratio in solution will decrease as well. Overall the pH will decrease (Figure 3-21).

At a ratio of 2.8:1 the precipitation is congruent. Congruent precipitation means that the solid phase has the same composition as the solids in the bulk solution. At this point, the program control will not change with hideout or return. Coordinated phosphate programs operated at 2.8:1 mole ratio are called congruent phosphate programs.

Another congruent point is the 2.2:1 ratio. As hideout lowers the ratio, it will approach 2.2:1 and then stay there because the precipitation is congruent with the bulk water ratio. Coordinated phosphate programs can operate between these two congruent points.

To help avoid hideout related problems, equilibrium phosphate programs have been developed. In these programs, phosphate levels are allowed to decrease until load changes no longer produce hideout behavior. This establishes the equilibrium point. The main drawback to this program is that phosphate levels can be so low that buffer capacity is seriously degraded (section 7.3.2). Systems with a history of leaks into the boiler cannot operate well under equilibrium phosphate conditions.

The key points to remember are:

1. Coordinated Phosphate is only applicable to high purity feedwater boilers
2. Program control is based on phosphate and pH measurements, plotted on a diagram like Figure 3-18. Sodium measurements are not valid for program control, because not all sodium is involved in the buffer chemistry.

7.4.4 All Volatile Programs

All volatile treatment (AVT) is applicable only to very high pressure boilers (>2400 psig) with very high purity feedwater and condensate polishing systems. Program control is based on using volatile amines and oxygen scavengers to maintain proper pH and oxygen levels in the feedwater and boiler. No nonvolatile solids are added to the boiler water.

There is no buffering capacity, so system leaks can not be tolerated. Condensate polishing is required to handle any impurity ingress. Electric utilities operating with sea water cooling systems cannot use AVT programs unless they are totally leak free (almost impossible), or have a very large polishing capacity.

Oxygen scavengers are covered in section 7.1. Only hydrazine can be used in AVT because it is volatile and breaks down only to safe species: NH_3 , N_2 , and H_2O . Species which contain carbon (carbohydrazide, hydroquinone, DEHA, MEKO) will break down to form carbonic acid in the condensate.

Likewise organic amines contribute carbon dioxide in the condensate. Consequently, most AVT programs use ammonia and hydrazine. Other amines, like morpholine and cyclohexylamine can be used, but condensate polishing is exhausted more frequently because of the carbonate loading.

The condensate polishers can be operated in the ammonia form instead of the hydrogen form. This prevents quick exhaustion or sodium breakthrough. But the tradeoff is poorer cation selectivity. This leads to higher sodium leakage rates.

High levels of ammonia can increase corrosion in the condensate system where there is copper based metallurgy, and if air inleakage is significant.

Boiler pH is maintained in the range of 9.5 to 10.5. Dissolved oxygen must be controlled to less than 5 ppb.

7.4.5 Neutral Oxygen Treatment

Most boiler treatment programs are based on maintaining a reducing environment in the boiler. Mechanical deaeration and chemical oxygen scavenging are used to maintain oxygen levels in the low part per billion range. Under these conditions, if the pH is maintained in the range of 9 to 12, magnetite forms a dense protective film.

Neutral oxygen treatment is a new development pioneered in Europe for high pressure utility boilers operating with the best possible purity feedwater. If the pH is maintained in the neutral range of 7 to 8 and the oxygen is controlled in the range of 100 to 250 ppb, a very dense and thin, but highly protective magnetite film will form. Boilers treated on this program have not needed a chemical cleaning in over a decade of operation in many cases.

A variant, called combined oxygen treatment or combined water treatment (CWT) involves maintaining the pH at a slightly higher range of 8 to 8.5 with ammonia, and reducing the oxygen level to 75 to 150 ppb. Similar results are seen as for neutral oxygen treatment.

System requirements are as follows:

- All ferrous metallurgy, no copper alloys in the feedwater or condensate system.
- Full flow condensate polishing.
- Mechanical deaeration to 5 ppb.

Operationally, the feedwater is polished, deaerated, and then oxygenated under controlled conditions to the proper level. Program control is by dissolved oxygen measurements at the deaerator outlet and boiler feedwater, pH measurement in the feedwater and boiler, and cation conductivity in the condensate and the steam.

Control levels are: pH 7-8.5, specific conductivity consistent with ammonia treatment at pH 7-8.5, oxygen levels of 75 to 250 ppb at the economizer inlet, cation conductivity of $<0.25 \mu\text{S/cm}$ in the main steam.

Combined water treatment systems have been used mainly in high pressure, field erected utility boilers, but smaller industrial boilers are beginning to use these programs successfully.

7.5 HOT WATER BOILER CHEMICAL TREATMENT

Most building hot water systems use city water. In some cases softened or partially softened water is used. Demineralized water is seldom used, but may be encountered in specialized cases such as pharmaceutical or microelectronics facilities, which may use the same water supply as for the process hot water heaters/boilers.

The use of city water (or well water) means that considerable amounts of sludge can form in these systems, much like home hot water heating systems. The sludge will accumulate in the heater, and to a lesser degree in the heat exchangers. Most treatments do not address sludge handling because these systems do not have mud drums or other convenient sludge removal systems. Sludge handling is usually done by periodic manual cleanings.

There are two modes of treatment usually involved. One is oxygen control, and the other is corrosion inhibition. Oxygen control focuses on the boiler-like environment, while corrosion inhibition approaches treat the system much like a closed loop cooling system. Each of these methods is discussed below. Chemical treatment of closed systems is also discussed in chapter 4.

