# Understanding corrosion in alkanolamine gas treating plants
## Part 1 & 2

Proper mechanism diagnosis
optimizes amine operations

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## PART 1

# Understanding corrosion in alkanolamine gas treating plants

## Proper mechanism diagnosis optimizes amine operations

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Corrosion in alkanolamine gas treatment plants results in unscheduled downtime, production losses, reduced equipment life and even injury or death. Although it is virtually impossible to eliminate, it can be controlled and minimized. Design engineers and plant operators must understand how corrosion affects an amine plant. Some key areas on which to focus are: corrosion mechanisms, different corrosion types, corrosion-contributing factors and preventive measures. Designers can emphasize preventive measures with design considerations, operating parameters and solvent choice.

Diagnosing the correct type(s) of corrosion that occur in amine systems is half of the problem. This simple review outlines the various corrosion types for alkanolamine processes and the conditions that frequently occur. Once you have determined your corrosion problem, the preventive design suggestions remedy most plant problems.

**Amine plants' history.** Regenerative processes have used alkanolamines for $CO_2$ and $H_2S$ removal since the early 1930s. However, removing $H_2S$ and/or $CO_2$ with alkanolamine-based gas conditioning solvents posed its own problems—corrosion. The amine itself isn't the culprit, but the acid gas that the amine absorbs is. It has been shown that carbon steel exposed to alkanolamines under an inert gas pad has lower corrosion rates than those exposed to a water solution under similar conditions.

Extensive corrosion data proves that acid gas with alkanolamines does affect corrosion rates. Fig. 1 for monoethanolamine (MEA) shows that not only does the acid gas have an effect, but the acid gas type and the ratio of $H_2S$ to $CO_2$ also impacts the corrosion rate.[1] Data suggest that MEA with $H_2S$ or $CO_2$ alone is more corrosive than a mixture of the two. In Fig. 2, the effect of acid gas loading is shown. As loading increases, corrosion rates also increase.[2] From Fig. 3, the data correlates elevated corrosion rates at higher temperatures.[3] Similar data (Fig. 4) for diethanolamine (DEA) reinforce the same effects of
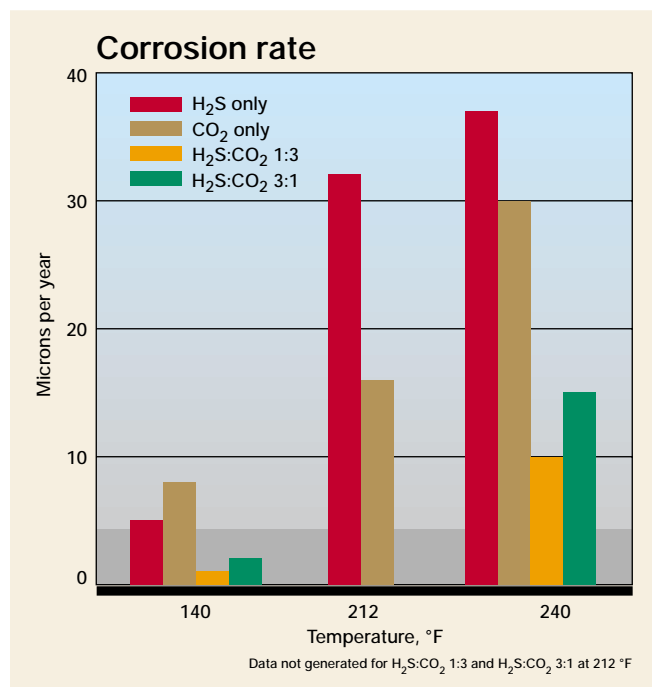


Fig. 1. Corrosion rates for 15% MEA with carbon steel.

acid gas and temperature as in Figs. 1 to 3. However, there is no correlation that predicts corrosion behavior with mixtures of $H_2S$ and $CO_2$ in MEA or DEA service. Nevertheless, plant data indicate that in predominantly $CO_2$ service, small quantities of $H_2S$ have a strong passive influence.[4] DEA corrosion data (Fig. 4) closely parallel the MEA data. DEA is generally considered less corrosive than MEA, but only in relative terms.

Corrosion testing of carbon steel with methyl diethanolamine (MDEA)/$CO_2$ indicates that there may be an advantage to using MDEA from a corrosion standpoint.[5] Fig. 5 compares corrosion results of MEA, DEA and MDEA. MDEA has significantly lower corrosion rates than MEA or DEA. Plant operating data confirm MDEA laboratory corrosion test results. Also, Fig. 5 indicates that higher amine concentrations are more corrosive. While MDEA is not
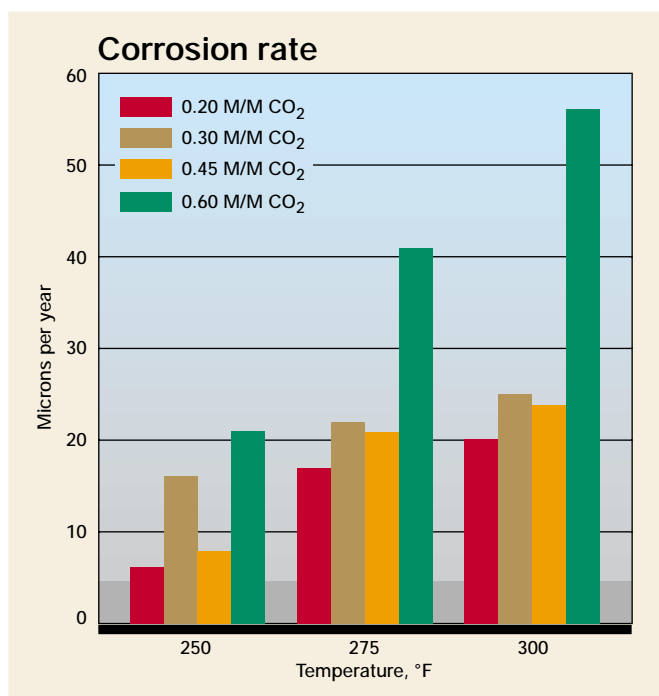
## Corrosion rate



