

A hand is shown from the top left, holding a small amount of water. The water is dripping into a calm lake, creating ripples. The background features a scenic landscape with snow-capped mountains and a clear blue sky. The sun is low in the sky, creating a lens flare effect. The overall mood is serene and natural.

EASTMAN

**Eastman
water treatment
solutions**

Eastman oxygen scavengers

Experts in the field of water treatment know the importance of treating boiler water to slow corrosion.

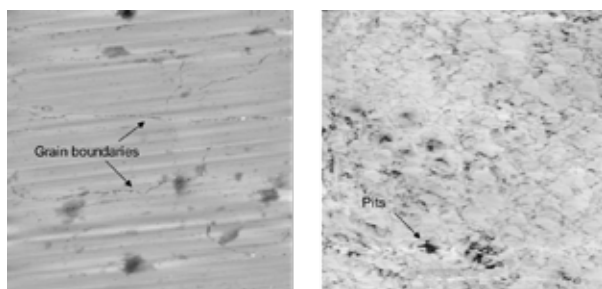
Two gases, oxygen and carbon dioxide, can cause severe problems in the boiler as well as steam condensate lines. As little as a few parts per billion (ppb) of dissolved oxygen (DO) is enough to cause pitting on the surface of the boiler. Carbon dioxide in condensate water may form carbonic acid, accelerating corrosion of steel and other metals used in steam condensate lines.

Oxygen scavengers from Eastman such as diethylhydroxylamine (DEHA) and our neutralizing amines such as diethylaminoethanol (DEAE), *N,N*-dimethylamino-2-propanol (DMA-2-P), and dimethylaminopropylamine (DMAPA) are effective in controlling corrosion in the boiler and steam lines, prolonging the service life of the boiler circuit.

Corrosion caused by dissolved oxygen (DO)

Dissolved oxygen in boiler feedwater can be corrosive if left untreated. It is common to use a deaerator to mechanically lower the DO to about 7–10 ppb. Even at this low level, DO can still cause corrosion to the feedwater system and boiler itself. If left untreated, the DO in the boiler water may cause pitting corrosion.

Figure 1.



Bare steel without exposure to air-saturated water

Steel after exposure to oxygen-containing water showing pits in surface

The general reactions involving pitting corrosion in boilers may be explained by the following reactions:



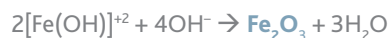
In the presence of DO, the ferrous hydroxyl species will oxidize to ferric hydroxyl:



DO is reduced to hydroxide:



And in the alkaline medium of the boiler, precipitation leads to the red rust, hematite, commonly seen on ferrous-based metal:



The overall corrosion of iron in the absence of oxygen scavengers is:



One way to slow the pitting corrosion of boilers is to minimize or eliminate the reduction of DO as previously discussed. Further removal of DO is accomplished using oxygen scavengers.

Common oxygen scavengers

Most oxygen scavengers provide two important functions in boiler water chemistry. First, they all remove as much DO from the water as possible, slowing pitting corrosion in the boiler.

By nature, oxygen scavengers are reducing agents in that they convert DO to hydroxide ion or water. For example, the removal of oxygen by DEHA:



The theoretical amount of DEHA required to remove oxygen is calculated as follows:

