



Corrosion and Corrosion Enhancers in Amine Systems

Presented at
The Brimstone Sulfur Conference
Banff, Alberta, April 2005

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ABSTRACT

Corrosion in alkanolamine gas treating solutions begins with the acid gases which are the target of the treating, and is enhanced by several physical and chemical factors. Corrosion causes and enhancers are reviewed as are suggestions for mitigating or minimizing corrosive effects. Particular attention is focused on the effects of amino acids (bicine), because of recent revelations of their presence in a broad range of alkanolamine systems.

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INTRODUCTION

Gas processing includes removing acids. Alkanolamine solutions are commonly used to remove acid gas contaminants from various process gas streams in the oil & gas industry, the steel industry, syngas plants, chemical plants, and many others. Corrosion is an inevitable result of dealing with acid gasses. Much work has been done to understand corrosion mechanisms in alkanolamine (“amine”) systems, so that corrective action may be taken to improve unit operation and reliability.¹⁻¹⁴ It is recognized that the major corrosive agents are the very acid gases (H₂S and CO₂) that are the reason for the existence of amine systems. Other chemicals enter with the gas or are produced within the amine system and contribute to corrosion either directly or indirectly. Physical conditions such as temperature, fluid velocities, suspended solids and metallurgy all play a role.

THEORY OF CORROSION IN AMINE SYSTEMS

A long list of parameters affecting corrosion in amine systems may be made.¹³ To reduce the problem to something manageable, parameters are grouped into fewer factors.¹³ The temptation is to eliminate some factors or groups of factors in order to focus on others. This is very useful, but places limitations on the applicability of the results.

If one is to apply a model to a general phenomenon such as amine system corrosion, the model must be robust enough, and flexible enough to explain the different varieties of occurrences without straying too far from its foundation. This particular way of viewing corrosion in an amine system follows this requirement.

Simply stated, corrosion rate in an amine system is a function of four factors. They are corrosive acid concentration, temperature, fluid velocity, and heat stable salt (HSS) anion concentration. Written as a mathematical expression:

$$\text{corrosion rate} = f(\text{acid gas conc.}, \text{temperature}, \text{velocity}, \text{HSS anion conc.})$$

There will also be some dependence on acid gas type and HSS anion type. Amine degradation products (results of chemical modification of alkanolamines) have been characterized as having no practical effect on corrosion⁸ and as promoting corrosion by complexing iron.^{5,12,16} Those that complex iron enhance the corrosion in amine systems in the same manner as HSS, so can be included in the HSS term of the expression.

Relating these variables to the physical process of corrosion is needed to validate the expression. In this case a model view of the physical process of corrosion is required. The model view in this case is built on more fundamental chemical and thermodynamic principles.

The fundamental building blocks are first, the oxidation of iron by some agent, and second, the interaction between the products of corrosion and the corrosive environment. In the case of the typical refinery H₂S amine system, the corrosive agent is a form of an acid gas in solution, either a form of H₂S in solution or possibly even CO₂ in solution. The “form” referred to here is the molecular form of the acid gas. The acid gasses mentioned are dibasic, that is they can give up two protons (hydrogen ions) and form two different ions in solution, as well as exist

in the dissolved, hydrated, un-ionized state. The forms of H₂S are hydrogen sulfide (H₂S), bisulfide (HS⁻) and sulfide (S⁼). For CO₂ they are carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻), and carbonate (CO₃⁼). The primary corrosion product referred to in this system is iron sulfide. The great benefit of iron sulfide formation is that this material is fairly insoluble in aqueous solutions and tends to adhere rather uniformly over the surface where the oxidation of the iron took place. If uniformly distributed and with minimal porosity to the solution, the iron sulfide layer affords a substantial barrier to additional corrosion by blocking access of the corrosive agent to the free metal. Iron carbonate is also fairly insoluble, but it does not form as tenacious a layer of corrosion product on the surface of the remaining free metal.

Iron Oxidation & Protective Layer Formation

Nature of the Acid. The oxidizing agents in the amine system are protonic acids (those which give up H⁺ or a proton). This seems rather odd since the solutions we are talking about are highly buffered, basic solutions. It is also odd because many corrosion control strategies are based on the neutralization of acids and maintaining a basic pH.

The key to understanding the acid attack then is understanding the acid. First H₂S enters the aqueous phase and is surrounded by water molecules. The H₂S then undergoes a two step reaction sequence, losing an H⁺ to form H⁺ and HS⁻ followed by losing the other H⁺ from the HS⁻ to form H⁺ and S⁼. Only an extremely small portion of the original H₂S undergoes the second step. Eventually, an equilibrium distribution of the three forms is established.