7.5.1 Dissolved Oxygen Control

Sulfite is the treatment of choice (chemistry in section 7.1.2). Sodium sulfite is added as a liquid solution of up to 60 percent sodium sulfite. Sulfite is controlled to around 50 to 70 mg/L in the system. Addition is usually by a pot feeder.

Because of air leaks that can occur, sulfite control requires frequent monitoring. The monitoring is done by iodate-iodide titration, supplemented with direct dissolved oxygen measurements.

The titration method involves addition of potassium iodide-iodate solution to an acidified sample of the test water to which a starch indicator has been added. The test water will oxidize the iodide-iodate to iodine, which turns the indicator blue. The residual sulfite will reduce the iodine to iodide. When the blue color persists all the sulfite has been exhausted.

Sulfite treatment of hot water boiler systems should be undertaken only after very careful consideration. Because of the lower temperatures involved as compared to boiler water, the reaction of sulfite with dissolved oxygen is slow. Even with substantial sulfite residuals in the water, it is sometimes possible to detect low levels of dissolved oxygen. This is especially true when the system loses water that must be replaced with fresh oxygenated water.

In some cases, corrosion control treatment of the hot water is not possible because of use or discharge requirements. IN such cases, sulfite is the treatment of choice. However, by far the majority of closed hot water systems are treated with corrosion inhibiting programs (section 7.4.2), rather than sulfite.

7.5.2 Corrosion Inhibition

Oxygen control is a means of corrosion inhibition by reducing the amount of corrodant. Corrosion inhibition here is meant as the introduction of chemicals which act to mitigate corrosion in the presence of the corrodant.

Building hot water heating systems can be treated like closed loop cooling systems because there is no change of phase, the water is generally not demineralized, and the system is closed. Because it is closed, certain types of inhibitors can be used which would be too expensive for use in open systems.

Inhibition choices include: nitrite and molybdate. See also chapter 4 on closed cooling systems.

- Sodium nitrite is added as a liquid product. The target range when used alone is about 1000 to 1500 mg/L as nitrite in hot water systems. The pH of the system should be from 8.5 to 10, and preferably above 9.0. The pH is buffered in the proper range with sodium metaborate. If borate cannot be used, as in some nuclear plants, then add caustic to adjust pH.

Testing is done by typical wet chemical methods for nitrite. The most common test is based on acidic ferrous sulfate. The ferrous ion reduces NO_2^- to NO , which then forms a colored complex with excess ferrous ion.

Because nitrite can decompose, it must be tested on a regular basis, and supplemented as needed. It can decompose to ammonia or nitrate, depending on conditions. It is useful to monitor nitrate or ammonia levels if nitrite levels regularly decrease. This will permit the assessment of what is causing the decomposition. Most nitrite will be lost via reaction with iron corrosion products or by slow oxidation if air can get into the system. Also, there can be some losses due to leaks.

Microbiological degradation of nitrite is not common in hot water systems.

Nitrite programs cannot be combined with sulfite due to the reaction in which nitrite oxidizes sulfite to sulfate.

- Molybdate treatment of hot water closed systems is based on the inhibiting power of molybdate at high concentrations, especially for localized corrosion.

When molybdate alone is used for hot water corrosion inhibition, the concentration should be at least 500 mg/L as MoO_4 . The pH should be between 8.5 and 10, as for nitrite programs.

Molybdate is sensitive to chloride and sulfate levels. Typically, the molybdate level should be greater than the sum of these two ions, but not less than about 250 mg/L. If one or both of chloride or sulfate are high molybdate should be at least 250 mg/L above the sum of the two ions.

Blends of sodium molybdate and sodium nitrite are sometimes used to lower the total chemical dosage requirement. For example, with 150 mg/L molybdate as MoO_4 , 500 mg/L nitrite as NO_2 is sufficient to provide good corrosion control.

Control is by testing for molybdate and nitrite. Again, nitrite may have to be supplemented, and molybdate may be needed if the system leaks significantly. The control pH range is 8.5 to 10.

7.5.3 Monitoring Hot Water Systems

Hot water boiler system performance is best monitored by inspections, coupons and pipe spools. Coupons should be used judiciously because water is lost from the system, and oxygen is added, every time the coupon rack is opened.

Pipe spools are placed in the main circulation with a bypass. The pipe spool is cleaned and weighed. After exposure it is removed, inspected for corrosion and fouling, cleaned and weighed, and then replaced.

Chemical levels are monitored as discussed in section 8.4.2. Iron monitoring is not reliable since many of these systems are old, and have copious amounts of iron oxide scale, which can occasionally slough off.

7.6 BOILER WATER CHEMISTRY LIMITS

Boiler chemistry control involves both the feedwater and the boiler section. The feedwater becomes the boiler water after it is chemically treated and cycled up. This section deals with the rationale for the various chemistry limits. The ASME consensus limits for boiler water chemistry are shown in Table 3-13.

7.6.1 Alkalinity

Alkalinity breaks down in the boiler to form carbon dioxide, hydroxide ions, and a small amount of carbonate ion. Carbonate is not critical, since a phosphate or chelant program can prevent calcium carbonate scaling. The hydroxide is important in adjusting pH to the proper range for precipitating programs to work.

