CONTROLLING CORROSION IN AMINE TREATING PLANTS

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ABSTRACT

The causes and the prevention of carbon steel corrosion in amine systems are reviewed. The corrosive agents are acid gases, oxygen, heat stable salts, amine degradation products, and, in refineries, gas contaminants such as ammonia and hydrogen cyanide. Corrosion mechanisms are provided for carbon steel exposed to amine solutions and for amine regenerator overhead systems containing aqueous condensate. Corrosion is prevented by purification of amines and feed gases, corrosion inhibitors, use of corrosion resistant materials in selected locations, modification of process variables, and use of inhibitors. Different modes of carbon steel cracking in amine service are also discussed along with measures for their mitigation.

Keywords: amines, alkanolamine, gas treating, corrosion, erosion, cyanide, water wash, ammonium polysulfide, acid gases, cracking, SSC, HIC, SOHIC, ASCC, ammonium bisulfide, chloride, heat stable salts

INTRODUCTION

Amine systems are subject to corrosion by carbon dioxide and hydrogen sulfide in the vapor phase, in the amine solution, and in the regenerator reflux, and amine degradation products in the amine solution. In refineries, amine systems suffer from corrosion by several agents not generally found in natural and synthesis gases, namely ammonia, hydrogen cyanide, and organic acids, some of which tend to accumulate in certain parts of the refinery amine system.

Amine units must be designed to overcome these special problems. This paper, which is based on a comprehensive review of the published literature,-explains both the causes of these problems and their solutions. It describes the locations within the units where the various contaminants cause corrosion, provides the corrosion mechanisms in these places, and reviews the design practices and preventive measures required to mitigate corrosion. These measures include control of velocities and impingement, process configuration changes, process control strategies, selective use of corrosion resistant materials, sidestream amine solution purification, and the choice of amine.

AMINE PLANT CORROSION

Figure 1 depicts a typical alkanolamine treating unit. The feed gas containing either CO_2 or H_2S or a mixture of both acid gases flows into the bottom of a trayed or packed column where it is contacted with an amine solution. Acid gas components are removed from the gas by chemical reaction with the amine. The purified gas is the overhead product while the rich amine solution flows from the bottom of the contactor on level control to a rich amine flash drum. In the flash drum, the rich amine is flashed to a lower pressure to remove dissolved and entrained hydrocarbons. The rich amine then flows on level control from the flash drum through the lean/rich amine heat exchanger and on to the amine regenerator. In the regenerator, the acid gas components are stripped from the solution using heat supplied by the regenerator reboiler. Acid gas components are the amine regenerator overhead product while lean amine solution is the bottom product. The hot lean amine from the regenerator is heat exchanged with the rich amine, cooled, and then pumped to the contactor.

As Figure 1 indicates, most of the equipment and piping in an alkanolamine plant is constructed of carbon steel. In fact, it is possible, in most cases, to build an alkanolamine plant entirely of carbon steel by keeping amine regenerator operating temperatures low and by minimizing the amine solution concentration and acid gas loading (moles acid gas/mole amine). However, as shown in Figure 1, it is common practice to construct certain sections of an amine plant with stainless steel or other alloy. Selective use of higher alloys permits operation at higher amine concentrations and acid gas loadings, allows better stripping of the lean amine solution and improved treating, reduces corrosion in susceptible areas, and improves process economics. Locations marked in bold on Figure 1 show where carbon steel is typically replaced by stainless steel. Areas marked with a crosshatch show where either process or mechanical design modifications or corrosion resistant materials may be required depending primarily upon the composition of the gas being treated. To comprehend these choices, it is necessary to understand why carbon steel corrodes in amine plants.

In the absence of inhibitors, carbon steel corrodes in aqueous solutions by an electrochemical mechanism. The anodic half reaction is the oxidation of iron to ferrous ion:

$$Fe = Fe^{2+} + 2e^- \qquad (1)$$

The cathodic half-reaction is the reduction of some form of hydrogen from the +1 oxidation state to the element.

$$2H^+ + 2e^- = H_2 \qquad (2)$$

The net chemical reaction is the sum of the two half reactions:

$$Fe + 2H^+ = H_2 + Fe^{2+} \qquad (3)$$

This is an irreversible reaction and, consequently, its rate is affected only by the concentration of the species on the left side of the equation. Therefore, the rate of Reaction (3) increases with increasing hydrogen ion concentration (i.e., decreasing pH), with increasing temperature, and, because the reaction is electrochemical, with increasing conductivity of the liquid medium.

Figure 1 indicates the principal areas where corrosion can occur in alkanolamine gas purification plants. As indicated in this figure, corrosion in amine plants can be divided into two broad categories:

1. Wet Acid Gas Corrosion

   Wet acid gas corrosion of carbon steel is the reaction of CO_2 and H_2S with iron through a thin liquid film.

2. Amine Solution Corrosion

Amine solution corrosion is the corrosion of carbon steel in the presence of aqueous amine.

MECHANISM OF CORROSION OF CARBON STEEL BY WET ACID GAS

Aqueous acid gas solutions are found in the overhead section of the amine regenerator and in the bottom of an amine contactor if the feed gas is water-saturated. Metal surfaces in these sections of the amine plant may, therefore, be contacted with aqueous acid gas solutions containing little or no amine. See Figure 1.

Wet CO_2 Corrosion

If there is a separate aqueous phase and if the only acid gas present is carbon dioxide, the CO_2 will dissolve in the water to form carbonic acid, $H_2 CO_3$. The predominant carbon steel corrosion reaction in wet CO_2 is thought to be the direct reduction of the undissociated acid to form ferrous carbonate, which is only slightly soluble and does not form a very protective film.(1)

$$Fe + H_2 CO_3 = FeCO_3 + H_2 \qquad (4)$$

Figure 2 shows the effect of temperature on the corrosion of carbon steel by aqueous carbon dioxide. This figure shows that the corrosion rate reaches a maximum for a given CO_2 partial pressure. The reduction in corrosion rate is thought to be due to the formation of a protective film, either $FeCO_3$ or Fe_3O_4, at higher temperatures.(1) De Waard and Lotz have developed a nomograph which can be used to predict the corrosion of carbon steel by aqueous carbon dioxide solutions.(1)

Wet H_2S Corrosion

If the acid gas includes hydrogen sulfide, the principal product of corrosion is ferrous sulfide, which is very insoluble, and forms a weakly adherent and somewhat protective iron sulfide film:

$$Fe + H_2S = FeS + H_2 \qquad (5)$$

The iron sulfide is more protective than iron carbonate, and, if the acid gas contains sufficient H_2S, a protective sulfide film can be formed. If contaminants which disrupt this iron sulfide film are not present and mechanical design minimizes erosion-corrosion, wet acid corrosion of exposed carbon steel surfaces will be limited. On the other hand, if the gas is predominantly CO_2, wet acid gas corrosion will occur and protective measures are required. As might be expected, there is disagreement on the exact CO_2/H_2S ratio where protective measures are required. API Recommended Practice 945 suggests that wet CO_2 corrosion occurs when the acid gas contains 95% or more CO_2.(2)

Wet Acid Gas Corrosion Due to NH_3 and HCN

In refineries, the amine regenerator overhead system is often affected by wet acid gas corrosion due to the combined presence of ammonia with CO_2 and H_2S. Wet acid gas corrosion of the overhead system is accelerated if HCN is also present.(3,4) In these circumstances, wet acid gas corrosion due to H_2S and CO_2 can occur when the CO_2 content of the acid gas is less than 90%. In fact, substantial corrosion can occur in the total absence of CO_2 if sufficient HCN and ammonia are present.

Ammonia and HCN are found in gas streams from Delayed Cokers, Visbreakers, and Fluid Catalytic Cracking Units (FCCU's). Ammonia, HCN, and H_2S are also produced during hydrotreating and hydrocracking operations. When gas from these units is treated, the ammonia is readily absorbed by aqueous alkanolamine solutions. HCN, which is a weak acid and very water soluble, is chemically absorbed by alkanolamine solutions and is released, along with the absorbed ammonia, in the amine regenerator.

In the regenerator overhead condenser, the gaseous ammonia and HCN are reabsorbed in the condensed reflux water. Ammonia dissolved in the reflux water reacts with H_2S to form ammonium bisulfide.

$$NH_3 + H_2S = NH_4^+ + HS \qquad (6)$$

Without a reflux water purge, HCN and ammonium bisulfide are trapped in the amine regenerator overhead system. CO_2 can be trapped in the overhead system in a similar manner as ammonium bicarbonate. If both ammonia and HCN are present, the net effect is a substantial increase of the HCN, H_2S, and $H_2\,CO_3$ concentrations in the amine regenerator overhead system.