**Fig. 2.** Corrosion rates for 20% MEA and $CO_2$ only with carbon steel.
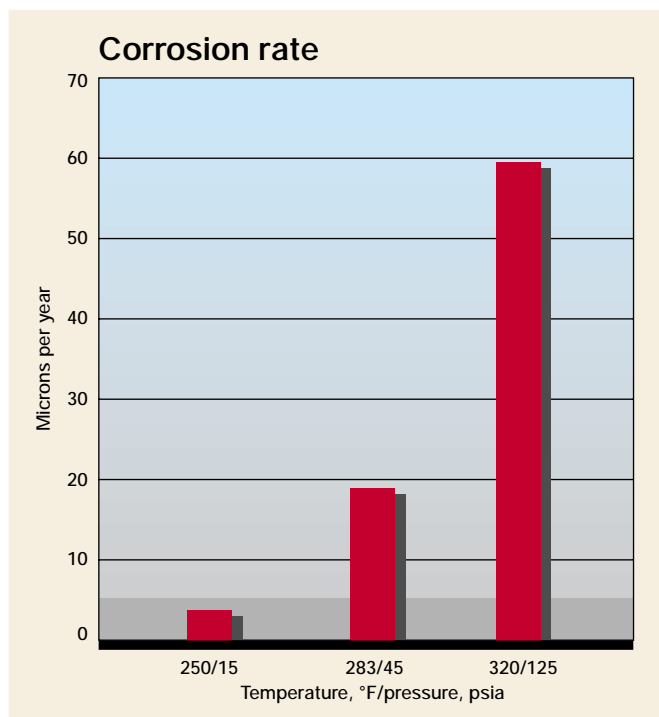
## Corrosion rate



**Fig. 3.** Corrosion rates for 20% MEA and $CO_2$ atmosphere with carbon steel.

immune to corrosion, it has inherently lower corrosivity and can be used in mixed acid gas applications to reduce corrosion tendencies. DEA has also exhibited good corrosion service in mixed acid gas situations.

Corrosion in alkanolamine gas treatment units generally focuses on the cross exchanger's rich side, rich-amine piping after the cross exchanger, the still and the reboiler, where free acid gas and higher temperatures are the main driving forces for corrosion.

**Types of corrosion.** Most corrosion failures in alkanolamine service are attributed to free acid gas and high temperature. Other factors account for many corrosion experiences. Studying different types of corrosion reveals other means by which corrosion occurs.

**General corrosion.** This is the most widely recognized form and is characterized by uniform material deterioration over the entire exposed area.[6] Although this corrosion type destroys a great deal of material annually, equipment life can be accurately monitored and predicted by simple corrosion tests. Tests include in-line corrosion probes, coupons or ultrasonic thickness testing. General corrosion rates have been established for amine treatment plants based on over 50 years of operating experience with different metallurgy types with corrosion allowances set accordingly.

Unfortunately, most corrosion failures in amine service are not general corrosion, but localized attack. Localized corrosion usually occurs in specific areas and goes undetected until an unexpected or premature failure occurs.[6]

**Galvanic corrosion.** When two dissimilar metals are coupled together through a conducting electrolyte, an electrical potential is set up between the two metals, which causes the less resistant metal to corrode.[6] For example, galvanic corrosion occurs when stainless steel trays are held together with carbon steel bolts. The small carbon steel bolts, acting as electrical anodes, preferentially corroded are over the more resistant stainless steel tray because of the difference in electrical potential between the two metals.[7] Another example of galvanic corrosion is pump shafts and valve stems made of steel, or more corrosion-resistant material failing because of contact with more noble graphite packing.[6] Area effects are also important when considering galvanic corrosion.[6] In the earlier tray example, if carbon steel trays were held together with stainless bolts, then corrosion would be minimized due to the very large anode (tray) and the small cathode (bolt).

**Crevice corrosion** results when a concentration cell forms in the crevice between two metal surfaces or a metal and a non-metallic material. Crevice corrosion is caused by oxygen depletion, changes in acidity or by inhibitor depletion in the crevice.[6] Chloride ions contribute greatly to this corrosion. Frequently, crevice corrosion is found at points where tubes are attached to the heat exchanger's tube sheet and is more common in the reboiler.[8] One way to prevent this type of corrosion is to weld tubes to the tube sheet rather than roll them.[6] Crevice corrosion also occurs under deposits in stagnant areas. Filtration can prevent solid deposition.

**Pitting corrosion** is a highly localized and intense corrosion that results in rapid and destructive penetration at relatively few spots. Equipment failures due to pitting are often quite sudden and unexpected. Halide ions, particularly chlorides, and stagnant areas usually promote pitting-type corrosion. For plants using corrosion inhibitors, inhibitor concentration is critical when controlling this type of corrosion. If the inhibitor does not completely stop the pitting, the intensity of the pitting can increase.[6] Carbon steel is more resistant to pitting corrosion than stainless steel.

**Intergranular corrosion** occurs selectively at metallic grain boundaries and is most frequently found in stainless steels. Chromium carbide precipitation promotes corrosion in grain boundaries by improper heat treatment or welding techniques. Heat treatment outside the sensitizing range and low carbon stainless steels such as 304L

and 316L have helped reduce intergranular corrosion. Two other forms of intergranular corrosion, weld decay and knife line attack, develop from improper welding or lack of post weld heat treatment. Use electric arc welding, instead of gas welding, to prevent weld decay and knife line attack on stabilized stainless steels.[6]

**Selective leaching** is the removal of one element from a metallic alloy by a corrosion-like process.[6] A classic example of this corrosion type is the selective leaching of copper out of Monel or 70/30 Cu/Ni when oxygen is present.[8] Generally, selective leaching is not a concern since copper-bearing alloys are not used frequently and oxygen is absent from most systems.

