AMINE LEVELS IN STEAM-HUMIDIFIED ROOM AIR

Corrosion within the boiler steam/condensate systems of commercial buildings is known to degrade their energy efficiencies and reliabilities and add to maintenance costs.

Corrosion may shorten the lives of boilers, coils, pumps, traps, and piping. It also generates iron and copper oxides and hydroxides that may concentrate within boilers, deposit on heat-flux areas, and may increase the potential for boiler tube overheating and failure.

Corrosion control throughout a boiler steam/condensate system, therefore, is imperative. Corrosion-inhibiting chemicals, such as neutralizing amines, should be introduced after a system has been analyzed for specific problems and the right combination of materials and injection locations selected. Regular analysis and chemical adjustments are essential for quality performance.

In recent years, questions have arisen regarding the safety of amine chemicals, especially those that are carried over into steam humidifiers, admitted to the room air and breathed or ingested with food.

Nalco recently conducted steam humidification tests involving several commonly applied amines under controlled conditions. It has determined that concentrations in room air normally are well below prescribed federal limits if sound application techniques are followed according to Nalco's written recommendations.

To best understand the results of the tests, how these results might be useful to building operators, and how amine corrosion inhibitor concentrations in room air can be minimized, it's necessary that corrosion phenomena and inhibiting techniques be explained in some detail.

Why corrosion occurs

Corrosion within a steam/condensate system is primarily caused by dissolved carbon dioxide (CO,) and oxygen (O_2) present in condensate. When CO2 dissolves in water, it creates carbonic acid:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

Because CO_2 possesses a high vapor/liquid (V/L) distribution ratio, the gas spreads easily throughout the steam system, forming carbonic acid almost everywhere. The acid may attack mild steel and copper alloys and is most often characterized by a trough-like thinning of the bottom of condensate piping (see Figure 1).

The major source of CO_2 is the thermal breakdown within the boiler of bicarbonate and carbonate present in feedwater.

$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + H_2O + CO_2$$
$$Na_2CO_3 + H_2O + \text{heat} \rightarrow 2NaOH + CO_2$$

Other sources of CO_2 include the breakdown of small amounts of organic materials that may be present in the make-up water.

High oxygen levels, on the other hand, most often are due to an improperly operating deaerator, underfeed of an oxygen scavenger, or air leakage across feedwater pump seals.

Oxygen also can enter the system through air leaks across condensing turbines in industrial systems, condensate pumps, vented receivers and traps. Oxygen corrosion often is characterized by localized pitting of metal surfaces (see Figure 2).

A third source of corrosion is ammonia in the condensate. In combination with oxygen in the condensate, ammonia forms ammonium hydroxide, a caustic material that is harmless to mild steel but may attack copper and other yellow metals. In addition, ammonia has a very high vapor/liquid (V/L) ratio, causing a high pH at the final condensate receiver, but providing little protection to the initial phase of the condensate system.

Inhibition techniques

To help control damage to a condensate system from dissolved CO_2, amines are fed into the feedwater or the steam header. Amines are alkaline compounds that work by neutralizing carbonic acid. The ideal pH range for condensate is generally maintained from 8.2 to 9.2 (moderately alkaline).

To help assure corrosion protection throughout the condensate system, blends of several amines having different V/L distribution ratios are often specified.

One having a low V/L ratio, such

Test results demonstrate that amine concentrations in the steam-humidified air of commercial buildings should not rise to hazardous levels. However, the authors warn, it's prudent to minimize exposures through judicious applications of all chemicals.

