

Hydrocarbon Processing®

March 1996 and April 1997

Effect of heat stable salts on MDEA solution corrosivity

Parts 1 & 2

New testing gives recommended limits of each species
and the impact of temperature and pH

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INEOS LLC

As part of a Federal Trade Commission mandated remedy to the merger of The Dow Chemical Company and the Union Carbide Corporation, INEOS plc was able to purchase both Dow's Ethanolamines and GAS/SPEC MDEA-based specialty amine businesses. This purchase became effective on February 12, 2001.

INEOS LLC was set up as the newly acquired company, which includes the GAS/SPEC Technology Group. All the key Ethanolamines and GAS/SPEC personnel were retained by INEOS LLC. All GAS/SPEC products, technology and know-how became the exclusive property of INEOS on a global basis.

Effect of heat stable salts on MDEA solution corrosivity

New testing gives recommended limits of each species and the impact of temperature and pH

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The formation of heat stable amine salts (HSAS) in amine solutions used in gas conditioning applications has long been a problem, particularly in refinery systems or when oxygen is present in the feed gas to an amine unit. In the absence of practical corrosion data concerning HSAS and the controversy surrounding neutralization of HSAS, a comprehensive coupon corrosion testing program was undertaken to address these issues as well as vapor corrosion issues.

HSAS are called heat stable since they are not regenerated in the amine unit's stripping section, as sulfide (H_2S) and carbonate/bicarbonate/carbamate (CO_2) salts are. These HSAS, such as formate, oxalate, acetate, thiocyanate, sulfate and chloride, decrease the amine solution's acid-gas carrying capacity and increase solution viscosity, thus increasing amine unit operating costs.

It is generally thought that the presence of HSAS increases the corrosivity of amine solutions. However, hard data has not existed that the industry could review and use to correlate HSAS and amine solution corrosivity. Emerging corrosion data have been conflicting,¹⁻³ especially when electrical polarization is used to measure solution corrosivity. Recent reports indicate that the very long time to reach chemical and steady-state equilibrium,⁴ along with interferences with H_2S and thiocyanate,^{4,5} preclude using much of the data that attempts to correlate electrical polarization and corrosion.

In addition, controversy exists regarding the benefits of neutralizing HSAS with caustic (which converts the amine salt to free amine to be used in acid gas treating along with the sodium salt that stays in solution). While neutralization certainly restores the lost-acid gas carrying capacity of the amine solution, the effect on solution corrosivity is still being debated. Again, most of the

previous work used electrical polarization probes, which further complicates the controversy.

Test procedures. Corrosion rates of different metals in 50 wt% methyldiethanolamine (MDEA) and 50 wt% MDEA containing various anions that concern the refining industry were measured. Weight loss coupons in 2-liter, 316 stainless steel (SS) pressure reactors (rated at 2,000 psi) with magnetic stirrer drives connected to temperature controllers were used. Each reactor head was custom fitted with a 316SS rack. Carbon steel, 304SS, 316SS and 410SS coupons were totally immersed in the liquid. Additional coupons were fully placed in the vapor space above the liquid. Each coupon was mounted to the rack using teflon spacers to fully insulate them from the rack.

The solution (1,000 g total solution was used in each test) was placed in the reactor and the head was then bolted to the reactor to seal it. Glass liners were not used in any of these tests since silicates are known corrosion inhibitors in industrial cooling-water systems⁶ and automotive cooling systems.⁷ Nitrogen was passed through each solution prior to heating to remove any trace oxygen. The solutions were heated to the desired temperature (180°F or 250°F) maintaining a stir speed of about 190 rpm throughout the test. After the test, the coupons were cleaned and weight loss was measured. Coupon weight loss was converted to a corrosion rate in mils per year (mpy) using the following formula:⁸

$$\text{Corrosion rate} = \frac{\text{Weight loss} \times 534}{(\text{Area}) (\text{time}) (\text{metal density})} \quad (1)$$

where weight loss is in milligrams, surface area of each coupon is in ² of metal surface exposed (each about 1.5-in. length \times 0.6-in. width \times 0.1-in. thick), time is in hours exposed and density is in g/cm^3 (carbon steel = 7.86 g/cm^3 ; 304 SS = 7.94 g/cm^3 ; 316SS = 7.98 g/cm^3 ; 410SS = 7.70 g/cm^3). One duplicate test was run at 180°F and 250°F to ensure result reproducibility.

Prior to the tests, C1018 carbon steel and 410SS coupons were cleaned with a 1:1 mixture of inhibited HCl and water for 2 to 3 min., scrubbed with warm water and then dried with acetone.

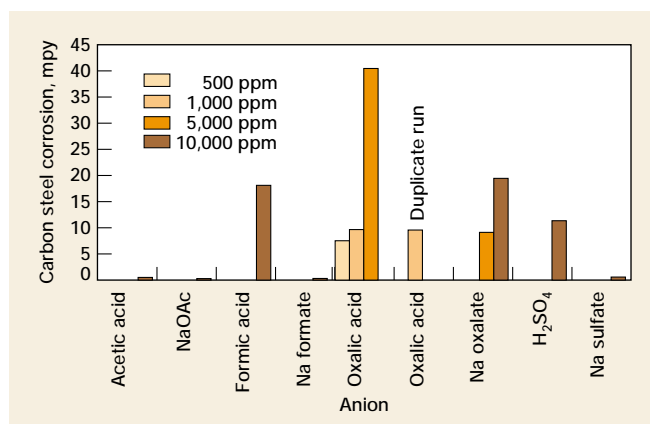


Fig. 1. Corrosivity of various anions at 180°F to carbon steel (liquid).

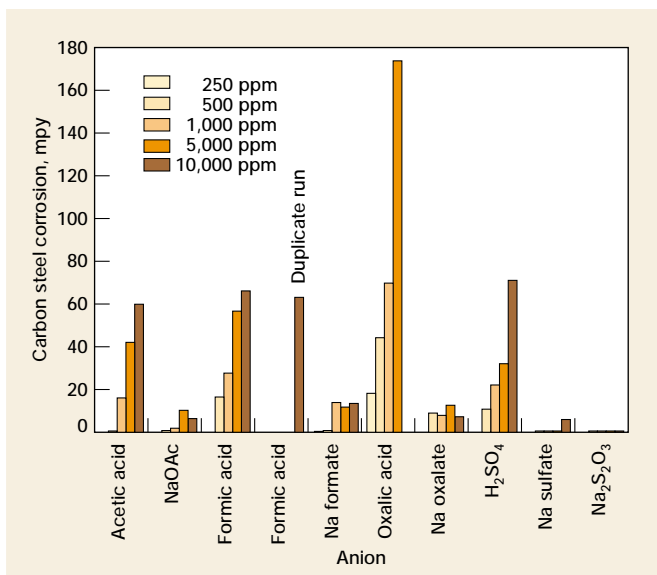


Fig. 2. Corrosivity of various anions at 250°F to carbon steel (liquid).