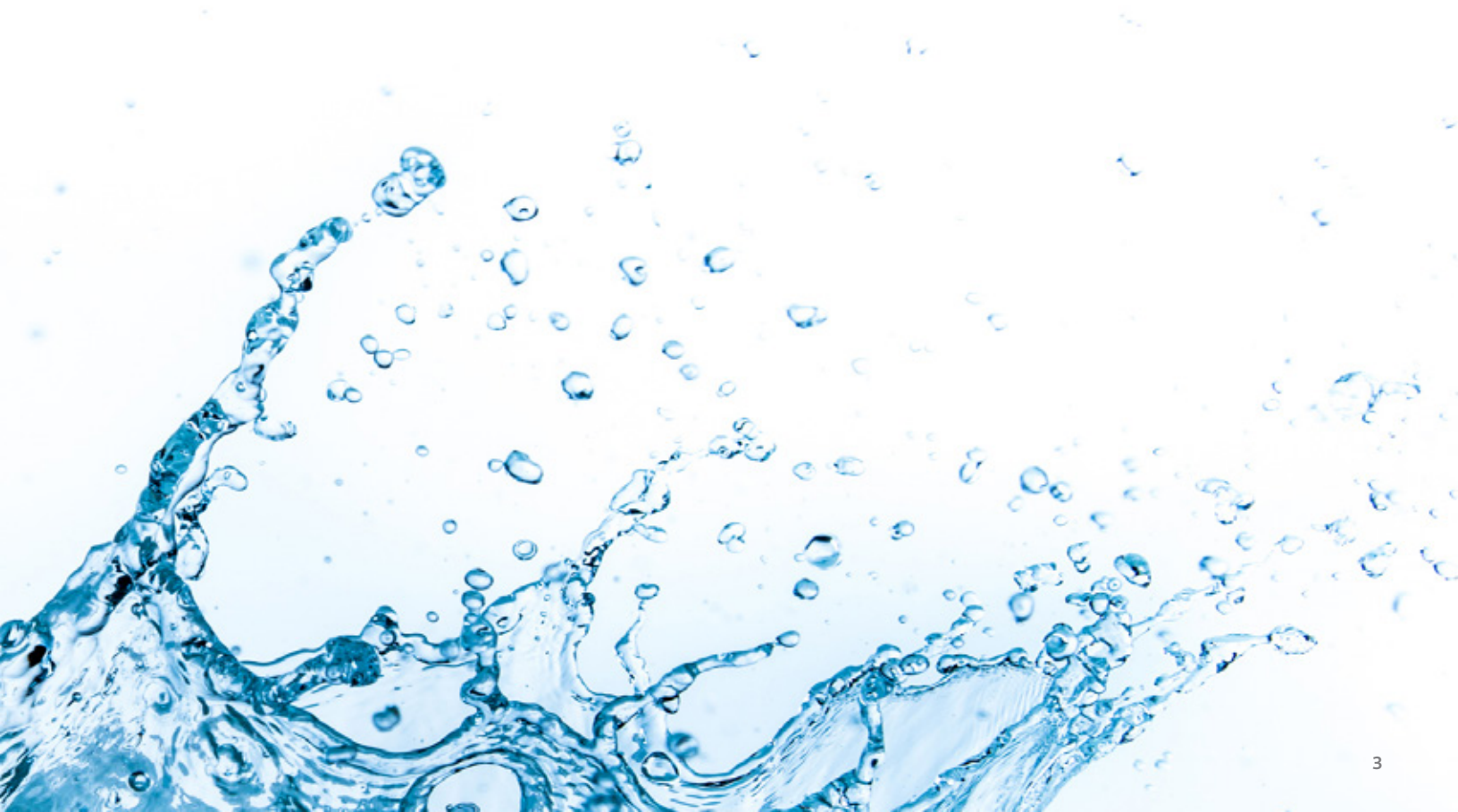
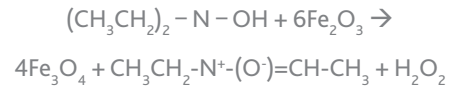
- Molecular wt DEHA: 89 g/mol
- Molecular wt O₂: 32 g/mol
- $[(4 \times 89.14)/(9 \times 32)] = 1.24$

Therefore, it requires about 1.24 times the amount of DEHA than DO. In practice, excess oxygen scavenger is added to ensure removal of the DO.

Second, it is impossible to eliminate all DO from water, and some degree of corrosion of the boiler walls and pipes is likely. Most oxygen scavengers may induce a passivating layer on the boiler walls.

For example, DEHA can induce a passivating layer on the boiler walls, further slowing corrosion. This passivating layer is the often-seen "black rust," magnetite (chemical composition Fe₃O₄). Notice that hematite is composed of iron only in the +3 oxidation state, whereas magnetite is a mixture of iron in the +2 oxidation state (FeO) and +3 oxidation state (Fe₂O₃).

Although the exact mechanism of the reduction of hematite to magnetite by DEHA is complex, it may be represented by:



Choice of oxygen scavenger

The choice of oxygen scavenger is dependent on many factors, including the pressure of the boiler, quality of the feedwater, its ability to produce magnetite, kinetics of removing DO, and its HES (health, environment, and safety) profile. For example, sulfite is an inexpensive oxygen scavenger and shows good kinetics in removing DO. But it is limited to low-pressure boilers as it is quickly oxidized to sulfate, possibly forming CaSO_4 or MgSO_4 and leading to more rapid blowdown cycles. Hydrazine is used in high-pressure systems requiring high-purity water, since its reaction products do not contribute any solids. However, hydrazine may pose a health concern to workers. Other common oxygen scavengers are seen in Table 1.

