Education Institute for

Equipment & Process Design

Neutralizing Amine

Condensate is not usually pure. Various substances carry over physically or by volatilization in the boiler. When the steam condenses, many of these substances will dissolve in the condensate. Often, they impart objectionable properties to the condensate. Particulates and ionic species can be removed by condensate polishing, which is both a filtration process and an ion exchange process (chapter 2).

The main substance to be chemically treated in the condensate is carbon dioxide. Carbon dioxide is formed by the breakdown of carbonate alkalinity in the boiler. Being very volatile, most of it passes into the steam, and then forms carbonic acid in the condensate. The pH of the condensate can be depressed to very low levels, often below 3, because the carbon dioxide is not in equilibrium with the atmosphere, where the limiting pH is about 5.8.

Carbonate alkalinity can be removed by dealkalization and decarbonation in the pretreatment train (chapter 2), but in most medium and low-pressure systems, this is not done. To prevent the resulting acidic corrosion in the condensate lines, the carbon dioxide must be neutralized. This is done by adding neutralizing amines to the feedwater. Amines adjust the feedwater pH to a range of 8.8 to 9.2, which is optimum for a mixed metallurgy system. Passing into the boiler, amines distribute into the steam, and condense with the steam and carbon dioxide.

There are three important factors to be aware of with neutralizing amines:

- Basicity
- Neutralizing capacity
- Distribution ratio

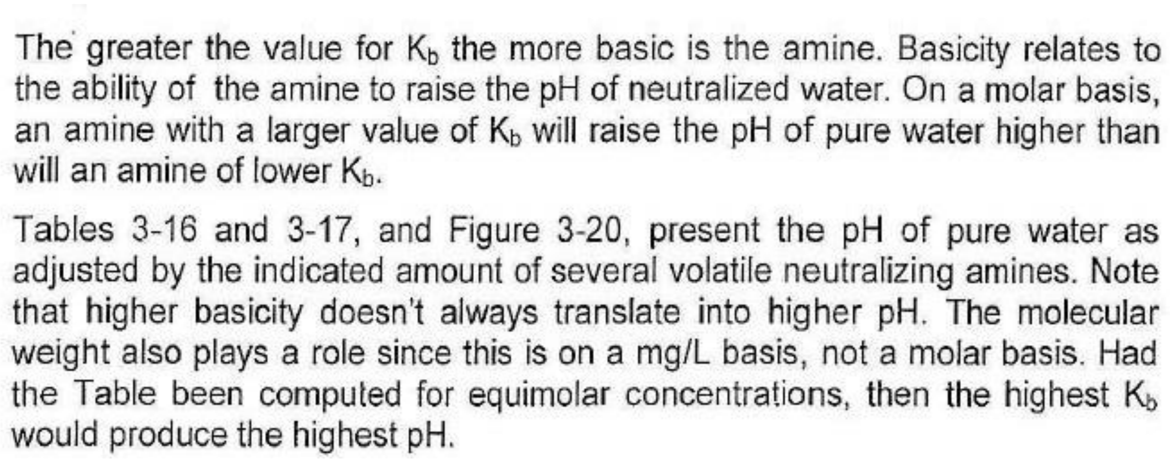
7.7.1 Basicity

The general reaction of amines with water is:

$$RNH_2 + H_2O = RNH_3^+ + OH^- \qquad (3\text{-}51)$$

The base hydrolysis constant for amines (chapter 1) is defined as:

$$K_b = [RNH_3^+]\,[OH^-] / [RNH_2] \qquad (3\text{-}52)$$



The greater the value for K_b the more basic is the amine. Basicity relates to the ability of the amine to raise the pH of neutralized water. On a molar basis, an amine with a larger value of K_b will raise the pH of pure water higher than will an amine of lower K_b.