The final distribution depends on the relative amounts of other acidic or basic species in solution and the amounts of positive or negative charge each contributes. Fortunately, this can be reduced to charge balances and equations using the acid and base dissociation constants. By simultaneously solving the equations, the pH of the solution and the concentrations of any species of any weak acid or weak base constituents can be determined.

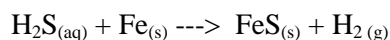
In the pH range normally encountered in an amine system, the majority of the H₂S in solution will be bisulfide ion, HS⁻. Under most amine conditions, HS⁻ will be more than 90% of the total H₂S in the solution (Figure 1). Now, the question of whether or not HS⁻ can be an acid in a basic solution must be answered.

The answer is yes. It is not that HS⁻ is a strong acid like HCl or H₂SO₄. Rather, it is that the sulfide also reacts with the oxidized iron to form insoluble iron sulfide. The reaction equation is written:



The stability of the reaction product FeS makes corrosion by bisulfide more probable than corrosion by other available proton donors.

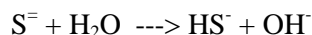
Undissociated, *dissolved* H₂S should be even more reactive than the bisulfide ion. The iron corrosion reaction becomes:



Unlike bisulfide corrosion, where two bisulfides likely attach themselves to adjoining sites on the free metal or a second proton donor is needed, only one H₂S is required to get the same effect. The corrosion rate with H₂S should be faster that with a similar concentration of HS⁻

because fewer molecules must come together at the reaction site. However, in amine solutions, the H₂S concentration is low relative to HS⁻ (Figure 1), and is dependent on pH, which can be affected by total acid gas and HSS concentrations.

Sulfide on the other hand, is not likely to be in significant quantities because it is stronger base than OH⁻. Stronger bases than OH⁻ will tend to be leveled in strength to OH⁻ by reacting with water as show below:



The solution pH will need to be greater than 13 for a significant amount of sulfide ion to be present. Sulfide has no protons to donate to hydrogen in the oxidation of iron, so there would be little tendency for sulfide to corrode. This is evidenced by the low corrosion rates in caustic treaters and prolific use of carbon steel.

Oxidation Rate. The rate of oxidation of the iron (not overall corrosion rate) is determined then by nothing more than the availability of free metal, the concentration of the corrosive forms of acid gas in solution, and the temperature. In kinetics terms:

$$\text{oxidation rate} = K_o e^{(-E_a/RT)} [H_2S]^n [HS^-]^p$$

Since the iron concentration is constant when free metal is present, its term is omitted. This establishes the first two parts of the fundamental corrosion rate equation, the dependence on acid gas concentration, and the dependence on temperature.

The only things that can retard the rate of oxidation are reduction of the concentration of oxidizer, or reduction of the availability of free iron. As stated before, the beneficial effect of the oxidation by HS⁻ or H₂S is the formation of a corrosion product layer that reduces the free metal availability and slows the overall corrosion rate.

The remaining factors in the overall corrosion rate are those that prevent the corrosion products from forming a protective layer or those that cause the layer to be removed exposing more free metal. These are the other two factors in the overall corrosion rate expression.

In the absence of H₂S, “wet CO₂” (Carbonic acid and bicarbonate) corrosion dominates analogously to the above described H₂S mechanisms. Iron Carbonate (FeCO₃) solids can form corrosion-inhibiting protective layers, but generally not a well as does iron sulfide. The pH ranges in which the carbonic acid ionic forms dominate differ from those of the H₂S forms, as can be see by comparison of Figures 2 and 1. Also unlike H₂S where the proton-less S⁼ ion is never significant, in the pH range of amine solutions a significant fraction of CO₂ in solution can be in the carbonate (CO₃⁼) form, particularly in lean amine solution. Thus one might expect corrosion rates in CO₂ systems to be much more pH dependent.

Factors Affecting the Protective Layer

Physical Interactions. The physical process of iron oxidation in this system takes place by transporting the acid from the bulk solution to the surface of the metal, adsorption of the acid on the surface, reaction, and transport of reaction products into the bulk solution. As long as free metal is present, the physical barriers to reaction are the rate of diffusion of acid, the rate of diffusion of hydrogen and, in the case of HS⁻, sulfide ion away from the reaction site. As the reaction proceeds, the surface of the iron is changed to a lattice work of iron and sulfide ions.

As the reaction takes place, the surface is expanded by the addition of the mass of sulfide. In addition, the flow of the surrounding fluid transporting material in and out of the reaction area, and the release of hydrogen gas at the reaction site, tend to expand the surface. So instead of a hard crystal lattice being built on the surface, a somewhat porous surface layer is built which adheres to the free metal surface. Another factor which affects the state of the iron sulfide layer is the non-stoichiometric proportions of iron and sulfur in the lattice. The defective crystal structure then allows for non-uniformity of the layer.

