CORROSION PROTECTION

OF

CONDENSATE SYSTEMS

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by

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INTRODUCTION

Condensate systems experience corrosion from two major impurities—carbon dioxide and oxygen. The combination of carbon dioxide & water provides the conditions that are necessary for uniform metal loss in the form of grooving, particularly in horizontal runs, and thinning at pipe threads, whereas oxygen corrosion manifests itself as deep pits.

Bicarbonates and carbonates in the fresh make-up water are the major sources of carbon dioxide contamination. Most natural waters contain sodium, calcium, and magnesium bicarbonates. When these minerals enter the boiler, heat causes them to break down as follows:

Ca(HCO ₃) ₂	+ Heat		+ H ₂ O	+	CO ₂	♠	(1)
Calcium		Calcium	Water		Carbon		
Bicarbonate		Carbonate			Dioxide		
		Sludge			Gas		

In zeolite softened waters, the problem of carbon dioxide evolution is often increased. The softening process converts all calcium & magnesium bicarbonate into sodium bicarbonate which breaks down as follows:



Unlike calcium carbonate, sodium carbonate is soluble and subject to further breakdown as follows:

Na ₂ CO ₃	+	H_2O	+	Heat	>	2NaOH	+	CO ₂	(3)
Sodium Carbonate	Э	Water				Sodium Hydroxide Gas		Carbon Dioxide	

These equations show that 2 molecules of sodium bicarbonate in the feedwater are a potential source of 2 molecules of carbon dioxide in the condensate.

Equation #3 illustrates that since soda ash (i.e., sodium carbonate) is also a source of carbon dioxide, sodium hydroxide (i.e., caustic soda) should be used for boiler water pH control rather than soda ash.

Carbon dioxide by itself is not corrosive; however, when it dissolves in water (i.e., condensate), carbonic acid is formed, and at the resulting low pH level of 4.5-5.5, iron is dissolved, thus resulting in the typical grooving attack in accordance with the following equations:

CO ₂	+ H ₂ O	>	H⁺ +	HCO ₃ ⁻	(4)
Carbon Dioxide Gas	Water		Hydrogen Ion (acid)	Bicarbonate ion	
2Fe +	3H ₂ O	H ⁺	Fe ₂ O ₃	+ 3H₂ ♠	(5)
Iron	Water	Hydrogen Ion (acid)	Ferrous (ire Oxide	on) Hydrogen Gas	

Oxygen in the fresh make-up water and the ambient air are the major sources of oxygen contamination. Most natural waters contain approximately 9 ppm of dissolved oxygen at room temperature; however, its solubility decreases as the water is heated. Therefore, the higher temperature in the boiler forces oxygen out of solution and into the steam. As steam condenses, it creates a vacuum which will tend to suck ambient air into the system. Steam traps, condensate drains, vents, and other areas where air in-leakage may occur are possible sources of oxygen contamination.

The oxygen corrosion reaction is as follows:



Reaction #6 occurs by a differential aeration mechanism and results in pitting under corrosion products. When carbon dioxide is also present, the condensate low pH will dissolve corrosion products, thus leading to additional differential aeration cells in uncovered crevices.

PREVENTING CORROSION IN CONDENSATE SYSTEMS

The two basic approaches for the prevention of corrosion in condensate systems are:

- Minimise carbon dioxide & oxygen contamination;
- Use chemical inhibitors to counteract corrosive conditions.

Various ion exchange methods are available for reducing or eliminating carbonates and bicarbonates from the fresh make-up water; however, in most cases, pretreatment of the water solely for removing carbonates and bicarbonates can not be justified from an economic standpoint.

Dissolved oxygen in the fresh make-up water can be eliminated or greatly reduced by de-aeration **plus** the use of an oxygen scavenger. In small systems with very little fresh water make-up, chemical oxygen scavenging alone is effective. However, in systems with extensive piping, it is difficult to completely eliminate air in-leakage into the steam condensate lines.

