One of the prime considerations in the operation of a boiler is feedwater quality. The better the feedwater, the less likely that water-related problems will occur. There are many sources of feedwater:

- Raw, untreated water
- Zeolite softened water
- Demineralized water
- Lime-soda softened water and of course, returned condensate.

Of all these sources, condensate is usually the best economic choice. Condensate, being condensed water vapor (steam) is extremely pure. Since condensate is usually 180°F (82.2°C) or greater, less fuel is needed to convert it back to steam because 148 Btu’s (82.2 Kcal) are in each pound (kilogram) of 180°F (82.2°C) condensate. And finally, because it is water that the plant has already treated (ion exchange processed, scale/corrosion treated, oxygen removed and evaporated to produce steam), it represents a valuable investment. Therefore, recovering and reusing this water is good management.

Condensate return can help improve the economics of boiler operation through:

**Feedwater temperature increases** — By increasing feedwater temperature, a plant can reduce the amount of fuel required to produce a pound (kilogram) of steam from a pound (kilogram) of water. Increasing the amount of returned condensate either increases the feedwater temperature directly, or decreases the amount of steam (deaerator) needed to preheat it.

**Cycles of concentration increase (blowdown decreases)** — Since condensate is low in dissolved solids, the more returned, the lower the concentration of feedwater solids. Boiler cycles of concentration increase, blowdown decreases, and so does the amount of heat lost in the blowdown.

**Reduced makeup water requirement** — As more condensate is returned, less makeup is needed for feedwater. Therefore, less money is spent on makeup water treatment (ion exchange regenerant, chemical treatment).

Now that reasons for returning condensate have been established, it is necessary to be aware of problems incurred in the condensate system. Almost all difficulties encountered in condensate systems can be traced to two gases:

- Carbon dioxide
- Oxygen

**CARBON DIOXIDE**

In most boiler feedwaters, some carbonate alkalinity is present. Under the pressures and temperatures encountered in the boiler, a portion of the alkalinity breaks down to form carbon dioxide. Carbon dioxide, being a gas, is carried out with the steam. When steam condenses, some of the carbon dioxide dissolves in the condensate and forms carbonic acid. Carbon dioxide is not harmful until it dissolves in condensate.

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-
\]

Carbonic acid will cause four characteristic problems:

- The pH of the condensate will drop
- Dissolved iron will increase
- Total dissolved solids will increase
- A trough-like thinning of the bottom of the condensate pipe may occur (Figure 1)

As little as 1 ppm carbon dioxide dissolved in condensate can result in a pH of 5.5 at typical condensate temperatures.

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A pH of 5.5 is 10,000 times more aggressive to mild steel than a pH of 7.5, and 1,000,000 times more aggressive than a pH of 8.5.

What is the impact? Iron is dissolved by low pH condensate and is then returned to the feedwater.

$$\text{Fe} + 2\text{H}^+ + 2\text{HCO}_3^- \rightarrow \text{Fe}(${HCO}_3$)_2 + \text{H}_2$$

Simply put, iron is removed from one part of the system (condensate piping) and is deposited in another area of the boiler system (boiler heat transfer surfaces — Figure 2).

The results of carbon dioxide corrosion include:

- Expensive replacement of condensate piping
- Reduced boiler tube life
- In some cases, unexpected boiler shutdowns and production losses

The net result is an outlay for maintenance on the condensate network, chemical cleaning of the boiler, and possible loss of plant production due to an unscheduled outage.

OXYGEN

Also present in boiler feedwater, this gas may be removed by conventional mechanical and chemical means. Mechanically, oxygen content is reduced by a deaerator, which atomizes the feedwater, and “scrubs” it with steam. The steam increases feedwater temperature, so oxygen becomes less soluble, and is released to the atmosphere at the deaerator vent. Typically, oxygen concentration drops to below 10 ppb.