Calcium phosphate forms best above a pH of 10, where the phosphate ion predominates. Similarly magnesium hydroxide forms above pH 10. In order to achieve the proper pH range, the hydroxide alkalinity needs to be in the range of 200 to 500 mg/L as CaCO₃. The main control parameter is M-2P (chapter 1).

To control the program, the boiler water M and P alkalinity are measured, and M-2P calculated. This value is the hydroxide alkalinity expressed as equivalent CaCO₃. A hydroxide alkalinity of 200 mg/L as CaCO₃ is an approximate pH of 11.5. At that pH, phosphate is efficient at precipitating calcium hardness, magnesium will precipitate as Mg(OH)₂, and silica will be soluble as SiO₃⁻² ion. This is the basis for control of phosphate precipitation programs (section 7.2.2).

Often it is necessary to add caustic to achieve the desired pH range if there is not enough natural alkalinity in the feedwater. This is also desirable from the condensate standpoint since less carbon dioxide will be formed and pass over into the steam. This reduces the need for neutralizing amines.

Table 3-13.
ASME consensus boiler operating guidelines

SUGGESTED WATER CHEMISTRY LIMITS INDUSTRIAL WATERTUBE, HIGH DUTY, PRIMARY FUEL FIRED, DRUM TYPE				SUGGESTED WATER CHEMISTRY LIMITS INDUSTRIAL WATERTUBE, HIGH DUTY, PRIMARY FUEL FIRED, DRUM TYPE				
Makeup water percentage: Up to 100% of feedwater Conditions: Includes superheater, turbine drives, or process restriction on steam purity Saturated steam purity target: See tabulated values below.				Makeup water percentage: Up to 100% of feedwater Conditions: Includes superheater, turbine drives, or process restriction on steam purity Saturated steam purity target: See tabulated values below.				
Drum Operating Pressure (1)(11)	psig 0-300 (0-2.07)	301-450 (2.08-3.10)	451-600 (3.11-4.14)	601-750 (4.15-5.17)	751-900 (5.18-6.21)	901-1000 (6.22-6.89)	1001-1500 (6.90-10.34)	1501-2000 (10.35-13.79)
Feedwater (7)								
Dissolved oxygen ppm (mg/l) O ₂ — measured before chemical oxygen scavenger addition (8)	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007
Total iron ppm (mg/l) Fe	≤0.1	≤0.05	≤0.03	≤0.025	≤0.02	≤0.02	≤0.01	≤0.01
Total copper ppm (mg/l) Cu	≤0.05	≤0.025	≤0.02	≤0.02	≤0.015	≤0.01	≤0.01	≤0.01
Total hardness ppm (mg/l) *	≤0.3	≤0.3	≤0.2	≤0.2	≤0.1	≤0.05	ND	ND
pH @ 25°C	8.3-10.0	8.3-10.0	8.3-10.0	8.3-10.0	8.3-10.0	8.8-9.6	8.8-9.6	8.8-9.6
Chemicals for preboiler system protection	NS	NS	NS	NS	NS	VAM	VAM	VAM
Nonvolatile TOC ppm (mg/l) C (6)	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Oily matter ppm (mg/l)	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Boiler Water								
Silica ppm (mg/l) SiO ₂	≤150	≤90	≤40	≤30	≤20	≤8	≤2	≤1
Total alkalinity ppm (mg/l) *	<350(3)	<300(3)	<250(3)	<200(3)	<150(3)	<100(3)	NS(4)	NS(4)
Free OH alkalinity ppm (mg/l) * (2)	NS	NS	NS	NS	NS	NS	ND(4)	ND(4)
Specific conductance (12) μmhos/cm (μS/cm) 25°C without neutralization	5400-1100(5)	4600-900(5)	3800-800(5)	1500-300(5)	1200-200(5)	1000-200(5)	≤150	≤80
Total Dissolved Solids in Steam (9)								
TDS (maximum) ppm (mg/l)	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

*as CaCO₃
 NS = not specified
 ND = not detectable
 VAM = Use only volatile alkaline materials upstream of attemperation water source.
 (10)

7.6.2 Silica

Silica is a volatile substance. It is generally considered that no more than 20 ppb of silica in the steam is permissible for the protection of turbines and other

downstream elements. Allowed silica levels are based on the volatility of silica as a function of temperature (Figure 3-19 and Table 3-14). As temperature (pressure) increases, the volatility of silica also increases. For that reason, the allowable limit of silica in the boiler decreases with increasing pressure so as to remain below the 20 ppb limit in the steam. By maintaining the pH high, most of the silica will be in the soluble silicate form. This minimizes the volatility of silica by restricting the concentration of the volatile SiO_2 form.

Table 3-14
Solubility of Silica vs. pH

pH	Solubility of amorphous SiO_2 (mg/L) at 77°F
6 - 8	120
9	138
9.5	180
10	310
10.6	876

Silica in the steam often spikes at a pressure of about 1500 psig. At that point, silica-containing dust and dirt solubilize and begin to volatilize as SiO_2 .