H_2S in the overhead system causes corrosion according to the following reaction:

$$Fe + H_2S \quad = \quad FeS + 2H^0 \qquad (7)$$

As noted by Ehmke,(3,4) the iron sulfide scale provides some protection at pH of 7 or 8, but is porous at a pH of 8 or 9. Also, if cyanide ions are present, the protective iron sulfide scale will be removed according to the reaction:(3,4,5)

$$FeS + 6CN- \quad = \quad Fe(CN)_6^{4-} + S^{2-} \qquad (8)$$

Removal of the protective iron sulfide scale by Reaction (8) is pH dependent, the rate increasing as the pH increases. (3,4) As Reactions (7) and (8) indicate, the higher the concentrations of H_2S and CN, the greater the rate of corrosion.

If CO_2 is trapped in the amine regenerator overhead system by ammonia, corrosion can result according to the following reaction:

$$Fe + 2H_2CO_3 = Fe^{2+} + 2HCO_3 + 2H^0$$

Reactions (7) and (9) produce atomic hydrogen, H^0. Under normal circumstances, the atomic hydrogen would combine at the metal surface to form molecular hydrogen. However, steel surface poisoning agents such as sulfide and cyanide anions prevent this recombination, and a significant fraction of the atomic hydrogen migrates into the metal lattice. (6) Most of the atomic hydrogen passes completely through the steel and forms molecular hydrogen on the opposite surface.

However, if the atomic hydrogen encounters an inclusion or a subsurface discontinuity in the base metal, it becomes trapped and recombines to form molecular hydrogen. As more and more molecular hydrogen is trapped at these locations, the pressure builds up past the yield strength of the steel. High molecular hydrogen concentrations at these locations can lead to hydrogen blistering/hydrogen induced cracking (HIC). In areas of high stress, such as weld heat affected zones, HIC may propagate in a planar manner, through thickness. This type of cracking is referred to as stress oriented hydrogen induced cracking (SOHIC). Also, atomic hydrogen dissolved in the steel lattice may embrittle areas of hard microstructures in carbon steel base metal or weldments. High atomic hydrogen concentrations in carbon steel can lead to sulfide stress cracking (SSC) of these hard areas.

Amine units treating gas from FCCU's are particularly susceptible to low temperature hydrogen attack because gas from these units can have a high cyanide content. According to Neumaier and Schillmoller, hydrogen attack should be expected whenever the organic nitrogen compounds in the FCCU feed are greater than 0.05 wt.%.(7) Wash or reflux water with a blue color (Prussian blue) after oxidation by air indicates that cyanide induced corrosion is taking place.(3,4) A simple plant test to detect cyanide using a dilute ferric chloride solution has been described by Neumaier and Schillmoller and by Ehmke.(3,4, 7)

PREVENTION OF WET ACID GAS CARBON STEEL CORROSION

Wet CO_2 and H_2S Corrosion Prevention

As shown in Figure 1, wet $C0_2$ corrosion can occur in either the bottom of the amine absorber or the amine regenerator overhead system. If the amine solution completely wets all the exposed carbon steel surface, it greatly raises the pH of the condensate and reduces its corrosiveness. In cases where the acid gas is 95% CO_2 or greater, an amine spray in the regenerator overhead has been recommended to minimize carbon steel corrosion.(2,8) Sufficient amine should be injected so that the reflux contains 0.5 wt.% amine. (8,9) In most refinery systems, wet CO_2 corrosion of the amine regenerator overhead system is not an issue because the acid gas is predominantly H_2S. However, an amine spray should be considered for amine regenerators in hydrogen plants using amine for CO_2 removal.

Wet CO_2 corrosion can also be a problem in hydrogen plant amine absorbers. In the bottom of the amine absorber, corrosion due to high CO_2 content of the acid gas can be prevented by introducing the gas through a distributor immersed in the amine absorber sump liquid.(10) The distributor orifices should be immersed in the rich amine solution so that the emerging gas causes amine solution to splash and wet the carbon steel surface. If the distributor breaks or is installed above the solution level, wet CO_2 can rapidly attack the shell of the absorber and its internal elements. If the absorber has trays, the underside of the bottom tray is attacked by acid gas until the tray collapses, whereupon the second tray is attacked, and fails in turn. As shown in Figure 1, all the trays can be saved if the bottom tray is stainless steel. If the mechanical design of either the bottom of the absorber or the amine regenerator overhead system is such that amine does not wet all exposed carbon steel surfaces, piping should be stainless steel and all equipment should be either made of or lined with stainless steel.

Another factor that should be considered for high CO_2 content gases is minimizing high velocity acid gas vapor impingement on carbon steel surfaces. Dupart et al. report one instance where impingement of a CO_2 rich gas led to corrosion in the bottom of an amine contactor.(10) This problem was corrected by modifying the feed gas distributor to minimize impingement of the acid gas on the amine contactor wall.

Preventing NH_3 and HCN Based Corrosion

Several different means have been employed to reduce ammonia and cyanide induced corrosion in the amine regenerator overhead system. These methods include:

A reflux water purge to reduce the concentration of cyanide and ammonium bisulfide in the amineregenerator overhead. See Figure 1.

A water wash upstream of the amine treating system to remove both ammonia and HCN.

Injection of either ammonium or sodium polysulfide upstream of the amine regenerator or into the amine regeneration overhead system.

Stripping corrosive components from the amine regenerator reflux.

Use of corrosion resistant materials in the amine regenerator overhead system.

Combinations of the above.

In general, the most economic solution is to modify the process conditions to permit the use of carbon steel. Elimination of HCN and ammonia upstream of the amine treating unit is usually the most effective solution. A brief review of each of these corrosion prevention methods follows:

Continuous Reflux Purge. Ammonia and cyanide build-up in the amine regenerator overhead system can be reduced and corrosion controlled if there is a continuous purge of amine regenerator reflux water. See Figure 1. A reflux purge is commonly used to reduce the cyanide and ammonia content of the overhead system and is effective if the cyanide and ammonia concentrations in the sour gas are low.(7) In fact, if the cyanide content of the reflux water or upstream wash water is less than 100 ppmw, cyanide induced blistering (HIC) of carbon steel will be minimal. (7) To minimize wet H_2S corrosion problems (SSC, HIC, SOHIC), the cyanide content of the wash water should be below 20 ppm.(11) Following guidelines developed for hydroprocessing unit air coolers, carbon steel can be used in the regenerator overhead condenser and downstream piping if the ammonium bisulfide concentration in the reflux water is less than 2-3 wt.% and exchanger tube and piping velocities are kept below 20 feet per second.(12) Inhibitor injection (ammonium polysulfide) may be required for the amine regenerator overhead system if the cyanide concentration is too high and, in refineries, a standby inhibitor injection system is often provided.(7) If a reflux purge is used to control the NH_3 and cyanide content of the reflux water, it may be desirable to avoid the use of return bends in either air or water cooled overhead condensers.(12)

The disadvantage of an amine regenerator reflux purge is that there may be very costly amine losses because amine concentrations in the reflux water can be between 0.5 and 2.0 wt.% depending on amine entrainment, the type of amine, and the number of water wash trays in the amine regenerator.(13) Also, the purge rate required to reduce cyanide and ammonia concentrations below corrosive levels is difficult to both determine and control. While amine losses can probably be reduced by installing a demister pad in the amine regenerator, corrosive conditions may exist even with a continuous reflux purge.

For that reason, when both ammonia and cyanide are present, amine units are typically designed with corrosion resistant materials of construction as shown in Figure 1. The amine regenerator is typically lined with type 304L integral cladding or weld overlay from two trays below the feed tray up to and including the upper head. The overhead piping is usually 304L SS, and titanium tubes have frequently been used in the overhead condenser. Ehmke notes that aluminum has been used successfully for the overhead condenser if pH, chloride ion content, impingement, and velocity are controlled.(14) Carbon steel is frequently utilized for the reflux accumulator, however, a conservative corrosion allowance is necessary and HlC-resistant material is sometimes used. The reflux pump casing and impeller should be 316 SS. All the reflux piping is typically 304L SS.

Upstream Water or Caustic Wash. Caustic washing was recommended by Polderman and Steele and used by Norris and Clegg for removal of formic and acetic acids from gas streams entering amine treating units.(14, 15) Since both formic and acetic acids are stronger acids than either H_2S or CO_2, they will replace the sulfide (or carbonate) salt. However, as noted by Polderman and Steele and Ehmke, caustic washing cannot remove HCN from gas streams because HCN is a weaker acid than H_2S or CO_2 and will be displaced from the caustic solution by either of these two acid gases.(14, 3, 4)

Since HCN is more soluble in water than either H_2S or CO_2, water wash has been used to remove hydrogen cyanide from gas streams.(7, 14, 16) Table 1 indicates that a single stage water wash alone is relatively ineffective in removing ammonia and cyanide.(3, 4, 7) This means that additional protective measures are required including a back-up inhibitor injection system (ammonium polysulfide) for the amine regenerator overhead system and a amine regenerator reflux purge.(7)

Upstream Ammonium Polysulfide Wash. Corrosion due to cyanide and ammonium bisulfide can be eliminated by washing the gas upstream of the amine absorber with an ammonium polysulfide solution.(3, 4) In the upstream water wash, the ammonia is dissolved in the wash water while the ammonium polysulfide reacts with CN- to form thiocyanate ion, SCN. Thiocyanic acid, HSCN, is a strong acid and is more water soluble than HCN. Ehmke(3, 4) presents data that show that ammonium polysulfide injection can reduce CN concentrations to less than 10 ppmw, which is below the threshold required to prevent both HIC and SSC.(7, 11)

$$S_X^{-2} + CN- \quad = \quad S_{x-1}^{-2} + SCN \tag{10}$$

Ammonium polysulfide is preferred over sodium polysulfide because it reacts faster with CN and does not raise the pH of the wash water.(3, 4) Design and operating guidelines for ammonium polysulfide wash systems are provided by Ehmke.(3, 4) With an upstream ammonium polysulfide water wash to remove both ammonia and HCN, the amine regenerator overhead system can be all carbon steel. Design principles of an ammonium polysulfide water wash system have been reviewed by Bucklin and Mackey who recommend the use of a multistage counter-current contactor with 8 to 10 actual trays.(13) The water wash system described in this reference uses stripped sour water containing 50 ppm NH_3 to reduce the ammonia in the washed gas to 0.1 ppm. Ammonium polysulfide is added to the wash water to convert the cyanide to thiocyanate.

