Neutralization Technology to Reduce Corrosion from Heat Stable Amine Salts

H.J. Liu and J.W. Dean
Union Carbide Corporation
P.O. Box 670
Bound Brook, New Jersey 08805

Sidney F. Bosen
Union Carbide Corporation
335 Pennbright, Suite 120
Houston, TX 77090

Technical Paper Number 572 Presented at:
NACE International, Corrosion/95
Orlando, Florida – March 26-31, 1995
Abstract

Laboratory experiments have demonstrated the corrosivity of a contaminated N-methyldiethanolamine solution from a refinery can be reduced by adding caustic or a proprietary neutralizer. A model formic acid contaminated amine solution was shown to have similar behavior.

Laboratory studies have shown there is a definite decrease in corrosivity as the pH of the amine solutions increase. Three possible mechanisms for the observed pH corrosivity behavior are discussed.

Plant experience that demonstrates the usefulness of neutralization and a novel method for dissolved solids removal are presented.

Keywords: amine, alkanolamine, heat stable amine salts, corrosion, neutralization, reclamation, undissociated acid

Introduction

Amine solutions have been used for over 60 years to remove acid gas contaminants, usually H₂S or CO₂, by reactive absorption from a wide variety of process gas streams¹, equation (1).

\[
\text{AMINE} + \text{HAcid} \rightarrow \text{AMINEH}^+ + \text{Acid}^-
\]

The acid gas is then desorbed from the amine solution in the regenerator by the reverse of equation (1). Corrosion in amine treating units has been a problem for plant operators and a topic for intensive study by corrosion engineers²⁻⁵. Much attention has been given to the effects amine type, acid gas removal service and loadings and amine degradation products.

Heat stable amine salts (HSAS) have also been implicated in causing corrosion in amine gas treating units⁴. HSAS are formed in the gas treating solution by the reaction of amine with acids, equation (1), forming salts that do not undergo the reverse of equation (1) under normal regenerator conditions. These acids mainly come from the process gas stream but can also be produced by oxidation of amines and other reactions in the amine solution. HSAS include formate, acetate, glycolate, propionate, oxalate, chloride, sulfate, thiosulfate, and thiocyanate. HSAS also impact the overall operating efficiency of the amine solution by reducing the amount of unprotonated amine. Only unprotonated amine will reactively absorb acid gases.

When corrosive or other detrimental amounts of HSAS accumulate in the solution remedial action must be taken. While there are a number of possible strategies, one that is easy to practice has been developed and incorporated into an overall Amine Management Program. This Amine Management Program includes neutralization of the HSAS with UCARSOL® DHM(¹), a proprietary neutralizer. To lessen the possibility of operational problems when concentrations of anions reach levels high enough that solids precipitate, causing fouling, under deposit corrosion and erosion, the UCARSEP® Process(¹)⁶ can be used to reduce the concentration of anions to acceptable levels without a system shut down. This paper presents laboratory and plant data that demonstrate the concepts of the Amine Management Program neutralization of MDEA HSAS and removal of ash by proprietary electrodialysis.
Experimental Procedure

Test Solutions
Reagent grade chemicals were used when possible. A used proprietary N-ethylidioethanolamine (MDEA) based amine (field) solution was obtained from a refinery system treating a cracked LPG stream. The chemical analysis is given in Table 1. The model amine solution was prepared gravimetrically to yield the following; 35 (wt%) virgin proprietary MDEA base amine, 5 wt% formic acid and balance liquid chromatography grade water. Both field and model amine solutions were neutralized to different HSAS levels with either 50 wt% sodium hydroxide or the neutralizer. Hydrogen sulfide was purchased as a mixture, 1.98 vol. % in nitrogen, from a specially gas supplier. Hydrogen sulfide content of solutions was determined by iodimetric titration and reported as mole per mol ratio to amine.

Corrosion Coupon Tests
Corrosion tests were conducted in 1 liter 304 stainless steel (UNS S31600) autoclaves equipped with an agitator and rated for 12.4 MPa (1800 psi) at 121°C (250°F) solution temperature. Autoclaves that previously contained sulfide solutions were not used for corrosion rate measurements of solutions that did not contain sulfide. Four mild steel (UNS G1018) corrosion coupons, 1.27 cm (0.5 in) X 2.54 cm (1 in), were installed at the bottom of the cell and isolated with Teflon holders to avoid any metal contact. The coupons were exposed to approximately 500 mls of test solution.