**Erosion corrosion** is an increase in the rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and a metal surface.[6] Solids particles or gas bubbles suspended in the liquid aggravate this type of corrosion. Erosion corrosion is prominent in plumbing bends, elbows, tees and valves as well as in pumps, blowers and impellers. Velocity, turbulence and the stability of protective films also affect the degree of erosion corrosion. Impingement attack (corrosion caused by turbulent flow) and cavitation damage (caused by vapor bubble formation and collapse in a liquid near a metal surface) are two examples of erosion corrosion.[6]

**Stress corrosion cracking** results from the simultaneous presence of tensile stress and a corrosive media. Stress can be either residual internal stress in the metal or an externally applied stress.[6] Chloride-induced stress corrosion cracking is a widely recognized form of this type of corrosion. Other factors that affect the extent of stress corrosion cracking are: operating temperature, amine solution's chemical composition, metal composition and structure.[9]

Stress corrosion cracking in amine units has received considerable attention since a recent catastrophic rupture of an MEA contactor at a U.S. refinery that resulted in 17 fatalities and extensive property damage.[10] Although this failure was later attributed to hydrogen-induced cracking, a joint API/NACE committee conducted a stress corrosion cracking survey of amine plants after this incident. Survey results indicated that stress corrosion cracking is most prevalent in MEA units and to a much lesser degree in DEA and MDEA units.[10]

**Hydrogen damage** refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen.[6] In amine service, hydrogen damage is limited to blistering, embrittlement or attack. Amine solutions containing hydrogen sulfide or cyanide can promote either hydrogen embrittlement or sulfide stress cracking.[6,10] Hydrogen blistering can occur in corrosive amine solutions that contain hydrogen evolution poisons, such as sulfides, arsenic compounds, cyanides and phosphorous-containing ions.[6] Often, hydrogen-associated failures are often mistaken for stress-corrosion cracking. This may account for the high rate of stress-corrosion cracking incidents reported in MEA service.

**Mechanical design considerations.** Several mechanical design criteria can minimize corrosion. Some criteria are based on common sense, but others have been developed from past operating experiences.

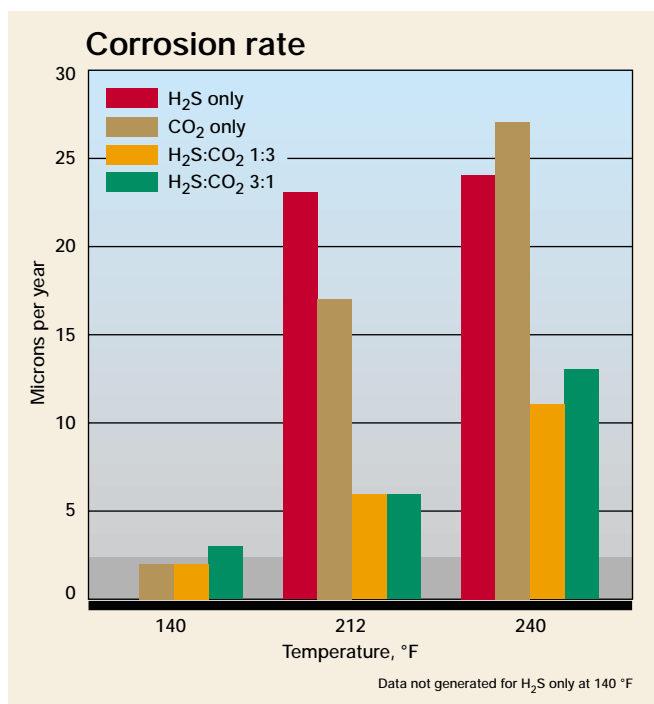**Metallurgy.** Ideally, from an up-front capital cost per-



**Fig. 4.** Corrosion rates for 20% DEA with carbon steel.
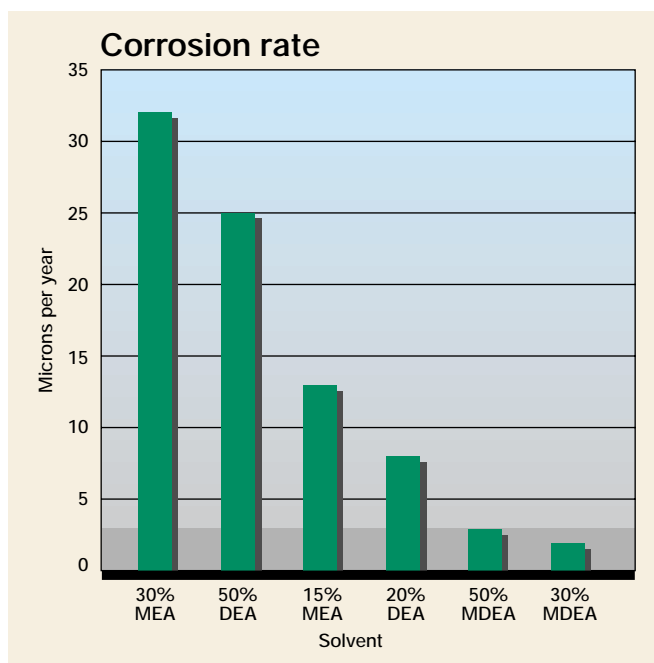


**Fig. 5.** Hot skin corrosion test with $CO_2$ atmosphere and carbon steel, 7-day test at 210°F.

**Table 1. Corrosion rates of MEA and DEA with various metals**

| | 20% MEA, 240°F No AG | 20% MEA, 240°F $CO_2$ sat'd | 20% MEA, 230°F $H_2S/CO_2$ | 15% DEA, 230°F $H_2S$ |
|---|---|---|---|---|
| Data source | Lab | Lab | Plant | Plant |
| Metal | Corrosion rate, microns per year | | | |
| Monel | 1.0 | 3.0 | 1.3 | 2.1 |
| 70/30 CU/NI | — | — | 10.0 | * |
| 304 SS | <1.0 | <1.0 | <1.0 | <1.0** |
| 316 SS | 1.0 | <1.0 | <1.0 | — |
| 410 SS | — | — | — | <1.0*** |
| Carbon steel | 1.0 | 103.0 | 5.4 | * |