Tables 3-16 and 3-17, and Figure 3-20, present the pH of pure water as adjusted by the indicated amount of several volatile neutralizing amines. Note that higher basicity doesn't always translate into higher pH. The molecular weight also plays a role since this is on a mg/L basis, not a molar basis. Had the Table been computed for equimolar concentrations, then the highest K_b would produce the highest pH.

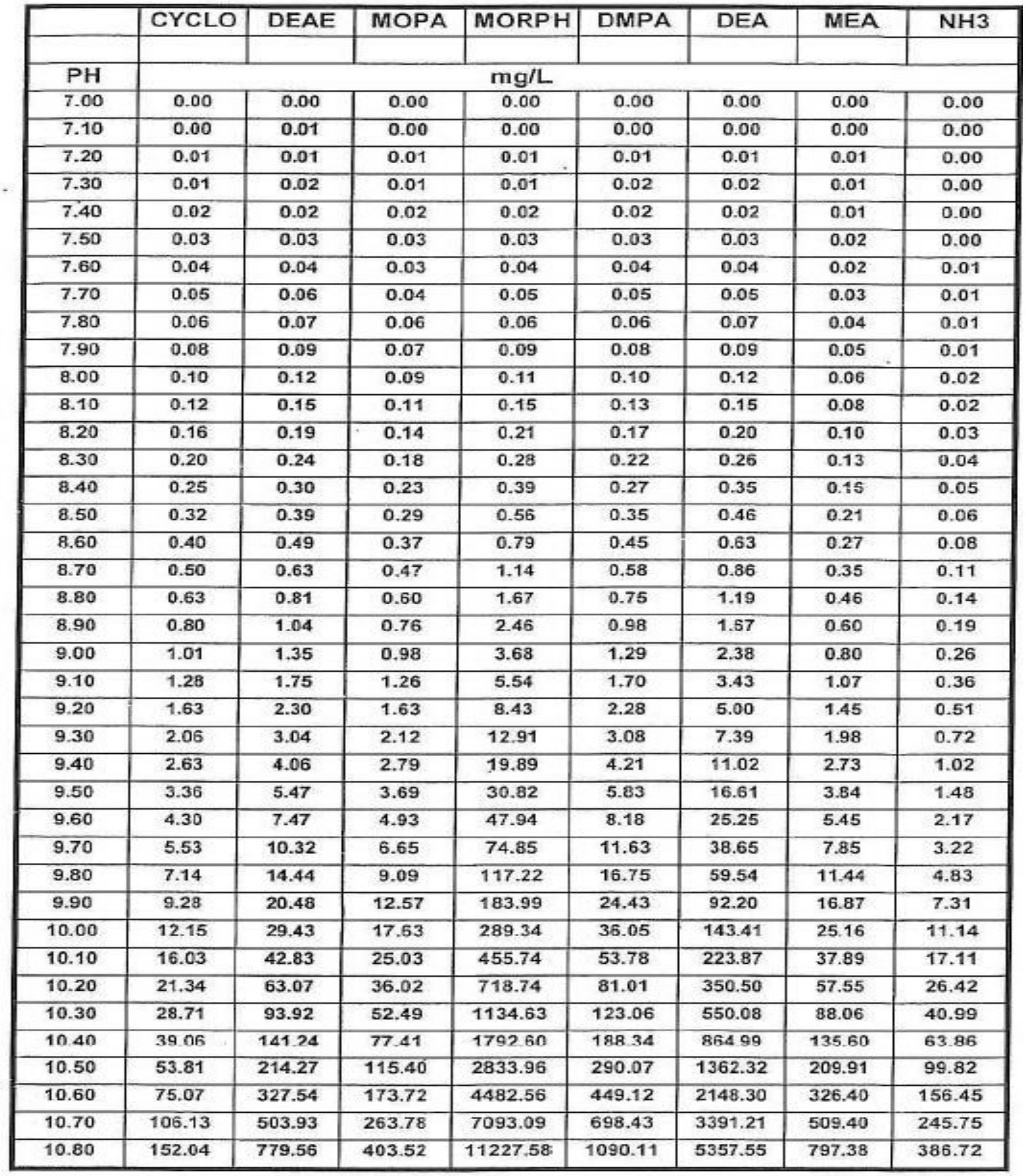
Table 3-16
pH Adjustment Capacity of Amines pH vs Amine Concentration