Stripping Corrosive Components from the Amine Regenerator Reflux. Neumaier and Schillmoller outline another method for eliminating corrosion by ammonia and cyanide in the amine regenerator overhead system.(7) In this method the amine regenerator reflux stream is directed to a dedicated sour water stripper. The ammonia and HCN are then stripped from the reflux water in the sour water stripper. The stripped reflux water is then returned to the amine regenerator. Since cyanide and ammonia are not returned to the amine regenerator, there is no build-up of these components in the amine regenerator overhead and the overhead system can be made of carbon steel.

AMINE SOLUTION CARBON STEEL CORROSION

Amine solution corrosion of carbon steel can be caused by a number of factors including:

- High operating temperatures
- High rich and lean amine loadings (moles acid gas/mole amine)
- The ratio of CO_2 to H_2S in the acid gas

- Amine solution contaminants including amine degradation products and heat stable salts.

- Amine solution concentration

- Amine type

As shown in Figure 1, amine solution corrosion is most significant in the hot bottom section of the regenerator. Amine solution corrosion also occurs in the line connecting the contactor level control valve to the rich amine flash drum, in the lean/rich amine exchanger, and in the piping from the rich amine flash drum level control valve to the regenerator. Amine solution corrosion in these areas can be minimized by selecting alloy materials of construction and process modifications.

Amine-Acid Gas Carbon Steel Corrosion Mechanisms

Pure amines and mixtures of only water and amines are not corrosive because they have either low conductivity and/or high pH.(10, 17) However, rich amine solutions, which have high conductivity and a pH significantly lower than lean amine solutions, can be quite corrosive.

Several mechanisms have been proposed for amine-acid gas corrosion. Riesenfeld and Blohm were the first to note that significant amine corrosion was usually associated with the evolution of acid gases from the rich amine solution.(18, 19, 20) Based on this observation, Riesenfeld and Blohm stated that amine solution carbon steel corrosion was due to the presence of the acid gases themselves. For example, acid gas is evolved from rich amine solutions according to Reactions (11) and (12):

$$R_3\,NH^+ \quad + \quad HCO_3 \quad = \quad R_3N \quad + \quad H_2O \quad + \quad CO_2 \tag{11}$$

$$R_2NH_2^+ \quad + \quad R_2NCO_2 \quad = \quad CO_2 \quad + \quad 2R_2NH \tag{12}$$

The acid gases can then react directly with exposed carbon steel to form iron carbonate according to Reaction (13):

$$Fe + H_2O + CO_2 = FeCO_3 + H_2 \tag{13}$$

Iron carbonate is only slightly soluble and forms a film over the active metal surface which offers limited protection from funkier corrosion. Similar corrosion reactions occur with H_2S; however, the iron sulfide film covering the active metal surface is much more protective than iron carbonate, and the iron sulfide film resists funkier corrosion.

This mechanism explains several observed corrosion phenomena. For example, primary amines such as monoethanolamine (MEA) and Diglycolamineâ . (DGA) are more corrosive than secondary and tertiary amines because higher temperatures, which lead to greater corrosion, are required to strip primary amines. Therefore, in amine systems employing primary amines, high concentrations of acid gases are present in the hottest areas of the process. Conversely, methyldiethanolamine (MDEA), a tertiary amine, is easily stripped of both CO_2 and H_2S. Therefore, it is less corrosive because the acid gases are evolved from solution at a lower temperature.

Although it is widely believed that the acid gases are responsible for carbon steel corrosion, the exact corrosion mechanism is unclear. As Reaction(13) indicates, it is uncertain which species, H_2CO_3 or HCO_{3-}, contributes hydrogen ions to the corrosion reaction. There is no definitive research in the public literature and, clearly, additional work is required to establish the exact mechanism if some carbonic acid species is responsible for the corrosion reaction. Although carbonic acid and bicarbonate ion are unlikely to be present in amine solutions at regenerator operating conditions; nucleating sites (crevices, pits, and intergranular boundaries) where CO_2 bubbles evolve from amine solution are vulnerable to corrosive attack and the CO_2 partial pressure at these nucleating sites may be substantially higher than in the bulk solution. Therefore, it is possible that bicarbonate and possibly even carbonic acid could be present at these sites. Also, it is possible that carbon steel corrosion may be due in part to CO_2 liberated from the amine forming corrosive aqueous CO_2 solutions when free CO_2 contacts water condensing in areas that are not wet by amine solution, e.g., uninsulated regenerator manways.

Kosseim et al. provide another explanation for amine-acid gas corrosion which includes a plausible source for the hydrogen ion needed to explain carbon steel corrosion.(21) The authors note that acid gases react with amines to form alkanolammonium ions and the anions of the acid gases:

$$H_2S + R_3N \;=\; R_3NH + \;HS \qquad (14)$$

$$CO_2 + R_3N + H_2O \;=\; R_3NH^+ + HCO_3 \qquad (15)$$

$$CO_2 + 2R_2NH = R_2NH\ 2+ + R\ 2\ NCO\ 1$$

Alkanolammonium ions are acids in that they can provide hydrogen ions for the corrosion reaction. The corroding metal (iron in this case) will react with the strongest or most concentrated acid in the solution. In amine solutions, the alkanolammonium ion is both the strongest and (excepting water) the most concentrated acid. Thus, Reaction (3) can be rewritten in the following form:

$$Fe + 2R\ 3NH^+ = Fe^{2+} + H_2 + 2R_3N \qquad (17)$$

Reaction (17) implies that corrosion rates should increase in proportion to the concentration of alkanolammonium ion and generally this is true. Richer solutions are more corrosive than leaner, other things being equal. The hydrogen ion does not appear in Reaction (17); therefore, pH does not directly affect the reaction rate. Consequently, undegraded MEA solutions are more corrosive than undegraded diethanolamine (DEA) solutions, because MEA, the stronger base, unloads less in the stripper and retains a higher concentration of alkanolammonium ions there so the stronger base retains more acid (alkanolammonium ions) and, therefore, forms a more corrosive solution.

Reaction (17), like Reaction (3), is irreversible; therefore, its rate cannot in principle be affected by the concentrations of its products. In particular, heat stable acid anions and amine degradation products which form complexes with ferrous ions should not affect its rate, yet experience shows that these contaminants often do aggravate corrosion. The reason probably is that Reaction (16) is an overall reaction composed of several steps, and the rate-determining step may involve attack of iron atoms on the carbon steel surface by complexing agents. Futhermore, those complexing agents which associate with ferric as well as ferrous ions are very likely to inhibit the active-to-passive transition by preventing the formation of an insoluble ferric oxide passive film. For these reasons, heat stable salts and amine degradation products may strongly affect corrosion rates, although they may not appear in the overall corrosion reactions.

Uncontaminated solutions of tertiary amines such as MDEA are generally not corrosive whatever the acid gas. According to API 945, solutions of most amines are not corrosive if the ratio of hydrogen sulfide to carbon dioxide is above roughly 1/20, because the corrosion reaction leads to formation of a protective sulfide film.(2) The most corrosive combinations are those of primary or secondary amines with carbon dioxide, either because the carbamate ions form complexes with the ferrous ion or because carbamate ions are difficult to regenerate. Consequently, with amines like MEA, alkanolammonium ions or, alternatively, corrosive acid gases, are present in the hottest section of the amine regenerator.

Effect of Amine Loadings and Temperature on Carbon Steel Corrosion

Figure 3 shows the effect of CO_2 loading on carbon steel corrosion.(22) At a given amine concentration, corrosion increases as the CO_2 loading increases. Through experience, general guidelines have evolved on the maximum acceptable lean and rich amine loadings. Table 2 summarizes recommended lean and rich solution loadings obtained from various sources. As might be expected, there are considerable variations in these recommendations. One reason for these differences is that the maximum loadings ignore the passivating effect of H_2S on the maximum allowable amine acid gas loading. Therefore, these recommendations usually err on the conservative side.