It is common to use a catalyst along with the oxygen scavenger to increase the rate of oxygen removal. For example, DEHA uses hydroquinone (HQ) as a catalyst while sulfite and others use metallic catalysts such as cobalt (II).

Table 1. Oxygen scavengers and common catalysts

O ₂ scavenger	Molecular formula	Common catalyst	Promotes magnetite?	Theoretical stoichiometry vs. DO (practical amount used)
DEHA	$(\text{CH}_3\text{CH}_2)_2\text{NOH}$	HQ, Cu	Yes	1.24x (2–3x)
Sodium sulfite	Na_2SO_3	Cobalt (II)	No	7.9x (8–10x)
Carbohydrazide	$(\text{NHNH}_2)_2\text{C}=\text{O}$	HQ, Cobalt (II)	Yes	1.4x (2–3x)
Hydrazine	N_2H_4	Cu (II), Mn (II), HQ	Yes	1.0x (2–3x)
Methyl ethyl ketoxime	$\text{C}_2\text{H}_5\text{C}(\text{=NOH})\text{CH}_3$	Cu, HQ	Weakly	5.5x (7–8x)
Hydroquinone	$\text{C}_6\text{H}_4(\text{OH})_2$	None, = pyrogallol	Yes	6.9x (7–10x)
Erythorbate	$\text{C}_6\text{H}_7\text{O}_6$	Cobalt (II), HQ	Yes	10.6x (12x)



Eastman neutralizing amines

Steam leaves the boiler through a network of pipes, so it can transfer its heat to some commercial or residential process. As the steam is traveling through the array of short, medium, or long and winding piping, it may cool to the point where some portion of the steam condenses, forming water in the transfer pipes. This condensed water is called condensate. As the condensate originates from steam, this water has very few impurities in it and, for all intents and purposes, this condensate is almost 100% pure water. Perhaps as important as its purity, condensate is also very hot, which is why it is often sent back to the boiler to serve as a portion of the feedwater going into the boiler. Since the boiler feedwater must be hot, a facility can save money on fuel by not having to heat so much room-temperature makeup water if using condensate water.

Role of neutralizing amines

While condensate water is an attractive source of feedwater, it may contain dissolved gases such as carbon dioxide, oxygen, and possibly ammonia, leading to corrosion of the condensate pipes if not properly treated. Carbon dioxide in steam condensate lines originates primarily from two sources. First, leaks in steam condensate lines may allow the ingress of CO_2 . Second, most carbon dioxide comes from the breakdown of carbonates and bicarbonates (e.g., alkalinity) under the intense temperatures and pressures encountered in boilers. Alkalinity in boiler water may be present in three forms: hydroxide (OH^-), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). In water softening systems, there may be moderate levels of HCO_3^- which acts as a latent form for CO_2 generation:

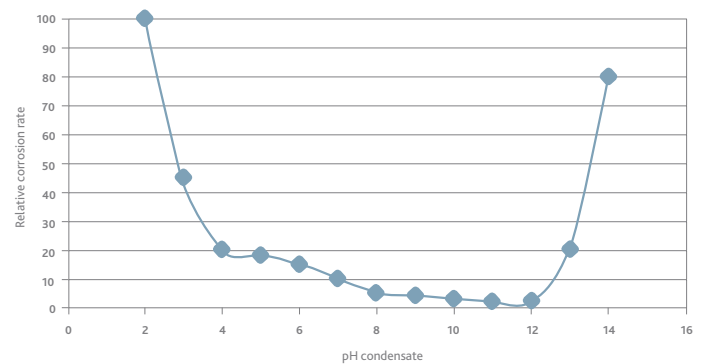


Once formed, free carbon dioxide mixes with condensate water and forms carbonic acid, lowering the pH of the condensate:



In fact, as little as a few ppb is enough to lower the pH of the high-purity condensate water, thereby accelerating condensate corrosion of the steam pipes. The rate of corrosion is influenced strongly by the pH of condensate water as seen in Figure 1.