	CYCLO	DEAE	MOPA	MORPH	DMPA	DEA	MEA	NH3
	pH							
mg/L								
0.2	8.32	8.25	8.36	8.21	8.29	8.23	8.49	8.91
0.5	8.71	8.62	8.74	8.48	8.65	8.54	8.84	9.20
1	9.00	8.89	9.01	8.67	8.91	8.75	9.08	9.40
2	9.29	9.15	9.28	8.85	9.16	8.96	9.31	9.58
3	9.46	9.30	9.43	8.95	9.29	9.07	9.43	9.68
4	9.57	9.40	9.53	9.02	9.39	9.14	9.51	9.75
5	9.66	9.47	9.61	9.08	9.45	9.20	9.58	9.81
6	9.73	9.53	9.67	9.12	9.51	9.25	9.63	9.85
7	9.79	9.58	9.72	9.16	9.56	9.29	9.67	9.89
8	9.84	9.62	9.76	9.19	9.59	9.32	9.71	9.92
9	9.89	9.66	9.80	9.22	9.63	9.35	9.74	9.95
10	9.93	9.69	9.83	9.24	9.66	9.38	9.77	9.97
11	9.96	9.72	9.86	9.27	9.69	9.40	9.79	10.00
12	10.00	9.75	9.89	9.29	9.71	9.42	9.81	10.02
13	10.03	9.77	9.91	9.30	9.73	9.44	9.83	10.04
14	10.05	9.79	9.93	9.32	9.75	9.46	9.85	10.05
15	10.08	9.81	9.95	9.34	9.77	9.48	9.87	10.07

In Table 3-16:

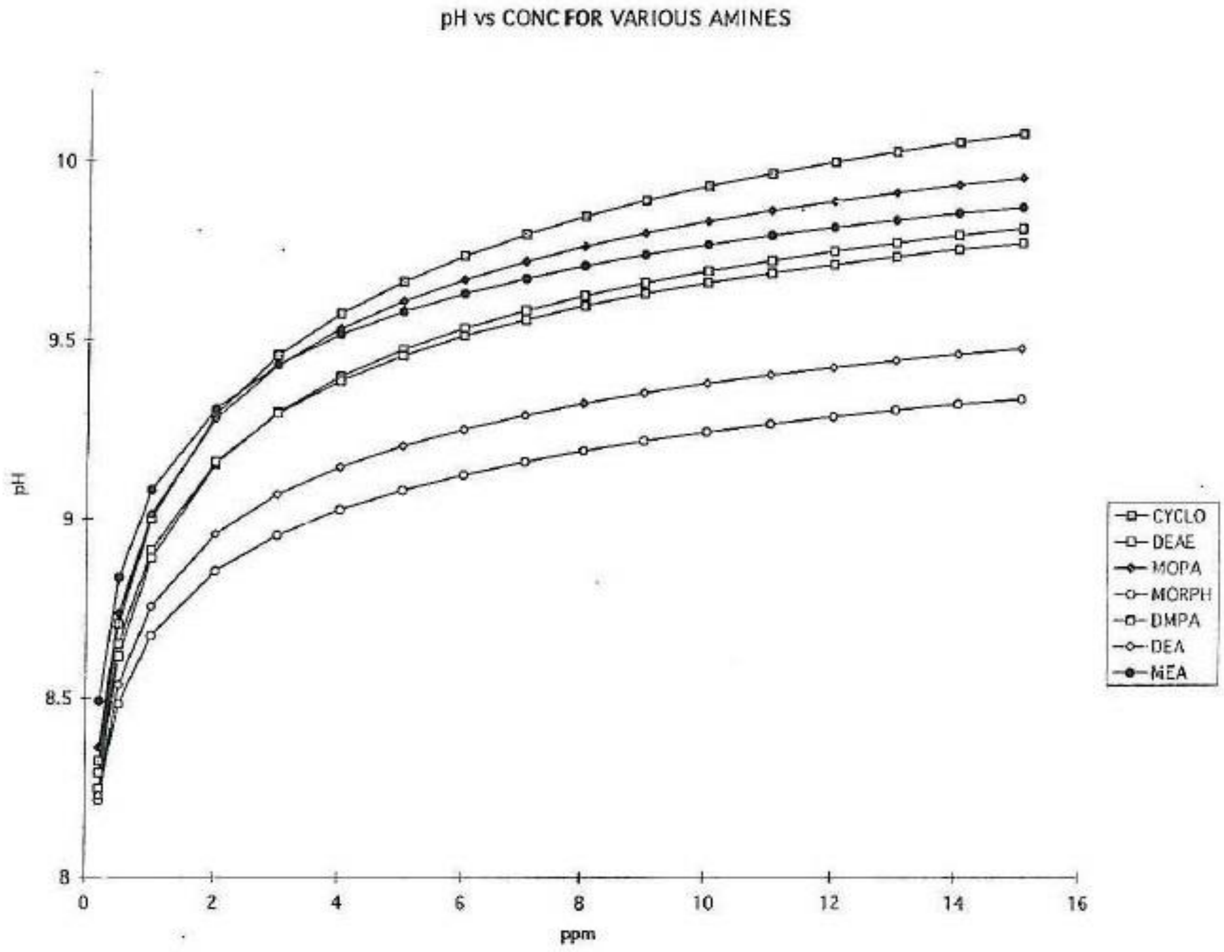
CYCLO = cyclohexylamine
DEAE = diethylaminoethanol
MOPA = methoxypropylamine
MORPH = morpholine
DMPA = dimethylpropylamine
DEA = diethanolamine
MEA = monoethanolamine
NH3 = ammonia

pH Adjustment by Amines: Amine Concentration vs pH



	CYCLO	DEAE	MOPA	MORPH	DMPA	DEA	MEA	NH3
PH	mg/L							
7.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.10	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7.20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00
7.30	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.00
7.40	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.00
7.50	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.00
7.60	0.04	0.04	0.03	0.04	0.04	0.04	0.02	0.01
7.70	0.05	0.06	0.04	0.05	0.05	0.05	0.03	0.01
7.80	0.06	0.07	0.06	0.06	0.06	0.07	0.04	0.01
7.90	0.08	0.09	0.07	0.09	0.08	0.09	0.05	0.01
8.00	0.10	0.12	0.09	0.11	0.10	0.12	0.06	0.02
8.10	0.12	0.15	0.11	0.15	0.13	0.15	0.08	0.02
8.20	0.16	0.19	0.14	0.21	0.17	0.20	0.10	0.03
8.30	0.20	0.24	0.18	0.28	0.22	0.26	0.13	0.04
8.40	0.25	0.30	0.23	0.39	0.27	0.35	0.16	0.05
8.50	0.32	0.39	0.29	0.56	0.35	0.46	0.21	0.06
8.60	0.40	0.49	0.37	0.79	0.45	0.63	0.27	0.08
8.70	0.50	0.63	0.47	1.14	0.58	0.86	0.35	0.11
8.80	0.63	0.81	0.60	1.67	0.75	1.19	0.46	0.14
8.90	0.80	1.04	0.76	2.46	0.98	1.67	0.60	0.19
9.00	1.01	1.35	0.98	3.68	1.29	2.38	0.80	0.26
9.10	1.28	1.75	1.26	5.54	1.70	3.43	1.07	0.36
9.20	1.63	2.30	1.63	8.43	2.28	5.00	1.45	0.51
9.30	2.06	3.04	2.12	12.91	3.08	7.39	1.98	0.72
9.40	2.63	4.06	2.79	19.89	4.21	11.02	2.73	1.02
9.50	3.36	5.47	3.69	30.82	5.83	16.61	3.84	1.48
9.60	4.30	7.47	4.93	47.94	8.18	25.25	5.45	2.17
9.70	5.53	10.32	6.65	74.85	11.63	38.65	7.85	3.22
9.80	7.14	14.44	9.09	117.22	16.75	59.54	11.44	4.83
9.90	9.28	20.48	12.57	183.99	24.43	92.20	16.87	7.31
10.00	12.15	29.43	17.63	289.34	36.05	143.41	25.16	11.14
10.10	16.03	42.83	25.03	455.74	53.78	223.87	37.89	17.11
10.20	21.34	63.07	36.02	718.74	81.01	350.50	57.55	26.42
10.30	28.71	93.92	52.49	1134.63	123.06	550.08	88.06	40.99
10.40	39.06	141.24	77.41	1792.60	188.34	864.99	135.60	63.86
10.50	53.81	214.27	115.40	2833.96	290.07	1362.32	209.91	99.82
10.60	75.07	327.54	173.72	4482.56	449.12	2148.30	326.40	156.45
10.70	106.13	503.93	263.78	7093.09	698.43	3391.21	509.40	245.75
10.80	152.04	779.56	403.52	11227.58	1090.11	5357.55	797.38	386.72