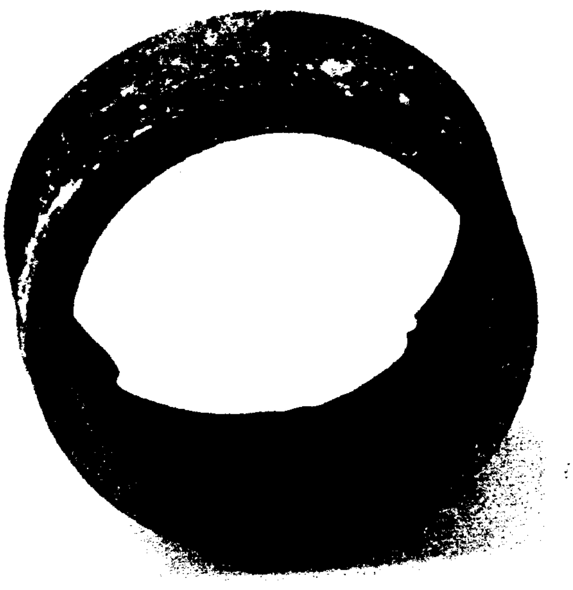

Figure 1. Corrosion resulting from the presence of carbon dioxide.

by David A. Grattan, Mary E. Koutek, and Stephen A. Russum

as morpholine,condenses sooner and helps protect the close-in piping. Another, such as cyclohexylamine, protects the far reaches of the condensate system. A third amine, such as diethylaminoethanol (DEAE), is used to aid in the preferential protection of the middle segments. Table 1 lists the V/L ratios of the three amines at various pressures.

Because of their complexity, certain condensate systems are very difficult to protect even with blended amines. In these cases, satellite feed of neutralizing amines may be required to provide pH control in localized areas.

In situations where CO2 levels are excessively high, and it's not practical to try to neutralize all of the carbonic acid, a combination of neutralizing and filming amines is specified.

A filming amine, such as octadecylamine, helps protect against both carbonic and oxygen corrosion by laying down a monomolecular barrier film on the metal surface. The barrier helps prevent both the migration of acid and the diffusion of O_2 through the surface.

Filming amines have very low V/L ratios and should be fed continuously to the steam header downstream of

EDITOR'S NOTE: David Grattan, group leader, and Mary Koutek, senior research chemist, are members of Nalco's research and development staff. Steve Russum is product manager at Nalco Chemical Co., Naperville, IL.

any turbines. Feeding ahead of turbines could leave deposits on the blades.

Corrosion protection from a filming amine depends on maintaining a continuous barrier (see Figure 3). For octadecylamine to form a film, condensate pH must range between 6.5 and 8.0 (slightly acidic to slightly alkaline). Outside of this range, the inhibitor either may not film or may strip off the surface.

Caution must be taken not to overfeed a filming amine because traps, strainers, and valves may plug and "gunk balls" may form in the boiler.

Caution must also be exercised when beginning a filming amine program. The chemical will remove iron oxide and scale deposits from condensate pipes, leading to high levels of solids in the return condensate and possible plugging problems.

To avoid this problem, the filming amine should be fed initially at very low doses, them gradually increased until residual limits are met.

Another method of controlling oxygen corrosion is to feed volatile O_2 scavengers, such as hydrazine or carbohydrazide, along with the neutralizing and/or filming amines. In addition to scavenging, these compounds have been reported to enhance the passivation of metal surfaces.

Pressure (psi)	Cyclohexylamine	DEAE	Morpholine
0	4.0	4.1	0.40
150	9.0	5.8	0.85
450	9.4	6.3	1.33
600	8.2	5.2	1.02
900	7.0	4.5	1.24

Table 1: Vapor/liquid distribution ratios at various pressures.