Figure 1.



The lower corrosion rates at neutral to slightly alkaline pH may be due to the formation of magnetite as seen on potential-pH diagrams. It is therefore important to maintain a condensate pH where corrosion is minimal—pH of about 8–9. If copper is part of the condensate pipe network, it is important not to have the pH greater than about 9 to minimize the propensity for copper corrosion.

Detailed electrochemical and analytical surface analysis clearly shows the effects of H_2O , HCO_3^- , and CO_3^{2-} on the corrosion of low-carbon steel. Atomic force microscopy (AFM) imaging of the surfaces of steel before and after being exposed to H_2O , HCO_3^- , and CO_3^{2-} are seen in Figures 2a–2d, respectively:

Figure 2a. Surface of bare steel, no treatment

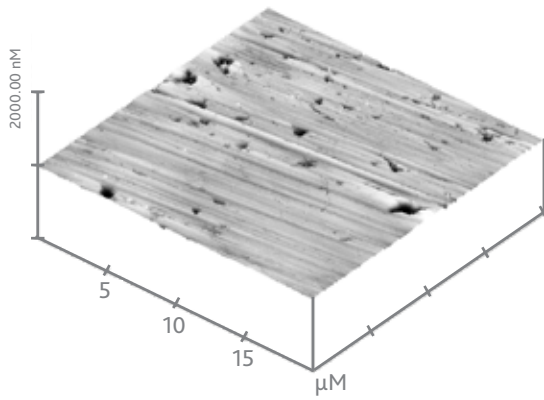


Figure 2b. Fe surface after immersion in ultrapure water only

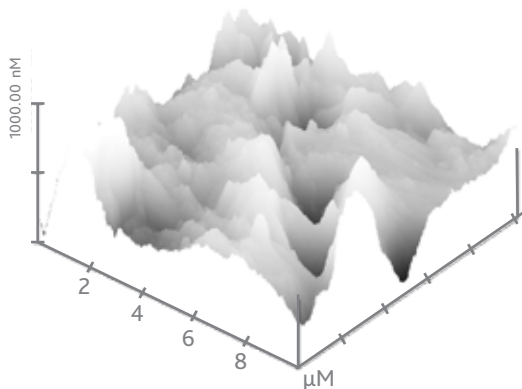


Figure 2c. Fe surface after immersion in water + HCO_3^-

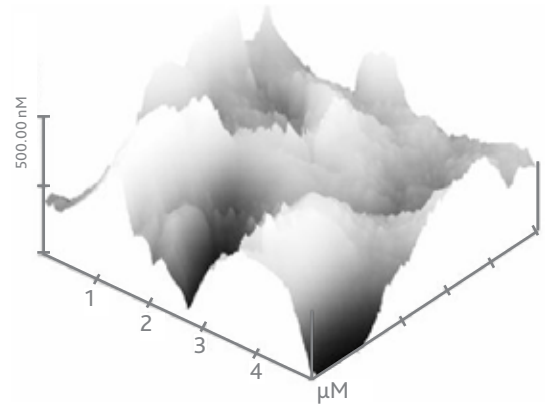
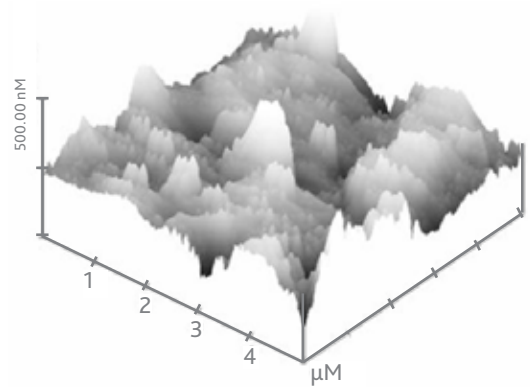


Figure 2d. Fe substrate with layer of carbonate



It is apparent from the depths of the pits in Figures 2c and 2d that steel is corroded by HCO_3^- and CO_3^{2-} . Confirmation of the corroded surfaces using electron spectroscopy for chemical analysis (ESCA) reveals the chemical composition of the corrosion layers (Table 2). The binding energies in electron volts (eV) are shown for various chemical surface elements. The presence of a carbonate-rich layer is indicated by the carbon 1(s) signal at about 287 eV—an indication of a C=O species originating from dissolved CO_2 . Even bubbling CO_2 gas through ultrapure water corrodes steel and results in the formation of a carbonate-rich layer on the steel surface.