pH Behavior of Amines in Pure Water



Neutralizing Capacity

This parameter relates to the capacity of the amine to neutralize CO_2. The neutralizing reaction is:

$$RNH_2 + H_2CO_3 = RNH_3^+ + HCO_3^- \qquad (3\text{-}53)$$

The reaction is stoichiometric. The lower the molecular weight of the amine, the greater the neutralizing capacity. It has nothing to do with the basicity of the amine. Generally, the more alkalinity in the feedwater, the greater amount of neutralizing amine of any type will be needed.

Volatile Amines and Distribution Ratios

Volatile amines (neutralizing amines) follow the steam into the distribution system. The distribution ratio (DR) is a measure of the volatility of the amine (equation 3-54). It describes the ability of the amine to carry over into the steam where it can neutralize CO_2 in the condensate. Since amines are fed to the feedwater for pH control, they must then volatilize and pass into the steam to neutralize the condensate. The selection of amine has to be balanced by a consideration of feedwater pH adjustment, and condensate treatment. Sometimes it is economical to feed a high basicity amine of low volatility to the feedwater, and inject a high neutralizing capacity amine into the steam with a satellite feed point. The drawbacks are more product inventory and more feed equipment to monitor and maintain. Table 3-18 shows neutralizing capacities and distribution ratios for common volatile amines.

Table 3-18
Neutralizing Amine Properties

Amine	MW	neutralizing capacity	K_b	Distribution Ratio (vs pressure psig)		
		ppm CO_2/mg/L amine		0	200	1000
Ammonia	35	2.59	1.8×10^{-5}	10	7.14	3.57
Cyclohexylamine	99	0.444	440×10^{-6}	4	23.3	9.3
DEAE	117	0.376	66×10^{-6}	1.7	4.5	3.4
MOPA	89	0.494	102×10^{-5}	1	2.4	2.5
Morpholine	87	0.506	3.1×10^{-5}	6.4	1.6	0.98
DEA	105	0.419	7.9×10^{-5}	0.004	0.11	0.07
MEA	61	0.720	32×10^{-6}	0.07	0.15	0.29

DEAE = diethylaminoethanol
MOPA = methoxypropylamine
DEA = diethanolamine
MEA = monoethanolamine

The distribution of the amine in the steam is straightforward. The distribution ratio expresses the ratio of the concentration of the amine in each phase, as shown in equation (3-54).

$$DR = [\text{amine in steam}] / [\text{amine in the boiler}] \qquad (3\text{-}54)$$

However, the concentration itself is not directly evident. From mass balance the entire amine is present either in the steam or in the boiler water. But the relative boiler blowdown and steam flow will affect the absolute concentration of the amine in each phase.