* Coupon completely destroyed during test period
** Pitted to a maximum depth of 0.002 in. during test period
*** Pitted to a maximum depth of 0.013 in. during test period

## Corrosion rate
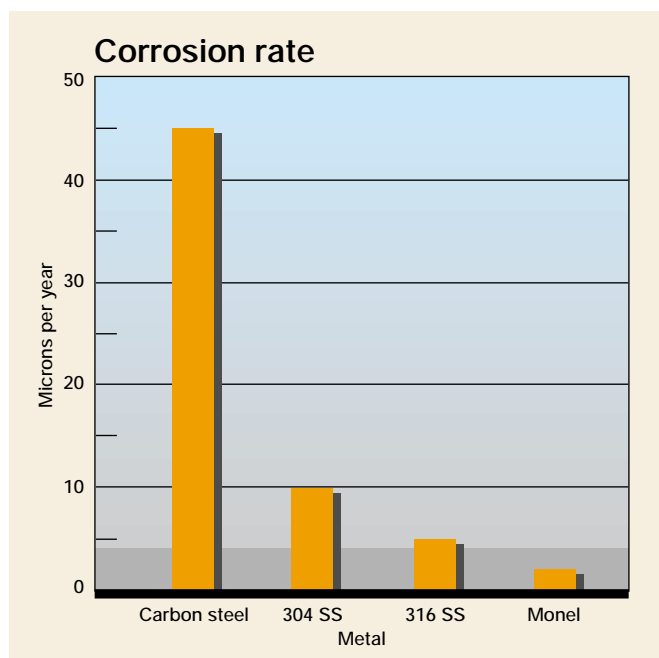


**Fig. 6.** Corrosion rates of different metals with 30% MEA at 250°F and $CO_2$ saturated.
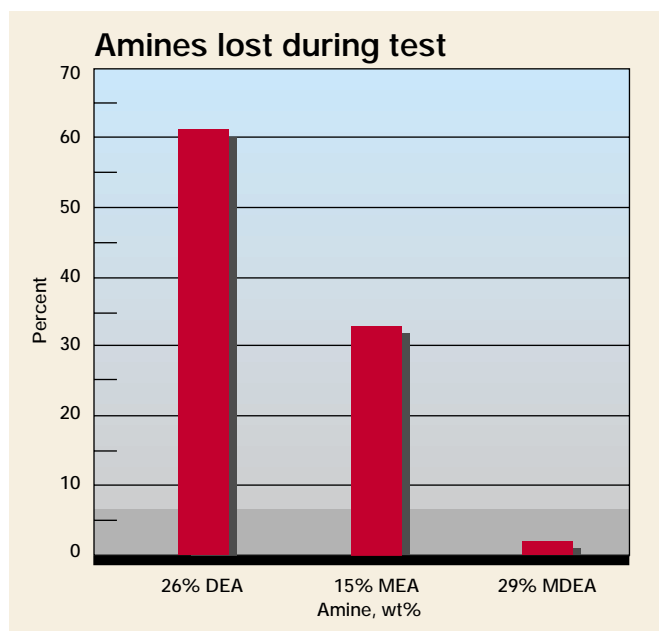
## Amines lost during test



**Fig. 7.** Oxygen degradation with MEA, DEA and MDEA.

spective, one would like to fabricate an amine plant solely from carbon steel. Plants constructed of carbon steel have operated successfully without corrosion problems, but process concessions required high energy consumption. Substituting stainless steel in key plant areas (rich-amine piping, cross exchanger tubes and internals of the reboiler and stripper) will provide adequate corrosion protection and allow the plant to be operated with optimum energy input. Table 1 and Fig. 6 show corrosion rates for different amines with various alloys under both laboratory and plant conditions.[11–13] Carbon steel exhibited corrosion rates, depending on the test conditions, from <1 mils per year to > 100 mils per year. Stainless steel, in particular 316, performed adequately under all test conditions. 410SS appears anodic to carbon steel in some applications. Always use caution when specifying this material.

While some investigators have shown acceptable cor-

rosion rates with Monel and other copper-bearing alloys,[11] its use is discouraged due to unfavorable plant experience. Other evidence suggests that oxidizers and amine degradation products enhance corrosion of these alloys. Table 2 lists general metallurgical guidelines for amine plant construction. Avoid dissimilar metals usage to minimize bimetallic or galvanic corrosion.[14]

**Flow in piping and vessels.** Minimizing acid gas flashing, which is keeping the $CO_2$ and/or $H_2S$ in solution, is a major factor when controlling corrosion in amine units. Several investigators have recommended 3 ft/s as the maximum solution velocity for carbon steel pipe.[14–16] Solution velocities of 5 to 8 ft/s can be used with stainless steel piping due to its higher inherent corrosion resistance. Other design practices that will reduce turbulence and localized pressure drop are: install long radius elbows and seamless pipe where the solution changes direction, eliminate flow restrictions (i. e. flange gaskets protruding into the line), repair tubes that are not flush with tube sheet, do not use threaded connections or socket weld fittings and install long tapered sections (optimum cone angle of 7°) when changing cross sectional area of flow.[16,17] Prevent pump cavitation by minimizing suction pressure drop (reduced velocity, straight runs of pipe, etc.) and providing sufficient NPSHA to inhibit small gas bubble formation.[14,17]