Carbon steel corrosion due to high lean amine loadings can be limited by controlling the stripping operation in the amine regenerator. The degree of stripping in amine regenerators is a function of two related variables:

1. The amount of stripping steam per unit volume of rich amine solution; or,
2. The mole ratio of the reflux water to the acid gas leaving the amine regenerator overhead.

Two methods of controlling the degree of lean amine stripping are in common use. The first uses flow ratio control to set the reboiler heat medium mass flow at a fixed value in relation to the rich amine flow (kg of steam per m^3 of solution or lb of steam per gallon of rich amine solution). Most rich amines can be adequately stripped using between 110 to 133 kg of steam per m3 of rich amine solution (0.9 to 1.1 Ib of steam per gallon).(23) The second control method uses the temperature between the top regenerator tray and the regenerator overhead condenser to reset the reboiler heat medium flow. This controls the moles of reflux water per mole of acid gas leaving the amine regenerator overhead because, at a fixed regenerator operating pressure, the temperature above the top tray is directly related to the mol.% water in the acid gas leaving the top tray. Usually, a reflux ratio of 1.0 - 2.0 moles of water per mole acid gas is adequate to strip most amines.(9, 10) Fitzgerald and Richardson provide guidelines for MEA stripping as a function of the H_2S/CO_2 ratio in the feed gas.(24, 25) According to Smith and Younger these guidelines can be used for DEA.(26)

As Figure 3 illustrates, high rich amine loadings can also lead to excessive corrosion. Figure 6 depicts a control strategy used to limit rich amine loadings and control corrosion.(27) As shown in Figure 6, in a typical amine absorber most of the heat of reaction is released in the bottom section of the tower. If there is too little amine in relation to the amount of acid gas, the temperature bulge moves up the column. If there is excessive amine, the temperature bulge moves to the bottom of the column and amine acid gas loadings are low. Using the temperature at the bottom of the amine absorber to reset the amine flow, as depicted in Figure 6, maintains a relatively constant rich amine loading. This minimizes the chance of severe corrosion due to temporary overloading of the rich amine solution and also minimizes lean amine pumping and rich amine stripping costs.

Butwell recommends that amine concentrations be increased in preference to increasing amine loadings.(28) Although more concentrated amine solutions are more difficult to strip, more concentrated solutions are preferred as long as the regenerator reboiler has enough capacity to regenerate the solution. Figure 5 also shows that at constant amine acid gas loading, carbon steel corrosion increases as the temperature increases. To minimize corrosion, operating and reboiler heat medium temperatures are generally limited to maximum values. Table 3 summarizes various recommendations. In most cases, it is desirable to limit the reboiler steam temperature to about 150 °C (300 °F).

The Effect of the H_2S/CO_2 Ratio on Carbon Steel Corrosion

It is generally agreed per guidelines in API 945 that solutions of most amines are not corrosive if the ratio of hydrogen sulfide to carbon dioxide is above about 1/19, because when sufficient H_2S is present a protective iron sulfide film is formed according to Reaction (18) (2)

$$Fe + H_2S = H_2 + FeS \tag{18}$$

The ferrous sulfide film is sufficiently adherent to prevent further corrosion as long as erosion-corrosion is prevented by good mechanical design, and gas impurities which remove the protective sulfide film, like cyanide, are not present. The lack of corrosion at high H_2S/CO_2 ratios has been exploited in the SNPA-DEA process where acid gas loadings of 0.77 to 1.0 moles of acid gas per mole of amine have been achieved.(23) High acid gas loadings might also be achieved with other amines at high H_2S/CO_2 ratios; however, no confirming data have been published. Without confirming data, the rich solution loadings of Dupart et al. as summarized in Table 2 should be followed for even though they ignore the effect of the H_2S/CO_2 ratio.(10)

Several studies have been published on the effect of the H_2S/CO_2 ratio on the corrosion of carbon steel by amine solutions.(29, 30, 31, 32) The results of Froning and Jones are summarized in Figures 4 and 5. Figure 4, which summarizes tests in a $N_2/H_2S/H_2O$/MEA environment, suggests that a minimal H_2S partial pressure is required to prevent carbon steel corrosion. Figure 5, which summarizes tests in a $N_2/H_2S/CO_2/H_2O$/MEA environment, shows carbon steel corrosion is minimal and independent of the H_2S/CO_2 ratio as long as the acid gas contains at least 5 vol% H_2S. Since the tests were run at atmospheric pressure, 5 vol% H_2S corresponds to a H_2 partial pressure of 5.1 kPa (0.74 psia). This suggests three possible interpretations of the results of Froning and Jones:

1. Carbon steel corrosion will be minimal as long as the H_2S partial pressure is greater than 5.1 kPa (0.74 psia).

2. To minimize carbon steel corrosion the H_2S/CO_2 ratio should be greater than 1:19 (the acid gas should contain at least 5 vol% H_2S).

3. For minimal carbon steel corrosion the H_2S/CO_2 ratio should be greater than 1:19 (the acid gas should contain at least 5 vol% H_2S) and the H_2S partial pressure should be greater than 5.1 kPa (0.74 psia).

Alternative 2 is the basis of guidelines provided in API 945.(33) However, Alternative 3 is the more conservative interpretation of the tests of Froning and Jones and is more consistent with the test data. In any case, the results of Figures 4 and 5 should be used with caution because Froning and Jones report that pitting occurred when both the hydrogen sulfide concentration and the H_2S/CO_2 ratio were low.(29)

Corrosion tests reported by Riesenfeld and Blohm confirm the conclusion of Froning and Jones that there is no correlation between the rate of carbon steel corrosion and the H_2S/CO_2 ratio as long as there is sufficient H_2S present to form a protective film and inhibit carbon steel corrosion.(18, 19, 20) McNab and Treseder have also investigated the effect of the H_2S/CO_2 ratio on amine solution carbon steel corrosion.(30) Their results, which are based on tests with diisopropanolamine (DIPA or ADIP) solutions, do not support the conclusions of Froning and Jones. It is possible that this discrepancy is due to the use by McNab and Treseder of sealed glass containers for the corrosion tests. Silica is known to inhibit amine solution corrosion, and silica from the glass containers may have affected the test results.(29)

Effect of Heat Stable Salts and Amine Degradation Products

Carbon dioxide and hydrogen sulfide are weak enough acids that their reactions with amines are thermally reversible. Acids which are sufficiently strong that their reactions with amines are not thermally reversible are called heat-stable salt forming acids. That is, products of their reactions with amines form heatstable salts. If heat-stable acids enter an amine unit or are generated there by reaction with trace amounts of oxygen or by thermal degradation of the amine, the heat-stable salts will remain in solution and accumulate there.

Heat-stable salts have several sources. In refineries, FCCU gases may contain trace amounts of formic and acetic acids. Traces of oxygen in various refinery gas streams (FCCU, Delayed Coker, Vacuum Unit, Vapor Recovery System), air leaking into gas gathering systems operating under vacuum, and oxygen in unblanketed amine storage tanks and sumps can react with the amine to form carboxylic acids and with H_2S to form elemental sulfur and thiosulfate. In refineries, elemental sulfur can then react with cyanide to form thiocyanate.

Heat-stable salts reduce the acid gas removal capacity of the amine solution because they react irreversibly with the amine. Amine solutions can also be corrosive if they are contaminated with heat-stable salts.(10) Heat-stable salts are corrosive because they lower the amine solution pH, increase solution conductivity, and may also act as chelating agents, dissolving the protective film covering the base metal. It is also possible that some of the weaker heat-stable acids, such as formic acid, recombine in the amine regenerator to form the free acid, which could then react with exposed carbon steel. Amine-CO_2 degradation products, some of which are strong chelating agents, may also contribute to amine solution corrosion by removing protective oxide or sulfide films.(34, 35) While it is generally agreed that heat-stable salts and amine degradation products contribute to amine solution corrosion, there is no definitive explanation of the corrosion mechanism. In fact, it is likely that several factors, including lowering of the amine solution pH and chelating effects, contribute to carbon steel corrosion by heat-stable salts and amine degradation products.