The amine in each phase is calculated from:

$$\text{mg/L in steam} = \text{mg/L in FW} \times DR / (DR \times S/FW + BD/FW) \quad (3\text{-}55)$$

$$\text{mg/L in BD} = \text{mg/L in FW} \times 1/(DR \times S/FW + BD/FW) \quad (3\text{-}56)$$

Where FW, BD, S, and DR are the feedwater flow, blowdown flow, steam flow and distribution ratio respectively.

Note that the sum of equation (3-55) times steam flow and equation (3-56) times blowdown flow is equal to the amount of amine in the feedwater, as it must for mass balance to be maintained.

In complex steam distribution systems with flash tanks, the application of neutralizing amines is very complicated. Amines will condense in the flash tanks, and redistribute according to the local relative flow rates and pressures. The proper pH in the flash tank blowdown is important for corrosion protection. Also, the persistence of amine in the steam phase downstream of the flash tanks must be considered.

It is common practice to blend amines for feedwater pH control. One amine is chosen for its ability to raise the pH of the feedwater (more basic amines), while another may be chosen for its neutralizing capacity and/or distribution into the steam.

Low DR amines will concentrate in the condensate, providing good tank protection, but are removed according to equation (3-51). Many satellite feeds may be needed. A high DR amine will remain in the steam, and not provide as good protection to the tank, but will travel further down the system, and provide better protection at distant locations. An amine with high basicity or neutralizing capacity might help overcome this problem, since it will produce a higher pH in the condensate at lower concentration.

Filming Amines

Filming amines are used for condensate systems only. Filming amines are high molecular weight amines with long hydrocarbon chains. Most are insoluble in water. The nitrogen end of the molecule is highly polar, and adheres to metallic oxides on the condensate line walls. The hydrocarbon chain is very hydrophobic, and provides protection for the metal surface by preventing contact with water.

The main filming amine is octadecylamine (ODA), $CH_3(CH_2)_{17}NH_2$. It is a very waxy material at room temperature, and must be heated in order to be fed. Feed is accomplished by heating the amine so that it flows freely, then mixing it in with demineralized water. It is then fed directly into the steam header with an injection quill. Stainless steel or Hastelloy is needed, as the concentrated solution is aggressive to steel or copper alloy metallurgy. ODA is sometimes fed as the acetate salt, which is more soluble. The acetate decomposes to liberate ODA and a small amount of acetic acid.

The feed rate is based on steam flow, and is typically about 1 to 5 mg/L active amine. The solution should be held at elevated temperature, around 100 °F. Make down water should be demineralized water or condensate. Solutions fed directly to steam should be free of dissolved solids. Also, since dissolved solids can coagulate filming amines, they should not be fed to systems with high carryover from the boiler.

The feed need not be continuous unless fed to high flow velocity areas. The films are persistent, and may need to be maintained only by intermittent feed. Once a day for a few hours may be enough to maintain good protection.

Use of filming amines in complex steam distribution systems is a problem. Many satellite feed points are needed, as the amine does not travel as far in the steam as the more volatile neutralizing amines.

