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# Boiler Water Treatment Chemical Guidelines—Part II

*By the AWT Boiler Water Subcommittee*





In Part I, we discussed deaerators and the chemistry used to remove dissolved oxygen from the boiler feedwater. Also discussed was general internal treatment utilizing carbonate technology and phosphate technology. We continue our discussion of other internal treatments and condensate chemical treatment programs.

### Chelating Technology

Chelating agents offer an opportunity for supplying better results in boiler water treatment (i.e., cleaner boilers). The important key to success is to use the same care in selecting, applying, and controlling the treatment program. Chelating programs are another variation of water treatment.

The word chelate derives from the Greek word *chele*, meaning claw. This was probably chosen because of the structure of the molecule, which holds tightly, in a ring structure, the metal that has been chelated. The resulting complex is quite soluble; and under the proper control conditions will not permit the hardness metals, calcium and magnesium, to deposit in the boiler as carbonates or sulfates (assuming there are not phosphates present).

In feedwater reactions with hardness, the specific reaction with a chelating agent is to tightly complex the calcium or magnesium, with the resulting reaction product being soluble. Although it is not the only chelating agent available for boiler water treatment, the tetra sodium salt of ethylenediaminetetraacetic acid (EDTA) is typical of the chelating agents being used today. In addition, it is probably the most widely used chelant available.

This complex is sufficiently soluble in the concentrations commonly used in boilers so that it effectively holds the calcium in solution. The reaction with magnesium is the same. The extra bonding of the calcium or magnesium is called coordinated covalence and is responsible for the "tightness" with which the metal ion is complex.

Iron can be chelated under strong alkaline conditions in the boiler feedwater, and only if it is in solution in the ferrous (divalent) form.

In the past, chelants have been misapplied, causing serious corrosion to metal when they were grossly overfed. They will cause corrosion problems if not properly controlled. Serious metal loss can take place in as little as 30 days.



Because of the associated corrosion problems, chelants are not the preferred treatment choice. However, if the system dictates the use of chelating agents, it can feed under “starvation” conditions, i.e., no free residual in the boiler. Based on the trace level of hardness in the boiler feedwater, substoichiometric levels of chelant are fed (approximately 90% of hardness equivalent). The hardness that does not combine with chelant (excess hardness) is allowed to precipitate and then is dispersed with a low molecular weight dispersant.

### Phosphonate Technology

The phosphonate ion has been shown to be a very powerful scale and sludge inhibitor. With the combined use of a phosphonate and a polymer dispersant, it is possible, in many instances, to increase sludge levels in the boiler water by as much as 30–50%. These increased levels can be carried continuously with outstanding boiler cleanliness.

An additional benefit of the phosphonate is its ability to disperse corrosion products, such as metallic iron oxides, so that they do not adhere to heat transfer surfaces and form deposits. Scale and deposits of high iron content can cause tube failure due to the high insulating factor of the deposit.

Phosphonates are much less aggressive toward boiler metal than chelants, such as EDTA, and feeding is much simpler. The ability of phosphonates to permit higher levels of suspended solids allows them to provide a superior onstream cleanup program.

One of the problems associated with the phosphonate HEDP use is the degradation to orthophosphate. The data collected show that although HEDP does not undergo instantaneous decomposition, it is not infinitely stable in boiler water. Rather, like many boiler chemicals, it has a limited stability that does not preclude its use in boilers. In field studies feeding HEDP or PBTC, there has always been a residual found, even when being applied at 800 psig and at 20 cycles of concentration. Temperature and corresponding pressure affect stability; as temperature rises, stability decreases. Stability is also adversely affected by residence time, which is the average time dissolved solids spend in the boiler before leaving via blowdown. Short residence times result in better stability. For a given boiler, residence times are a function of cycles of concentration; as cycles decrease, residence

time decreases. The effect of residence time or cycles of concentration are, at a given pressure, stability decreases as cycles increase from 5 to 20.