**Control valves.** The location of control valves helps to reduce acid gas flashing and related corrosion. Locate stripper or reboiler level control valves downstream of the lean amine cooler.[14] Locate the absorber level control valve downstream of the lean/rich cross exchanger if a rich amine flash tank is not included. If a flash tank is used, then install the valve between the absorber and exchanger. [14,16] When two-phase flow exiting a control valve is inevitable, closer attention to the design of the control valve and

**Table 2. Metallurgical guidelines
for amine plant construction**

| Item | Material | Alternate material |
|---|---|---|
| Absorber | | |
|   Shell | Carbon steel | — |
|   Internals | Carbon steel | Stainless steel |
| Lean/rich exchanger | | |
|   Tubes (rich) | Stainless steel | — |
|   Shell (lean) | Carbon steel | — |
| Lean amine cooler | | |
|   Tubes | Carbon steel | Stainless steel |
|   Shell | Carbon steel | — |
| Carbon bed | | |
|   Shell | Carbon steel | — |
|   Internals | Stainless steel | — |
| Regenerator | | |
|   Shell | Carbon steel | — |
|   Internals | Stainless steel | — |
| Reboiler | | |
|   Tubes | Stainless steel | — |
|   Shell | Carbon steel | — |
|   Tube sheet | Carbon steel | — |
|   Steam side channels | Carbon steel | — |
| Reflux condenser | | |
|   Tubes | Carbon steel | Stainless steel |
|   Shell | Carbon steel | — |
| Reflux drum | Carbon steel | — |
| Pumps | | |
|   Cases | Carbon steel | — |
|   Impellers | Stainless steel | — |
| Piping | | |
|   Rich amine | Stainless | — |
|   Lean amine | Carbon steel | Stainless steel |

General carbon steel, 304 SS, 304L SS, 316 SS and 316L SS are recommended for general use. Do not use copper, brass or other copper bearing alloys.

downstream piping will minimize the potential effects of high velocity two-phase flow.

**Filtration.** Adequate mechanical and carbon filtration can significantly reduce corrosion in amine units. Not only can filtration reduce particles that promote erosion corrosion and abrasion of passive films, it can effectively remove hydrocarbons and, to a lesser extent, amine degradation products.[18] Filter arrangements should remove all particles greater than 5 microns.[14] In dirty service, incorporate a spare parallel mechanical filter into the design. Exercise caution with paper and sock-type filters. These filters can collapse and recontaminate the solution.[14]

Mechanical filters should be installed upstream and downstream of the carbon bed. The upstream filter acts as a "guard" filter and extends carbon life. The downstream filter prevents carbon fines from entering the system. In sour service, a full rich stream filter is recommended. In $CO_2$-only applications, a slip stream filter on the lean stream is adequate. Some plants have incorporated both rich and lean filtering with particular success.

**Stress relieving** of amine plant hardware has been recommended for many years.[14,19] Although cracking does occur in vessels and piping that were stress-relieved, the NACE/API survey showed that most cracking occurred in nonstress-relieved equipment. Stress relieving should be applied for all types of amine service and is particularly important in MEA units due to their poor cracking record. And strong evidence suggests that they are specially prone to cracking.[20,21]

**Miscellaneous.** There are a few other design considerations that can minimize corrosion. Inlet knockouts are useful in preventing brine from entering the amine solution. Remember, chlorides can promote pitting, stress corrosion cracking and crevice corrosion. Inert or sweet gas blanketing of the surge drum and storage tank will minimize oxidation of the amine and prevent degradation product formation.[14] DEA is particularly susceptible to oxygen degradation and extra attention should be given to excluding oxygen in DEA plants (Fig. 7).[22]

Regeneration pressure should be kept low with the bulk amine temperature not exceeding 255°F and the reboiler heat source not exceeding 300°F. Operating within these guidelines will minimize thermal degradation of the amine. Designing or modifying reboiler tube bundles to minimize binding by omitting tubes in an "X" or "V" pattern can reduce localized overheating. Tubes arranged in a square pitch tube pattern simplify cleaning. Install multiple vapor-exit lines to prevent stagnant areas of acid gas.[14,16]

**Next month: Part 2.** Corrosion case histories in amine treatment look at actual plant problems. These are excellent examples on how to troubleshoot potential corrosion problems in your plant. Also, each example has observa-tions and recommended corrections. The examples are definite plant notebook additions for later reference.

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## The authors

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**Tom Bacon** is a project manager for the GAS/SPEC Technology Group of Dow Chemical, USA. His responsibilities focus on development and use of formulated amine solvents and licensed technologies for removing acid gas impurities from liquid and gas streams. He has 17 years of varied experience at Dow in research, manufacturing, process engineering, capital project management, and technical service and development. He holds a BS degree in chemical engineering from Texas A&M.

**David J. Edwards** is a senior development engineer for the GAS/SPEC Technology Group of Dow Chemical, USA. He is responsible for technical service and development of MDEA-based formulated amine solvents used to remove acid gas impurities from natural gas and synthesis gas streams. Prior to joining GAS/SPEC in 1989, he had 6 years of experience in technical sales of ion exchange resins for Dow Chemical USA. He holds a BS degree in chemical engineering from Mississippi State University.

PART 2

# Understanding corrosion in alkanolamine gas treating plants

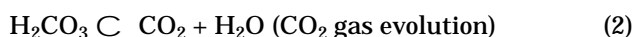## Case histories show actual plant problems and their solutions

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Proper diagnosis is half the problem and solution in alkanolamine corrosion. In Part 1, several common corrosion mechanisms were identified with amine systems. With many possible mechanisms to choose from, proper corrosion diagnosis is a cumbersome task. Unfortunately, the designer or the operations engineer must knowledgeably sift through the plant data and correctly match the symptoms or observations with the probable cause and prescribe corrective action(s).