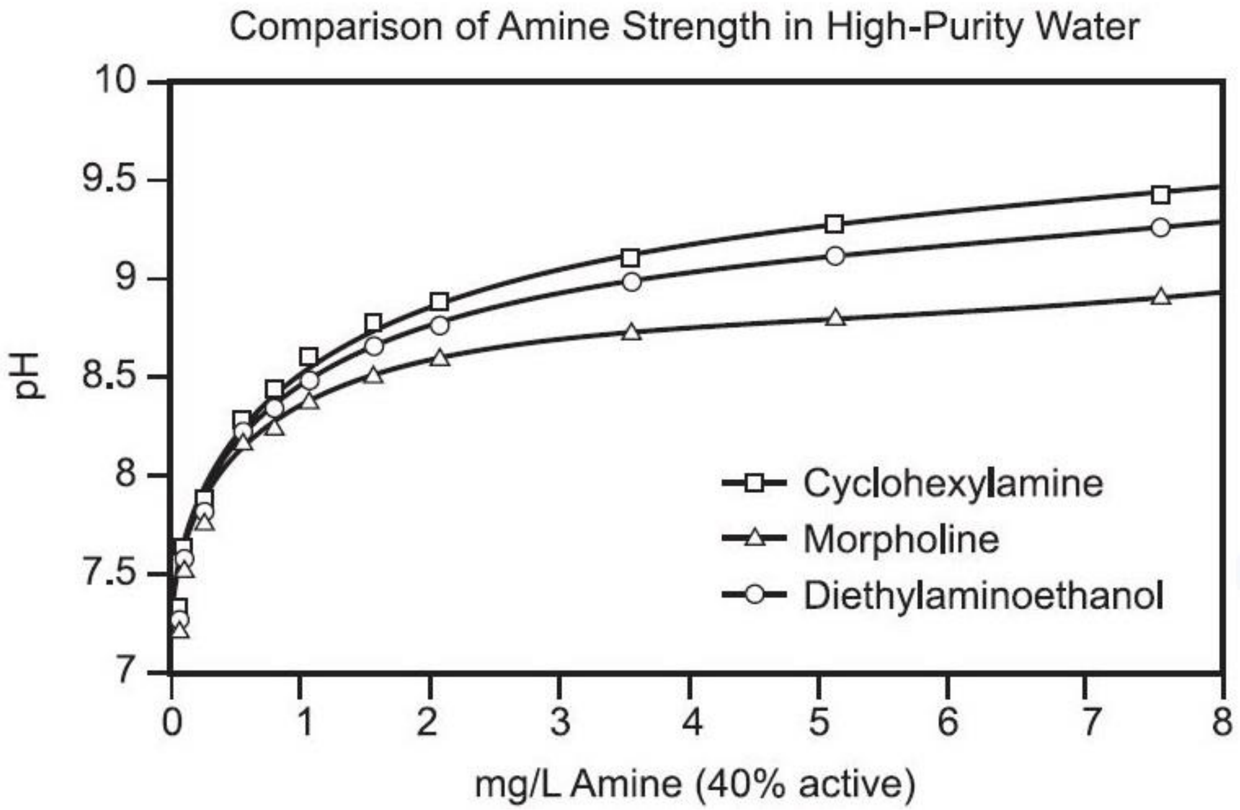
Filming amines can undercut old oxide deposits and cause them to slough off. The deposits then travel at high velocity in the steam line, leading to erosive wear or clogging of steam traps and valves. For that reason, use of filming amines in older systems should be carefully considered before a decision is made to feed them.

Notes

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

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

$$RNH_3^+ + OH^- + H^+ + HCO_3^- \rightleftharpoons RNH_3HCO_3 + H_2O$$



Thermal Stability

All organic molecules, including amines, have specific temperature limitations, above which they thermally decompose. Most water treatment chemicals commonly used in boiler systems have been chosen for their exceptional thermal stability, yet all eventually break down in the boiler system given sufficient heat and holding time.