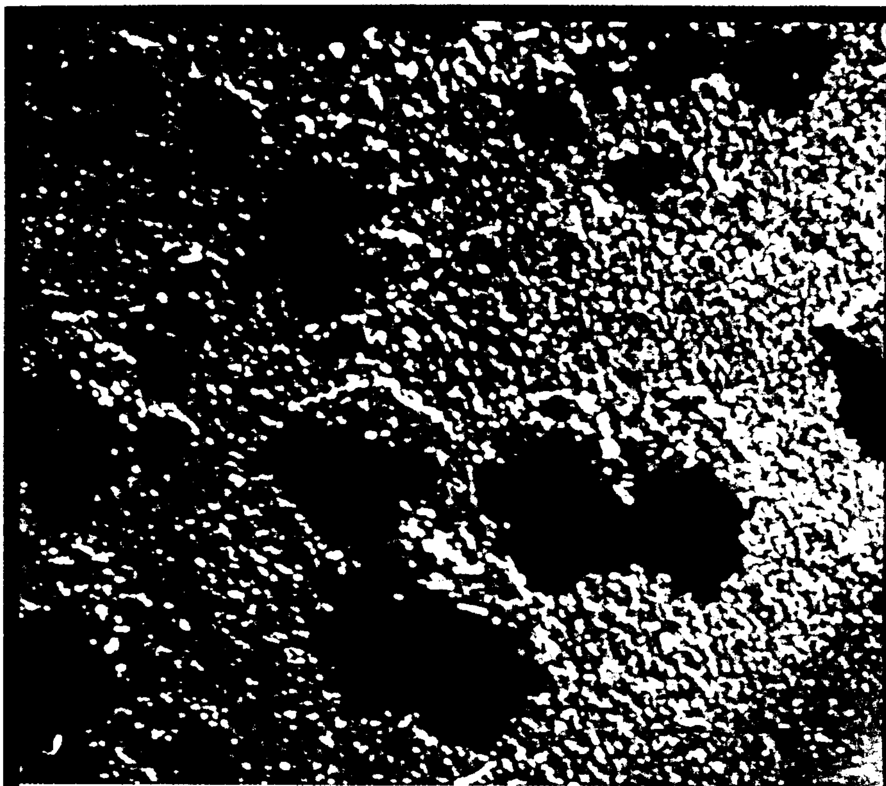

Figure 2. Corrosion resulting from the presence of oxygen.

Steam humidification

Hospitals, office complexes, and industrial plants routinely use steam humidification for climate control. Steam containing the Food and Drug Administration-approved neutralizing amines morpholine, cyclohexylamine, and diethylaminoethanol (DEAE) is acceptable for such humidification[1,2,3].

(Morpholine, cyclohexylamine, DEAE, and octadecylamine are the only amines approved by FDA for use in boilers whose steam comes in direct contact with food, with the exception of milk and milk products. maximum levels of amine permitted in such steam are 10 ppm for morpholine and cyclohexylamine, 15 ppm for DEAE, and 3 ppm for octadecylamine — Code of Federal Regulations, 21 CFR 173.310).

The Occupational Safety and Health Administration (OSHA), the American Conference of Governmental and Industrial Hygienists (ACGIH), and FDA have established permissable exposure limits (PELs) for these chemicals which are based on an 8-hour day and. 40-hour week[4,5].

The allowable concentrations in air are:

Morpholine	20 ppm
Cyclohexylamine	10 ppm
DEAE	10 ppm

Concern has been expressed about whether airborne concentrations in room air humidified with steam containing amines actually comply with OSHA/ACGIH guidelines. To address this concern, Nalco conducted a research study to determine what levels of amine might be found in room air humidified with steam containing morpholine, cyclohexylamine, and DEAE.

The room selected for the study was a 15-ft by 25-ft climate-controlled laboratory in which stringent environmental conditions are required for experimental work. Relative humidity was constantly maintained between 49% and 50%, temperature between 22" and 23°C (71.6" and 73.4°F).

Test Amine	Amine conc. steam (ppm)	Room airborne amine conc. (ppm) Location A	Location B
A Morpholine	19.2	0.004	0.004
B Morpholine	64.8	0.018	0.015
C DEAE	11.6	0.010	0.008
D DEAE	19.8	0.031	0.029
E Cyclohexylamine	30.6	0.041	0.033
F Cyclohexylamine	87.7	0.039	0.066

Table 2. Airborne amine concentration in steam-humidified room air.