Once coupons and the test solution were in place, the autoclave was sealed. Atmospheric oxygen was removed by filling the autoclave with nitrogen to 138 kPag (20 psig) and venting to atmospheric pressure a total of five times, followed by pressuring to 690 kPag (100 psig) for one hour to ensure complete seal. Pressure was then released to atmospheric pressure prior to heating the test solution. When H₂S was needed, it was added after the pressure test with solution agitation to the desired loading, as determined by iodimetric titration. No additional fluid was added to the autoclave to make up for the small amount of liquid removed for analysis. The agitator was turned on at 200 rpm and heating initiated to a final temperature of 121°C (250°F) which was maintained for the 14 day test period. At the end of each experiment the autoclave was cooled to room temperature, and a N₂ purge applied before the autoclave was opened. Solution pH was measured at room temperature using an Orion Model 610 pH meter and an Orion combination glass electrode. Weight loss corrosion rates from the coupons were determined by following ASTM G1-90 Standard Practice by the chemical cleaning option. Reported corrosion rates are the average of three or four individual coupon measurements.

Some of the coupons were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), Energy Dispersive X-ray Spectroscopy (EDS), and Electron Spectroscopy for Chemical Analysis (ESCA) to identify surface scales.

Results

Model Solvent vs. Field Solvent
Similarity with low H₂S: Figure 1 gives corrosion rates versus HSAS content of the field solution and the model amine solutions without added H₂S. Both amines show very consistent results that corrosion rates decrease with decreased HSAS. At 12% HSAS the corrosion rate is 406 μm/y (16 mpy), at 9-10% HSAS the rate drops to 305 μm/y (12mpy) and when neutralized to 6% or lower the rate is further reduced to 25 μm/y (1 mpy) or lower. Both the field and model amine solutions exhibit similar behavior.

Similarity with H₂S: The effect of H₂S loadings at a constant 12% formate HSAS level in field and model amine solutions is given in Figure 2. Again the behavior of both amine solutions is very similar.
At 0 to 0.002 mole/mole H₂S loadings corrosion rates for both are from 381-406 μm/y (15-16 mpy), 0.01 mole/mole H₂S loading corrosion rates are reduced to 127-152 μm/y (5-6 mpy) and at 0.05 mole/mole H₂S loading corrosion rates fall to 51-76 μm/y (2-3 mpy). The reduction of corrosion rates with increased H₂S loadings indicates the iron sulfide corrosion product on the metal surface, as determined by FTIR, EDS, and ESCA, inhibits corrosion under these test conditions for both the field and model amine solutions.

The model amine shows very good quantitative consistency with the field amine, both having 12% formate HSAS, see Table 1. This suggests that the remaining 20% of HSAS in the field amine solution does not significantly contribute to the corrosion rate.

Effect of pH: Corrosion rates versus solution pH for the model amine with and without H₂S are given in Figure 3. Corrosion rates increase as solution pH values decrease, whether H₂S is present or not. It appears that as long as the amine solution has a pH above 9.5-9.6, corrosion rates are minimized. This also suggests that when these low acid gas content high HSAS amine solutions reactively absorb acid gases, the corrosivity of the solution will increase due to the lower pH of the rich amine solution.

Caution should be used in trying to generalize from this specific result to systems with different amines, anions, temperatures and concentrations. Work is in progress in our laboratories that will attempt to address these issues in a broader context.

Possible Mechanisms
The variation in corrosion rate observed as the amine solution pH is changed by adding alkali must be the result of either: 1) formation of a passivating reaction product film, or 2) change in cathodic polarization. Since iron formate salts are soluble, these can’t be responsible for passivation. Other possibilities are discussed below.

Iron oxide film hypothesis: The formation of a protective iron oxide film is generally accepted as the most common mechanism for steel passivation. Usually conditions exist where an inhibitor is present that results in the formation of an insoluble ferrous salt. While amines don’t form insoluble iron salts and the experiments excluded both inhibitors and oxygen, the formation of a protective oxide film can not be rigorously as there is a significant quantity of water present.

Weakened iron sulfide film hypothesis: Two papers ⁹,¹⁰ discuss the inhibitive properties of some forms of iron sulfide. Both conclude that some forms of iron sulfide solids are more protective than others and in the aqueous systems worked with, claim the wrong kind of iron sulfide forms are produced when solution pH is above 6.2 and below 8.8-9.5. Since the cited work was done in purely aqueous media, it is difficult to completely accept that this is also the case in an amine solution. A major flaw of this hypothesis is the behavior of the model amine solutions that contain no sulfide.