The 304SS and 316SS were cleaned with a mixture of 1:1 nitric acid for 2 to 3 min., scrubbed with warm water and then dried with acetone. After the tests, all coupons were cleaned with a 1:1 mixture of inhibited HCl, scrubbed with warm water and dried with acetone.

Each solution was made with commercial-quality MDEA and distilled water. All the carboxylic acids and their sodium salts were the highest purity available. Note that 5,000 and 10,000 ppm sodium oxalate and sodium sulfate at >1,000 ppm were not completely soluble in the MDEA solution at room temperature. Although the solubility of sodium oxalate in 50 wt% MDEA is not known at elevated temperatures, based on the solubility of sodium oxalate in water (3.7g/ml at 20°C versus 6.33g/ml at 100°C),⁹ it is likely that the sodium oxalate was mostly, if not completely, soluble at the elevated temperatures used in this study. Sodium sulfate, however, has a maximum solubility at 33°C (91.4°F) in water and decreases with rising temperature.¹⁰ Therefore, it is possible that the sodium sulfate remained insoluble in the MDEA at the temperatures used in this study.

Corrosivity of various anions at 180°F. Results of the 7-day, 180°F carbon steel liquid corrosivity test are in Fig. 1. Tests were performed with 500, 1,000 and 5,000 ppm anion concentrations using oxalic acid, 500, 1,000, 5,000 and 10,000 ppm anion concentrations using sodium oxalate, and 10,000 ppm for each of the remaining anions. Oxalic acid, which reacts with MDEA to form MDEA oxalate, had higher corrosivity to carbon steel at 5,000 ppm (40 mpy) than all the other anions at 10,000 ppm. Sodium oxalate at 5,000 ppm had a reduced rate (9 mpy), although 10,000 ppm sodium oxalate had a corrosivity similar to 10,000 ppm H₂SO₄ (MDEA and H₂SO₄ react to form MDEA sulfate) and 10,000 ppm formic acid (present as MDEA formate).

Corrosivity of each anion to the 304, 316 and 410SS (both liquid and vapor) were all less than 0.5 mpy. For reference, pure 50 wt% MDEA has a corrosivity rate of 0.1 mpy or less to all the liquid and vapor coupons.

Corrosivity of various anions at 250°F. The same procedure used in the 180°F tests was performed at 250°F (Fig. 2). Tests were performed with 250, 500, 1,000 and

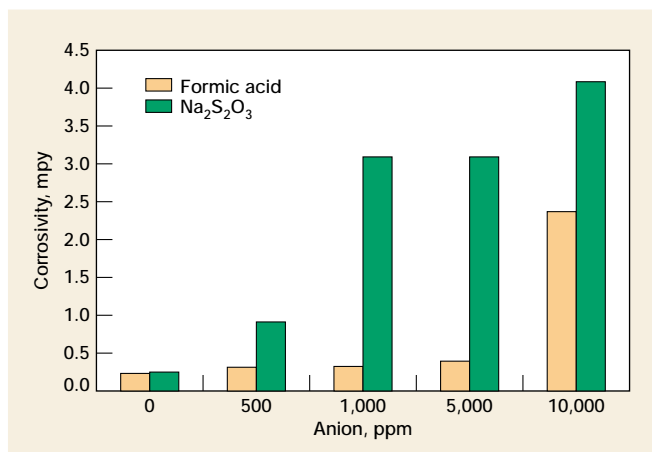


Fig. 3. Corrosivity of formic acid and sodium thiosulfate to carbon steel (vapor) at 250°F.

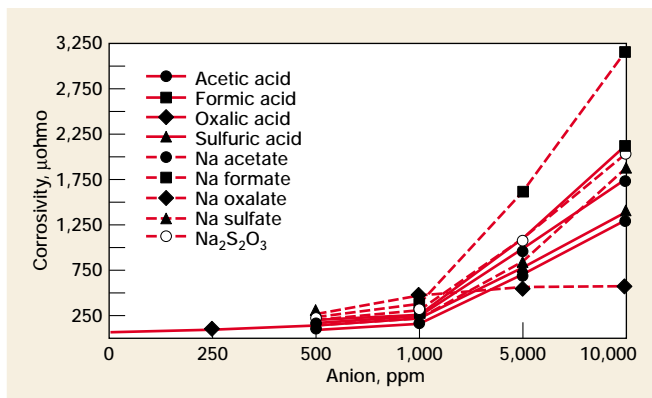


Fig. 4. Conductivity measurements for 50 wt% MDEA containing various concentrations of added acid or salt.

5,000 ppm anion concentrations using oxalic acid and 500, 1,000, 5,000 and 10,000 ppm anion concentrations using each of the remaining anions. As expected, measured carbon-steel liquid corrosivities are generally much higher at 250°F than 180°F. Acetic acid, formic acid, oxalic acid and H₂SO₄ all show increased corrosivities as the MDEA heat stable salt concentration increases. The sodium salts all had reduced corrosivities to carbon steel compared to the MDEA heat stable salts.

As was seen for the 180°F tests, oxalic acid had extremely high corrosivity even at 5,000 ppm. Based on these results, to maintain about 10 mpy or less corrosivity to carbon steel in the liquid phase, the acetic acid concentration must be less than 1,000 ppm; formic acid and sulfuric acid must be less than 500 ppm; and oxalic acid less than 250 ppm. Neutralization with caustic appears to reduce corrosion to carbon steel to about 10 mpy or less as is seen by the sodium salt results in Fig. 2.