The case histories review actual plant situations and the observations from inspection. They give great insight into a costly problem. The examples are definite plant notebook additions for later references.

As in many processes, better designs reduce costly downtime and lost production, improve equipment life and minimize operation accidents or injuries. A better understanding of parameters affecting corrosion with amines present improves process operations and allows a better amine selection.

**Amine and process parameters.** Careful selection of amine and process parameters can have a positive impact when reducing corrosion incidence. Since "free" acid gas is the primary contributor to corrosion, a brief discussion about the actual mechanism is appropriate. $CO_2$ corrosion in amine units is caused by the reduction of undissociated carbonic acid in turbulent areas where a passive ferrous carbonate scale is unable to be laid down.[23] The carbonic acid can undergo any one of these reactions:

$$H_2CO_3 + e^- \subset HCO_3^- + H \text{ (corrosion cathode)} \quad (1)$$

$$H_2CO_3 \subset CO_2 + H_2O \text{ (}CO_2\text{ gas evolution)} \quad (2)$$

The basic corrosion reaction for $H_2S$ is more straightforward:

$$Fe + H_2S \subset FeS + H_2 \quad (3)$$

However, corrosion reactions become quite complicated in mixed acid gas service. Variation in corrosion experience may be related to the dissimilarity in iron sulfide films formed. Some films are tightly adhering while others are soft or jelly-like.[24]

**Amine choice.** MEA, DEA and MDEA are the three most popular amines used for acid gas treating (Fig. 8). Historically, MEA has the worst reputation for corrosion problems. However, several investigators have shown that there is no difference in corrosion rates between the different amines when acid gas is absent.[1,3,11,25,28] MEA and DEA form degradation products when reacted with $CO_2$, but MDEA does not.[26–28] One investigator claimed that MEA/$CO_2$ degradation products can enhance corrosion, but are not responsible for corrosion alone.[2] Other studies have shown that DEA/$CO_2$ degradation products without acid gas present do not enhance corrosion.[28] If MEA, DEA and MDEA have similar corrosion rates with pure solutions and with basic degradation products with no acid gas, particularly $CO_2$, how does one explain plant and laboratory corrosion results that show MEA is more corrosive than DEA? Also, why is DEA more corrosive than MDEA? Teevens[21] may have the best answer to this question. He proposes that since MEA is a stronger Lewis base than DEA and MDEA is the weakest, reactivity plays a strong role:
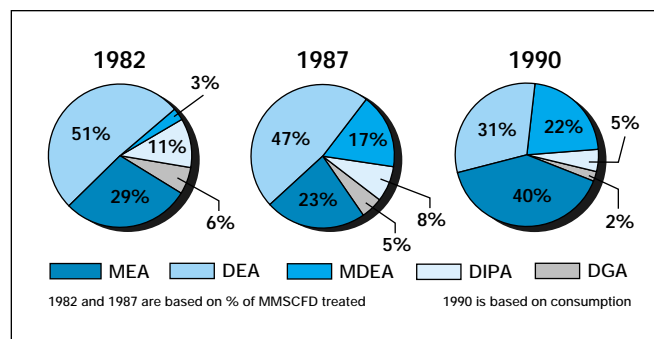


**Fig. 8.** Comparison of amine market share.

"The formation of basic degradation products is directly attributable to the reaction of $CO_2$ with primary amines and secondary amines which react to form intermediate amides, and, subsequently, their amine-carbamates which in turn, undergo internal dehydration to yield various basic degradation products. Since MEA is a much stronger Lewis base, then it is likely to form more carbamate than DEA. The production of carbamates from tertiary amines is impossible, since they fail to yield amides necessary in carbamate ion formation. The presence of amine carbamates as viable intermediary salts, may, somehow impact the corrosivity of MEA and DEA. The inability of tertiary amines to react with $CO_2$ to form amides and subsequently amine carbamates may be the vital clue as to why solvents such as MDEA are indeed

less corrosive in all aspects."

MEA, DEA and MDEA plants have proved that operating under proper conditions can minimize corrosion. However, from plant experience and laboratory corrosion data, the relative corrosivity of amines would be ranked as: MEA ○ DEA ○ MDEA with MDEA being the least corrosive. MDEA is the most forgiving amine from a corrosion standpoint.

**Amine strength and acid gas loading.** Previous data showed that as amine strength and acid gas loadings increase, corrosivity also increases. Plant histories support this trend. Higher strength amines cannot achieve high mole/mole equilibrium-rich loadings like lower strength amines can. This condition can increase the potential for acid gas flashing. Table 3 lists recommended maximum ranges for amine strength and acid gas loadings that have historically addressed corrosion concerns.

Consideration should also be given to maximum lean loadings. Table 4 lists the recommended loadings that minimize acid gas flashing in the lean circuit. These loadings should be easily achieved with a 1.0 to 2.0 m/m stripper reflux ratio.

Anions such as formate, oxalate, thiosulfate, thiocyanate and chloride that tie up the amine and are not regenerated in the plant's stripping section are called heat stable salts (HSS). While there is conflicting data on HSS's effect on corrosivity, the consensus is that HSS will enhance corrosion in alkanolamine gas treating solutions. For this reason and because HSS also reduce the acid gas carrying capacity of the amine, they should be minimized. Table 5 lists common sources for the anions and is a guide for minimizing HSS formation. As a rule, HSS should not exceed 10% of the total amine concentration.

**Corrosion inhibitors.** For many years, considerable research has been devoted to developing corrosion inhibitors, particularly for high strength amine systems. The most effective inhibitors developed were based on heavy metals such as arsenic and vanadium. However, their popularity waned due to the environmental concerns associated with heavy metals. In addition, the heavy metal inhibitors provided excellent corrosion protection for wetted areas, but they did not always protect splash and vapor regions. "Off the shelf" corrosion inhibitors based on film-forming amines have been used with limited success. These inhibitors addressed general corrosion, but were inadequate for correcting or preventing other corrosion forms. Also, inhibitors are frequently difficult to maintain. If they are not properly controlled, they can lead to more severe corrosion problems. Proper plant design and operation are the best approaches to managing amine unit corrosion.