Undissociated acid hypothesis: General acid corrosion of mild steel will be considered here and since the most common material of construction in amine units in refineries is mild steel, anoly corrosion iron will be considered.

Corrosion of mild steel in acidic (pH <7) aqueous media can be described by the following reactions:

<table>
<thead>
<tr>
<th>Anode</th>
<th>Fe -&gt; Fe²⁺ + 2e⁻</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>2HX + 2e⁻ -&gt; H₂ + 2X⁻</td>
<td>(3)</td>
</tr>
<tr>
<td>Net Reaction</td>
<td>Fe + 2HX -&gt; FeX₂ + H₂</td>
<td>(4)</td>
</tr>
</tbody>
</table>
In general, the aggressiveness of a medium relates to the strength of the acid HX, since it tends to affect the degree of cathodic polarization. In amine wetted areas of the scrubbing process, acid corrosion should not occur since the pH is always alkaline, and indeed in uncontaminated systems this is the case. However, some heat stable amine salts, such as formates, are slightly regenerable to the undissociated acid and amine at high temperatures. If this occurs especially under deposits or in crevices in heat transfer areas, acid corrosion may be significant.

In a gas treating solution, it can be shown from the definitions of the two equilibria involved that at a given temperature, the concentration of undissociated HA produced by a heat stable amine salt AmH+A is:

\[
[\text{HA}] = \frac{K_1 [\text{AmH}^+] [\text{A}^-]}{K_2 [\text{Am}]}
\]

where \([\ ]\) denotes concentration in moles/liter
HA is undissociated acid
\(K_1\) is the acid dissociation equilibrium constant for the protonated amine
\(K_2\) is the acid dissociation constant of HA
AmH+ is protonated amine
Am is free base amine
A- is the anion from acid HA

For the case of 5 wt% MDEA as the formate salt in 30 wt% MDEA, at a stripper temperature of 121°C (250°F) with no acid gas loading, the undisocciated formic acid is calculated as (using 1.05 gm/l as the density and 119 as the molecular weight for MDEA):

\[
[\text{FormicAcid}] = \frac{10^{-7} \times 0.05 \times 1050 \times 0.05}{1.07 \times 10^{-4} \times 0.30 \times 119} = 6.87 \times 10^{-5} \text{ molar} = 3 \text{ ppm wt}
\]

While this may not seem high, in the context of corrosion inhibitors being effective at 20 ppm, it may be sufficient to produce corrosion. If corrosion does consume undissociated acid, it is immediately replaced by re-establishment of the equilibrium so that corrosion can proceed continuously.

Using the above relationships, amounts of undissociated formic acid were calculated and are plotted versus corrosion rate in Figure 4. The data for the field and model solvents were combined and categorized on whether or not sulfide was present. As was seen earlier, sulfide inhibits corrosion under these test conditions.

Work is continuing in our laboratories on other HSAS anions to further test these hypotheses. If the undissociated acid hypothesis is correct then other organic and inorganic acids with different acid pKa's should have corrosion rate versus solution pH profiles that are similar to the one obtained for formic acid but have different pHs where corrosion rates sharply increase. These pHs should also follow the same trend as the pKa of the acid. If the pH where corrosion rates rapidly increase is roughly the same for these other HSAS, then the mechanism has to be related to weakening of the protective film(s).
Neutralization Advantages
Comparison between the neutralizing agent and caustic neutralization: No discernible differences in corrosion rates were observed when the two amine solutions were neutralized with either caustic or the neutralizer. What has been observed in field practice is that plant personnel using caustic can more easily over neutralize the amine solution which results in poorer acid gas removal and in some cases rapid and catastrophic production of solids.

Both caustic and the neutralizer increase the amount of amine available in the circulated amine solution for acid gas removal.

The neutralizing agent was used to neutralize heat stable amine salts of an MDEA-based solvent in a second refinery. Figures 5 and 6 shows the before and after effects of neutralization on some operational measurements such as heat exchanger efficiency, pressure drop on tube sides of heat exchanger, and pressure drop in the absorber in a six month time period. Without using neutralization (Figure 5), the system experienced difficulties in maintaining steady operation conditions. With neutralization (Figure 6), the operation upsets were drastically reduced. Table 2 also gives the number of times remedial action (washing heat exchangers, absorber trays, and changing filters) was needed to correct an operational problem before and after neutralization with the neutralizing agent at this refinery. Remedial action was reduced after neutralization was implemented.