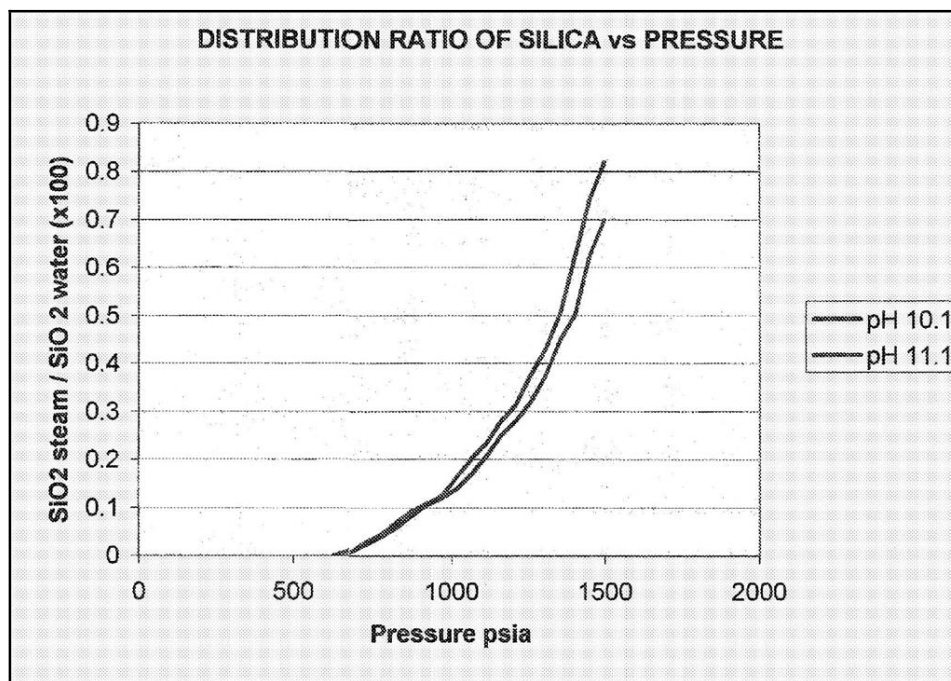


Figure 3-19. Volatility of Silica vs. Pressure

7.6.3 Magnesium Hydroxide

Magnesium does not precipitate well as the carbonate or the phosphate. The control of magnesium is effected by pH control to a pH of >11 to precipitate

$\text{Mg}(\text{OH})_2$. If magnesium is not well controlled, it can form precipitates with silica which are hard to remove.

Ordinarily, magnesium is not specifically tested. If the feedwater is suspected of having a high level of magnesium, steps should be taken to remove it by partial or full flow softening of the makeup water. The actual limits will vary due to boiler cycles and silica content.

7.7 CONDENSATE TREATMENT

Condensate is not usually pure. Various substances carry over physically or by volatilization in the boiler. When the steam condenses, many of these substances will dissolve in the condensate. Often, they impart objectionable properties to the condensate. Particulates and ionic species can be removed by condensate polishing, which is both a filtration process and an ion exchange process (chapter 2).

The main substance to be chemically treated in the condensate is carbon dioxide. Carbon dioxide is formed by the breakdown of carbonate alkalinity in the boiler. Being very volatile, most of it passes into the steam, and then forms carbonic acid in the condensate. The pH of the condensate can be depressed to very low levels, often below 3, because the carbon dioxide is not in equilibrium with the atmosphere, where the limiting pH is about 5.8.

Carbonate alkalinity can be removed by dealkalization and decarbonation in the pretreatment train (chapter 2), but in most medium and low pressure systems, this is not done. To prevent the resulting acidic corrosion in the condensate lines, the carbon dioxide must be neutralized. This is done by adding neutralizing amines to the feedwater. Amines adjust the feedwater pH to a range of 8.8 to 9.2, which is optimum for a mixed metallurgy system. Passing into the boiler, amines distribute into the steam, and condense with the steam and carbon dioxide.

There are three important factors to be aware of with neutralizing amines:

- Basicity
- Neutralizing capacity
- Distribution ratio

7.7.1 Basicity

The general reaction of amines with water is:



The base hydrolysis constant for amines (chapter 1) is defined as:

$$K_b = [\text{RNH}_3^+] [\text{OH}^-] / [\text{RNH}_2] \quad (3-52)$$

The greater the value for K_b the more basic is the amine. Basicity relates to the ability of the amine to raise the pH of neutralized water. On a molar basis, an amine with a larger value of K_b will raise the pH of pure water higher than will an amine of lower K_b .

Tables 3-15 and 3-16, and Figure 3-20, present the pH of pure water as adjusted by the indicated amount of several volatile neutralizing amines.

Note that higher basicity doesn't always translate into higher pH. The molecular weight also plays a role since this is on a mg/L basis, not a molar basis. Had the Table been computed for equimolar concentrations, then the highest K_b would produce the highest pH.

Table 3-15
pH Adjustment Capacity of Amines pH vs. Amine Concentration

	CYCLO	DEAE	MOPA	MORPH	DMPA	DEA	MEA	NH3
mg/L				pH				
0.2	8.32	8.25	8.36	8.21	8.29	8.23	8.49	8.91
0.5	8.71	8.62	8.74	8.48	8.65	8.54	8.84	9.20
1	9.00	8.89	9.01	8.67	8.91	8.75	9.08	9.40
2	9.29	9.15	9.28	8.85	9.16	8.96	9.31	9.58
3	9.46	9.30	9.43	8.95	9.29	9.07	9.43	9.68
4	9.57	9.40	9.53	9.02	9.39	9.14	9.51	9.75
5	9.66	9.47	9.61	9.08	9.45	9.20	9.58	9.81
6	9.73	9.53	9.67	9.12	9.51	9.25	9.63	9.85
7	9.79	9.58	9.72	9.16	9.56	9.29	9.67	9.89
8	9.84	9.62	9.76	9.19	9.59	9.32	9.71	9.92
9	9.89	9.66	9.80	9.22	9.63	9.35	9.74	9.95
10	9.93	9.69	9.83	9.24	9.66	9.38	9.77	9.97
11	9.96	9.72	9.86	9.27	9.69	9.40	9.79	10.00
12	10.00	9.75	9.89	9.29	9.71	9.42	9.81	10.02
13	10.03	9.77	9.91	9.30	9.73	9.44	9.83	10.04
14	10.05	9.79	9.93	9.32	9.75	9.46	9.85	10.05
15	10.08	9.81	9.95	9.34	9.77	9.48	9.87	10.07