Amine Reclaiming. The operation of sidestream purification units (reclaimers) makes it possible to maintain a constant concentration of active amine in the treating solution and prevent the accumulation of corrosive heat-stable salts and amine degradation products. Commercial techniques used to reclaim amine solutions include: batch distillation under vacuum; atmospheric or higher pressure distillation (thermal reclaiming); ion exchange; and electrodialysis. Atmospheric or higher pressure batch distillation can only be used for MEA and DGA which are primary amines. Secondary amines (DEA and DIPA) and MDEA, a tertiary amine, must be reclaimed by vacuum distillation, ion exchange, or electrodialysis because these amines decompose at atmospheric distillation temperatures. Design and operating guidelines for MEA thermal reclaimers are provided in several references.(9, 36, 37, 32, 38) DGA reclaiming is reviewed by Kenney et al., ion exchange by Keller et al., and electrodialysis is discussed by Union Carbide.(39, 40, 41) Reclaiming of secondary and tertiary amines is usually on a contract basis while primary amines are reclaimed as a part of normal operation. Amine reclaiming should be considered when the heat stable salt content is greater than 10% of the active amine concentration.(10)

Heat Stable Salt Neutralization. Soda ash is often added to DEA and MDEA solutions to neutralize heat-stable salts, and there is considerable plant evidence that this is an effective means of reducing corrosion.(26, 42, 43) Adding soda ash reduces amine solution corrosiveness by raising the solution pH. Caustic soda addition might also reduce corrosion by preventing the recombination of weaker acids such as formic acid to the molecular form during amine regeneration. Although caustic soda addition can limit corrosion, the amount of soda ash that can be added is limited because solids will eventually be precipitated, plugging equipment and piping. However, solids precipitation can be avoided if caustic soda addition is combined with amine solution reclaiming using either batch distillation, ion exchange, or electrodialysis. Caustic soda addition is particularly attractive for secondary and tertiary amines like DEA and MDEA since these amines cannot be reclaimed during normal operation. Therefore, for these amines, caustic soda addition can be used to control corrosion until a contract reclaimer arrives at the plant site.

According to Scheirman, soda ash should be first added to DEA solutions when the heat stable salt concentration reaches 0.5 wt.%.(44) Nearly 20 wt.% sodium salts can be tolerated before any solids precipitate. Potassium carbonate can also be used to neutralize heat stable salts and has the advantage of being about 25% more soluble by weight than sodium compounds.(44)

For MDEA solutions, Liu and Gregory recommend that soda ash be added to keep the amine heat stable salts content below 2 wt.%.'43' The MDEA solution should be reclaimed when the total heat-stable salt anion content reaches 40,000 ppm.(43)

Effect of Amine Type on Amine Solution Corrosion

It is well known that the choice of amine affects corrosion.(10, 17) Primary amines like MEA and DGA are more corrosive than secondary amines like DEA and DIPA. In turn, DIPA and DEA are more corrosive than tertiary amines like MDEA. Exactly why this is so is not known. As noted by DuPan et al.,(10, 17) several investigators have shown that all amines are equally non-corrosive when no acid gas is present.(29, 30, 31, 45, 46) Therefore, differences in corrosion cannot be due to the amine alone. MDEA differs from MEA, DEA, DIPA, and DGA in that it does not form amine-$C0_2$ degradation products. However, investigations by Polderman et al. for MEA and by Chakma and Meisen for DEA suggest that while amine-CO_2 degradation products contribute to corrosion, they are not the primary cause.(34 35) As noted by DuPart et al., it is possible that the ability of primary and secondary amines to form carbamates according to Reaction (16) may account for the differences in corrosion.(10, 17) Perhaps the more basic amines such as MEA are more corrosive due to the presence of alkanolammonium ions in the hottest sections of the amine regenerator.

$$\mathrm{Fe} + 2\mathrm{R_3NH} + \quad = \quad \mathrm{Fe^{2+}} + \mathrm{H_2} + 2\mathrm{R_3N} \tag{19}$$

Less basic amines such as DEA are easier to strip, and since alkanolammonium ion concentrations are low in the bottom section of the amine regenerator, less basic amines are less corrosive.

Erosion-Corrosion

Erosion-corrosion is caused by the high amine solution velocities, solution turbulence, and the impingement of gas and amine on metal surfaces. Erosion-corrosion removes the protective sulfide or iron oxide film protecting the piping and equipment from corrosion. Areas that are subject to erosion-corrosion include the piping from the amine contactor pressure let-down valve to the rich amine flash drum, the piping from the rich amine flash drum level control valve to the amine regenerator, and the lean amine pump. Other areas that are affected include heat exchanger tubes near the inlet nozzle, the amine contactor near the sour gas inlet, and the amine regenerator rich amine inlet. Erosion-corrosion is aggravated by "dirty" amine solutions containing suspended particulates. Erosion-corrosion can be reduced by choosing the correct materials of construction and mechanical design details which minimize impingement, reduce turbulence, and lower amine solution velocities. Amine solution mechanical filtration to remove particulates also reduces erosion-corrosion.

Erosion-Corrosion of Piping. API 945 recommends designing both lean and rich amine carbon steel piping for velocities less than 1.8 m/see (6 ft/sec).(2) Table 2 summarizes piping velocity recommendations from other sources. As noted, recommended velocities range from 0.9 to 1.8 m/see (3 to 6 ft per see). While there is no published research to support these recommendations, it is thought that API 945 represents good practice because it is an industry consensus document. Sheilan and Smith and Dingman et al. recommend the use of seamless pipe and long-radius elbows to reduce amine piping erosion-corrosion.(47, 48) Sheilan and Smith also suggest that threaded connections or socket weld fittings be avoided.(47)

Erosion-Corrosion of Heat Exchanges and Reboilers. Ballard and Dingman et al. recommend the use of multiple inlets and outlets to reduce corrosion of kettle and horizontal thermosyphon reboilers.(9, 48) Sheilan and Smith recommend perforated inlet bafffles for heat exchangers to prevent corrosion due to impingement.(47) Ballard and Connors suggest designing reboilers with liberal disengaging space to minimize violent boiling and resulting erosion-corrosion.(9, 49) Both recommend removal of tube rows to form a "V" or "X" in existing installations where violent boiling is a problem. Ballard recommends designing exchangers and reboilers with square pitch to facilitate cleaning and reduce erosion-corrosion while Connors, Dingman et al., and Smith and Younger advise keeping amine velocities in carbon steel heat exchangers below 0.9 m/see (3 ft/sec).(9, 49, 48, 26) However, this guideline may be too conservative as the velocity recommendations for piping (1.8 m/see or 6 ft/sec) summarized in Table 4 should apply to heat exchangers as well. Ballard also advises that the reboiler bundle should be covered with 15 to 20 cm (6 to 8 inches) of liquid to prevent localized drying and overheating.(9) He also recommends locating the reboiler tube bundle about 15 cm (6 inches) above the bottom of the reboiler shell to allow free circulation of the amine through the tube bundle.(9) The reboiler steam control valve should be located on the reboiler inlet not the condensate outlet to prevent high localized temperatures due to steam side reboiler flooding and resulting corrosion.(9) As shown in Figure 1, the lean/rich amine exchangers should be located upstream of the rich amine flash drum level control valve to minimize acid gas evolution inside the exchangers, and the rich amine should be on the tube side. If the lean/rich amine exchangers are stacked, rich amine should flow up through the bottom exchanger to the top shell.

Erosion-Corrosion of Lean Amine Pumps. To minimize turbulence and erosion-corrosion of the lean amine pump impeller and casing, Sheilan and Smith recommend a minimum of 8 to 9 pipe diameters of straight pipe upstream of the pump suction. As shown in Figure 1, lean amine pumps should be located downstream of the lean/rich amine exchanger as the hot lean amine solution leaving the regenerator is often near saturation at the elevation corresponding to the lean amine pump suction. Placing the lean amine pumps downstream of the lean/rich amine exchanger ensures that the lean amine is subcooled before it enters the pump.

Erosion-Corrosion of Pressure Let-Down Valves. To reduce erosion-corrosion of pressure let-down valves downstream of absorbers, Graff recommends the use of carbon steel bodies with type 316 SS internals and stellited trim when the valve pressure drop is above 7 to 14 berg (100 to 200 psig).(50) Scheirman recommends carbon steel globe body valves with stellited 316 SS internals, but also suggests that valves be selected with the maximum possible valve body size to minimize the amine velocity through the valve body.(51)

CRACKING OF CARBON STEEL IN AMINE SERVICE

Four carbon steel cracking mechanisms in alkanolamine gas treating units have been identified. Reviews of these cracking mechanisms have been provided by Merrick, Buchheim, Gutzeit, and in API 945.(52, 53, 54, 2) The first three cracking mechanisms are connected with the entry of atomic hydrogen into the carbon steel lattice. These three cracking mechanisms are known as sulfide stress cracking (SSC), hydrogen induced cracking (HIC), and stress oriented hydrogen induced cracking (SOHIC). All three of these cracking mechanisms require the production of atomic hydrogen in an aqueous-H_2S solution. While there is no established lower H_2S concentration limit, industry practice has been to assume that aqueous solutions containing more than 50 ppmw H_2S can lead to cracking.(11) In the vapor phase, a commonly used threshold for SSC is a H_2S partial pressure of 0.34 kPa (Q05 psia). What distinguishes these three cracking mechanisms from each other is what entraps the atomic hydrogen inside the metal lattice, whether it recombines to form molecular hydrogen, the orientation and features of the resulting cracks, and the corrective measures required to minimize each type of cracking. The fourth mode of cracking is alkaline stress corrosion cracking (ASCC). It is thought that ASCC is caused by a film rupture mechanism. Stressed areas such as heat affected zones slip, breaking the passive film and exposing bare steel, which corrodes to form cracks. The passive film reforms, but residual stresses cause the film to rupture again, leading to more corrosion. Repetition of this process leads to cracking. A summary of each cracking mechanism follows. Examples of each cracking mechanism are provided in API 945, Appendix A.(2)