Electrodialysis Process
When the inorganic salts resulting from neutralization (not amine salts) accumulate to a certain level, fouling and foaming may occur due to solids precipitation. A clean-up of the solvent is required. There are a number of choices available to remove excessive amounts of dissolved solids such as, purge and make up, amine solution change out, ion exchange and electrodialysis.

Electrodialysis technology: The electrodialysis process uses specially selected ion exchange membranes arranged in an electric field to remove electrically charged species from the solution. Two types of ion exchange membranes are used simultaneously - one type selective to cations such as sodium, and potassium; the other type selective to anions such as chloride, nitrate, formate, acetate, oxalate, thiocyanate, phosphate, citrate, and sulfate. Figure 7 illustrates the separation of cations and anions by means of selective ion transport across permeable membranes under the influence of an electrical potential. Cation or anion permeable membranes allow concentration of the impurities in a "waste brine" stream.

HSAS have an amine molecule tied up in the protonated cation form. When salts are removed by this commercial process, the amine can be also removed. This increases the amount of amine lost to the brine solution. Ash salts are salts that have an inorganic cation. These salts are formed by adding the neutralizing agent or caustic to HSAS (neutralization) to release amine. Thus it is desirable to neutralize all HSAS prior to electrodialysis.

Advantages of the electrodialysis process: The electrodialysis process will typically be applied after heat stable amine salts neutralization with the neutralizing agent or caustic has resulted in ash levels of over 5 wt%. This process has successfully removed 10 wt% heat stable amine salts/ash salts down to less than 0.5 wt%.
Several features and advantages of this electrodialysis process are indicated as follow:

- Very low energy costs and solvent losses as compared to other separation technologies such as ion exchange and vacuum thermal distillation.
- The on-line process technology can be applied to a slipstream of the operating solution so that the amine unit does not have to be shut down while reclaiming.
- The flow to the electrodialysis unit is so small that it will not affect the regular operation conditions in the amine unit.

Case study of the electrodialysis process: Table 3 shows changes in solution analysis of an MDEA-based solvent with electrodialysis treatment. Formate was reduced from 58,000 ppm to 10,500 ppm; acetate from 4,000 to 2,400 ppm; thiocyanate from 21,500 to 900 ppm. The total anions were reduced from 83,000 ppm to only 13,800 ppm. Total ash salts were reduced from 11.6% to 1.6%. Heat stable amine salts remained almost constant and low enough to not cause any observed unit corrosion.

Conclusions

An Amine Management Program to resolve corrosion issues of HSAS in MDEA based amine gas treating units has been developed and demonstrated. Laboratory studies have shown neutralization of formic acid HSAS reduces the corrosivity of MDEA based amine solutions. Plant experience indicates the laboratory data can be extended to plant situations with MDEA base amine solutions. A novel method for removal of accumulated inorganic salts (ash) has also been presented.

Acknowledgments

The authors wish to express their appreciation to the following people for their dedicated work and helpful discussions: M. G. Pavelcha, P. J. Kroposky, G. Latyschow for providing laboratory experiments, Dr. D. Back for analytical assistance, Dr. L. Hakka for anion chemistry and undissociated acids, Dr. R. G. Asperger and M. Fortin for consulting on corrosion testing, Dr. R. A. Gregory and Dr. D. Burns for providing information on the electrodialysis process and other colleagues for plant samples and data.

References

Table 1
Composition of Field MDEA Amine Solution Before Neutralization and HSAS Contribution of Each Anion Present.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit of Measurement</th>
<th>Found</th>
<th>% HSAS&lt;sup&gt;(a)&lt;/sup&gt; Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine</td>
<td>Weight %</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>mol/mol</td>
<td>.002</td>
<td></td>
</tr>
<tr>
<td>Formate</td>
<td>Ppmw</td>
<td>45,000</td>
<td>11.88</td>
</tr>
<tr>
<td>Acetate</td>
<td>Ppmw</td>
<td>5,000</td>
<td>1.01</td>
</tr>
<tr>
<td>Chloride</td>
<td>Ppmw</td>
<td>200</td>
<td>0.07</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Ppmw</td>
<td>100</td>
<td>0.02</td>
</tr>
<tr>
<td>Oxalate</td>
<td>Ppmw</td>
<td>100</td>
<td>0.02</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>Ppmw</td>
<td>600</td>
<td>0.12</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>Ppmw</td>
<td>3,500</td>
<td>0.72</td>
</tr>
<tr>
<td>Total anion</td>
<td>Ppmw</td>
<td>54,500</td>
<td></td>
</tr>
<tr>
<td>Total HSAS</td>
<td>Weight %</td>
<td>13.84</td>
<td></td>
</tr>
</tbody>
</table>