Formic acid and sodium thiosulfate both show some corrosion to carbon steel in vapor (Fig. 3). Very likely, formic acid and SO₂ (from breakdown of sodium thiosulfate) are the active corrosion agents to the carbon steel vapor coupons. Although 10,000 ppm of each of these two anions resulted in <10 mpy carbon steel vapor corrosivity in the autoclave, plant experience suggests that the autoclave may understate true plant vapor corrosion for these two compounds. Unlike the plant stripper where constant vapor is produced by boiling the solution, the autoclave prevents solution boiling by pressurizing the reactor to maintain constant temperature. The amount

Table 1. Acid dissociation constants of weak acids at 25°C¹¹

Acid	Equilibrium	pKa
Formic acid	$\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$	3.75
Acetic acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$	4.76
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{H}^+$	1.27
	$\text{HC}_2\text{O}_4^- \rightleftharpoons \text{C}_2\text{O}_4^{2-} + \text{H}^+$	

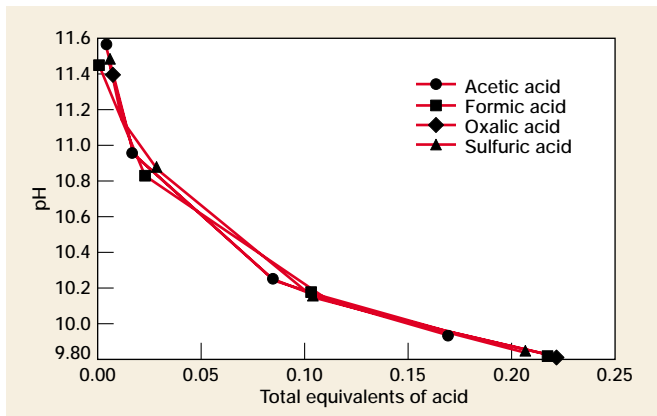


Fig. 5. Correlation of pH versus total acid concentration for 50 wt% MDEA.

of formic acid and SO_2 constantly generated in the stripper, therefore, is significantly more than the amount of formic acid and SO_2 vapor in the autoclave.

All the anions except formic acid and sodium thiosulfate had <0.4 mpy corrosivity to carbon steel in the vapor. All the anions (including formic acid and sodium thiosulfate) had corrosivities less than 0.4 mpy to 304, 316 and 410SS in the liquid and vapor. For reference, pure 50 wt% MDEA had a corrosivity rate of 0.2 mpy or less to all the liquid and vapor coupons.

Effect of MDEA solution conductivity on corrosion. Conductivity measurements were taken of the 50 wt% MDEA solutions to determine the effect of added anion on corrosion rate (Fig. 4). Conductivities were measured at room temperature using a 0 to 200,000 μhmo conductivity meter connected to a conductivity probe. Traceable conductivity calibration standards were used to calibrate the conductivity meter. Distilled water further treated with a ion exchange system was used (18.2 megaohm resistance) to dilute the MDEA solutions. Note that 5,000 and 10,000 ppm sodium oxalate and sodium sulfate at $>1,000$ ppm were not completely soluble in the MDEA solution at room temperature. For the purpose of these experiments, conductivity was measured with the solids in the solution. The fact that these two compounds had solubility problems at room temperature does not affect the fact that room temperature conductivity does not correlate with corrosivity.

Although it may be reasonable to think that solutions with higher conductivity might result in higher measured corrosion rates, these results show little correlation of room temperature conductivity and corrosion. For example, sodium formate (carbon steel corrosion rate at 250°F = 13.3 mpy at 10,000 ppm) has a higher conductivity than formic acid (carbon steel corrosion rate at 250°F = 63 to 66 mpy at 10,000 ppm). Sulfuric acid (carbon steel corrosion rate at 250°F = 71.4 mpy at 10,000 ppm) has a lower conductivity than the less corrosive anions sodium acetate,

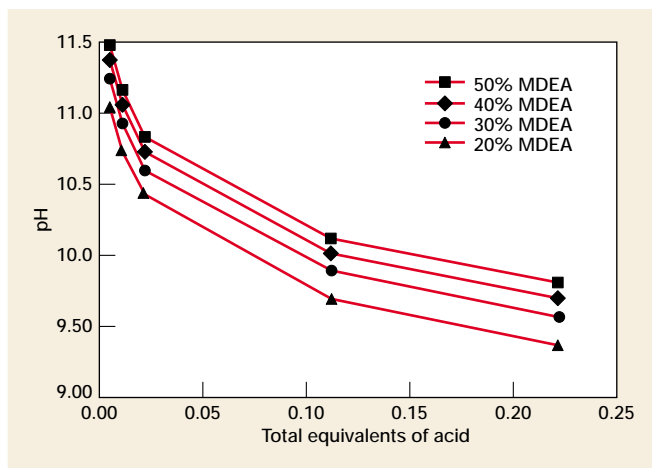
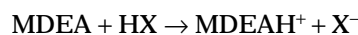


Fig. 6. Effect of total added acid on the pH of various MDEA concentrations.

sodium formate and sodium thiosulfate (carbon steel corrosion rate at 250°F = 6, 13 and 0.1 mpy, respectively).

Effect of solution pH on corrosion. For the reaction:



where HX is a weak acid such as acetic, formic or oxalic acid. If the solution pH is much greater than the pKa of the weak acid, then that weak acid can be considered to act like a strong acid (i.e., sulfuric acid) in that all the protons of the acid (the H^+) will react with MDEA to form heat stable salts. For 50 wt% MDEA at room temperature, the assumption that the above acids completely react with MDEA is true given the much greater concentration of MDEA (4.2 mol/l) compared to 10,000 ppm acid (<0.25 mol/l) and the acids' pKas used in this study (see Table 1).

The effect of added acid concentration on the MDEA solution pH can then be calculated from the equation:

$$\text{pH} = \text{pKa} - \log \left[\frac{[\text{MDEAH}^+]}{[\text{MDEA}]} \right] \quad (2)$$

where pKa refers to MDEA (8.56 at 25°C).¹² $[\text{MDEAH}^+]$ is the same as the added acid concentration (diprotic acids such as oxalic and sulfuric acid have twice the number of protons compared to monoprotic acids such as acetic and formic acid) used to form the MDEA heat stable salt. $[\text{MDEA}]$ refers to the total concentration of MDEA not neutralized by acid.

From Eq. 2, the 50 wt% MDEA solution's pH at room temperature depends solely on the total acid concentration, independent of whether the acid is acetic acid, formic acid, oxalic acid or sulfuric acid (Fig. 5). The pH is lowered even more by total acid added when lower concentrations of MDEA are used due to the log function in Eq. 2 (Fig. 6). At higher temperatures, the calculation of solution pH becomes more complicated due to very different equilibrium constant equations for each acid as well as the much higher solution ionic strengths.