Table 2. ESCA binding energies for different surface elements

Steel-electrolyte and binding energies (eV)	Fe 2p _(3/2)	O 1s	C 1s
Fe-UPW only	707.81 709.92 711.81	529.75 530.33	284.15
Fe-HCO ₃	709.09 710.22 711.56	529.21 530.62 531.72	284.22 287.94
Fe-CO ₃	708.60 711.53	529.13 530.96 531.53	284.92 287.28
Fe-CO ₂ (bubbling CO ₂ gas through UPW)	708.89 710.06 711.41	529.31 530.27 531.11	284.92 287.28

Note: Metallic Fe has the lowest binding energy (BE), followed by FeO then Fe₂O₃. Similarly, for oxygen, metal oxides have a lower BE vs. metallic carbonates. All surfaces usually have a thin layer of carbon (BE about 284 eV), and the O-C=O BE is about 287 eV.

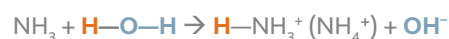
Slowing the rate of condensate corrosion

The boiler water industry uses neutralizing amines to control condensate corrosion. The amines do not have any adverse effects on copper or copper alloys under normal treatment conditions where pH is maintained between about 8.0 and 9.0. There are several amines to choose from, including Eastman's diethylaminoethanol (DEAE), DMA-2-P, and dimethylaminopropylamine (DMA).

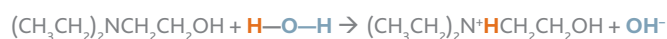
The properties of neutralizing amines must be considered when determining which one is best suited for a given condensate circuit. Three of the most important properties are basicity (K_b), neutralizing capacity, and vapor-liquid equilibrium distribution.

Basicity

Dissolution of a neutralizing amine into water results in a basic solution. The extent of the basicity is determined by the concentration of the amine and its properties. For example, dissolution of 10 ppm ammonia (NH₃) and 10 ppm DEAE will produce basic solutions with two different pH levels. The degree of basicity of neutralizing amines (and ammonia) on dissolution into water is due to the generation of the hydroxide ion (OH⁻) from water (H-O-H):



Similarly, the proton from water is transferred to the neutralizing amine, forming the protonated amine and free OH⁻. Dilution of DEAE in water produces the free hydroxide ion according to:



Increasing the concentration of free OH⁻, by the addition of a more basic amine than ammonia such as DEAE, the more basic the condensate water.

The extent of the preceding reactions can be quantified based on equilibrium calculations. Equilibrium of DEAE and the protonated form of DEAE is:

$$K_{\text{eq}} = \frac{[(\text{CH}_3\text{CH}_2)_2\text{N}^+\text{HCH}_2\text{CH}_2\text{OH}][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]}$$

In acid-base reaction, the equilibrium constant, K_{eq} , is replaced with either the acid or base dissociation constant, K_a or K_b , respectively. Using the base dissociation constant for DEAE, the extent of the equilibrium reaction is:

$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_2\text{N}^+\text{HCH}_2\text{CH}_2\text{OH}][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]} = 10^{-4.05}$$

Taking the log of both sides:

$$\log(K_b) = pK_b = \log[(\text{CH}_3\text{CH}_2)_2\text{N}^+\text{HCH}_2\text{CH}_2\text{OH}] + \log[\text{OH}^-] - \log[(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}] = 4.05$$

In water at pH 7, the OH^- concentration, $[\text{OH}^-]$, is 1×10^{-7} . Using this value, one can now calculate the extent of the DEAE equilibrium:

$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_2\text{N}^+\text{HCH}_2\text{CH}_2\text{OH}][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]}$$

$$K_b / [\text{OH}^-] = \frac{[(\text{CH}_3\text{CH}_2)_2\text{N}^+\text{HCH}_2\text{CH}_2\text{OH}]}{[(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]}$$

$$10^{-4.05} / 10^{-7} = \frac{[(\text{CH}_3\text{CH}_2)_2\text{N}^+\text{HCH}_2\text{CH}_2\text{OH}]}{[(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]} = 891$$

The large positive equilibrium value of 891 implies the dilution of DEAE in water results in a large fraction of free OH^- and therefore a basic solution. Amines with even smaller pK_b values than 4.05 will produce even more basic solutions at similar molar concentrations.