<sup>(a)</sup> HSAS expressed as wt% MDEA

Table 2.
Neutralization of the Second Refinery MDEA Base Solution with the Neutralizing Agent

<table>
<thead>
<tr>
<th>Type of remedial action</th>
<th>6 months prior to neutralization</th>
<th>6 months after neutralization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of heat exchanger water washes</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Number of absorber tray water washes</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Number of particulate filter changes</td>
<td>16</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3
Plant Trial of Electrodialysis<sup>6</sup> Salt Removal

<table>
<thead>
<tr>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formate ppmw</td>
<td>57,747</td>
</tr>
<tr>
<td>Acetate ppmw</td>
<td>3,789</td>
</tr>
<tr>
<td>Thiocyanate ppmw</td>
<td>21,462</td>
</tr>
<tr>
<td>Total Anions ppmw</td>
<td>82,998</td>
</tr>
<tr>
<td>HSAS %</td>
<td>1.6</td>
</tr>
<tr>
<td>Total ash</td>
<td>11.6</td>
</tr>
</tbody>
</table>
Figure 1
Effect of formate HSAS on corrosion rate for field and model MDEA solutions

Figure 2
Effect of H$_2$S loading on field and model MDEA solution corrosion rates
Figure 3
Effect of H$_2$S on model MDEA solution rate versus room temperature pH

Figure 4
Relationship between corrosion rates and calculated undissociated formic content of MDEA solutions with and without H$_2$S present.
Figure 5
Plant operating parameters versus time before neutralization

Figure 6
Plant operating parameters versus time after neutralization with the neutralizing agent
Figure 7
Schematic of the electrodialysis cell

![Schematic of the electrodialysis cell](image)
When considering the use of any Dow products in a particular application, you should review Dow’s latest Material Safety Data Sheets and ensure that the use you intend can be accomplished safely. For material Safety Data Sheets and other product safety information, contact your Dow representative or the nearest sales office at the numbers listed below. Before handling any other products mentioned in the text, you should obtain available product safety information and take necessary steps to ensure safety of use.

No chemical should be used as or in a food, drug, medical devise, or cosmetic, or in a product or process in which it may contact a food, drug, medical device, or cosmetic until the user has determined the suitability and legality of the use. Since government regulations and use conditions are subject to change, it is the user’s responsibility to determine that this information is appropriate and suitable under current, applicable laws and regulations.

Dow requests that the customer read, understand, and comply with the information contained in this publication and the current Material Safety Data Sheet(s). The customer should furnish the information in this publication to its employees, contractors, and customers, or any other users of the product(s), and request that they do the same.

To learn more, contact
The Dow Chemical Company
Midland, Michigan 48674 U.S.A.

For More Information
In the United States: call toll-free 1-800-447-4369 or 1-800-UCARSOL
In Canada: call toll-free 1-800-447-4369 • call 1-403-267-3508 • fax 1-989-832-1465
In Northern Europe: call +32 89 51 1022
In Southern and Eastern Europe, Middle East and India: call 49 7227 91 3814
In the Pacific: call toll-free +800-7776-7776 • fax toll-free +800-7779-7779
In China: call toll-free +10-800-600-0015 • fax toll-free +10-800-600-0017
In South and Latin America: call 55 11 5188 9555
In Mexico: call 52 55 5201 4700
In Other Global Areas: call 1-989-832-1560 (USA) • fax 1-989-832-1465
Or visit us at www.dowgas treating.com

NOTICE: No freedom from any patent owned by Seller or others is to be inferred. Because use conditions and applicable laws may differ from one location to another and may change with time, Customer is responsible for determining whether products and the information in this document are appropriate for Customer’s use and for ensuring that Customer’s workplace and disposal practices are in compliance with applicable laws and other governmental enactments. Seller assumes no obligation or liability for the information in this document. NO WARRANTIES ARE GIVEN; ALL IMPLIED WARRANTIES OR MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ARE EXPRESSLY EXCLUDED.

Published Month Year.