When the calculated pH of each MDEA solution is plotted against the 250°F carbon steel corrosivity results, carbon steel corrosivity increases with lower pH (higher total acid added) for formic, acetic and sulfuric acid (Fig. 7). Oxalic acid, however, has a much higher rate of corrosion than would be expected from pH alone. As is seen in Table 2, the equilibrium constant for the complexation of oxalic acid and Fe^{3+} is about 4 to 5 orders of magnitude larger than the complexation of acetic acid, formic acid and sulfuric acid with

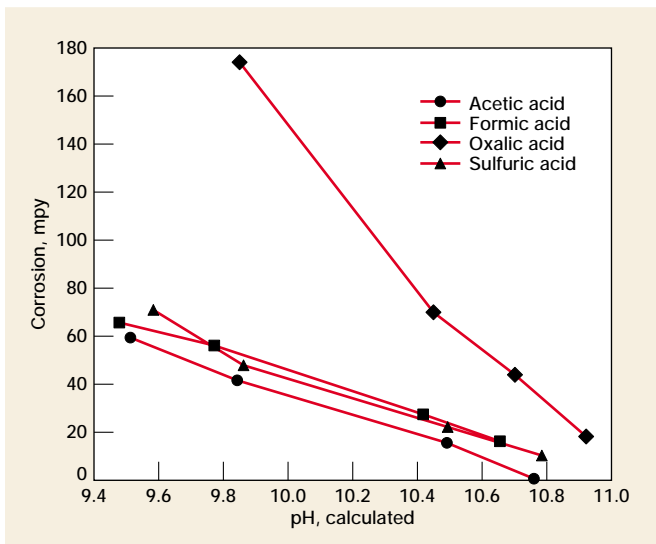


Fig. 7. Effect of pH on carbon steel liquid corrosivity at 250°F.

Fe³⁺. This means that as freshly exposed Fe of the carbon steel is oxidized (by the acid in solution or oxygen), the oxalic acid will chelate this oxidized metal and expose new metal to further oxidation. The net result is a significantly increased rate of corrosion than what would be expected from total acid concentration or pH alone. If this chelation theory is true, then it is reasonable to predict, based on equilibrium constants of Fe³⁺ and other species, that malonic acid and succinic acid will also have much greater corrosivity to carbon steel than predicted by pH alone (Table 2).

Plant operating solution results. Corrosion results of two refinery plant solutions before and after caustic neutralization are shown in Table 3. All corrosion testing was performed at 250°F for seven days. Both plant solutions had high HSAS that resulted in high solution corrosivity to carbon steel. Total neutralization of these plant solutions with caustic significantly reduced corrosion.

Recommendations. Based upon our results, recommended limits of individual species of heat stable salt are:

Oxalate	250 ppm
Sulfate	500 ppm
Formate	500 ppm
Acetate	1,000 ppm
Thiosulfate	10,000 ppm

In addition, we recommend that chlorides and thiocyanates not exceed 500 ppm and 10,000 ppm, respectively. The total HSAS level should not exceed 0.5% of the total solution.

When the limit of any species or total HSAS is reached, look for symptoms of problems caused by HSAS. Foaming, diminished filter run time, solution color change and iron sulfide suspended in the solution are typical warning signs of corrosion problems caused by HSAS.

Caustic additions can be considered when signs of corrosivity appear that are related to HSAS. The addition of chloride-free caustic (25° Baume or 19 wt% is a handy form of addition) should be continuous, thoroughly mixed and 0.1% of circulation rate. Thus, for a circulation rate of 100 gpm, a caustic addition of 6 gph into the lean amine through an injection quill would be a maximum addition rate.

The amount of caustic to add should be based on calculations to free half of the HSAS. Analysis after addition will

Table 2. Equilibrium constants for the complexation of iron and various acids¹²

	log K (25°C, μ = 1.0)
Oxalic acid	
Fe ²⁺ [ML]/[M.L.]	3.05
Fe ³⁺ [ML]/[M.L.]	7.59
Malonic acid	
Fe ²⁺ [ML]/[M.L.]	2.17, 2.24
Fe ³⁺ [ML]/[M.L.]	7.50
Succinic acid	
Fe ²⁺ [ML]/[M.L.]	—
Fe ³⁺ [ML]/[M.L.]	6.88 (μ = 0.5)
Acetic acid	
Fe ²⁺ [ML]/[M.L.]	—
Fe ³⁺ [ML]/[M.L.]	3.2
Formic acid	
Fe ²⁺ [ML]/[M.L.]	—
Fe ³⁺ [ML]/[M.L.]	3.1
Sulfuric acid	
Fe ²⁺ [ML]/[M.L.]	—
Fe ³⁺ [ML]/[M.L.]	2.0

Table 3. Comparison of corrosivity of two refinery plant solutions before and after caustic neutralization

	Plant 1 operating solution	Plant 1 operating solution after caustic neutralization	Plant 2 operating solution	Plant 2 operating solution after caustic neutralization
CO ₂ (M/M)	—	—	.0022	—
H ₂ S (M/M)	0.0002	—	—	—
%MDEA by GC	31.0	—	55.0	—
Titration	30.4	—	52.9	—
%HSAS	1.69	—	4.37	—
Anion, ppm				
Acetate	560	—	480	—
Chloride	110	—	1,200	—
Oxalate	<25	—	<25	—
Formate	3,475	—	8,545	—
Sulfate	110	—	220	—
Thiocyanate	1,490	—	1,200	—
Corrosion, mpy				
Carbon steel liquid	42	0.2	26	0.1
Carbon steel vapor	1.6	0.1	1.3	0.1
304SS liquid	0.1	0.1	0.1	0.1
304SS vapor	0.1	0.1	0.1	0.1
316SS liquid	0.1	0.1	0.1	0.1
316SS vapor	0.1	0.1	0.1	0.1
410SS liquid	42.5	0.1	0.2	0.1
410SS vapor	0.2	0.1	0.4	0.1

confirm the actual amount of amine freed and allow for corrections to estimated solution inventory and actual amount of caustic added. Limiting the freed amine to a maximum of 80% of the original HSAS will provide further safeguards against excess addition of caustic. Although caustic dramatically reduces corrosion, the amount of NaOH that can be added to plant solutions is limited without increasing the solution viscosity or insoluble sodium salts. In general, a maximum of about 10% of the total MDEA concentration can be neutralized with caustic before viscosity problems and solids problems appear.

Anion exchange is an excellent way to reduce high HSAS to extremely low levels. Of course, if high amounts of Na or K are in the solution (due to NaOH or KOH neutralization), then a cation exchange resin may also have to be used to fully clean the alkanolamine solution. Solution reclaiming by distillation (or vacuum distillation) will also remove HSAS to very low levels. In addition, reclaiming by distillation can remove other contaminants (e.g., ethylene glycol, triethylene glycol) to very low levels that anion exchange will not remove.