Note: The easiest way to quantify the basicity of an amine is to look at the pK_a of its conjugate acid, the protonated form of the amine. The larger the pK_a of the conjugate acid, the stronger the amine. Or the smaller the pK_b , the stronger the amine.

Neutralizing capacity of amines

Neutralizing amines react with carbonic acid (carbon dioxide dissolved in water) on a 1:1 molar basis. The amount of the neutralizing amine required to neutralize a given amount of dissolved carbon dioxide is inversely proportional to the molecular weight of the amine. For example, CO_2 weighs 44 g/mol and DMA-2-P weighs 103.16 g/mol. The amount of DMA-2-P required to neutralize CO_2 is $102.14/44 = 2.32$. So, knowing the amount of CO_2 , it requires 2.32 times as much DMA-2-P.

Similarly, if using carbonic acid in the calculation, H_2CO_3 , ($\text{CO}_2 + \text{H}_2\text{O}$) weighs 62 g/mol. DEAE, $(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}$ weighs 117 g/mol. If 5 ppm CO_2 is entrained in the condensate circuit, it will produce 7.05 mg/L H_2CO_3 ($62 \text{ g/mol H}_2\text{CO}_3 / 44 \text{ g/mol CO}_2 = 1.41 \times 5 \text{ ppm CO}_2 = 7.05 \text{ ppm H}_2\text{CO}_3$). The amount of DEAE required to neutralize this 7.05 mg/L H_2CO_3 is:

$$(7.05 \text{ mg/L}) / 62 \text{ mg/mmol H}_2\text{CO}_3 \times 117 \text{ mg/mmol DEAE} = 13.3 \text{ mg/L (13.3 ppm) DEAE}$$

Recall: (mg/L = ppm)

Similar calculations for carbonic acid show the amount of DMA-2-P required for the same 5 ppm CO_2 is 11.7 ppm. The slightly lower amount of DMA-2-P necessary for complete neutralization is due to the lower molecular weight of DMA-2-P vs. DEAE.



Vapor-liquid (VL) equilibrium distribution

The VL distribution ratio is a concentration ratio representing the amount of the neutralizing amine in the vapor phase (steam) to the concentration of the amine in the water phase: $[Amine_{vapor}]/[Amine_{water}]$. The greater the ratio, the more amine will be in the steam along the condensate circuit. It is known that only amines that are deprotonated (exist as the free amine) are volatile, and the extent of deprotonation is governed by the pH of the boiler water and steam condensate.

If the neutralizing amine is added to the boiler feedwater, then the pH of boiler water is sufficient to ensure neutralizing amines are mostly deprotonated. The percent of the free amine at the pH of boiler water, 10–12, that is deprotonated and carried away with the steam and CO₂ is easily calculated by:

$$\% \text{ deprotonated} = 100 / (1 + 10^{(pK_a - pH)})$$

For example, for MOPA with pK_a 10.15 and the pH of the boiler water at 11, the fraction of MOPA that is deprotonated is:

$$\% \text{ deprotonated} = 100 / (1 + 10^{(10.15 - 11)}) = 87.62\%$$

The fractions of other neutralizing amines in their unprotonated form at boiler-water pH is shown in Table 3.

Table 3. Fractions of neutralizing amines in unprotonated form at boiler-water pH

Amine	pKa	pH 9.5	pH 10.0	pH 10.5	pH 11.0
DEAE from Eastman	9.87	29.9%	57.4%	81.0%	93.1%
DMA-2-P from Eastman	9.53	48.3%	74.7%	90.3%	96.7%
DMAPA from Eastman	9.33	61.3%	83.4%	94.1%	98.0%
Morpholine	8.34	93.2%	97.8%	99.3%	99.8%
CHA	10.64	6.8%	18.6%	42.0%	69.6%
MOPA	10.15	18.3%	41.5%	69.1%	87.6%

Although the fraction of deprotonated morpholine is greater than cyclohexylamine, the VL for CHA is much greater than that of morpholine. In fact, morpholine exhibits the lowest VL of any common neutralizing amines.

Laboratory measurement values for VL of the neutralizing amines listed vary with pressure. See Table 4.