In Table 3-15:

CYCLO = cyclohexylamine
 DEAE = diethylaminoethanol
 MOPA = methoxypropylamine
 MORPH = morpholine
 DMPA = dimethylpropylamine
 DEA = diethanolamine
 MEA = monoethanolamine
 NH3 = ammonia

Table 3-16
pH Adjustment by Amines: Amine Concentration vs. pH

pH	CYCLO	DEAE	MOPA	MORPH	DMPA	DEA	MEA	NH3
				mg/L				
7.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.10	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00
7.30	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.00
7.40	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.00
7.50	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.00
7.60	0.04	0.04	0.03	0.04	0.04	0.04	0.02	0.01
7.70	0.05	0.06	0.04	0.05	0.05	0.05	0.03	0.01
7.80	0.06	0.07	0.06	0.06	0.06	0.07	0.04	0.01
7.90	0.08	0.09	0.07	0.09	0.08	0.09	0.05	0.01
8.00	0.10	0.12	0.09	0.11	0.10	0.12	0.06	0.02
8.10	0.12	0.15	0.11	0.15	0.13	0.15	0.08	0.02
8.20	0.16	0.19	0.14	0.21	0.17	0.20	0.10	0.03
8.30	0.20	0.24	0.18	0.28	0.22	0.26	0.13	0.04
8.40	0.25	0.30	0.23	0.39	0.27	0.35	0.16	0.05
8.50	0.32	0.39	0.29	0.56	0.35	0.46	0.21	0.06
8.60	0.40	0.49	0.37	0.79	0.45	0.63	0.27	0.08
8.70	0.50	0.63	0.47	1.14	0.58	0.86	0.35	0.11
8.80	0.63	0.81	0.60	1.67	0.75	1.19	0.46	0.14
8.90	0.80	1.04	0.76	2.46	0.98	1.67	0.60	0.19
9.00	1.01	1.35	0.98	3.68	1.29	2.38	0.80	0.26
9.10	1.28	1.75	1.26	5.54	1.70	3.43	1.07	0.36
9.20	1.63	2.30	1.63	8.43	2.28	5.00	1.45	0.51
9.30	2.06	3.04	2.12	12.91	3.08	7.39	1.98	0.72
9.40	2.63	4.06	2.79	19.89	4.21	11.02	2.73	1.02
9.50	3.36	5.47	3.69	30.82	5.83	16.61	3.84	1.48
9.60	4.30	7.47	4.93	47.94	8.18	25.25	5.45	2.17
9.70	5.53	10.32	6.65	74.85	11.63	38.65	7.85	3.22
9.80	7.14	14.44	9.09	117.22	16.75	59.54	11.44	4.83
9.90	9.28	20.48	12.57	183.99	24.43	92.20	16.87	7.31
10.00	12.15	29.43	17.63	289.34	36.05	143.41	25.16	11.14
10.10	16.03	42.83	25.03	455.74	53.78	223.87	37.89	17.11
10.20	21.34	63.07	36.02	718.74	81.01	350.50	57.55	26.42
10.30	28.71	93.92	52.49	1134.63	123.06	550.08	88.06	40.99
10.40	39.06	141.24	77.41	1792.60	188.34	864.99	135.60	63.86
10.50	53.81	214.27	115.40	2833.96	290.07	1362.32	209.91	99.82
10.60	75.07	327.54	173.72	4482.56	449.12	2148.30	326.40	156.45
10.70	106.13	503.93	263.78	7093.09	698.43	3391.21	509.40	245.75
10.80	152.04	779.56	403.52	11227.58	1090.11	5357.55	797.38	386.72