### Stability of Phosphonate in an Industrial Boiler

An important consideration regarding the use of chemicals in a boiler is its decomposition products. Sulfite, for example, is not recommended for use in boilers operating above 900 psig because corrosive hydrogen sulfide and sulfur dioxide are formed upon decomposition. On the other hand, HEDP and PBTC breakdown into orthophosphate, a relatively harmless boiler constituent. The primary reason the orthophosphate is harmless is because of the small amount formed. The short residence times in the feedwater lines and economizers result in negligible amounts of orthophosphate being formed from the phosphonate in the feedwater line. In the boiler, hydrolysis contributes larger quantities of orthophosphate, but these levels are still very small.

### Polymer Technology

The major advantages of using the newer synthetic polymers over natural organics such as the tannins, lignates, starches, etc., are that:

1. They require a far smaller dosage than the natural organics.
2. They allow for more complete dispersancy at all dosage levels. Polymer dispersants distort crystal structure to prevent scale deposits and sludge buildup.
3. They are corrosion inhibitors that form a monomolecular protective film on internal metal surfaces.
4. They have a superior thermal stability. Most polymers are stable up to 600 °F. When they do decompose, the normal black carbonized deposits associated with natural organics are not formed.
5. They create very little waste disposal problems and some are suitable for the food processing industry.
6. They are far more compatible with other water treatment products than phosphates or chelants.

Polymer reactions are related to colloidal technology. When hardness starts to precipitate, it must pass through a colloidal (particle size) range. In the absence of a dispersant, the hardness will fuse into dense sludge with a very high cohesive (adherent) strength.

When there is some dispersant present, the aggregates are prevented from touching each other (electrical and mechanical repulsion). This produces a fluffy network, which is easily removed from the boiler by blowdown.

Some of the polymers will coat or film metal surfaces and thereby repel sludge aggregates, thus preventing scale from forming.

As a polymer is used in the boiler water, it will absorb a heavy water layer, which also carries an electrical charge. Through this phenomenon, the polymer functions in two ways:

1. The electrical charge of the polymer that is absorbed on to the particles is identical (all negative or all positive) causing them to repel each other.
2. The heavy water layer that is absorbed mechanically prevents close contact of the particles. This is an extremely important point of any polymer application when used with a treatment program that removes hardness by precipitation.

There are very few methods for monitoring the residual levels of a polymer in a boiler. They are usually formulated with other internal treatments so that they will exist when the other residual is present. A common blend is polymer and phosphates.

### Steam/Condensate Treatment

The postboiler, or the steam distribution and condensate return system, can be effectively treated to reduce metal loss caused by carbon dioxide and oxygen corrosion. The chemical treatment scheme may consist of neutralizing amines, filming amines, and oxygen scavengers.

### Neutralizing Amines

Neutralizing amines neutralize the acid formed by the solution of carbon dioxide in the water. In effect, they hydrolyze in water to generate hydroxide ions needed for neutralization.

By regulating the feedrate of the amine, the pH of the system can be maintained in a range of 8.2-9.0.

There are several amines available for condensate neutralization. The selection of an appropriate amine depends upon several different requirements. Primarily, choice is made based on the distribution ratio.

At a given point in the steam system where condensation begins, there will be portions of the amine present in the steam and portions present in the condensate. The degree or ratio of an amine in these two phases is called the distribution ratio. Therefore, the distribution ratio of a given amine is expressed as follows in Table 2:

Table 2: Relationship Between Distribution Ratio and Dosage

Amine	Published Distribution Ratio	Dosage mg/L
AMP-95	0.3:1	13.0
Morpholine	0.4:1	10.6
DMPO	0.4:1	11.6
DEAE	1.1:1	9.8
Cyclohexylamine	2.6:1	7.6
Methoxypropylamine	1.0:1	NA

Amines with a distribution ratio of more than 1.0 will have more amine present in the steam phase, while amines with a distribution ratio of less than 1.0 will have more amine present in the condensate phase.

It must be noted that the distribution ratios will change as pressure changes. Table 3 gives the various ratios of the amines currently used at different pressure levels.