Which reclaiming method to use for your plant will depend on the amount and type of HSAS that needs to be removed as well as whether other contaminants also need to be removed. In either case, it is very important that chelating anions such as oxalate are removed as much as possible (<250 ppm) and that other anions are reduced to levels well below the recommended guidelines given above.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Ken Willbanks (Dow Chemical Metals Department, Freeport, Texas) for making the custom autoclave coupon racks, preparing and weighing all the coupons for testing and for his expert advice on metal corrosion.

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Tom Bacon is a project manager in the GAS/SPEC technology group, Dow U.S.A., Freeport, Texas. His responsibilities since joining the group in 1982 have included managing special projects, facilitating the research and development of Dow's gas treating technologies and the application of technical service to customers using these technologies. During his 30-year career with The Dow Chemical Company, he has served in a number of engineering and management roles including process research, plant operations, management of process technology, design, construction and startup of newly developed technologies, and development of and technical service for gas treating processes for the natural gas, geothermal power, oil refining and coal fired power industries. His experience includes three years with Texaco in gas production and processing. He received his BS in chemical engineering from Texas A&M in 1961.



Mike DuPart is a development associate in the GAS/SPEC Technology Group of The Dow Chemical Company, Freeport, Texas. He has a wide range of experience in gas processing, from corrosion inhibitor research to process optimization of amine plants. He holds four U.S. patents and has coauthored several papers on gas processing. Mr. DuPart received a BS degree in metallurgical engineering from The University of Texas, El Paso.

Part 2

Effect of heat stable salts on MDEA solution corrosivity

As a follow-up to research presented in a March 1996 article, more anions were tested for recommended levels

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A comprehensive coupon corrosion testing program was undertaken to address the effect of various heat stable salts on methyldiethanolamine (MDEA) corrosivity to carbon steel and various stainless steels.¹ Corrosion rates of carbon steel, 304SS, 316SS and 410SS liquid and vapor coupons towards MDEA, and MDEA containing various anions, at 180°F and 250°F, were measured in a reactor. Corrosion results of two refinery plant solutions before and after caustic neutralization were also performed.

Based on these results, guidelines were determined for heat stable amine salt (HSAS) levels of oxalates, sulfates, formates, acetates and thiosulfates. In addition, caustic neutralization guidelines for MDEA heat stable salts were determined. Ongoing results include MDEA corrosivity with succinates, malonates, glycolates, SO₂ and ammonia.

TEST PROCEDURES

Corrosion rates of different metals in 50 wt% MDEA and in 50 wt% MDEA containing various anions that concern the refining, hydrogen and natural gas industries were measured. Weight-loss coupons in a 2-liter 316SS pressure reactor (rated at 2,000 psi) with a magnetic stirrer drive connected to temperature controllers (Fig. 1) were used. Each reactor head was custom-fitted with a 316SS rack. Carbon steel, 304SS, 316SS and 410SS coupons were

totally immersed in the liquid and additional coupons were fully placed in the vapor space above the liquid. The coupons were mounted to the rack using Teflon spacers to fully insulate them (Fig. 2).

The solution studied (1,000 g total solution was used in each test) was placed in the reactor and the head was then bolted on to seal it (Fig. 3). Glass liners were not used in any of these tests since silicates are known corrosion inhibitors in industrial cooling water² and automotive cooling systems.³ Nitrogen was passed through each solution prior to heating to remove any trace oxygen. The solutions were heated to the desired temperature (180°F or 250°F) maintaining a stir speed of about 190 rpm throughout the test. After the test, the coupons were cleaned and weight loss was measured. Coupon weight loss was converted to corrosion rate in mils per year (mpy) using:⁴

$$\text{Corrosion rate} = \frac{\text{Wt. loss} \times 534}{(\text{Area})(\text{time})(\text{metal density})}$$

where corrosion rate is in microns per year (mpy), weight loss is in milligrams (mg), surface area of each coupon is in. ² of metal surface exposed (each about 1.5-in. long × 0.6-in. wide × 0.1-in. thick), test duration time is in hours exposed and density of each steel is in g/cm³ (carbon steel = 7.86 g/cm³, 304SS = 7.94 g/cm³, 316SS = 7.98 g/cm³, 410SS = 7.70 g/cm³). Duplicate tests were run at 180°F and 250°F to ensure result reproducibility.

Prior to testing, the carbon steel and 410SS coupons were cleaned with a 1:1 mixture of inhibited HCl (HCl containing 1,000 ppm of a corrosion inhibitor) and water for 2 to 3 min., scrubbed with warm water and dried with acetone. The 304SS and 316SS were cleaned with a mixture of 1:1 nitric acid for 2 to 3 min., scrubbed with warm water and dried



Fig. 1. The testing apparatus showing the temperature and mixer controller.

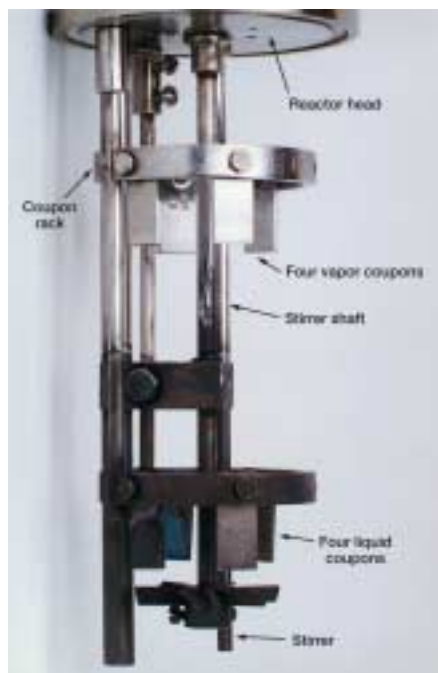


Fig. 2. Coupons mounted to the rack with Teflon spacers. The bottom coupons are immersed in liquid while the top coupons are in the vapor space.

with acetone. After the tests, all the coupons were cleaned with the 1:1 mixture of the inhibited HCl, scrubbed with warm water and dried with acetone.