SSC (Sulfide Stress Cracking)

Carbon steel is embrittled by atomic hydrogen dissolved in the metal lattice. In the heat affected zones adjacent to welds, there are often very narrow hard zones combined with regions of high residual tensile stress which may become embrittled to such an extent by dissolved atomic hydrogen that they crack. SSC is directly related to the amount of atomic hydrogen dissolved in the metal lattice and usually occurs at temperatures below 90 °C (194 °F).(54) SSC is also dependent on the composition, microstructure, strength, and residual and applied stress levels of the steel.(53) SSC has been found in attachment and seam welds in the amine regenerator overhead system, in the bottom of the amine absorber, in the top of the amine regenerator column, and on the rich side of the lean/rich amine exchanger.(54) These locations suggest that SSC is due mainly to wet acid gas corrosion. See Figure 1. This form of cracking can generally be prevented by limiting the carbon steel weld metal hardness to less than 200 Brinell (BHN) and by restricting the steel tensile strength to less than 621 MPa (90 ksi).(55, 56) Post weld heat treatment (PWHT) is beneficial in mitigating SSC because it reduces hardness and relieves stresses.(52, 53)

HIC (Hydrogen Induced Cracking)

When hydrogen atoms dissolved in carbon steel meet a non-metallic inclusion, e.g., a sulfide or oxide panicle, a slag inclusion, a lamination, or other discontinuity, they often combine irreversibly to form molecular hydrogen. The molecular hydrogen, unlike atomic hydrogen, cannot escape; therefore, it accumulates and builds up high pressure inside the metal. Eventually, the pressure causes the metal-inclusion interface to separate, resulting in cracking or blistering. The blisters are parallel to the steel surface because the carbon steel laminations or inclusions are typically elongated parallel to the carbon steel surface when the steel is rolled during manufacture. HIC rarely occurs in product forms other than plate or plate products.

HIC is also called hydrogen blistering cracking or stepwise cracking. HIC depends on steel cleanliness and composition. It has been found primarily in the bottom of absorber towers, in the amine regenerator overhead system, and in the top section of the amine regenerator tower.(54) These locations suggest that the principal cause of HIC is wet acid gas corrosion. HIC may be avoided by using specially manufactured "clean steel" plates that are more HIC-resistant than conventional carbon steel. HIC-resistant carbon steel is made by ladle treating with either calcium or a rare earth metal for residual sulfide inclusion shape control. A recently published NACE International Technical Committee Report reviews the manufacturing and test methods for HIC-resistant steel."" Since hydrogen induced cracking depends on the cleanliness of the carbon steel and its method of manufacture, HIC cannot be prevented by PWHT.(53)

SOHIC (Stress Oriented Hydrogen Induced Cracking)

As in HIC, SOHIC is caused by atomic hydrogen dissolved in the carbon steel combining irreversibly to form molecular hydrogen. The molecular hydrogen collects at imperfections in the metal lattice, just as in HIC. However, due to either applied or residual stresses, the trapped molecular hydrogen produces microfissures which align and interconnect in the through-wall direction. SOHIC can propagate from blisters caused by HIC, SSC, and from prior weld defects.(53, 54) However, neither HIC nor SSC are preconditions for SOHIC.(53) In amine systems, SOHIC has been found mostly in the upper section of the amine regenerator tower, in the amine regenerator overhead system, and in the bottom section of the absorber below the bottom tray.(54) As with HIC, these locations suggest that the primary cause of SOHIC is probably atomic hydrogen produced by wet acid gas corrosion. See Figure 1. PWHT improves the resistance of carbon steel to SOHIC, but does not totally eliminate it (Buchheim, 1990). In recent years, many users have specified

HIC-resistant carbon steels, with PWHT, for SOHIC resistance. However, under very corrosive laboratory conditions even HIC-resistant steels have been shown to be susceptible to SOHIC.(55) Therefore, carbon steel plate clad with austenitic stainless steel has been used to eliminate the risk of SOHIC. Since SOHIC is most prevalent in the amine regenerator overhead system, cladding this area, as shown in Figure 1, can prevent both SOHIC and HIC.

(ASCC) Alkaline Stress Corrosion Cracking

As noted earlier, it is thought that ASCC is caused by a film rupture mechanism. In areas of high residual stress, such as heat affected zones, slip causes the passive film to break, exposing bare steel, which corrodes to form cracks. If the corrosion rate is greater than the rate of passive film formation, the protective film will not reform, and pitting or some other form of localized corrosion will occur. However, if the passive film forms faster than the metal corrodes, the protective film will be restored. Repetition of this process results in alkaline stress corrosion crack growth. ASCC is the most common cracking mechanism in alkanolamine gas treating plants. It can occur in plants treating CO_2, H_2S, or mixtures of both acid gases.(56, 57)

ASCC in amine gas treating plants was first reported in 1951 by a NACE Committee.(58) In 1953, Garwood reported ASCC in MEA plants treating natural gas.(59) Cracks were found in heat exchanger heads, amine absorbers, piping, and amine regenerators. The cracks were intergranular and oxide-filled. Since the cracking occurred only in highly stressed, heat affected zones, PWHT was recommended to eliminate ASCC. As a result of this early work, the industry adopted a general policy of PWHT for all piping and equipment (except storage tanks) in contact with amine above a certain temperature. Depending upon the company and the amine, the selected temperature varied between 38 and 93 °C (100 and 200°F;) with 66 °C (150 °F) being a common choice.(56, 57)

In 1982, Hughes reported ASCC in non-PWHT treated carbon steel equipment in a MEA refinery unit.(60) ASCC had occurred in welds in contact with amine at temperatures ranging from 53 to 93 °C (127 to 200 °F), while no cracking had occurred in PWHT welds operating at temperatures as high as 155 °C (311 °F;). Hughes concluded that PWHT for all carbon steel piping and equipment in amine service would eliminate ASCC. (60)

In 1984, an amine LPG treater at an USA refinery ruptured, causing an explosion and fire that killed 17 people.(61, 62) Although the disaster was apparently caused by a combination of HIC and SOHIC, this disaster and reports of extensive cracking in other amine systems initiated investigations of carbon steel cracking in amine units.(63, 64) These investigations, which revealed many instances of ASCC, were undertaken by NACE Group Committee T-8 on Refining Corrosion in cooperation with the API.

Results of an industry survey by this group were reported in 1989 by Richert et al.(56) This survey included 294 amine units, 272 of them in refineries, and most of them MEA and DEA units. This survey indicated that cracking occurred primarily in MEA service. Nearly every crack was associated with a weld that had not been PWHT. Cracks occurred in every type of equipment and at temperatures as low as ambient. However, no conclusive correlation was found between cracking and most process variables, including source of gas, amine concentration or acid gas loading, use of filters or reclaimers, use of corrosion inhibitors, type of carbon steel, or addition of caustic to neutralize heat stable salts. ASCC was found to be generally independent of the H_2S/CO_2 ratio. However, all amine plants with less than 1% mol.% H_2S in their feed experienced cracking. This suggests that at least 1 mol.% H_2S in a predominantly CO_2 stream has some tendency to inhibit ASCC. This conclusion was confirmed by later laboratory investigations.(65, 66, 67) The survey data could not be used to demonstrate that ASCC was temperature dependent because most of the equipment operating at higher temperatures was PWHT. However, the experience documented by Garwood suggests that ASCC increases with increasing temperature when equipment and piping are not PWHT.(59) Since 98% of the cracks reported in the survey occurred in carbon steel welds that had not been PWHT or at nozzles where PWHT is difficult, PWHT of all carbon steel piping and equipment in amine service was judged to be the single most effective measure to prevent ASCC. Later additional data on DEA and DIPA gas treating units, which reported ASCC below 66 °C (150 °F) for both DEA and DIPA, emphasized the need for PWHT to prevent ASCC.(68)

A report by the Southwest Institute and a related article point out that the NACE survey include data from only 16 natural gas treating units out of a total of 294 units of all kinds.(67, 69) These references state that a more comprehensive survey was made for natural gas treating units, but gave the results of the survey only in brief summary, and did not state how many units had been surveyed. Both reports did, however, give detailed results of a laboratory study, which concluded that ASCC of carbon steel was inhibited by the presence of H_2S. Also, according to both reports, ASCC in refineries occurs predominantly in lean amine solutions while ASCC cracking in natural gas plants occurs primarily in rich amine solutions.

CHLORIDE ATTACK OF STAINLESS STEEL IN AMINE SERVICE

Impurities such as chloride gradually build-up in amine systems until a steady-state concentration is reached. Since most amine systems contain some stainless steel, it is of interest to know what chloride levels can cause pitting of stainless steels. Limited information is available in the literature. Experiments reported by Seubert and Wallace indicate little or no pitting tendencies with 304 SS exposed to DGA solutions containing up to 4000 ppm chloride.(70) Based on these experiments, the maximum acceptable chloride level for DGA plants containing type 304 SS was set at 1000 ppm.