Since the velocity of a fluid, along with its physical properties control the rate of mass transfer (diffusion), and velocity of the fluid controls the concentration gradients (driving force), then the velocity of the fluid should play a significant part in the oxidation rate and the quality of the iron sulfide layer formed on the surface of the metal. As the velocity of the fluid containing reactants increases, more corrosion causing material can diffuse to the surface. The amount of fluid passing the site increases, which increases the chances that the iron sulfide is deposited unevenly by distorting the crystal growth. Increased fluid velocity also increases the rate of transport of reaction products away from the reaction site providing driving force for the oxidation reaction to continue. An increase in oxidation rate caused by increased acid availability will make more hydrogen. Evolution of additional hydrogen will also affect the crystal growth and porosity of the layer. There may also be erosion effects which occur from solids which are transported by the fluid which make additional free metal available.

Chemical Interactions. As previously mentioned, the iron sulfide deposited on the surface is a lattice of iron and sulfide ions. The ions are in equilibrium with iron and sulfide species in solution. The distribution between solid and fluid is described in an equilibrium by the solubility product (K_{sp}) relationship.

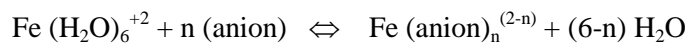


Iron forms the hexaquo ion while sulfide reacts with water to form bisulfide and hydroxide as described above. Any chemical relationship that can change the effective iron or sulfide ion content in solution can change the net direction of the dissolution reaction.

At amine system pH values, OH⁻ concentrations are regulated by the relative concentrations of the bound and free amine, which vary with amount of acid gas and HSS loading. The HS⁻ concentration is primarily dependent on the location in the amine system. In rich amines, there will be less tendency for iron ion to move into solution as the high concentration of HS⁻ forces the reaction to the left. In lean amines, the low HS⁻ concentration will allow more sulfide to enter the solution moving the reaction to the right.

Another way to move the reaction toward ions in solution is to stabilize the ionic iron in solution so that it will not go back to iron sulfide by simple reversal of the reaction above. This is accomplished by displacing the water in the hexaquo iron ion with other species. Ammonia, amine, hydroxide ion, and heat stable salt anions are the typical 'replacements' for water.

In the amine solution, amine is highly concentrated, but this seems to have little effect as tenacious iron sulfide layers are formed. Ammonia is usually in low concentrations in all but the regenerator overhead system. There may be some complexing effect here. Hydroxide is likely to be freely exchanged with water and its concentration will be small and vary little under these conditions. It is likely not to effect the solid/ion distribution. Many heat stable salt anions are well known to make complexes with iron.^{3,15,17} The complexes are formed by the reaction:



where n = 1 to 6

The reaction will be shifted toward complexation by increasing the anion concentration or by increasing the hexaquo iron ion in solution. Anions such as thiocyanate, formate, and acetate, common amine heat stable salt anions readily form iron complexes. The complexes then cause the dissolution of iron sulfide to shift to the right providing more iron ions for complexation. Addition of a large amount of H₂S in solution will shift the iron sulfide dissolution reaction back to iron sulfide solid which will cause the complexation reaction to shift to the left.

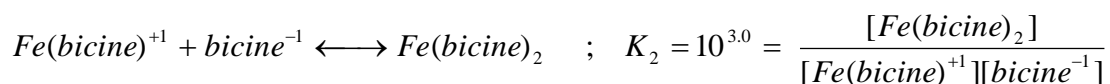
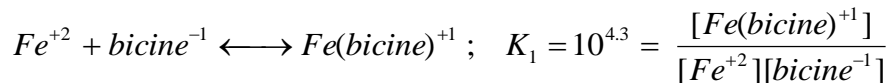
Cyanide ion, the quintessential complexer of iron, is known to remove FeS protective layer by this reaction, and the rate increases with increasing pH.¹ However, the Fe-cyanide complexes are rarely found in amine systems, because at the pH of amine solutions, cyanide hydrolyses to formate and ammonia and/or reacts with H₂S or thiosulfate to form thiocyanate (SCN⁻). Still, Fe-cyanide complexes have been reported in some syngas plant amine solutions which are treating gas containing CO, CO₂, a trace of cyanide, but no H₂S.