Each solution was made with commercial-quality MDEA and distilled water. All the carboxylic acids and their sodium salts were the highest purity available. Sulfurous acid (a solution of 6% SO₂ in water) was used as the SO₂ source. Ammonium hydroxide (a solution of 28% to 30% NH₃ in water) was used as the ammonia source. pH measurements were performed using a meter connected to a combination pH electrode and an

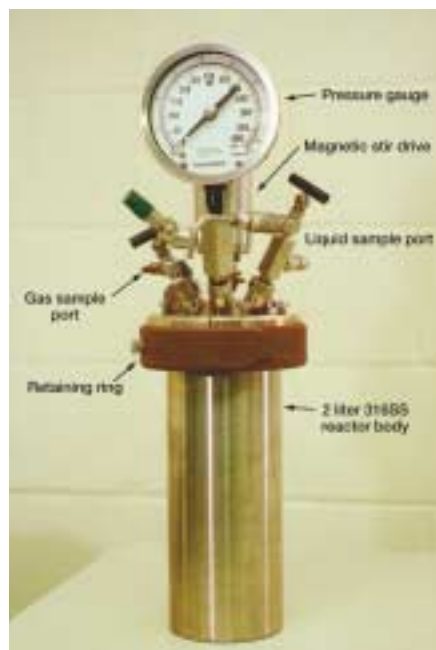


Fig. 3. The reactor with the head bolted on.

automatic temperature compensation probe. A two-point calibration was performed, using pH 7.00 buffer and pH 11.00 buffer concentrate.

Corrosivity of various anions at 250°F. Results of the 7-day 250°F carbon steel liquid corrosivity tests of 50 wt% MDEA with various added acids or sodium salts are in Figs. 4 and 5. Tests were performed with 250, 500, 1,000 and 5,000 ppm anion concentrations of oxalic acid, and 500, 1,000, 5,000 and 10,000 ppm anion concentrations of the remaining anions.

Acetic, formic, glycolic, oxalic, sulfuric, malonic and succinic acids all show higher corrosivities as the MDEA heat stable salt concentration

increases. The sodium salts all had reduced corrosivities to carbon steel compared to the MDEA heat stable salts. Our earlier work¹ showed that solution conductivity had no correlation with corrosion. However, when the calculated pH of each MDEA solution is plotted against the 250°F carbon steel corrosivity results, carbon steel corrosivity increases with lower calculated pH (higher total acid added) for formic, acetic and sulfuric acid. Oxalic acid had a higher corrosivity to carbon steel than could be attributed to pH alone.

As seen in Table 1, the equilibrium constant for the complexation of oxalic acid and Fe³⁺ is about 4 to 5 orders of magnitude larger than the complexation of acetic, formic, glycolic and sulfuric acid with Fe³⁺. As freshly exposed Fe in the carbon steel is oxidized (by the acid in solution or oxygen), the oxalic acid will chelate this oxidized metal and expose new metal to further oxidation. The net result is a significantly increased rate of corrosion than what is expected from total acid concentration or pH alone. Based on the equilibrium constants of Fe³⁺, we postulate that malonic and succinic acid might also act as chelants and, therefore, have much greater corrosivity to carbon steel than predicted by pH alone. However, as seen in Fig. 6, succinic and malonic acid corrosivities directly correlate with solution pH.

Based on these results, to maintain about 10 mpy or less corrosivity to carbon steel in the liquid phase the concentration of acetate and succinate must be less than 1,000 ppm; formate, glycolate, malonate and sulfate must be less than 500 ppm; and oxalate less than 250 ppm. Neutralization with caustic appears to reduce corrosion to carbon steel to about 10 mpy or less, as was seen by the sodium salt results in Fig. 5.

All the anions except formic acid, malonic acid and sodium thiosulfate had <0.4 mpy corrosivity to carbon steel in the vapor. All the anions (including formic acid, malonic acid and sodium thiosulfate) had corrosivities less than 0.4 mpy to 304, 316 and 410SS in the liquid and vapor. For reference, pure 50 wt% MDEA has a corrosivity rate of 0.2 mpy or less to all the liquid and vapor coupons.

As mentioned, only when the 50 wt% MDEA had added formic acid,

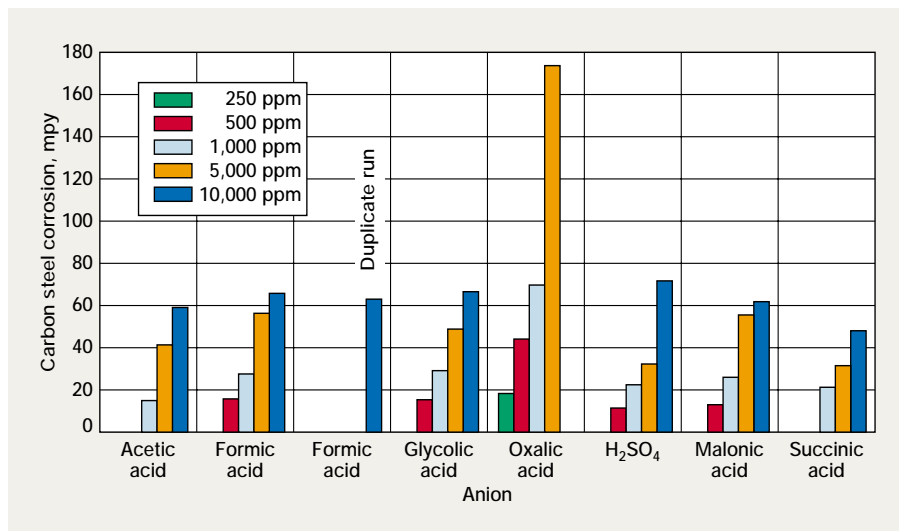


Fig. 4. Corrosivity of various added acids to MDEA towards carbon steel (liquid) at 250°F.

VARIOUS ANIONS WERE TESTED AT 180°F AND 250°F

malonic acid and sodium thiosulfate does the carbon steel vapor corrosivity exceed 0.4 mpy (Fig. 7). Malonic acid is known⁶ to decompose (presumably to CO₂) near its 275°F melting point. Very likely, CO₂ (generated from malonic acid), formic acid and SO₂ (from the breakdown of sodium thiosulfate) are the active corrosion agents to carbon steel vapor coupons. Although 10,000 ppm of each of these anions result in <10 mpy carbon steel vapor corrosivity in the autoclave, plant experience (at least with formates and SO₂) suggests that the autoclave may understate true plant vapor corrosion for these compounds.

Unlike the plant stripper where constant vapor is produced by solution boiling, the autoclave prevents boiling by pressurizing the reactor to maintain constant temperature. The amount of formic acid and SO₂ constantly generated in the stripper, therefore, is significantly more than the amount of formic acid and SO₂ vapor in the autoclave.