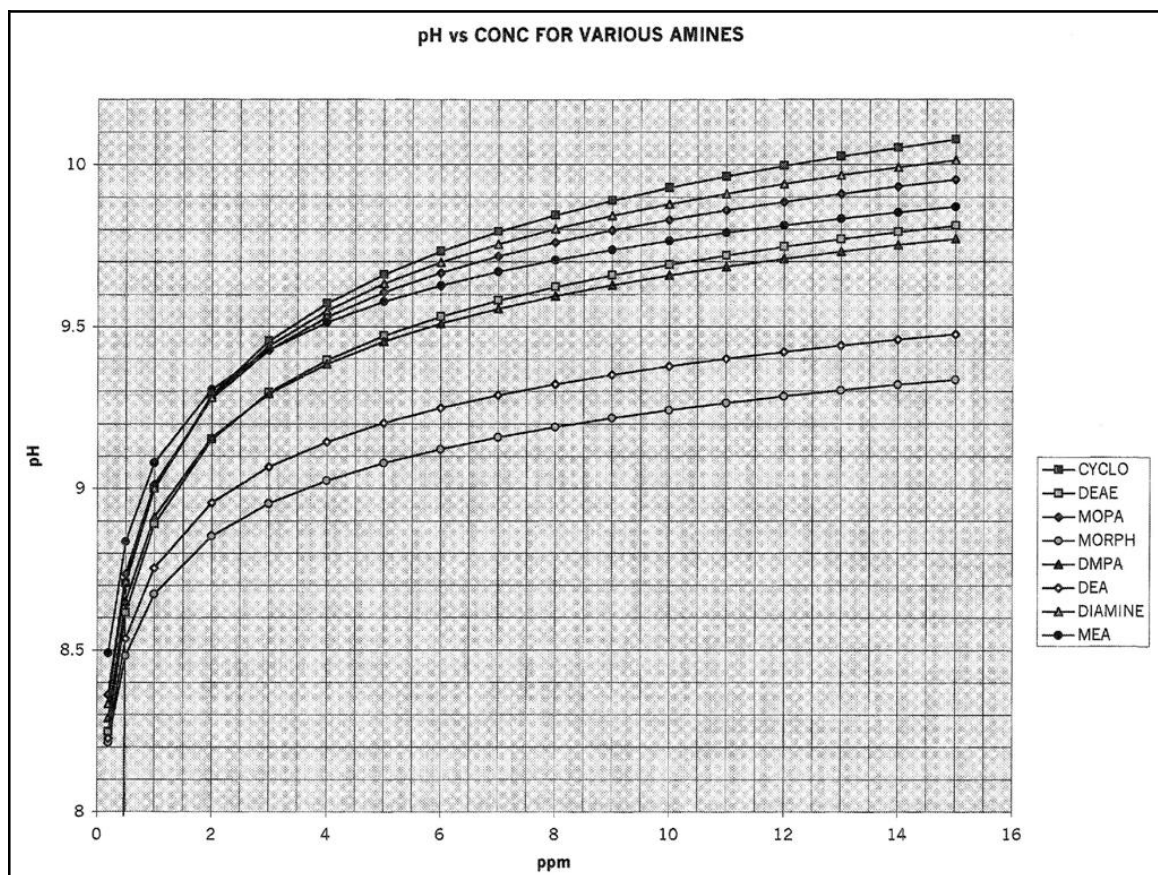
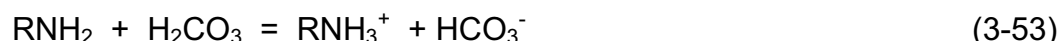


Figure 3-20. pH Behavior of Amines in Pure Water

7.7.2 Neutralizing Capacity

This parameter relates to the capacity of the amine to neutralize CO_2 . The neutralizing reaction is:



The reaction is stoichiometric. The lower the molecular weight of the amine, the greater the neutralizing capacity. It has nothing to do with the basicity of the amine. Generally, the more alkalinity in the feedwater, the greater amount of neutralizing amine of any type will be needed.

7.7.3 Volatile Amines and Distribution Ratios

Volatile amines (neutralizing amines) follow the steam into the distribution system. The distribution ratio (DR) is a measure of the volatility of the amine (equation 3-54). It describes the ability of the amine to carry over into the steam where it can neutralize CO_2 in the condensate. Since amines are fed to the feedwater for pH control, they must then volatilize and pass into the steam to neutralize the condensate. The selection of amine has to be balanced by a consideration of feedwater pH adjustment, and condensate treatment.

Sometimes it is economical to feed a high basicity amine of low volatility to the feedwater, and inject a high neutralizing capacity amine into the steam with a satellite feed point. The drawbacks are more product inventory and more feed equipment to monitor and maintain. Table 3-17 shows neutralizing capacities and distribution ratios for common volatile amines.

Table 3-17
Neutralizing Amine Properties

Amine	MW	Neutralizing Capacity (ppm CO ₂ /mg/L amine)	K _b	Distribution Ratio (vs. pressure psig)		
				0	200	1000
Ammonia	35	2.59	1.8x10 ⁻⁶	10	7.14	3.57
Cyclohexylamine	99	0.444	440x10 ⁻⁶	4	23.3	9.3
DEAE	117	0.376	66x10 ⁻⁶	1.7	4.5	3.4
MOPA	89	0.494	102x10 ⁻⁶	1	2.4	2.5
Morpholine	87	0.506	3.1x10 ⁻⁶	6.4	1.6	0.98
DEA	105	0.419	7.9x10 ⁻⁶	0.004	0.11	0.07
MEA	61	0.720	32x10 ⁻⁶	0.07	0.15	0.29

DEAE = diethylaminoethanol

MOPA = methoxypropylamine

DEA = diethanolamine

MEA = monoethanolamine

The distribution of the amine in the steam is straightforward. The distribution ratio expresses the ratio of the concentration of the amine in each phase, as shown in equation (3-54).

$$DR = [\text{amine in steam}] / [\text{amine in the boiler}] \quad (3-54)$$

However, the concentration itself is not directly evident. From mass balance the entire amine is present either in the steam or in the boiler water. But the relative boiler blowdown and steam flow will affect the absolute concentration of the amine in each phase.

The amine in each phase is calculated from:

$$\text{mg/L in steam} = \text{mg/L in FW} \times DR / (DR \times S/\text{FW} + \text{BD}/\text{FW}) \quad (3-55)$$

$$\text{mg/L in BD} = \text{mg/L in FW} \times 1/(DR \times S/\text{FW} + \text{BD}/\text{FW}) \quad (3-56)$$

Where FW, BD, S, and DR are the feedwater flow, blowdown flow, steam flow and distribution ratio respectively.