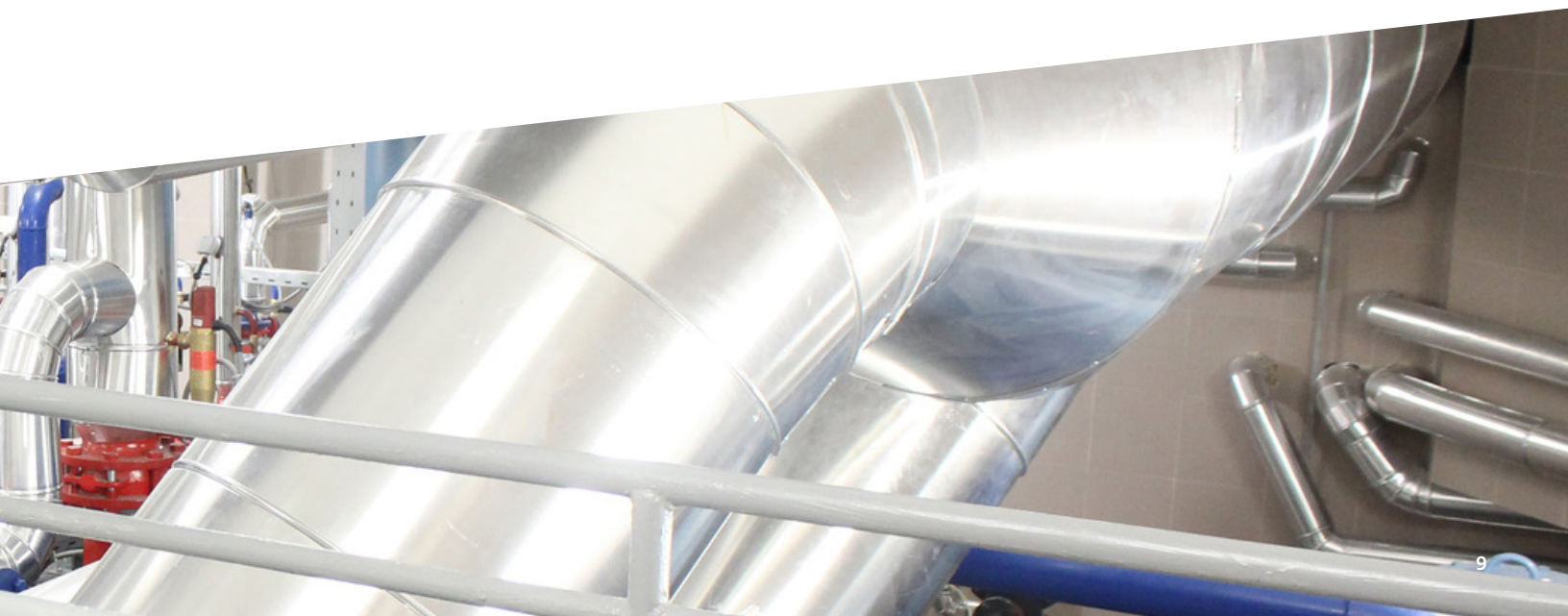


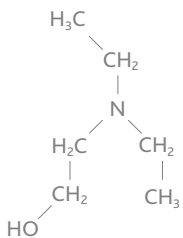
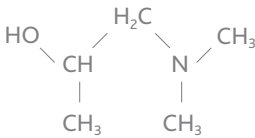
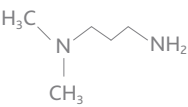


Table 4. VL value ranges for neutralizing amines

Amine	Maximum VL
DEAE from Eastman	2–4
DMA-2-P from Eastman	5–8
DMAPA from Eastman	1–3
Morpholine	0.2–0.5
CHA	10–12
MOPA	1–2

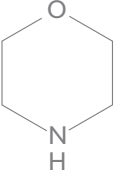
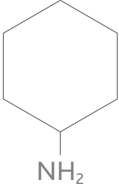
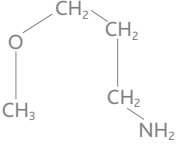
To fully protect a complicated steam circuit, it is common to use a blend of neutralizing amines to take advantage of the different basicity, neutralizing capacity, and VL properties. For example, if using only CHA with a high VL value, most of the amine remains within the steam and may not condense with the steam in the steam circuit. Thus, the condensate water is not truly protected from possible corrosion by carbonic acid. Therefore, if using a blend of neutralizing amines such as DEAE + CHA, it is likely some DEAE remains in the condensate, protecting the piping from corrosion while CHA travels further with the steam to protect the steam pipes further down the circuit.