Corrosivity of ammonia and SO₂ in MDEA at 250°F. Results of the 7-day 250°F carbon steel liquid and vapor corrosivity tests of 50 wt% MDEA with 500, 1,000, 5,000 and 10,000 ppm added SO₂ or ammonia are in Fig. 8. Adding up to 10,000 ppm ammonia in 50 wt% MDEA results in <0.6 mpy corrosivity to carbon steel liquid and vapor coupons. Adding ammonia to MDEA slightly increases solution pH (the measured pH for 50 wt% MDEA with 500, 1,000, 5,000 and 10,000 ppm added ammonia was 11.58, 11.60, 11.68 and 11.79, respectively) relative to the 50 wt% MDEA (measured pH = 11.57). Low measured corrosivities of added ammonia are consistent with our results showing that raising the pH of the MDEA solution lowers solution corrosivity and that added caustic also lowers corrosivity in plant solutions.¹

Adding even 500 ppm SO₂ (in the form of sulfurous acid, H₂SO₃, in water) into the 50 wt% solution results in high carbon steel liquid corrosivity at 250°F. It appears, however, that corrosivity decreases somewhat as the SO₂ concentration increases to 10,000 ppm. Since added acid increases MDEA solution corrosivity (Fig. 6), and the pH of 500, 1,000, 5,000 and 10,000 ppm added SO₂ was measured as 11.05, 10.67, 10.05 and 9.68, respectively, we expected that the 5,000 and 10,000 ppm added SO₂ would result in substantially higher corrosivity than observed. (Duplicate runs of added SO₂ at 5,000 ppm resulted in 10.0 and 11.1 mpy, confirming the unexpected lower corrosivity to carbon steel liquid).

It is not known if higher concentrations of SO₂ or sulfite (both good reducing agents) act as mild corrosion inhibitors or if the potentially produced sulfides, dithionites or

polythionates act as mild corrosion inhibitors in this system. The initial reaction of MDEA with sulfurous acid is to form an MDEA-sulfite heat stable salt. This MDEA-sulfurous acid reaction is an equilibrium reaction, meaning that some free SO₂ is present in the MDEA solution. The actual MDEA-sulfite/SO₂ solution composition may be even more complex, since the sulfite may undergo any of a variety of disproportionation reactions to yield MDEA-sulfates (SO₄²⁻) and MDEA-thiosulfates

Table 1. Equilibrium constants for the complexation of iron and various acids⁵

	log K (25°C, μ = 1.0)
Oxalic acid	
Fe ²⁺ [ML]/[M.L.]	3.05
Fe ³⁺ [ML]/[M.L.]	7.59
Malonic acid	
Fe ²⁺ [ML]/[M.L.]	2.17, 2.24
Fe ³⁺ [ML]/[M.L.]	7.50
Succinic acid	
Fe ²⁺ [ML]/[M.L.]	1.4 (37°C, μ = 0.15)
Fe ³⁺ [ML]/[M.L.]	6.88 (μ = 0.5)
Acetic acid	
Fe ²⁺ [ML]/[M.L.]	—
Fe ³⁺ [ML]/[M.L.]	3.2
Formic acid	
Fe ²⁺ [ML]/[M.L.]	—
Fe ³⁺ [ML]/[M.L.]	3.1
Glycolic acid	
Fe ²⁺ [ML]/[M.L.]	1.33
Fe ³⁺ [ML]/[M.L.]	2.90
Sulfuric acid	
Fe ²⁺ [ML]/[M.L.]	—
Fe ³⁺ [ML]/[M.L.]	2.0

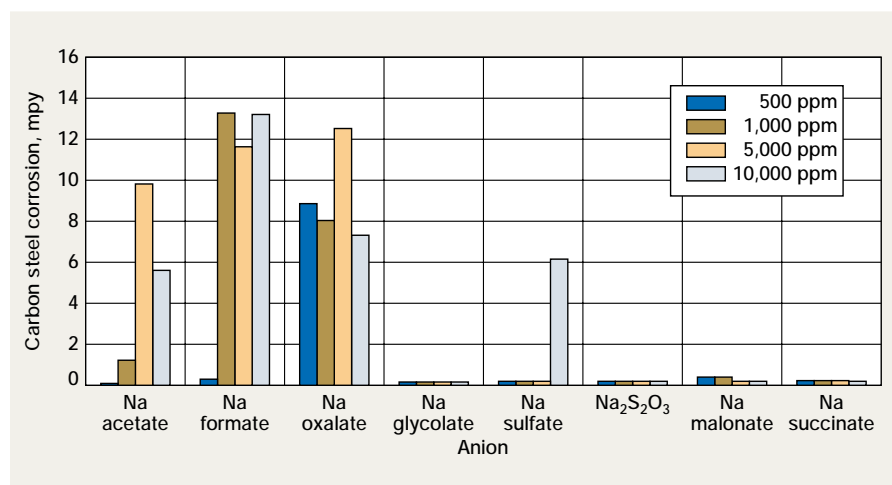


Fig. 5. Corrosivity of various added sodium salts to MDEA towards carbon steel (liquid) at 250°F.

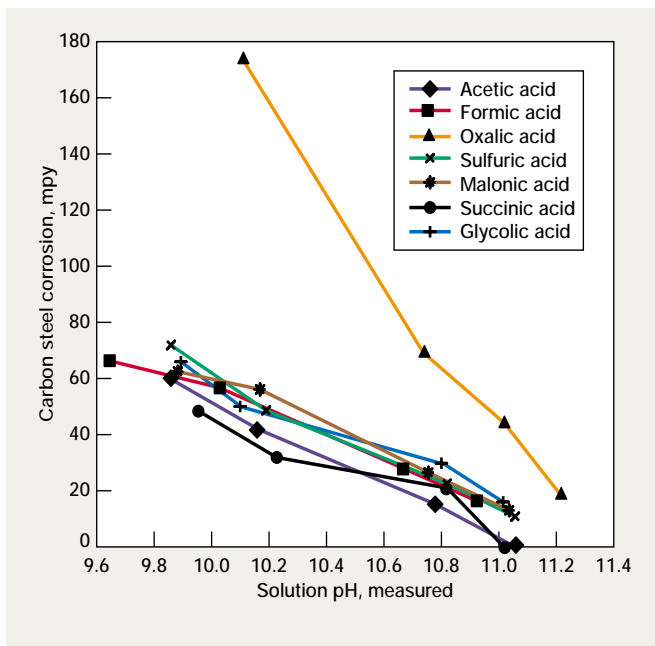


Fig. 6. Effect of pH on carbon steel liquid corrosivity at 250°F.