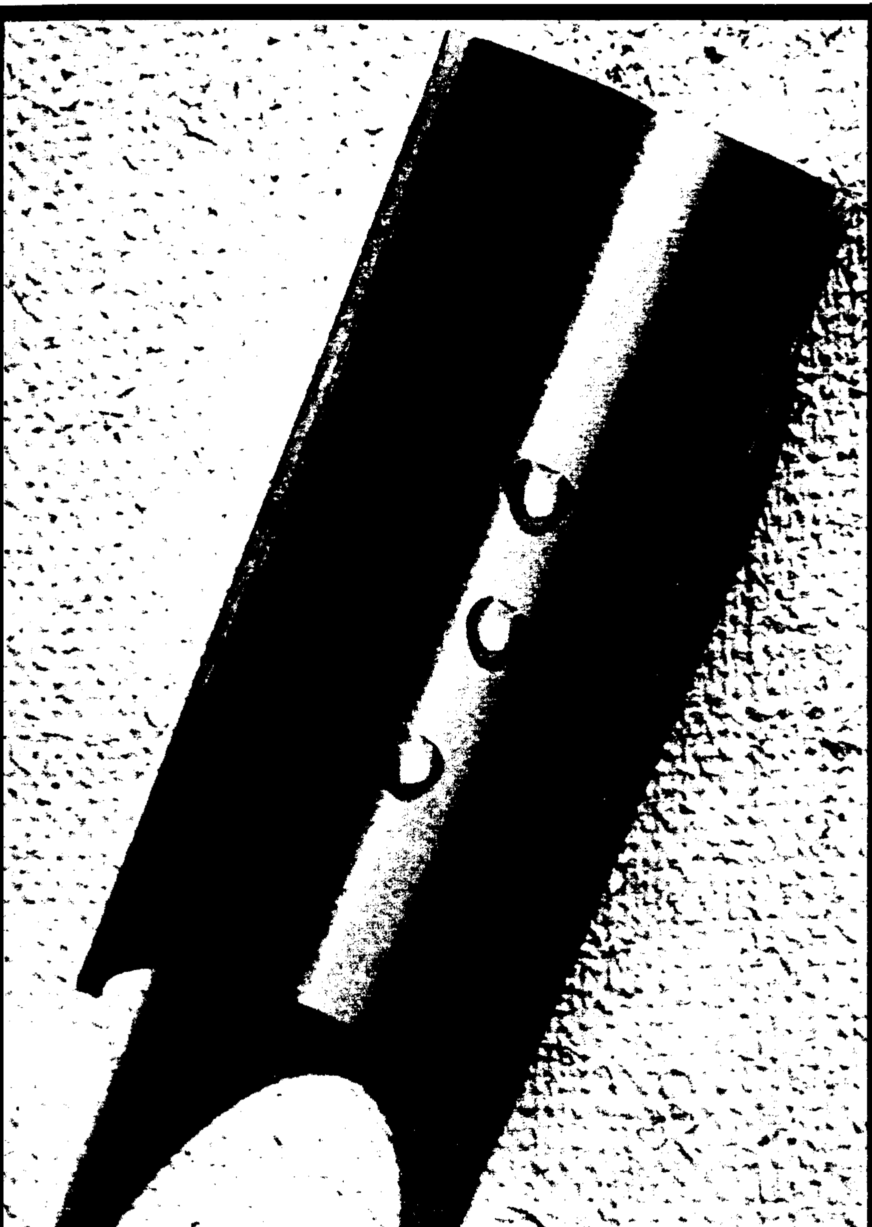

Figure 3. This section of condensate pipe, treated with a filming inhibitor shows complete repellence to the three drops of water.

The room was supplied with once-through building air turned over 16 times per hour. For the study, main-plant steam to the room was disconnected and a small once-through boiler was installed to provide continuously injected steam humidification.

This arrangement offered flexibility in varying amine concentrations in the steam. The boiler was operated at 15 psig, and all of the steam was used for humidification. The three FDA-accepted neutralizing amines were then fed individually to the feedwater.

During each test, the room was humidified for 32 hours prior to an air sample being taken. The sample was collected continuously over an 8-hour period using an air suction pump (Gillian LFS 113D) calibrated to 250 cc/min and attached to a Sep-Pak C-18 amine absorption cartridge (Waters Association No. 51910). Samples were taken from two fixed locations in the room. Table 2 lists the results.

In general, increasing the concentration of amine in the steam resulted in higher airborne amine concentrations. For instance, raising the dosage of morpholine in the steam from 19.2 ppm to 64.8 ppm increased the airborne amine level of morpholine from 0.004 ppm to 0.018 ppm.