CORROSION INHIBITORS

Corrosion inhibitors are often classified as cathodic inhibitors, which inhibit reaction (2), anodic inhibitors, which inhibit reaction (1), and oxidizing passivators, which are discussed separately below. Cathodic and anodic inhibitors are often adsorbed on the corroding metal, like filming amines, or plated out on it, like arsenic and antimony. They have been recommended and patented at various times, but none has much current commercial success in amine units.(2)

Oxidizing passivators are considerably stronger oxidizing agents than hydrogen ion, and they operate by shifting the potential of the steel to a more positive value where reactions (1) and (2) do not occur. Instead, a passivator oxidizes the iron on the surface to the trivalent state, i.e., to a form of ferric oxide which is very adherent and protective. This oxide is called the passive film. Such inhibitors work well in units removing carbon dioxide only, reducing the corrosion rate practically to nil, and they are the only effective inhibitors for MEA in the absence of hydrogen sulfide.(2) Conversely, they are destroyed by hydrogen sulfide.

While oxidizing passivators work extremely well when they are properly maintained, they have several drawbacks. First, they must be analyzed for and their concentration maintained. Second, they must be protected against impurities which destroy them, including hydrogen sulfide and large amounts of iron corrosion products, both soluble and insoluble. Third, when they fail, they often permit local attack, or even aggravate it. Finally, many of them are toxic heavy metals, and make it expensive to discard their solutions.

CONCLUSIONS

During the past forty years a significant amount of literature has been published regarding amine system corrosion. A review of this literature is a useful starting point in arriving at an overall view of corrosion in amine systems and proven preventive measures. As this paper indicates, amine system corrosion is caused by many factors including the acid gases themselves, heat stable salts, oxygen, amine degradation products, and, in refineries, trace gas impurities such as organic acids, ammonia, and hydrogen cyanide. Corrosion can be prevented by various combinations of conservative design velocities, selective use of corrosion resistant materials, upstream washing of feed gases, purging of regenerator reflux, side-stream purification (reclaiming) of the amine, and PWHT.

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TABLE 1
REMOVAL OF CORROSIVE COMPONENTS FROM A FCCU GAS STREAM BY A SINGLE STAGE WATER WASH FOLLOWED BY AMINE CONTACTING(7)

		Removed by Total Water		Absorbed by Diethanolamine Solution		Balance to Gas Plant	
Constituents	Total Constituents (Pounds per Day)	(Pounds per Day)	(Per-cent)	(Pounds per Day)	(Per-cent)	(Pounds per Day)	(Per-cent)
Ammonia	7,400	6,300	85	700	10	400	5
Sulfides	86,000	21,100	24	64,200	75	700	1
Carbonates	32,000	4,000	12	21,500	67	6,500	20
Cyanides and Thiocyanates	2,000	1,000	50	400	20	600	30
Phenols	7,100	1,750	25	100	1	5,250	74
Aliphatic Acids	6,500	1,850	28	1,600	25	3,050	47
TOTAL	141,000	36,000	25	88,500	63	16,500	12

TABLE 2
RECOMMENDED AMINE SOLUTION CONCENTRATIONS AND MAXIMUM RICH AND LEAN AMINE SOLUTION LOADINGS

		Mol. Acid Gas/Mol. Amine		
Amine	Maximum Wt.% Concentration	Lean Loading	Rich Loading	Reference
MEA	15-20	0.10-0.15	0.30-0.35	10
MEA	15-20	0.08-0.12	0.35-0.40	48
MEA*	18	0.13	-	71
MEA	18	-	0.3-0.4	9
MEA	10-20	-	0.25-0.45	42
MEA	<20	<0.10*	<0.4	72
DEA	25-30	0.05-0.07	0.35-0.40	10
DEA	20-30	-	0.33-1.0	26
DEA	20-30	-	0.77-1.0	23
DEA	20-40	-	0.50-0.85	42
MDEA	50-55	0.004-0.010	0.45-0.50	10
DGA	50-65	-	0.25-0.45	42
DIPA	20-40	-	0.50-0.85	42

* For CO_2 only.

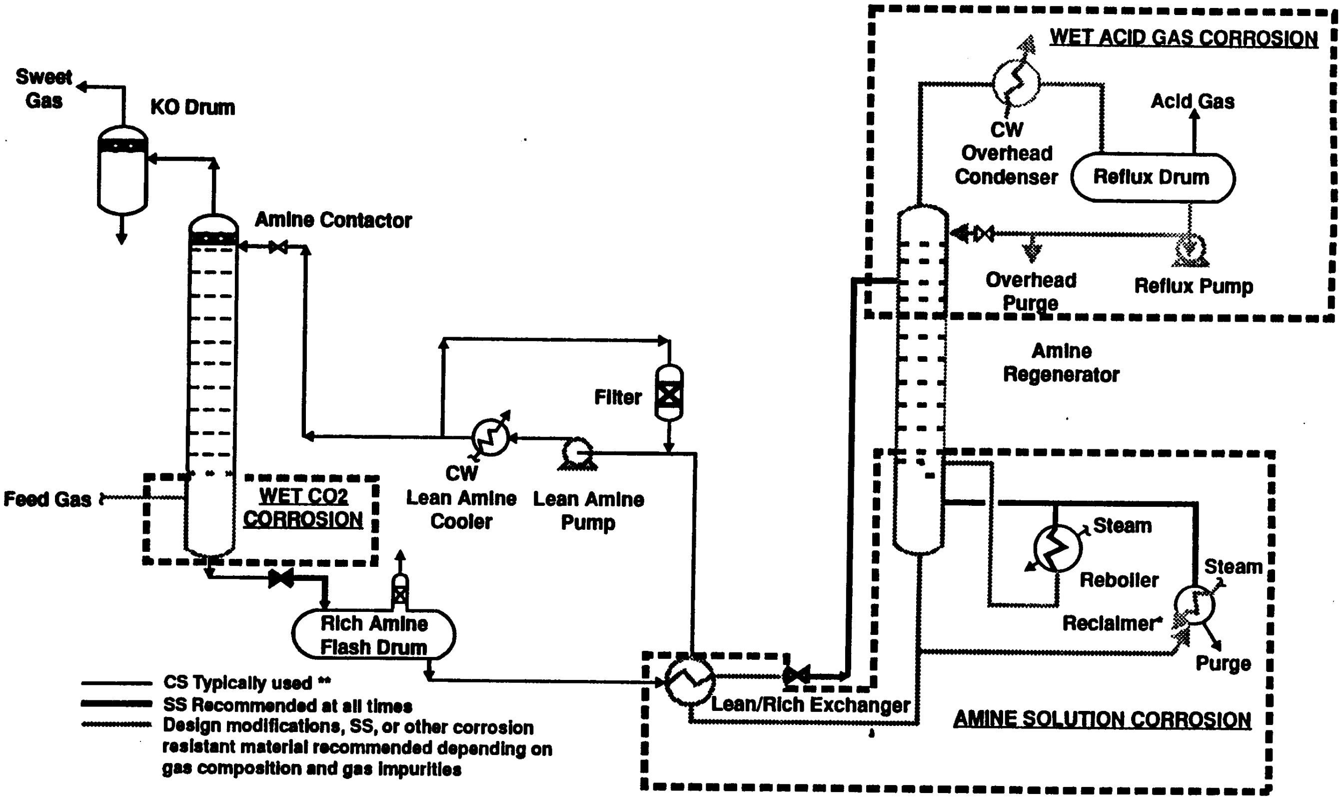
TABLE 3
RECOMMENDED MAXIMUM PROCESS AND HEAT MEDIUM TEMPERATURES

		Maximum Heat Medium Temp, °C (°F)		
Amine	Maximum Process Temp, °C (°F)	Hot Oil	Steam	Reference
All	124 (255)	-	149 (300)	17
MEA	127 (260)	-	149 (300)	48
MEA	121 (250)	-	149 (300)	49
MEA	127 (260)	-	141 (285)	9
MEA/DEA	116-117 (240-260)	<230 (<450)	-	73
MEA	-	188-227 (370-440)	-	74
MEA	121 (250)	-	135 (275)	72

TABLE 4
RECOMMENDED AMINE SOLUTION PIPING* VELOCITIES FOR RICH AND LEAN AMINE SOLUTIONS

	Velocity, m/sec (ft/sec)		
Amine	Rich Solution	Lean Solution	Reference
All	1.8 (6)	1.8 (6)	2
All	0.9 (3)	0.9 (3)	75
MEA	0.9 (3)	0.9 (3)	48
All	1.5 (5)	- (-)	10
DGA	1.5 (5)	1.5 (5)	70

* Figures also generally apply to heat exchanger tubing.