Chemical Inhibitors

There are two basic chemical inhibitors that are used for minimising corrosion in condensate systems—neutralising amines and filming amines. Neutralising amines are volatile, alkaline chemicals that increase the condensate pH level. They offer protection against carbonic acid attack, but do not completely prevent oxygen corrosion. Filming amines form a barrier between the metal and the condensate, thus preventing both carbonic acid and oxygen attack. The choice between neutralising and filming amines, or both, depends on the particular operating conditions. That is, if there is air leakage into steam condensate lines, generally filming amines are better suited, whereas in tight systems with low fresh water make-up, neutralising amines are usually more practical.

Neutralising Amines

The most common neutralising amines are listed in Table 1 below. Each one functions by neutralisation, and is effective only in controlling corrosion caused by low pH. Neutralising amines volatise from the boiler water, carry-over with the steam, and dissolve in the condensate where they react with carbonic acid to form amine carbonate or amine bicarbonate. Excessive amine carbonate/bicarbonate concentrations may result in their precipitation. However, in most cases the amine carbonates/bicarbonates dissolve in the condensate and are returned to the boiler where heat causes them to break down into amine and carbon dioxide, and the cycle is repeated.

The amine vapour/liquid distribution ratio (DR)—defined as the ratio of the amount of amine in the steam to the amount of amine in the condensate—is used to determine which amine, or groups of amine, that is best suited for a particular condensate system. The amine DR's are listed in Table 1 below.

Amine	Vapour/Liquid Distribution Ratio (at 0 psig)	Vapour/Liquid Distribution Ratio (at 600 psig)
Ammonia	10.0/1.0	4.2/1.0
Cyclohexylamine	4.0/1.0	6.6/1.0
Diethylaminoethanol (DEAE)	1.7/1.0	3.8/1.0
Dimethylaminoethanol (DMAE)	1.0/1.0	1.9/1.0
Morpholine	0.4/1.0	1.3/1.0

Table 1: Distribution Ratios of Neutralising Amines

Since the object of volatile amine treatment is to neutralise the carbonic acid that is formed in the condensate, it is important to note that only that portion of the amine that dissolves in the condensate is capable of complying with this objective. The amine in the steam phase does not neutralise acid in the condensate. Therefore, if most of the steam condenses early in the system, morpholine with its low DR of 0.4/1.0 (i.e., 0.4 part morpholine in the steam; 1.0 part morpholine in the condensate) would be the amine of choice because of its higher concentration in the condensate. Cyclohexylamine with its higher DR of 4.0/1.0 would be more effective for longer far reaching condensate systems due to its higher concentration in the steam phase. Similarly, DEAE or DMAE would be the amine of choice for moderately sized condensate systems because of their intermediate DR's. In complex steam systems, the prevention of deposits from excessive amine carbonate/bicarbonate concentrations may be best accomplished by feeding a mixture of amines.

The volatility of neutralising amines dictates that they should be purchased at a concentration that is in keeping with due regard to the fire hazard associated with their low flash point temperatures (i.e., 40% for morpholine & cyclohexlyamine). They are usually added to the boiler feedwater, along with the boiler water scale & corrosion inhibitors, and continuous injection is required.

The primary means for controlling neutralising amines is by adding sufficient amine to maintain condensate pH levels within the range of 8.5-9.5 pH for systems without steam humidification and 8.0-8.5 pH in systems where a portion of the steam is used for space humidification. However, control can also involve the monitoring of condensate iron concentrations, the use of corrosion coupons, and visual examination. Whichever method(s) is used, it is important to monitor as many condensate streams as possible.

Filming Amines

The most common filming amine is octadecylamine (ODA). It is a large molecule that has both hydrophilic—water attracting—and hydrophobic—water repelling—ends in its structure. Bonding at the hydrophilic end forms an adherent nonwettable organic film on the metal surface, thus preventing contact between that surface and the corrosive condensate. The monomolecular film thus formed inhibits attack from both oxygen and carbonic acid. A clean surface is required for filming amines to work properly because the presence of deposits on the metal surface inhibits film formation; therefore, either areas under the deposits are not protected, or the deposits are undercut and sloughed off, thus resulting in blockage of steam traps and valves in the condensate system.

Because high velocities could potentially erode the protective film, a continuous amine feed directly to the main steam supply at a typical concentration of 1-3 ppm is required.

The control of filming amines is accomplished by monitoring condensate iron concentrations, the use of corrosion coupons, and visual examination. Whichever method(s) is used, it is important to monitor as many condensate streams as possible.