Table 5. Neutralizing amines offered by Eastman

Amine	DEAE*	DMA-2-P	DMAPA
Structure			
CAS number	100-37-8	108-16-7	109-55-7
Type amine	Tertiary	Tertiary	Primary, tertiary
Molecular wt (g/mol)	117.19	103.16	102.18
pK _a	9.87	9.53	10.6, 8.7
pK _b	4.13	4.47	3.4, 5.3
DR	~3	~5	~2
Boiling point (°C)	162	121	135
Neutralizing capacity (ppm amine/ppm CO ₂)	2.66	2.34	2.32
Azeotrope formation	Yes	Yes	—
pH 1 ppm	9.44	9.3	9.2
10 ppm solution	9.94	9.8	9.7

*DEAE under Title 21 CFR Sec 173.310(d) is cleared by the FDA for the use in boiler water not to exceed 15 ppm in steam and excluding use of such steam in milk and milk products.

Table 6. Other common neutralizing amines

Amine	Morpholine	CHA	MOPA
Structure			
CAS number	110-91-8	108-91-8	5332-73-0
Type amine	Secondary	Primary	Primary
Molecular wt (g/mol)	87.12	99.17	89.14
pK _a	8.36	10.64	10.15
pK _b	5.64	3.36	3.85
DR	~0.3	~12	~1.5
Boiling point (°C)	129	135	116
Neutralizing capacity (ppm amine/ppm CO ₂)	1.98	2.25	2.03
Azeotrope formation	No	Yes	—
pH 1 ppm	8.71	9.85	9.6
10 ppm solution	9.21	10.35	10.1

Choice of neutralizing amine

DEAE from Eastman vs. morpholine

- The VL is much greater for DEAE than morpholine, providing greater corrosion protection down the steam condensate circuit.
- Since DEAE is more volatile, less blowdown loss is achieved with DEAE.
- DEAE is a stronger base than morpholine, so a higher pH is achieved at equal concentrations.
- The flash point of DEAE (50°C) is greater than morpholine (31°C), ensuring safer handling.
- The FDA allows 50% greater concentrations for DEAE than morpholine in food contact applications.*

DEAE from Eastman vs. cyclohexylamine (CHA)

- DEAE does not form salts with bicarbonate; CHA may form insoluble salts with bicarbonate.
- DEAE is not lost as fast from the deaerator as CHA due to the lower VL and higher boiling point of DEAE.
- The flash point of DEAE (50°C) is greater than CHA (27°C), ensuring safer handling.
- FDA allows 50% greater concentrations for DEAE than CHA in food contact applications.*

*Please see 21 CFR Sec. 173.310(d).

DMA-2-P from Eastman vs. morpholine

- DMA-2-P has a higher VL compared to morpholine, protecting the long steam condensate circuits.
- The basicity of DMA-2-P is greater than that of morpholine, so less DMA-2-P is required to achieve a similar pH.
- The "equilibrium pH" of DMA-2-P is low enough that little is lost during deaeration.

DMA-2-P from Eastman vs. CHA

- DMA-2-P having a lower VL will protect the steam condensate circuits closer to the boiler better than CHA.
- The "equilibrium pH" of DMA-2-P is low enough that little is lost during deaeration compared to CHA.



Other Eastman products for water treatment

Hydroquinone (HQ): commonly used as a catalyst for DEHA and other scavengers in boiler water

Methylamines: Eastman is the world's largest producer of methylamines, including dimethylamine, which is used as a raw material for the production of coagulants used in industrial and municipal wastewater treatment.

DMAE/DMAPA: amines used in the synthesis of ion exchange resins

DMAE: Eastman is the world's largest producer of dimethylaminoethanol a key raw material in the production of polyacrylamides used in wastewater treatment.

DMF: dimethylformamide is a solvent used to make reverse osmosis (RO) membranes, which are vital for water desalination and purification.

For more information, visit www.eastman.com or contact your local Eastman account manager or distributor.





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