As shown in Table 3, at 150 psig there would be twelve times the amount of cyclohexylamine in the steam phase as in the condensate phase. However, with MPA, there would be equal amounts in both the condensate and steam phase.

Table 3: Condensate Corrosion Inhibitors Vapor/Liquid Distribution Ratio at Various Pressures

psig	MPA <sup>1</sup>	CHA <sup>2</sup>	Morpholine	AMP-95 <sup>3</sup>	DEAE <sup>4</sup>
0	0	2.0	0.4	0.1	1.0
150	1.03	12.0	0.85	0.95	3.4
450	3.10	9.4	1.2	0.85	3.8
600	4.14	6.6	1.3	0.85	3.9
900	6.21	7.0	1.24	0.91	3.3

1. Methoxypropylamine
2. Cyclohexylamine
3. 2-amino-2-methyl-1-propanol
4. Diethanolamine

This is very important when choosing an effective overall treatment program for corrosion control. For example, with only using cyclohexylamine, the condensate returning to the system would have most of the amine

remain in the steam phase, which would not provide very good protection of the condensate return system.

Therefore, it is common to feed a blend of amines to protect the entire system. It is very important to have a good understanding of the system being treated so that the best amine or combination of amines can be applied for maximum protection.

Another important point is that cyclohexylamine and DEAE form an azeotrope with water and will volatilize at less than 1 psig. This is important when one of the major areas for amine loss from a system is in the deaerator heater section. Since deaerator temperatures are not uncommon at 220 °F, amines<sup>1</sup> that form azeotropes can accompany the gases vented from the deaerator. AMP95 and morpholine do not form azeotropes. They require pressure of about 75 psi before they will carry-over into the steam system. This is very important when considering that most of the neutralizing amines are fed directly into the boiler along with the other chemicals. In fact, one of the benefits of a neutralizing amines is that they will carryover from the boiler into the steam and do not require a separate feed system connected to the steam header. However, when they are fed directly into the boiler, a percentage of the amine will be lost through blowdown (approximately equal to the blow-down percent). Feeding directly to the steam header can prevent this loss.

Since carbon dioxide is being generated continuously, and the neutralizing amines function by reacting with the carbon dioxide, it is essential to feed the amine continuously for maximum protection.

Feedrate is controlled by the pH of the condensate. As the amines react with the carbonic acid, the pH of the system will be raised according to the amount of amine fed. Since carbonic acid can exist up to a pH of 8.2, it is important that 8.2 be the very minimum pH in the system.

#### Neutralizing Amine Notes

##### 1. pH Control Range: 8.2-9.0.

A maximum pH of 8.8 should be used if the system contains a large percentage of copper.

##### 2. Conductivity Range: Less than 20 µS/cm (micromhos).

If the condensate conductivity is higher, perform a hardness test to determine if there is carry-over taking place. An alkalinity test should also be conducted. The alkalinity should not be more than 5-10 mg/L Total Alkalinity and there should be no phenolphthalein alkalinity.

##### 3. Total Alkalinity Range: 5-10 mg/L.

A slight amount of alkalinity will be present in the condensate if all the carbonic acid has been neutralized by the amine. The range of 5-10 mg/L usually is at a pH of approximately 8.4. If the pH test is less than 8.2 and there is no alkalinity present, then CO<sub>2</sub> is in the condensate. If the pH is low and there is some alkalinity present, then there is excess CO<sub>2</sub> in comparison with the amine.

##### 4. Total iron and copper limits in feedwater is shown in Table 4.

**Table 4: Iron and Copper Limits**

psi	Iron mg/L	Copper mg/L
0 - 300	0.1	0.05
301 - 450	0.05	0.025
451 - 600	0.03	0.020
601 - 750	0.025	0.020
751 - 1000	0.020	0.015
1001 - up	0.010	0.010

##### 5. Insoluble Iron Filter Test: The Millipore® Filter test can be used to establish corrosion trends in the system. Using the Babcock and Wilcox charts, Table 5 shows the established limits for feedwater.