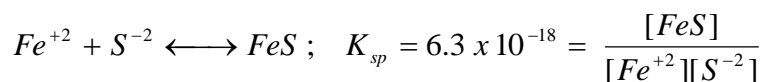
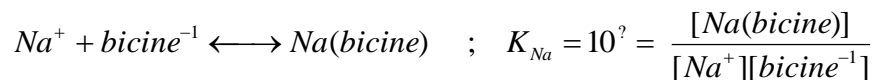
Degradation Products of amines – chemicals that result from chemical alterations of the amine – are also known to make complexes with iron, and could be substituted for “anion” in the above equation. Amino acids (bicine)⁹⁻¹¹, formamides⁵, diamines¹², have all been shown to contribute to corrosion in amine solutions.

Bicine was been found in a great number of gas treating plant amine samples, both generic and formulated amines.^{18,19} Another amino acid, hydroxyethyl sarcosine (HES) has been identified along with bicine.¹⁸ While most authors have shown or confirmed that bicine contributes to corrosion in amine systems, one suggested that corrosion is not associated with bicine, and proposes that complexation of iron by bicine can be reduced significantly by addition of potassium or sodium caustic.¹⁹ Unfortunately, the presumption of non-corrosion is based entirely on a lack of known complaints from refinery personnel, and the benefit of caustic (potassium or sodium) is derived from an overly optimistic application of an otherwise admirable theoretical treatment. We have worked through the same theory and find some comparisons and contrasts worth mentioning.

The solubilities of iron in amine solutions were calculated in a manner similar to that of reference 19 by solving the equilibrium and mass balance equations for the concentration of iron sulfide in solution under various conditions. As with that work, the pH of the amine solution was taken to be 10

The equilibria that are occurring under these conditions are:





To be consistent with the previous paper¹⁹, the equilibrium constant (K_{Na}) for the interaction of sodium and bicine varied from $10^{0.1}$ to $10^{0.5}$. Table 1 shows the results of our analysis as compared to the previous work. Note that the results of our calculations are very close to the previously reported numbers for 0.097 M bicine and various sodium concentrations and bicine-alkali metal complexation constants.

The solubility of iron sulfide without bicine or sodium in the system was not reported in the previous work. In our calculations, we found it to be very low at 1.4×10^{-7} M (Case 0, Table 1). When 0.097 M bicine is added to the system, the solubility of iron sulfide increases by a factor 443 to a concentration of 6.2×10^{-5} M (FeS is 443 times more soluble). This is a huge increase in the solubility of iron sulfide when bicine is in the system. Since the prior work did not calculate the solubility of iron sulfide with no bicine, this large increase in the solubility of iron sulfide was not noted.

Continuing down Table 1, we also calculated the effect of ‘neutralizing’ the bicine by addition of sodium hydroxide and found that, like the previous paper, the solubility of iron sulfide decreased. Our solubility data closely track the prior data and we found that the solubility of iron sulfide with 0.54 M sodium is about 40% of the solubility without sodium, if $K_{Na}=10^{0.5}$. At first glance this might seem like a large decrease in iron solubility. However when compared to the no bicine case, the decreased solubility is of little importance. The solubility of iron sulfide would still about 180 times more soluble with 0.097 M bicine and 0.54 M sodium as compared with the no bicine case.

Thus, it does little good to add sodium (or potassium) to the system to ‘neutralize’ the bicine. It is much better to remove the bicine from the system and make efforts to prevent its formation.

In the foregoing, we have repeated the model calculations reported by Bosen and Bedell¹⁹ and used their estimated complexation constant for the interaction of bicine with sodium in order to reproduce their work. However, closer examination of complexation constant data shows that the complexation constant they chose for bicine-alkali metal is probably too large. The ligand that they chose as model for estimating bicine’s K_{Na} did not have a molecular structure similar to bicine. This may be because there is very little published data on the chelation of sodium with relatively simple ligands like bicine, because the complexation constants are very small and hard to measure accurately. However, we were able to obtain chelation data from a NIST Data Base¹⁷ for bicine and similar ligands for a number of metals. Table 2 shows the molecular structure of bicine and some other ligands along with their complexation constants with selected metals.

There is a very close correlation of the complexation constants of bicine and glycine for magnesium, iron, copper and nickel. The other ligands have similar structure and similar complexation constants for the metals for which there was available data. It seems logical that if the complexation constants of bicine, glycine, and other similar ligands with a variety of metals are similar, the complexation constants for bicine and these ligands with sodium should be

similar. The complexation constant for glycine with sodium has been measured to be $10^{-0.5}$ and so it is likely that the bicine-sodium complexation constant is also about $10^{-0.5}$. Table 2 shows a complexation constant for alkali metal – alanine of $10^{+0.3}$ taken from reference 19. This value has to be called into question because alanine's complexation constants with the other selected metals are so similar to that of glycine. The complexation constant of bicine with alkali metals such as sodium and potassium should be in the range of $10^{-0.5}$ to $10^{-0.1}$ rather than the $10^{+0.1}$ to $10^{+0.5}$ chosen by Bosen and Beddel.

