EnviroAqua CONSULTANTS INC.

Water Talk

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Neutralizing Amines

This paper discusses the factors that go into the choice and use of neutralizing amines to neutralize the pH in the condensate system which include: basicity, neutralizing capacity, distribution ratio, and USDA and FDA requirements.

Carbon dioxide is formed by the breakdown of carbonate alkalinity in the boiler and is very volatile. This means that most of it passes into the steam, then forming carbonic acid in the condensate. The pH of the condensate can then reach low levels, sometimes below 3 because the

carbon dioxide is not in equilibrium with the atmosphere. The limiting pH in the atmosphere is about 5.8

Carbonate alkalinity can be removed by dealkalization and decarbonation in the pretreatment train. In most medium and low pressure systems the carbon dioxide is neutralized by adding neutralizing amines to the feedwater. The amines can also be fed directly into the steam lines. These amines adjust feedwater pH to an optimum range of about 8.8 to 9.2. Amines are distributed into the steam as they pass through boilers and condense with the steam and carbon dioxide.

BASICITY

The general reaction of amines with water is:

$RNH_2 + H_2O = RNH_3^+ + OH^-$

The base hydrolysis constant for amines is defined as:

$K_b = [RNH_3^+][OH^-]/[RNH_2]$

The greater the value for K_b the more basic the amine will be. 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 a lower K_b.Higher basicity doesn't always mean that the pH will be higher. The molecular weight will also play a role due to the fact that it is in mg/L.

Tables 1 and 2 show the pH of pure water as adjuste by the indicated amount of four volatile neutralizing amines.

CYCLO= cyclohexylamine
DEAE= diethylaminoethanol
MORPH= morpholine
NH3= ammonia

pH adjustment capacity of amines pH vs/ Amine concentration

	CYCLO	DEAE	MORPH	NH3
		pH		
Mg/L				
0.5	8.71	8.62	8.48	9.20
2	9.29	9.15	8.85	9.58
4	9.57	9.40	9.02	9.75
6	9.73	9.53	9.12	9.85
8	9.84	9.62	9.19	9.92
10	9.93	9.69	9.24	9.97
12	10.00	9.75	9.29	10.02
14	10.05	9.79	9.32	10.05

pH adjustment by amines: amine concentration vs pH

	CYCLO	DEAE	MORPH	NH3
pH		**Mg/L**		
7.00	0	0	0	0
7.30	0.010	0.02	0.01	0.00
7.60	0.04	0.04	0.04	0.01
7.90	0.08	0.09	0.09	0.01
8.20	0.16	0.19	0.21	0.03
8.50	0.32	0.39	0.56	0.06
8.80	0.63	0.81	1.67	0.14
9.10	1.28	1.75	5.54	0.36
9.40	2.63	4.06	19.89	1.02
9.70	5.53	10.32	74.85	3.22
10.0	12.15	29.43	289.34	11.14
10.3	28.71	93.92	1134.63	40.99
10.6	75.07	327.54	4482.56	156.45

NEUTRALIZING CAPACITY

The formula to express the capacity of the amine to neutralize CO_2 is expressed as:

$RNH_2 + H_2CO_3 = RNH_3^+ + HCO_3^-$

The reaction is stoichiometric; the lower the molecular weight of the amine, the greater the neutralizing capacity.

VOLATILE AMINES & DISTRIBUTION RATIONS

Neutralizing amines follow the steam into the distribution system and the distribution ratio is a measure of the volatility of the amine that shows the ability of the amine to carry over into the steam where it can neutralize the carbon dioxide in the condensate. The higher the distribution ratio (like cyclohexylamine), the more the amines carries through the steam lines to the far end of the condensate system.

The amines with a low distribution ratio (like morpholine) tend to condense close to the boiler. The distribution ratio of amines is pressure dependent. The attached chart summarizes the properties of the neutralizing amines and lists the distribution ratio at 200 psig.

Neutralizing amine properties

Amine	MW	Neutralizing capacity	K_b	Distribution Ration (vs Pressure psig)		
		ppm CO_2/mg/L amine		0	200	1000
NH3	35	2.59	$1.8x10^{-6}$	10	7.14	3.57
CYCLO	99	0.44	$440x10^{-6}$	4	23.3	9.3
DEAE	117	0.376	$66x10^{-6}$	1.7	4.5	3.4
MORPH	87	0.506	$3.1x10^{-6}$	6.4	1.6	0.98

When choosing an amine, or amine combination, the length of the condensate lines and amount of carbon dioxide generated in the boiler need to be considered.

FDA AND USDA LIMITATIONS

The four amines that are discussed in this water talk are acceptable for use in meat and poultry plants according to the FDA and USDA. The limitations of the amine in steam, as determined by the FDA, for steam contacting food is listed below:

Substance	**Limitations**
MORPH	10 ppm
DEAE	15 ppm
CYCLO	10 ppm
NH3	Good manufacturing practices