EnviroAqua CONSULTANTS INC.

# Water Talk

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## *Neutralizing Amines and Ammonium Hydroxide*

## NEUTRALIZING AMINES AND AMMONIUM HYDROXIDE

Selecting and applying a neutralizing amine in a steam system requires both technical and work environment considerations. This article briefly discusses the technical considerations, but emphasizes the government regulations as well as non-regulatory factors in choosing a treatment program.

The basis for using neutralizing amines or ammonium hydroxide in a steam system is to prevent carbon dioxide corrosion on steel or copper condensing coils and condensate return lines. When calcium bicarbonate { $Ca(HCO_3)_2$ }, magnesium bicarbonate { $Mg(HCO_3)_2$ }, or sodium bicarbonate {$NaHCO_3$} in boiler feedwater is heated, the bicarbonate ion { $HCO_3^-$ } will decompose into carbonate ion { $CO_3^{2-}$ }, carbon dioxide gas { $CO_2$ }, and water { $H_2O$ }. These chemical reactions are shown below.

### Hardwater Makeup

$Ca(HCO_3)_2 \xrightarrow{heat} CaCO_3 \downarrow + CO_2 \uparrow + H_2O$

$Mg(HCO_3)_2 \xrightarrow{heat} MgCO_3 \downarrow + CO_2 \uparrow + H_2O$

### Softened Makeup

$2\,NaHCO_3 \xrightarrow{heat} Na_2CO_3 \downarrow + CO_2 \uparrow + H_2O$

When bicarbonate alkalinity is decomposed in the boiler water, carbon dioxide gas is formed and released with the steam. For softened water systems or hard water systems being treated with caustic soda, the carbonate alkalinity { $CO_3$ } will further decompose into carbon dioxide and hydrate alkalinity.

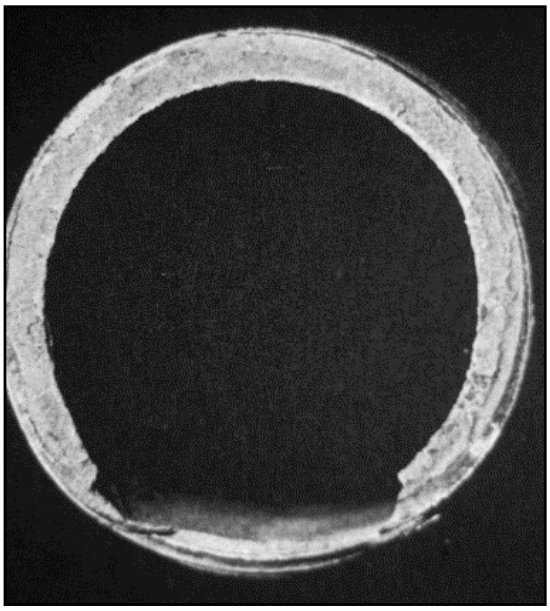

Fig. 1 Grooving of steel condensate line is typical of carbonic acid corrosion.

$Na_2CO_3 + H_2O \xrightarrow{heat} 2\,NaOH + CO_2 \uparrow$

This reaction is temperature dependent, which means the higher the operating pressure of the boiler, the greater is the conversion from carbonate alkalinity to carbon dioxide. Typically in very low-pressure boilers under 25 PSIG, the conversion rate is 25 to 50 percent. At 100 PSIG the conversion is 60 to 80%. At 200 PSIG and above, the conversion is 95+%.

Carbon dioxide is a non-condensable gas and prefers the steam phase. However, as the operating pressure of the boiler system increases, the concentration of carbon dioxide dissolved in the condensate phase as

carbonic acid also increases. The typical condensate pH is below 6.0.

Neutralization of dissolved carbon dioxide in the returning condensate is done with either volatile organic amines or ammonium hydroxide. Typically the pH is adjusted to > 7.0. Over the years, many different amines have been used in this application. The organic amines most commonly used as condensate line corrosion inhibitors are morpholine, diethylaminoethanol (aka diethylethanol-amine) and cyclohexylamine. The reason for the broad acceptance of these three amines is because they have approval from the Food and Drug Administration (FDA) for use in food processing applications. Further, the U.S. Department of Agriculture (USDA) permits the use of the amines in meat and poultry plants.

In addition to the government approvals for the use of these amines, another non-technical reason is that these neutralizing amines have a mild odor as compared to the sharp odor of ammonium hydroxide.

The Food and Drug Administration has issued approvals on the three organic amines for use as boiler water additives, which may be safely used in the preparation of steam that will contact food. This regulation can be found in Title 21, Code of Federal Regulations, Subpart D, Section 173.310, Boiler Water Additives. However, organic amines are excluded from steam which contacts milk or milk products. Therefore, ammonium hydroxide (aka ammonia) is used in dairies. In the FDA regulations under Section 184.1139, the use of ammonium hydroxide as a boiler water additive is permitted without exclusions. The following table lists the limitations of the amine in steam as determined by the FDA for steam contacting food.

| **Substance** | **Limitations** |
|---|---|
| Morpholine | 10 ppm |
| Diethylaminoethanol | 15 ppm |
| Cyclohexylamine | 10 ppm |
| Ammonia | Good manufacturing practice |

There are no government agencies that regulate amines used in humidification. However, the concentration of organic amine in the humidified air is regulated by OSHA (Occupational Safety and Health Administration). The following table lists the limitations based on a time weighted average exposure of 8 hours. The units are milligrams of substance per cubic meter of air.

| **Substance** | **Limitation (TWA 8 hrs.)** |
|---|---|
| Morpholine | 70 mg / $m^3$ |
| Diethylaminoethanol | 50 mg / $m^3$ |
| Cyclohexylamine | 40 mg / $m^3$ |
| Ammonia | 18 mg / $m^3$ |

During the 1980's, extensive inhalation studies were conducted on the three organic amines. They were also evaluated with respect to carcinogenicity. These amines were found not to be carcinogens.

A list of other non-regulatory work environment considerations for the application of neutralizing amines includes the following:

1. Odors in indoor air.
2. Staining of fabrics or instruments.
3. Interference with electronic equipment operation.
4. Incompatibility with materials such as rubber.

In general, odors associated with the application of steam for humidification result from the overfeed of an amine. Keeping the amine concentration at or below the OSHA TWA Value shown above will minimize odor problems. Staining of fabrics or instruments may be a result of iron oxide in the steam line being picked up by the amine or, possibly the amine reacting with residual laundry detergents in the fabric. In regard to electronic equipment operations, this has become less of a problem today than in the past.

For more information on neutralizing amines and other products, contact your local representative at the numbers listed below.