The rest of the oxygen (even at 10 ppb, still capable of causing severe corrosion) may be scavenged chemically using one or more of the following compounds:

- Sulfite
- Hydrazine
- Other proprietary organic reducing agents

Usually, these two processes, mechanical and chemical feedwater oxygen elimination, are sufficient to prevent oxygen from flashing into the steam. However, in large, extensive condensate systems, air can be drawn in through condensate pumps, improperly operating heat exchangers or tank vents. This air in-leakage brings in both carbon dioxide and oxygen, causing more corrosion problems than either gas individually.

Oxygen attack is characterized by pitting of the condensate pipe (Figure 3).

$$\text{4Fe} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}({\text{OH}})_3$$

The combined action of carbon dioxide and oxygen can cause accelerated corrosion rates of 10 to 40% more than the sum of the rates of the individual gases (Figure 4).

$$2\text{Fe}(${HCO}_3$)_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{CO}_2 + 2\text{H}_2\text{O}$$

The impact of oxygen attack is the same as that of carbon dioxide – equipment damage, expensive maintenance, unexpected boiler shutdown, and possible costly production losses.

PROBLEM PREVENTION

The best way of dealing with these two corrosive gases is to prevent their entry into the boiler system. Simple mechanical measures include:
• Good deaeration and properly operating condensate pumps and tank vents can keep oxygen and atmospheric carbon dioxide out of the system.

• Demineralization or dealkalization can greatly reduce the amount of alkalinity in boiler feedwater, and thus the amount of carbon dioxide generated by alkalinity breakdown.

• Condensate polishing, that is, using ion exchange resin to remove and filter hardness and corrosion products, is an effective way to eliminate the results of in-leakage and corrosion, but it does not correct the causes.

Not all problems can be cured mechanically, and due to budget constraints, chemical treatment may be selected. There are chemical answers to carbon dioxide and oxygen corrosion in the condensate.

**NEUTRALIZING AMINES**

These products do just what their name indicates: neutralize carbonic acid formed in the condensate. Neutralizing amine programs are generally effective when fed to maintain a minimum pH of 8.5 (suggested range: 8.5 to 9.0). In systems containing no copper alloys, somewhat higher pH values will improve mild steel corrosion control.

Neutralizing amines are added in direct proportion to the amount of carbon dioxide in the steam. In high alkalinity feedwater systems where CO₂ generation is appreciable, excessive amounts of neutralizing amines may be required to neutralize the carbonic acid. (Filming amines should be considered in these instances.) Neutralizing amines are characterized by a specific volatility, acid neutralization ability, and basicity.

**VOLATILITY**

Every gas in a condensate system has a specific volatility or vapor-to-liquid distribution ratio (V/L). The V/L distribution ratio is defined by:

$$V = \frac{\text{concentration in the vapor or steam phase}}{L}$$

(L (concentration in the liquid or condensate phase)

The V/L distribution ratio indicates whether the species will condense with the condensate or stay with the steam. For example, a V/L ratio of 4.0 indicates that 4.0 ppm of amine must be present in the steam to get 1.0 ppm in the condensate. The higher the V/L ratio, the more amine will be in the steam. To neutralize carbonic acid, the amine must be in the condensate as the CO₂ dissolves.

V/L ratios vary with pressure, pH, temperature, and other operating conditions. Table 1 indicates the V/L ratio of two common neutralizing amines and carbon dioxide.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Cyclohexylamine</th>
<th>Morpholine</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 psig</td>
<td>2.7</td>
<td>0.4</td>
<td>3.0</td>
</tr>
<tr>
<td>50 psig</td>
<td>3.0</td>
<td>0.4</td>
<td>4.8</td>
</tr>
<tr>
<td>150 psig</td>
<td>4.0</td>
<td>0.5</td>
<td>8.5</td>
</tr>
<tr>
<td>600 psig</td>
<td>10.0</td>
<td>1.2</td>
<td>15.8</td>
</tr>
<tr>
<td>900 psig</td>
<td>6.6</td>
<td>1.2</td>
<td>&gt;99.0</td>
</tr>
</tbody>
</table>

It is important to realize that V/L ratios are only significant when a phase separation occurs. For example, in a flash tank, condensate enters the vessel while both condensate and steam exit the vessel. Low volatility amines such as morpholine will tend to be present in greater concentration in the condensate exiting the flash tank. High volatility cyclohexylamine will tend to be present at higher concentrations in the steam exiting the flash tank.