**Table 5: Babcock & Wilcox Feedwater Limits for Iron**

psi	Maximum µg/L (ppb) Iron
0 - 600	100
601 - 1000	50
1001 - up	10

By dividing the limit by the percent of condensate return, the allowed limit of iron in the return system can be determined.

##### 6. Corrosion coupons and nipples: The preferred method is to insert the coupon directly into the line at midpoint by an appropriate length rod holder. A test nipple can be used to monitor the grooving effect that is a result of carbonic acid corrosion.



## Filming Amines

Filming amines are commonly used when oxygen leakage is a problem and/or the system is very extensive in length. This type of amine forms a molecular film on the metal. The molecule has one hydrophobic and one hydrophilic tail in its structure. The hydrophilic end attaches to the metal surface, leaving the hydrophobic end exposed to the steam and condensate. The hydrophobic end repels water preventing the water from adhering to the metal surface. This physical barrier prevents water and oxygen to contact the metal.

The most commonly used filming amines are octadecylamine and ethoxylated soya amine. The use of octadecylamine is an older technology and has some drawbacks, which include: inability to form a film over existing pits; relatively poor distribution in long or branched systems; acts as a boilersludge binder if overcycled or overfed; and it is more pH dependent than neutralizing amines. The film will begin to strip off when the pH falls below 6.5, while the ethoxylated soya amine has been found to be stable down to a pH of about 5.0.

In most cases, a filming amine will be fed in combination with a neutralizing amine to increase the stability of the film. The filming amines are more cost effective than neutralizing amines, primarily because of the lower dosage required. A basic control range is from 0.5-1.0 mg/L as active amine.

There are several drawbacks associated with filming amines. They require a separate feed system tied into the steam header since they are not volatile. They are very sensitive to iron contamination, oil, and to minerals such as those present in the boiler TDS. When these conditions exist, the filmer will polymerize or degrade to form a sticky deposit, which will impair the operation of steam traps, among other things. Table 6 shows a comparison between neutralizing amines and filming amines.

## Carryover

Carryover or entrainment of boiler water and boiler water solids must be prevented. It causes deposits on control valves, turbine blades, superheater tubes, and steam traps.

As little as 0.1 mg/L of solids can cause control valves to stick, leading to over-speed of rotating or reciprocating equipment. The same small amount can lead to turbine

blade deposits, which result in imbalance and excessive wear of high-speed machines and loss of efficiency in low speed machines. When the carryover gets as high as 1.0 mg/L, deposits can form in the superheater tubes resulting in reduced heat transfer, which may lead to tube ruptures.

**Table 6: Amine Comparison**

System Parameter	Neutralizing Amine	Filming Amine
Feed	Can be fed in the feedwater, boiler or steam header. Can be mixed with other chemicals.	Must be mixed with condensate and can only be fed into steam header. Requires separate feed system.
Deposits	Does not form or contribute to deposits. Not affected by contaminants.	Can degrade or polymerize if overfed or comes in contact with contaminants.
Oxygen corrosion	Not effective against O <sub>2</sub> corrosion.	Will provide protection against O <sub>2</sub> corrosion.
Control Test	Controlled by pH of condensate.	Very difficult test. Feed usually based on steam rate.
Heat transfer	No effect on heat transfer.	Can significantly impeded heat transfer.
Cost	Generally more expensive based on use.	Less expensive on product use basis
Results	Good protection from CO <sub>2</sub> corrosion.	Superior protection when properly applied for both CO <sub>2</sub> and O <sub>2</sub> corrosion.
Feedrate	Requirements based on CO <sub>2</sub> .	Based on steam production.

Carryover will increase the potential for corrosion and erosion-corrosion in the steam/condensate system. It can also lead to process contamination when live steam is required. In large slugs, it can cause thermal and mechanical shock, which is damaging to equipment and structures. This carryover, surging, splashing, foaming, misting, etc., can be either mechanical or chemical related.

There are seven reasons for mechanical carryover and only one of them can be corrected by chemical means. They are: 1) improper boiler design, 2) improper maintenance, 3) high water level in boiler or steam drum, 4) exceeding operational limits, 5) extreme or sudden load surges, 6) uneven firing, and 7) improper water composition.