Note that the sum of equation (3-55) times steam flow and equation (3-56) times blowdown flow is equal to the amount of amine in the feedwater, as it must for mass balance to be maintained.

In complex steam distribution systems with flash tanks, the application of neutralizing amines is very complicated. Amines will condense in the flash tanks, and redistribute according to the local relative flow rates and pressures. The proper pH in the flash tank blowdown is important for corrosion protection. Also, the persistence of amine in the steam phase downstream of the flash tanks must be considered.

It is common practice to blend amines for feedwater pH control. One amine is chosen for its ability to raise the pH of the feedwater (more basic amines), while another may be chosen for its neutralizing capacity and/or distribution into the steam.

Low DR amines will concentrate in the condensate, providing good tank protection, but are removed according to equation (3-51). Many satellite feeds may be needed. A high DR amine will remain in the steam, and not provide as good protection to the tank, but will travel further down the system, and provide better protection at distant locations. An amine with high basicity or neutralizing capacity might help overcome this problem, since it will produce a higher pH in the condensate at lower concentration.

7.7.4 Filming Amines

Filming amines are used for condensate systems only. Filming amines are high molecular weight amines with long hydrocarbon chains. Most are insoluble in water. The nitrogen end of the molecule is highly polar, and adheres to metallic oxides on the condensate line walls. The hydrocarbon chain is very hydrophobic, and provides protection for the metal surface by preventing contact with water.

The main filming amine is octadecylamine (ODA), $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$. It is a very waxy material at room temperature, and must be heated in order to be fed. Feed is accomplished by heating the amine so that it flows freely, then mixing it in with demineralized water. It is then fed directly into the steam header with an injection quill. Stainless steel or Hastelloy is needed, as the concentrated solution is aggressive to steel or copper alloy metallurgy. ODA is sometimes fed as the acetate salt, which is more soluble. The acetate decomposes to liberate ODA and a small amount of acetic acid.

The feed rate is based on steam flow, and is typically about 1 to 5 mg/L active amine. The solution should be held at elevated temperature, around 100°F. Make down water should be demineralized water or condensate. Solutions fed directly to steam should be free of dissolved solids. Also, since dissolved solids can coagulate filming amines, they should not be fed to systems with high carryover from the boiler.

The feed need not be continuous unless fed to high flow velocity areas. The films are persistent, and may need to be maintained only by intermittent feed. Once a day for a few hours may be enough to maintain good protection.

Use of filming amines in complex steam distribution systems is a problem. Many satellite feed points are needed, as the amine does not travel as far in the steam as the more volatile neutralizing amines.

Filming amines can undercut old oxide deposits and cause them to slough off. The deposits then travel at high velocity in the steam line, leading to erosive wear or clogging of steam traps and valves. For that reason, use of filming amines in older systems should be carefully considered before a decision is made to feed them.

7.7.5 Volatile Oxygen Scavengers

All the scavengers discussed in section 7.1 in this chapter, except for sulfite and ascorbate, are volatile. They will pass over into the steam and provide metals passivation in the condensate system. As was noted in that section, the scavengers have the ability to reduce unprotective oxides to the passive magnetite and cuprite forms. Sometimes volatile oxygen scavengers are fed to the steam directly for passivation of the condensate system. Because parts of the condensate system may be under vacuum, air leakage is always a problem.

The combination of filming/neutralizing amines with a metals passivator (oxygen scavenger) can be a very potent approach to condensate system protection.

In all cases, the selection of any material for direct injection must take into account the possible health and safety effects of these products. Steam is used for air heating and humidification, and direct and indirect contact with food or food packaging materials

7.8 CHEMICAL FEEDPOINTS

Boiler chemicals are fed to the feedwater, deaerator, boiler, and steam, depending on their intended use.

7.8.1 Internal Treatments

Internal boiler water treatments include various phosphates, phosphonates, polymers, chelants, caustic, nitrite, molybdate, and nitrate. They can be fed to the feedwater based on boiler cycles, or to the boiler. If attemperator water is taken from the feedwater, injection of any non-volatile components should be done after the attemperator takeoff.

If orthophosphate is used as an internal treatment, it should never be added to the feedwater line, to avoid possible plugging with calcium phosphate.

If chemicals are fed to the boiler, the feed rate is based on boiler blowdown. In some cases, where blowdown is very intermittent, feed is done in slugs. The chemicals enter the boiler in the drum. Good design will preclude close proximity of the feed line with drum internals. Often the concentrated forms of these chemicals can be aggressive to steel.

7.8.2 Oxygen Scavengers

Oxygen scavengers are fed to the deaerator down comer or storage tank. The feed rate is based on oxygen residuals. Feed upstream of the deaerator is uneconomical because of the mechanical action of the deaerator. Always feed downstream of the deaerating section of the deaerator.

- In steam systems, oxygen scavengers can be fed to the main steam header or satellite points as needed.
- With hydrazine or carbohydrazide, avoid the use of stainless steel or molybdenum containing alloys.

7.8.3 Condensate Treatments

Condensate treatments are fed to the feedwater after the deaerator and after any polishers. This will avoid uneconomical removal of some of the chemical in these units. Direct injection into the steam header is also used. An exception is feed of filming amines to deaerators (rarely done). The low distribution ratios of these amines limit their loss due to stripping by the deaeration steam.

Satellite feed points are used to allow condensate treatments to reach distant parts of a complex steam distribution system, or to provide targeted treatment to parts of the system that require special treatment.