* Only required for MEA and DGA

** Sometimes HIC-resistant CS plate materials are used.

Figure 1. Typical materials of construction for refinery amine plants

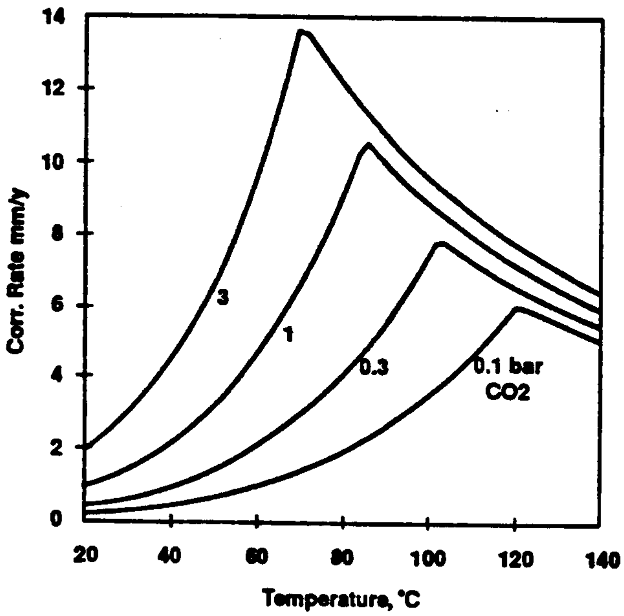


Figure 2. Effect of temperature on carbon steel corrosion at various CO_2 partial pressures (Reference 1).

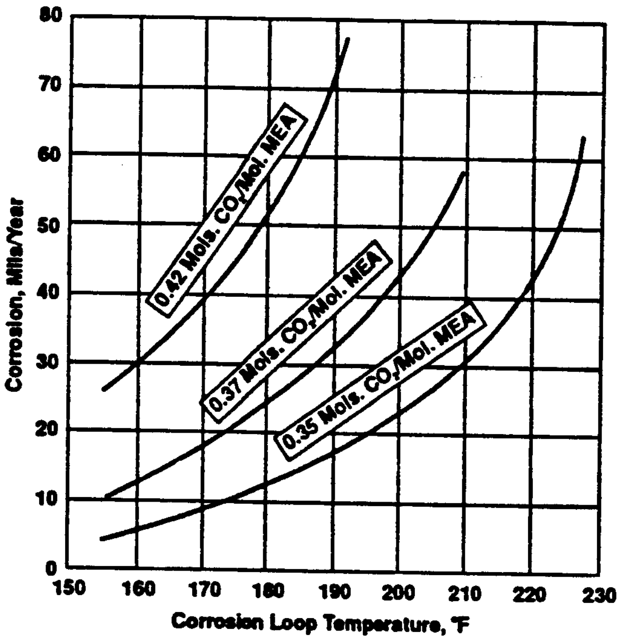


Figure 3. Results of pilot plant tests showing the effect of temperature and acid gas loading on carbon steel corrosion (Reference 22).

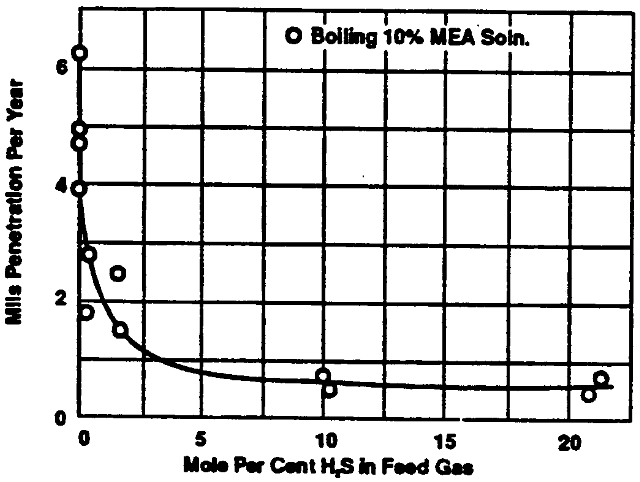


Figure 4. Corrosion of carbon steel in a H_2S-N_2-MEA-H_2O environment (Reference 29).

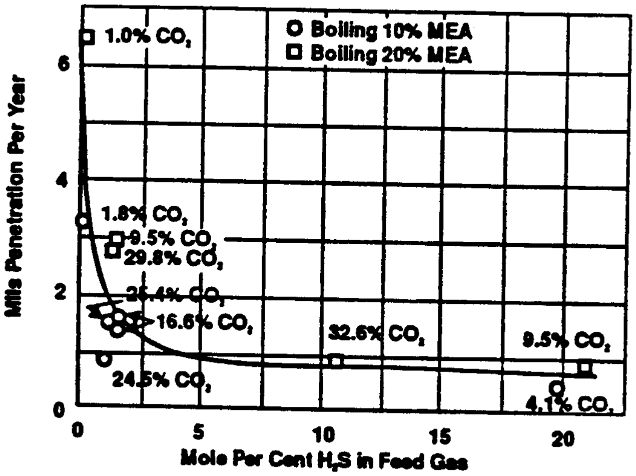


Figure 5. Corrosion of carbon steel in a H_2S-CO_2-N_2-MEA-H_2O environment (Reference 29).

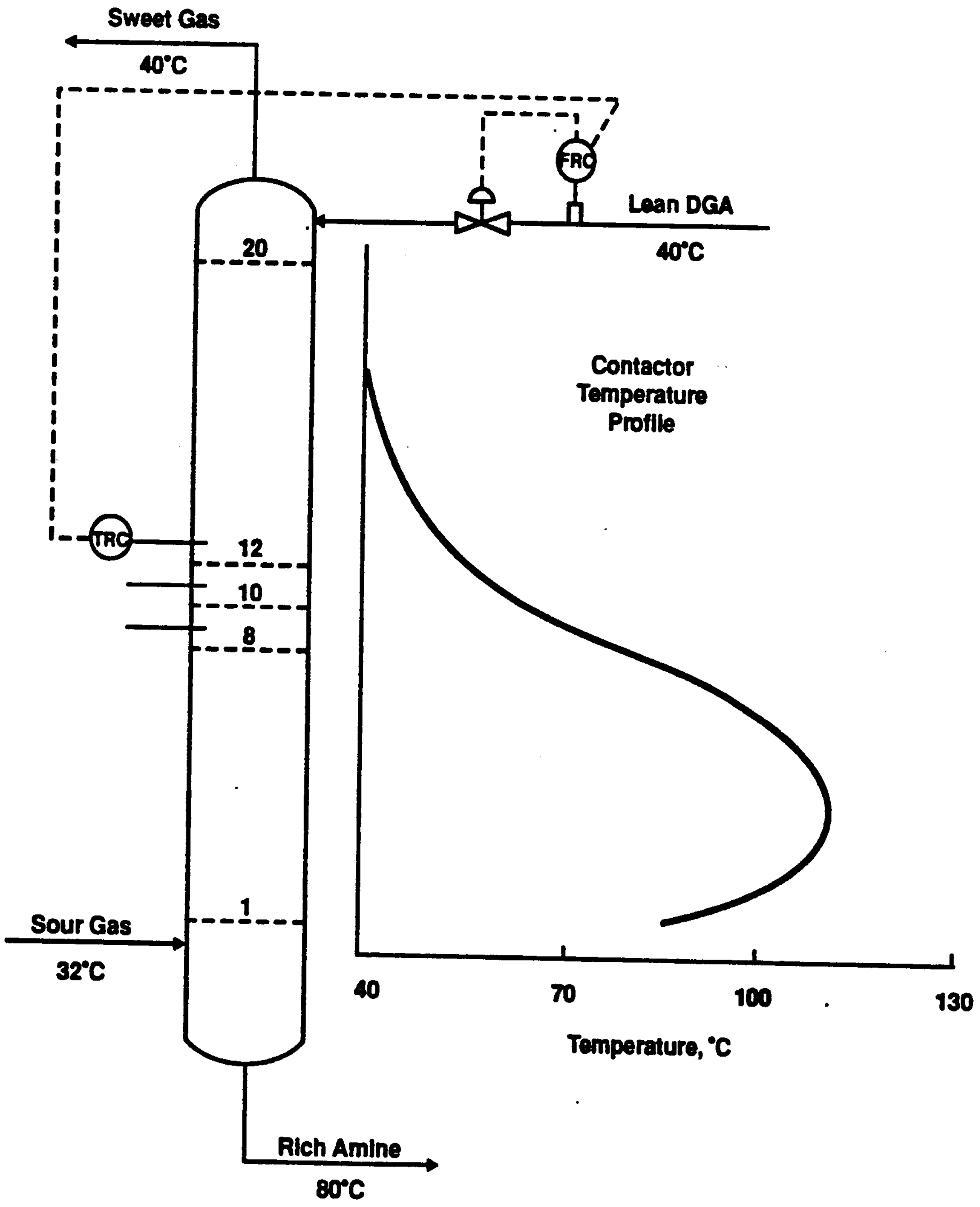


Figure 6. Use of absorber temperature to control the lean amine flow rate and rich amine loading (Reference 27).