**Makeup water.** Poor makeup water is often the source of chlorides and other contaminants that will foster corrosion. Using good quality water cannot be overemphasized. Table 6 lists minimum water quality standards.

## CASE HISTORIES

Now, here are some specific plant situations that will further explain where and how corrosion occurs in amine units.

### Table 3. Acid gas loadings

| Amine | wt% | Rich loading, m/m |
|---|---|---|
| MEA | 15 to 20 | 0.30 to 0.35 |
| DEA | 25 to 30 | 0.35 to 0.40 |
| MDEA | 50 to 55 | 0.45 to 0.50 |

### Table 4. Maximum lean loadings

| Amine | Total lean loading, m/m |
|---|---|
| MEA | 0.10 to 0.15 |
| DEA | 0.05 to 0.07 |
| MDEA | 0.004 to 0.010 |

### Table 5. Heat stable salts—common sources for the anion

| Anion | Source |
|---|---|
| Chloride | Makeup water/brine with inlet gas |
| Nitrate/nitrite | Makeup water/corrosion inhibitors |
| Sulfate/sulfite thiosulfate | Sulfur species oxidation products/ $H_2S + O_2 \subset S_2O_3$/component in gas |
| Formate/oxalate acetate | Acid in the feed gas/$O_2$ degradation/ thermal degradation |
| Thiocyanate | Reaction product of $H_2S$ and CN |
| Phosphate | Corrosion inhibitors/phosphoric acid activated carbon |

### Table 6. Water quality for amine plants

| | |
|---|---|
| Total dissolved solids | < 100 ppm |
| Total hardness | < 3 grains/gal |
| Chloride | < 2 ppm |
| Sodium | < 3 ppm |
| Potassium | < 3 ppm |
| Iron | < 10 ppm |

**Case 1. Problem:** Pitting and erosion corrosion in high loaded rich formulated MDEA at pressure letdown points. **Situation:** Treating was required for 300 psig gas with 45% $CO_2$ and 20 ppm $H_2S$ to produce fuel gas. Process design called for high rich loadings created by recirculating semi-lean and using partial stripping via 10 psig flash of the rich to the semi-lean stream. Final stripping was accomplished with a fired reboiler serviced stripper. This was a grassroots plant with all new equipment. The plant metallurgy was predominantly carbon steel with 304 SS for flashing service, but it was only found in the cross exchanger and its immediate downstream piping and the circulating pumps. Within weeks after plant startup, leaks appeared in:

• The liquid level control valve on the line transferring rich solvent from the absorber to the flash drum

• A similar valve on the line transferring semi-lean solvent from the flash drum to the stripper

• The inlet piping of the semi-lean solvent circulating pump that takes suction from the flash drum and feeds the stripper and booster pump feeding the absorber

• The valve adjusting semi-lean solution flow to the absorber.

**Observations:** An internal inspection found the corrosion was localized and characterized as pitting and erosion. Corrosive effects were specific to the carbon steel metallurgy and flashing conditions. The absorber bottom showed no corrosion and still had mill markings on the wall. Amine solution analysis indicated very high $CO_2$ loadings (> 0.8 moles $CO_2$/mole solvent and > 100% equilibrium) in the rich and semi-lean solutions. Corrosivity tests indicated a greater corrosivity (7 vs. 1 mil/yr) of the plant solution vs. virgin solution. The circulating pump suction strainer was fouled with rust

and scale and created additional pressure drop between the flash drum and pump suction. Piping design used socket weld fittings and velocities in the problem areas were 10 to 40 ft/s except at the circulating pump suction, which was 3 ft/s.

**Conclusions:** The corrosion mechanism was diagnosed as:

- $CO_2$ flashing caused pitting due to the corrosivity of the wet $CO_2$ and cavitation erosion from bubble collapse.
- Erosion was caused by the combination of corrosion and abrasion at high velocity impingement points in the system.

**Corrections:**

- Change piping in flashing service from carbon steel to 304 SS and size the pipe for two-phase flow.
- Limit carbon steel piping velocity in the rich and semi-lean circuits to 5 ft/s.
- Limit flow disruptions causing turbulence by using butt weld, long radius fittings and improved piping geometry.

**Case 2. Problem:** Erosion corrosion in bottom of ammonia plant amine contactor. **Situation:** Treating synthesis gas at 350 psig with 17% $CO_2$ to remove $CO_2$ to a 100-ppm target. Converting inhibited MEA to formulated MDEA with less basisity requires increasing mass transfer of $CO_2$ from the gas to the amine. The amine liquid level in the contactor was raised from approximately 4 ft below the inlet gas distribution header to 6 in. above the header.

> **MEA, DEA and MDEA plants have proved that operating under proper conditions can minimize corrosion.**

**Observations:** After the conversion, an annual internal inspection of the contactor found erosion patterns on the contactor wall. These patterns corresponded to the impingement of inlet gas from the farthest holes from the ladder-type distributor's center. The erosion had consumed most of the vessel's corrosion allowance.

**Conclusions:** The corrosion mechanism was diagnosed as turbulent interaction between the inlet gas and liquid surface that prevented the normal passivation layer from forming.

**Corrections:** The farthest holes in the inlet distributor were welded closed. Eroded areas were cleaned and filled with a metal impregnated epoxy material for protection from future attack. Subsequent annual inspections verified no further corrosion.