Most satellite feed systems involve direct injection into steam lines. They are used to feed filming amines, metal passivators, and neutralizing amines. Usually an injection quill is used. The quill is inserted about halfway into the line, and oriented to feed in the downstream direction.

Filming amines do not distribute well in the steam, and so must be fed at points relatively near where their actions are needed. High velocities degrade amine films, and so they must be fed continuously in these areas. In lower flow areas intermittent feed can be effective.

7.9 FEEDING AND CONTROL EQUIPMENT

There is a variety of OEM equipment for feeding, controlling and monitoring boiler chemical treatments and boiler systems in general.

7.9.1 Pumps and Feed Tanks

Feed pumps are positive displacement types to eliminate slippage at the high discharge pressures required for boiler feed pumps. The pumps must be able to pump against the pressure, which can range from 15 psi to over 2000 psi, depending on the boiler. Typical pump rates are a few tenths of a gallon per day. Most pumps are controllable with a 4-20mA current loop control system. Some pumps are strokable with an external signal generator. Drawdown glasses are often used in these feed systems.

The typical feed arrangement is to use a day tank. This is a cylindrical tank with a condensate feed line for dilution water, a mixer, a sight glass, a cover, and a drain to the pump intake. Enough chemical is added to last for one to a few days' operation. Dilution water is added to dilute the chemical to the appropriate concentration for feed with the existing pump, based on target feed rates.

Example: Given the following: (1) a 90% active amine product with a specific gravity of 1.05 is fed to the feedwater at 3 mg/L active; (2) the feedwater rate is 12,000 gph; (3) a three day supply of chemical is desired using a pump controllable to 0-0.5 gph and a tank 32 inches in diameter.

How much amine is needed? How much water is added? What pump speed is used?

- First, determine the amount of amine needed:
 $12,000 \text{ #FW} / \text{hr} \times 3 \times 10^{-6} \text{ #amine} / \text{#FW} \times 72 \text{ hr} = \mathbf{2.6 \text{ #amine}}$
 - Next, determine the concentration needed in the day tank at maximum pump speed:
 $2.6 \text{ #} / 72 \text{ hr} \times 1 \text{ hr} / 0.5 \text{ gal} = \mathbf{0.072 \text{ #/gallon}}$
 - Next, determine the gallons of chemical feed needed:
 $2.6 \text{ #amine} / 0.072 \text{ #} / \text{gallon} = \mathbf{36 \text{ gallons}}$
 - Next determine the depth of water in the tank:
 $36 \text{ gal} \times 144 \text{ in}^2 / \text{ft}^2 \times 12 \text{ in/ft} / (7.48 \text{ gal} / \text{ft}^3 \times 162 \text{ in}^2) = \mathbf{10.35 \text{ inches}}$
 - Finally, determine the volume of amine to be added:
 $2.6 \text{ #amine} \times 1 \text{ # product} / 0.9 \text{ #amine} \times 1 \text{ gal product} / (8.34 \times 1.05) \text{ #} = 0.33 \text{ gallons} = \mathbf{1245 \text{ cc}}$
- Now, it isn't good practice to operate at the extreme limit of the equipment. So, instead, pick a pump speed of 0.35 gph (70% of the maximum). Now, the amount of amine stays constant. The # / gallon must increase to compensate for the lower pump speed. The total #/gallon will now be $0.072 \times 0.5/0.35 = \mathbf{0.103 \text{ #/gal}}$. The total volume now decreases to $36 \times .35/.5 = \mathbf{25.2 \text{ gallons}}$. This will require a depth of $10.35 \times .35 /.5 = \mathbf{7.25 \text{ inches}}$.
- Finally, use 15-25 % excess of product in the tank to prevent running out of product. The amount of amine increases by 15-25%, the gallons in the day tank increase similarly, and the depth also increases by the same factor.

7.9.2 Controls

Controls are rapidly changing. Many OEM systems are available. Tank level sensors, pump controllers and flow sensors can be used to control feed rates. On-line analyzers for dissolved oxygen, oxygen scavenger, phosphate, iron, sodium, silica, and pH and conductivity are available. All require sample cooling.

Control schemes can utilize either feed back or feed forward mode:

Feed back: A feed back controller uses a signal proportional to the quantity to be controlled, e.g. phosphate. If the signal is below the desired level, then feed is initiated at a constant rate. When the signal reaches the desired level the feed stops. The concentration of the desired species oscillates about the desired level. The oscillation is dependent on the dead band of the equipment and the size of the system and equipment. Typically, the oscillations are larger than for feed forward systems.

Feed forward: A feed forward control scheme uses a signal from a control parameter other than the desired parameter itself. For example, to control phosphate a flow signal or pH signal can be used. The feed of product is proportioned to the signal by an appropriate algorithm. Additionally, a secondary signal can be used as a trim control. For example, flow can be the primary signal, and pH can be a trim. The feed rate is proportioned to the flow and is adjusted based on pH. That is, the feed rate changes with flow to maintain a constant feed concentration, but the concentration is changed based on system chemistry changes. Feed forward systems anticipate variances in system performance and adjust accordingly. They tend to lead system changes. Characteristically, they have smaller control fluctuations.

Feed back controllers tend to lag system changes. Typically, the control band is broader, with a greater fluctuation amplitude. Feed forward controllers are more complex and expensive, but they can provide more precise and uniform control within a smaller band.