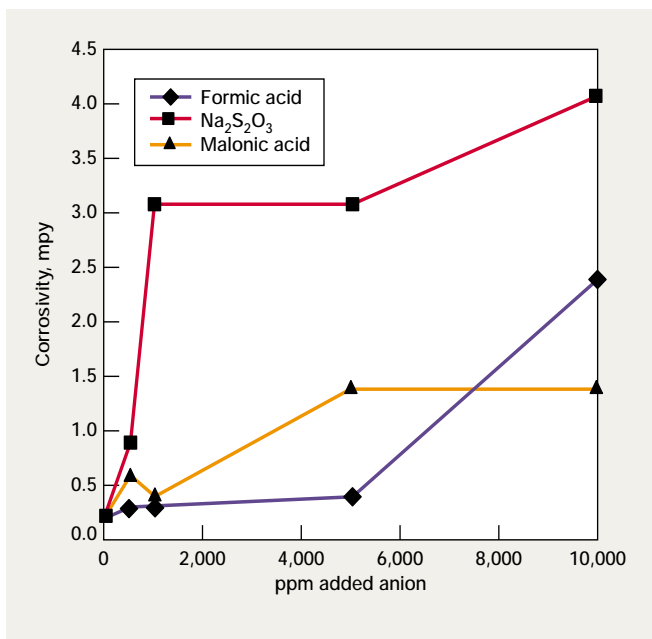


Fig. 7. Corrosivity of added formic acid, malonic acid and sodium thiosulfate to 50 wt% MDEA towards carbon steel (vapor) coupons at 250°F.

($S_2O_3^-$), MDEA-dithionites ($S_2O_4^-$), MDEA-polythionates, ($S_nO_6^-$) and MDEA-sulfides.^{7, 8}

Carbon steel vapor corrosivity rose with higher concentrations of added SO_2 . Although the corrosivity of even 10,000 ppm added SO_2 resulted in relatively low vapor corrosivity (2.5 mpy), as was explained earlier for formic acid, malonic acid and sodium thiosulfate vapor corrosivities, higher stripper corrosivities may be experienced in actual plant situations.

Stainless steel (304, 316 and 410SS) corrosivities in the liquid and vapor were all less than 0.1 mpy for 500, 1,000, 5,000 and 10,000 ppm added ammonia or SO_2 in the 50 wt% MDEA at 250°F.

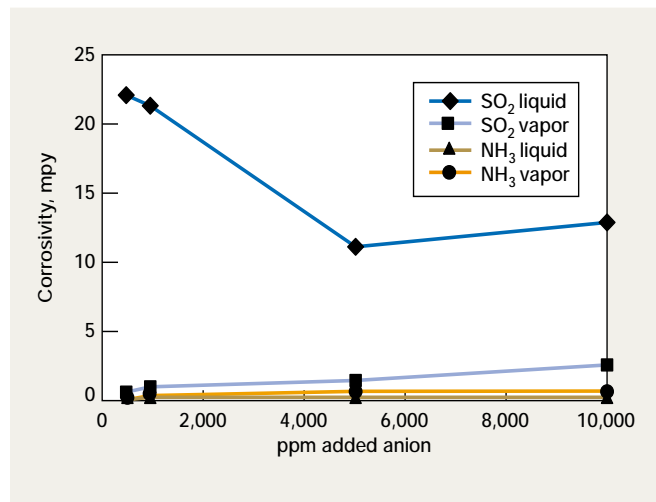


Fig. 8. Corrosivity of added SO_2 and NH_3 to 50 wt% MDEA towards carbon steel liquid and vapor coupons.

RECOMMENDATIONS

Based on these and previous¹ results, it is clear that MDEA solution corrosivity—measured by carbon steel weight loss coupons—increases as added acid lowers MDEA pH. Added oxalic acid significantly increases MDEA solution corrosivity due to chelation of the oxalate with iron. Carbon steel vapor corrosion weight loss occurs only at relatively high levels of added formic acid, thiosulfate or SO_2 . Stainless steel corrosivities (304SS, 316SS and 410SS weight loss coupons) in the liquid and vapor are less than 0.4 mpy for all the species studied. For reference, pure 50 wt% MDEA has a corrosivity rate of 0.2 mpy or less to all the liquid and vapor weight loss coupons.

Recommended levels of individual HSAS, based on limiting carbon steel coupon weight loss corrosion to less than about 10 mpy are:

Oxalate	250 ppm
Formate, glycolate, malonate, sulfite or sulfate	500 ppm
Acetate or succinate	1,000 ppm
Thiosulfate	10,000 ppm

Total HSAS level should not exceed 0.5% of the total solution. When the limit of any of these species or total HSAS is reached, pay more attention to symptoms of problems caused by heat stable salts. Foaming, diminished filter run time, solution color change and iron sulfide (or other solids) suspended in the solution are typical warning signs of corrosion problems caused by heat stable salts.

Low solution corrosivities observed when sodium salts are added to MDEA, and when caustic is added to neutralize HSAS are effective in extending the life of the MDEA solution. The amount of base added is limited by the increased solution viscosity as well as the insoluble salts formed. In general, a maximum of about 10% of total MDEA concentration can be neutralized with caustic before viscosity problems and solids problems occur.

Corrosion results with SO_2 are, to some degree, academic. Any level of SO_2 in the inlet gas will form various HSAS (i.e. sulfates and thiosulfates), for which corrosivity data has been reported. As little as 500 ppm and 1,000 ppm added SO_2 in MDEA results in 20 to 23 mpy

corrosion to carbon steel liquid coupons, so any SO₂ breakthrough should be avoided.

Added ammonia (up to 10,000 ppm) into 50 wt% MDEA results in less than 0.6 mpy corrosivity to carbon steel and stainless steel liquid and vapor coupons. Ammonia and other amines are added to boiler feed water to lower vapor corrosion by neutralizing CO₂ in steam condensate. This suggests that, by itself, small amounts of ammonia should not result in increased vapor corrosivity in amine reboilers. However, if enough ammonia is present to raise the pH of the water above 13, rapid corrosion may result.⁸

ACKNOWLEDGMENT

We gratefully acknowledge Ken Willbanks (Dow Chemical Metals Department, Freeport, Texas) for making the custom autoclave coupon racks, preparing and weighing all the coupons for testing, and for his expert advice on metal corrosion. Acknowledgment is also made to Tonni Laine (GAS/SPEC TS&D) for performing pH measurements.

Based on a presentation at The 1996 Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, March 4-6, 1996.

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