**Case 3. Problem:** Severe general and galvanic corrosion in bottom of ammonia plant amine contactor. **Situation:** Treating synthesis gas at 348 psia with 18% $CO_2$ to < 100 ppm with 25% MEA with a heavy-metal corrosion inhibitor. Contactor used 36 two-pass trays. Oxygen was injected into a catalyst vessel upstream of contactor to convert CO to $CO_2$ in the synthesis gas. After a catalyst failure, the amine solution experienced a dramatic increase of iron concentration that allowed 2,000 to 3,000 ppm oxygen to enter the contactor bottom with the feed gas for 3 to 5 days.

**Observations:** An internal inspection found "leopard-spot" corrosion: dark circular passive areas surrounded by active general and galvanic corrosion regions around the entire vessel ID in the vapor area between the liquid level in the bottom of the tower and the first contact tray. The liquid level in the tower was maintained at 12 in. below the inlet gas distributor. Corrosion in the active areas had progressed into the carbon steel vessel's corrosion allowance. A similar corrosion type, but at a lesser degree, was also found in the vapor region between the bottom five trays and was not present by tray 31 (five trays from the bottom). The bottom three tray downcomers in the vapor region also showed similar corrosion.

**Conclusions:** The corrosion mechanism was diagnosed as penetration of the passive iron carbonate film in the vapor region by this reaction:

$$4FeCO_3 + O_2 + 10H_2O \subset 4Fe\,(OH)_3 + 4H_2CO_3$$

Once the passive film had been compromised in a few areas, further corrosion was helped by galvanic action of active and passive regions in close proximity.

**Corrections:** The bottom five trays were removed and the inlet gas distributor turned upside down with the exit holes pointed down. The liquid level in the contactor was maintained above the inlet gas distributor and the corroded area in subsequent operation of the plant to prevent direct contact with the inlet gas and allow the inhibited MEA to provide corrosion protection. The plant continued using the catalyst bed and oxygen injection in upfront processing, but exercised caution in its operation. Later inspections showed the corrective actions were successful.

**Case 4. Problem:** Pitting and erosion corrosion of stripper internals, cross exchanger tubes and booster pump in formulated MDEA plant. **Situation:** Treating natural gas at 800 psig with 1.5% $CO_2$ to a treated gas specification of 100 ppm in a grassroots facility. The stripper internals were carbon steel trays and 304 SS valves. Cross exchanger arrangement based on rich amine flow consisted of two shells in series with 316 SS tubes in the first and carbon steel in the second. Lean amine $CO_2$ loadings were consistently between 0.15 to 0.20 m/m with stripper overhead temperature below 180°F. The plant operated in this mode for 1½ years. Plant design also incorporated a 10% slip stream carbon filter in the lean circuit, preceded by a sock filter. Solution corrosivity test suggested a corrosion rate of 35 mils/yr.

**Observations:** An internal corrosion inspection of the stripper revealed severe pitting and erosion corrosion of the carbon steel tray decks and enlargement of the valve openings. Deterioration of valve openings resulted in 90% of each tray's valves deposited on the tray below. Light pitting was also evident on the absorber's liquid feed tray. Also, pitting corrosion to the point of penetration from the shell side was discovered on the carbon steel cross exchanger tube bundle. Severe erosion corrosion was present on the booster pump impeller and case. Large quantities of carbon granules were found in the bottom of the stripper and surge tank and on the shell side of both bundles in the cross exchanger. However, very little carbon was found in the carbon filter vessel.

**Conclusions:** The corrosion mechanism was diagnosed as:

• Flashing $CO_2$ in the cross exchanger from excessive pressure drop and high lean loadings due to plugging by the carbon and insufficient stripping steam resulted in pitting-type corrosion.

• Erosion corrosion of the booster pump impeller and case was caused by carbon solids circulating in the system.

• Galvanic and erosion corrosion of stripper tray decks was due to 304 SS valves coupled with carbon steel decks and carbon circulating around the system.

**Corrections:**

• Stripper internals were replaced with 316 SS trays and valves.

• Carbon steel cross exchanger bundle was replaced with 316 SS tubes and baffle plates.

• Support screen was installed in carbon bed and personnel trained on proper carbon installation.

• A full flow mechanical filter was installed downstream of the existing slip stream carbon and sock filters.

• Plant personnel were trained in proper stripper operations (maintain sufficient reflux ratio to achieve a 0.015 to 0.020 m/m lean $CO_2$ loading).

• Plant switched solvent suppliers and put a new load of formulated MDEA in the plant.

**Case 5. Problem:** Intergranular corrosion in a heat-affected zone of 304 SS stripper shell welds. **Situation:** An ammonia plant's stripper shell for $CO_2$ removal was fabricated with carbon steel for the lower courses and 304 SS for the upper courses. The internals were inspected one year after conversion from inhibited MEA to a formulated MDEA solvent.

**Observations:** Corrosion was found in the heat-affected zone of longitudinal and circumferential welds of the 304 SS shell.

**Conclusions:** The corrosion was diagnosed as intergranular corrosion caused by sensitization of the stainless steel from fabrication techniques or metallurgy used in the vessel. The shell was not a low carbon grade of stainless. The weld metal chosen was unknown. Sensitization or carbide precipitation results in depletion of chromium and lowers the corrosion resistance in areas next to the grain boundary. The heat-affected zone was previously protected by the heavy-metal inhibitor dissolved by the formulated solvent. In effect, the previous inhibitor compensated for the reduced corrosion protection of the stainless steel in the heat-affected zone.

**Corrections:** A correct weld procedure was specified to maintain the corrosion resistance of the 304 SS and the affected welds repaired. Subsequent annual inspections showed no further attack.

**Summary.** Corrosion in alkanolamine gas treating plants can be controlled and minimized with proper plant design, correct operating parameters and monitoring the operation frequently for unplanned process and amine excursions. The keys are minimizing acid gas flashing and understanding other factors that can enhance corrosivity of amine solutions.

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