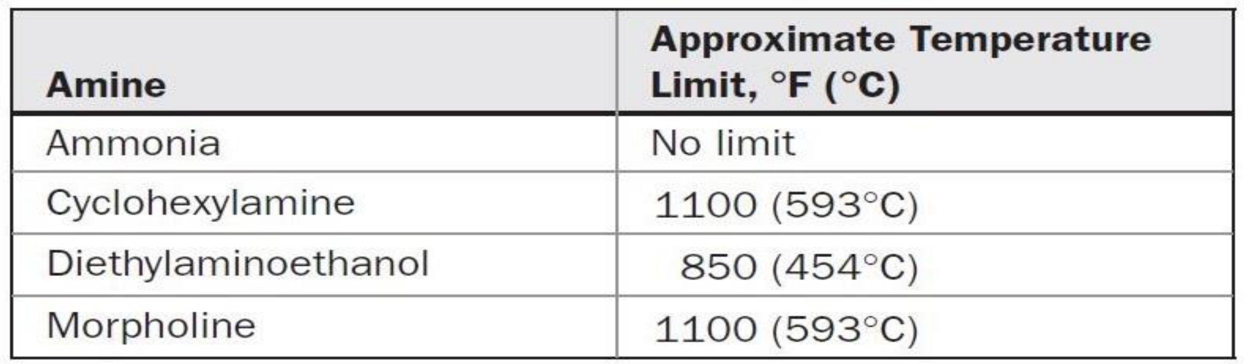
Amine thermal stability is primarily dependent on time at temperature, but system oxygen can also be a factor. The superheater is typically the location of highest heat within the boiler system. Because exposure time to superheat temperatures is extremely short, many amines can be used at temperatures above their known decomposition temperatures without appreciable loss. Amines used in systems with reheat have significantly more exposure time at high temperatures and typically see a higher percentage loss.

In work reported by the Electric Power Research Institute (EPRI) in the early 1990s, the relative stability of several amines was listed as:

Monoethanolamine > methoxypropylamine > morpholine

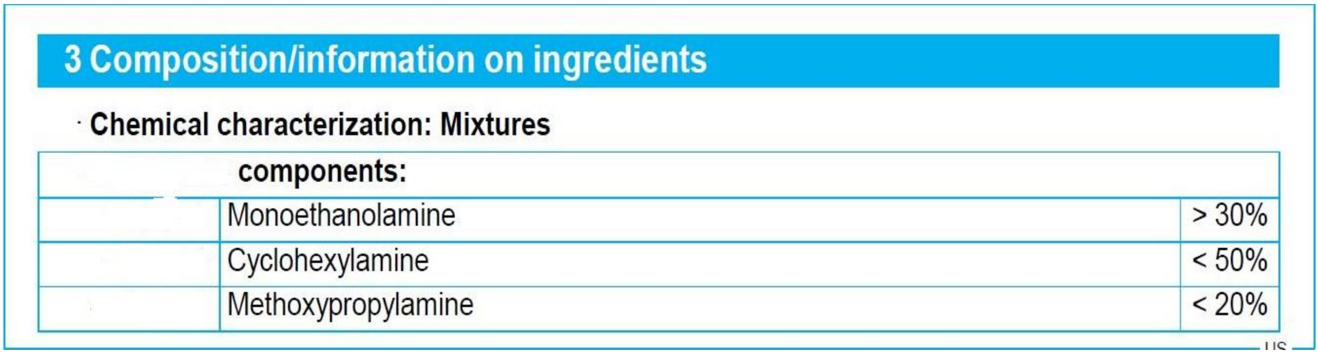
Table 13.5 shows suggested temperature limitations for some of the neutralizing amines commonly used.

Thermal degradation of the neutralizing amines typically results in the generation of lower molecular weight amines and organic acids, as well as ammonia.



Amine	Approximate Temperature Limit, °F (°C)
Ammonia	No limit
Cyclohexylamine	1100 (593°C)
Diethylaminoethanol	850 (454°C)
Morpholine	1100 (593°C)

TABLE 13.5 Recommended Temperature Limitations for Neutralizing Amines



3 Composition/information on ingredients

· **Chemical characterization: Mixtures**

	components:	
	Monoethanolamine	> 30%
	Cyclohexylamine	< 50%
	Methoxypropylamine	< 20%