V/L ratios are not significant when total condensation occurs. Total condensation occurs when all the carbon dioxide and amines in the steam entering a unit are dissolved into the condensate (no phase separation exists).

**ACID NEUTRALIZING ABILITY**

In addition to V/L ratio, which determines the distribution of an amine in a system, another very important aspect of amine choice is its acid neutralizing ability. This is the amount of amine required on a weight basis to neutralize the carbonic acid present. The amine reacts with the carbonic acid in solution to form an amine bicarbonate:

$$RNH_2 + H^+ + HCO_3^- \rightarrow RNH_3^+ + HCO_3^-$$

This characteristic is primarily dependent upon the molecular weight of the amine. On a pound-for-pound basis, lower molecular weight amines will neutralize more carbonic acid than higher molecular weight amines.

**BASICITY**

Once all the acid in the condensate system has been neutralized (at a pH of about 8.3), amine basicity becomes important. This is a measure of amine hydrolysis. Any additional amine added to the condensate system will hydrolyze, raising the condensate pH:

$$RNH_2 + H_2O \rightarrow RNH_3^+ + OH^-$$

Basicities of neutralizing amines also vary. For example, cyclohexylamine is a much stronger base than morpholine. Past a certain pH, additional quantities of the weaker neutralizing amines, such as morpholine, will do little to further increase pH.
Figure 5 shows the combined effect of acid neutralizing ability and basicity for three amines.

The V/L ratio, acid neutralizing ability, and the basicity of each amine must be considered when selecting a condensate corrosion inhibitor program. Common neutralizing amines are morpholine, cyclohexylamine, diethylaminoethanol (DEAE), aminomethylpropanol (AMP), dimethylisopropanolamine (DMIPA), and methoxypropylamine (MOPA). As mentioned earlier, neutralizing amines neutralize carbonic acid. Their effect on oxygen is negligible.

FILMING AMINES

Filming amines are used to protect condensate piping from both oxygen and carbonic acid attack. This is done by laying down a very thin film on the condensate pipe (Figure 6).

In order for the filmer to work, the condensate pH must be high enough for the film to form. Octadecylamine is a commonly used filmer, but the pH must be controlled at a range of 6.5 to 8.0. Outside this range, the film strips off, and can cause deposits in the steam traps and condensate lines (and even the boiler). Also, octadecylamine is difficult to feed.

Another filmer, a proprietary compound is stable over a wider pH range of 6.5 to 9.5, making it much easier to use, and overall, a more flexible program.

In almost all cases, the filmer must be supplemented with a neutralizing amine. Filmers alone do not have enough neutralizing capability to buffer condensate pH into the range where filming can effectively take place. Most filmers are offered as a combination treatment of filming/neutralizing amines to alleviate this problem.

The fact that a filmer/neutralizer program can provide protection at a lower pH than a straight neutralizer may allow a plant to use less neutralizer, and thus reduce treatment costs. It should be noted that the ultimate
basis for this decision is the individual plant’s treatment performance and operating history.
Another benefit of filming amines noted by some users is an improvement in heat transfer, due to the film promoting nucleate condensation.

**OXYGEN SCAVENGERS/METAL PASSIVATORS**

An alternative to filming amines for condensate oxygen corrosion protection is an oxygen scavenger/metal passivator (Figure 7).

These compounds work by the same mechanisms as the feedwater oxygen scavengers mentioned earlier. The oxygen problem is addressed directly by using an oxygen scavenger/metal passivator to treat the steam/condensate system. Some oxygen scavengers enhance metal passivation. At condensate temperatures, metal passivation generally occurs preferentially over oxygen scavenging. However, carbonic acid attacks the passive magnetite film, so passivation improves above pH 8.3, where the acid is not present.

A combination of neutralizing amines and metal passivator can be ideal for many plants. However, if feedwater alkalinites are high, a neutralizer/filmer program may be more economical. The trade-off between ease of control (which favors neutralizer/metal passivator) and economics (which favors neutralizer/filmer) is system dependent.