However, under the conditions studied, the maximum room air concentration seen in any test was 0.66 ppm amine or less — substantially below the current OSHA/ACGIH guidelines.

Although the test results demonstrate that amine concentrations in the steam-humidified air of commercial buildings should not rise to hazardous levels, it is prudent to minimize exposures through judicious application of all chemicals.

Monitoring is vital

Steam/condensate systems should be continuously monitored for corrosion problems and process leaks. Typical problem areas include heat exchangers, reboilers, surface condensers, condensing turbines, vented condensate receivers, flash tanks, and driers.

Sample points should be installed at various locations throughout the system to obtain the best diagnostic profile of system conditions. Use stainless steel sample lines and

Table 3

Boiler pressure: 10 to 18 psig reduced to 5 psig at room inlet

Room dimensions: 25 ft, 10 in. by 15 ft, 4 in. by 8 ft, 6 in. = 3,600 ft^3

Air turnovers: 16.1 times per hour.

Fan capacity:

Fan No. 1 = 238 cu ft/min (cfm)
Fan No. 2 = 198 cfm
Fan No. 3 = 233 cfm
Fan No. 4 = 234 cfm
Total = 903 cfm

Steam flow: 8 lb/hour

Air volume sampled: 120 L at 250 cc/min per cartridge.

Sampling

Cooled samples of the steam, feedwater, boiler water, and condensate were taken twice per day during each amine test segment. The temperature and humidity were continuously monitored.

Air sampling was done using Gillian LFS 113D air pumps calibrated at 250 cc/min. The air samples were adsorbed onto SepPak C-18 cartridges. These cartridges were refrigerated before and after sample collection. Air samples were collected from two fixed locations in the room for each amine dosage.

Sampling protocol

The room was purged with amine-free steam for 40 hours prior to the addition of the first amine. Two blank cartridges were collected during the last eight hours of this purge period. The purge time between amine sampling segments was also fixed at 40 hours (640 room air turnovers).

The steam during this purge time contained the next scheduled amine. This was followed by an 8-hour air-sampling period. This test schedule was designed to eliminate contamination by the previous chemical.

Sample analysis

Amine analyses of the feedwater, boiler water, and steam samples were performed using a modified version of a colorimetric procedure developed by PA. Sanford, et al[6].

Ion chromatography also was used to verify the amine concentrations of several of the feedwater, boiler water, and steam samples. Air-sampling cartridges were analyzed by Illinois Institute of Technology Research Institute (IITRD using a procedure developed for this evaluation[7,8]. The amines were eluted off the cartridges and analyzed via gas chromatography.

Results

The measured airborne amine concentrations were significantly lower than the OSHA PEL as presented in Table 2.

coolers, and. keep condensate samples flowing continuously. Cool samples to below 90°F to prevent flashing off the dissolved gases and amines.

It is recommended that condensate samples be taken frequently and tested for pH, conductivity, corrosion products, dissolved oxygen, and carbon dioxide. If a filming amine program is in use, it's necessary to test the condensate for residual filmer levels.

Other contaminants such as hardness, silica, and organics, are important to evaluate because their presence in condensate may indicate boiler carryover problems or a cooling water/process leak. On-line continuous conductivity meters and total organic carbon (TOC) analyzers are frequently chosen to monitor these contaminants.

Iron and copper levels can be measured using wet chemical analysis test methods, on-line turbidimeters, or through visual estimation using filtration methods.

Another effective monitoring tool is the instaliation of corrosion coupons in the condensate system. Corrosion rates are normally measured after a minimum of 30 days of exposure.

Control necessary

Proper feed, dosage, and control of amine condensate corrosion inhibitors are critical for several reasons:

- To assure compliance with FDA, OSHA, and ACGIH guidelines regarding the levels of amine permissible in steam-humidified room air.
- To minimize corrosion in steam and condensate systems, and prevent unscheduled outages.
- To optimize boiler efficiency by reducing the corrosion byproducts returned to the boiler via the condensate return system.

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