Consider what happens when a steam bubble reaches the water surface. The thin skin forming the top of the bubble breaks, leaving a concave or cavity in the water surface. The water rises to fill this void that is left. As the water rises, the center of the riser is moving faster and the result is that a small droplet snaps off and is thrown upward. This is commonly referred to as "misting" and is found in all boiler systems.

This mist, or droplets in the steam, must be removed mechanically. One method is the installation of a dry-pipe. The principle is that a sudden change in the flow direction of the steam will throw out the heavier entrained water and allow it to fall back into the bulk water. The same principle is employed in baffling, chevron screens, and centrifugal separators. In some boiler designs, the steam comes in contact with the boiler feedwater, which washes out the entrained water particles.

The most common chemical compound used is a class of polymers called polyamides, which have proven to be excellent foam suppressors. The addition of 3-5 mg/L of polyamide can reduce the solids in the steam to less than 0.5 mg/L.

Priming is a form of mechanical carryover. This is caused by gross surges of water in the steam drum that literally throw water into the steam space where it can be carried into the steam header. This can be caused by either improper design or improper operation. Priming, at times, can be corrected by changing the firing pattern, correcting false level indicators, or installing vertex breakers.

In addition to mechanical carryover, there can be a chemical carryover. Above 600 psig silica can volatilize along with the water, and thus be carried over into the steam. Silica content in the steam can be directly related to the amount of silica in the boiler water. Once in the steam, silica will deposit at pressure drop points, particularly on turbine blades.

It has been found that if the silica content of the steam remains below 0.02 mg/L, then deposition will not occur. Once silica deposits, it is very difficult to remove. The maximum amount of silica in boiler water is shown in Table 7.

**Table 7: The American Boiler Manufacturers Association (ABMA) Established Limits for Silica Concentration in Boiler Water**

psig	Maximum Silica mg/L
0-300	150
301-150	90
451-600	40
601-750	30
751-900	20
901-1000	8
1001-1500	4
1501-2000	1

Table 8 shows the feedwater quality limits.

**Table 8: Feedwater Quality Limits**

Drum Pressure psig	0-600	600- 1000	1000- 1500	1500- 2000
pH @ 25 °C (77 °F)	8.0-9.5	8.0-9.5	8.5-9.5	8.5-9.2 <sup>1</sup> 9.3-9.5 <sup>2</sup>
Oxygen, mg/L	0.007	0.007	0.007	0.007
Iron, mg/L	0.1	0.1	0.1	0.1
Copper, mg/L	0.05	0.03	0.005	0.005
Total hardness, mg/L	0 <sup>3</sup>	0 <sup>3</sup>	0	0
Organic, mg/L	0 <sup>4</sup>	0	0	0

#### Notes

1. With copper alloys in feedwater heaters
2. With carbon steel feedwater heaters
3. A total hardness limit of zero mg/L is taken to mean as close as possible to zero
4. An organic limit of zero mg/L is taken to mean as close as possible to zero total organic (TOC). Analyzers are commercially available with detection limits of 40 µg/L.

Boiler water limits are listed in Table 9.

**Table 9: Boiler Water Limits**

Drum Pressure, psig	TDS <sup>1</sup> Boiler Water mg/L	Total Alkalinity <sup>2</sup> Boiler Water mg/L
0-300	700-3500	140-700
300-450	600-3000	120-600
450-600	500-2500	100-500
600-750	400-2000	80-400
750-900	300-1500	60-300
900-1000	250-1250	50-250
1000-1500	100	Note 3
1500-1800	100	Note 3
1800-200	50	Note 3

#### Notes

1. Actual values within the range reflect the TDS in the feedwater. Higher values are for high solids, lower values are for low solids in the feedwater.
2. Actual values within the range are directly proportional to the actual value of TDS, of boiler water. Higher values are for high solids; low values are for low solids in the boiler water.
3. Dictated by boiler water treatment.
4. Alkalinity should not exceed 10% of specific conductance. 3.

*The AWT Boiler Water Subcommittee is chaired by John Zibria, Zibex, Inc. The Committee meets the third Friday of each month at 9:00 am ET. To join the Committee, please contact Angela Pike at (240) 404-6477.*



**Boiler Water Treatment Chemical Guidelines – Part II**  
AWT Boiler Water Subcommittee  
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**Question #1**

Certain natural organic and synthetic polymers are used as boiler water sludge conditioners, but often decompose at higher temperatures. Which of the following sludge conditioners is expected to have the best thermal stability?

- a. Sulfonated Lignin
- b. Polyacrylate
- c. Starch
- d. Chestnut Tannin
- e. Quebracho

**Question #2**

Neutralizing Amines are often used to control carbonic acid corrosion in steam condensate systems with the amines' *distribution ratio* being one of the main selection criteria. Based on distribution ratio, which of the following amines would carry furthest in a large, complex steam system?

- a. Aminomethylene propanol (AMP)
- b. Morpholine
- c. Diethylamineoethanol (DEAE)
- d. Methoxypropylamine (MPA)
- e. Cyclohexylamine (CHA)

**Question #3**

When treated steam condensate, containing un-reacted neutralizing amine, is recycled as boiler feedwater and deaerated, some of the amine will be lost through the deaerator vent. Which of the following amines will experience the lowest vent loss?

- a. Aminomethylene propanol (AMP)
- b. Morpholine
- c. Diethylamineoethanol (DEAE)
- d. Methoxypropylamine (MPA)
- e. Cyclohexylamine (CHA)

#### Question #4

The preferred point of injection for neutralizing amines is directly to the steam header. However, in smaller systems, the neutralizing amine is often mixed with other treatment chemicals and fed to the boiler feedwater line or to the boiler steam drum. This causes some of the amine to be lost in the continuous boiler blowdown. Which of the following amines will experience the least blowdown loss?

- a. Aminomethylene propanol (AMP)
- b. Morpholine
- c. Diethylaminoethanol (DEAE)
- d. Methoxypropylamine (MPA)
- e. Cyclohexylamine (CHA)

#### Question #5

In addition boiler water carryover, steam can also be contaminated by vaporized silica carryover in higher pressure boilers. At what boiler pressure does this type of silica carryover begin to occur?

- a. 150 psig
- b. 300 psig
- c. 450 psig
- d. 600 psig
- e. 750 psig

#### Question #6

Vaporized silica in high pressure steam is controlled by limiting the level of silica in the boiler water. According to ABMA, what is the recommended maximum boiler water silica level for a boiler operating at 800 psig?

- a. 1 mg/l SiO<sub>2</sub>
- b. 4 mg/l SiO<sub>2</sub>
- c. 8 mg/l SiO<sub>2</sub>
- d. 20 mg/l SiO<sub>2</sub>
- e. 30 mg/l SiO<sub>2</sub>



### Question #7

The ABMA also provides TDS and Total Alkalinity guidelines to help prevent boiler water carryover. What is their recommended maximum boiler water TDS limit for a water tube boiler operating at 150 psig?

- a. 3500 mg/l
- b. 3000 mg/l
- c. 2500 mg/l
- d. 2000 mg/l
- e. 1500 mg/l

### Question #8

Which of the following boiler treatment chemicals, shown by their common acronyms, belong to a group whose name is derived from the Greek word 'chele'?

- a. HEDP
- b. PAA
- c. EDTA
- d. PBTC
- e. DEAE

### Question #9

Which of the following boiler treatment chemicals will thermally decompose, with one of the decomposition products being ortho phosphate?

- a. HEDP
- b. PAA
- c. EDTA
- d. DMPO
- e. DEAE

### Question #10

Which of the following steam condensate treatments will have the lowest cost, especially in systems that have relatively high amounts of carbon dioxide?

- a. Aminomethylene propanol (AMP)
- b. Morpholine
- c. Diethylamineoethanol (DEAE)
- d. Octadecylamine
- e. Cyclohexylamine (CHA)