Table 3 shows the same data as in Table 1 except that the sodium-bicine complexation constants have been changed to more realistic values of $10^{-0.5}$ to $10^{-0.1}$. A comparison of Tables 1 and 3 shows that iron sulfide solubility depression by alkali metal addition cannot be called significant, when the more realistic complexation constant values are chosen. When bicine is 0.097 M with the extreme choice of 0.54 M Na^+ , the iron sulfide solubility is still 71% of the zero sodium case with a K_{Na} of $10^{-0.5}$ and 85% with a K_{Na} of $10^{-0.1}$. A more important item to note is the fact that the total FeS solubility is now 300 - 400 times more than when bicine is not in the amine solution. Clearly the addition of sodium or potassium will not be beneficial to systems containing bicine or other amino acids.

There are a large number of gas plant amine systems that have very little if any hydrogen sulfide and are used to remove carbon dioxide. We extended our modeling of the chelation of iron to systems in CO_2 service (without H_2S). Carbonate was substituted for sulfide in model and the appropriate acid disassociation constants (carbonic acid versus hydrogen sulfide) and solubility product constant of iron carbonate were employed. We modeled both lean and rich conditions to estimate the iron solubility in the contactor and the stripper.

Iron carbonate is very insoluble in both rich (2.5 M amine and 0.3 mole of total CO_2 ($\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$) per mole of amine) and lean (0.01 M/M) conditions. At pH 10, the concentration of FeCO_3 is 1.5×10^{-10} M in the rich case and 4.5×10^{-9} M in the lean case. When bicine is added at 0.097 M, the solubility of iron carbonate increased by a factor of nearly 200,000 in both the lean and the rich cases. This shows that there is a large potential for increased corrosion due to the increased iron solubility when bicine is added to the system.

Table 4 shows the CO_2 modeling results for bicine alone and for bicine with sodium addition. From the table, it is clearly seen that the addition of sodium does not really help much because iron carbonate solubility is still much more soluble with bicine than without bicine in all cases.

The last column in Table 4 shows the ratio of iron carbonate solubility in the lean side to the rich side solubility. It can be seen that iron carbonate is thirty times more soluble on the lean side. This can be problematic because bicine will cause iron carbonate to become soluble in the lean side of the system. When the amine is circulated back to the contactor and picks up CO_2 , the iron carbonate will precipitate out leaving bicine free. This free bicine is circulated back to the lean side where it picks up more iron. This cycle can repeat itself over and over and may cause severe corrosion on the lean side of the amine treating system. Furthermore, the precipitated iron carbonate can plug trays in the contactor dramatically impacting operation.

We have not done these rich lean calculations for H_2S service but it is expected that the same phenomenon will be experienced. Iron sulfide will be more soluble in the lean amine and less soluble in the rich amine. This again can result in corrosion in the areas where there is lean amine and precipitation and solids problems where there is rich amine.

Another contributor to bicine induced corrosion is the formation of iron-hydroxide-bicine complex. We have just begun to model the effect of iron hydroxide (not complete yet). The complexation constant of bicine with iron (III) and two hydroxides ($\text{Fe}(\text{OH})_2\text{bicine}$) is 10^{30} and the complexation constant of bicine with iron (III) and three hydroxides ($\text{Fe}(\text{OH})_3\text{bicine}$) is 10^{38} . These numbers are very large as compared to the complexation constant of $10^{7.3}$ for bicine with iron (II) alone (from $K_1 \cdot K_2$). At pH 10 there is 0.0001 M OH^- and, even though $\text{Fe} - \text{OH}_x$ complexes may not be strong enough to cause significant iron solubility, any $\text{Fe}(\text{OH})^-$ that forms in the presence of bicine could be stabilized in a very strong FeOHbicine complex. While $\text{Fe}(\text{III})$ is not likely in H_2S systems, in the absence of H_2S , where iron oxide and iron hydroxide corrosion products may form¹⁹, the formation of FeOHbicine complex should actively contribute to corrosion.

The concentrations of caustic that would be required to have significant benefit, by Bosen & Biddel calculation (although the foregoing discussion shows that there is not a significant benefit), could only be tolerated in systems containing very high concentrations of Heat Stable Salts. Most gas plants would never approach such HSS levels. Refineries with which we are acquainted which do carry such high HSS levels to accommodate such high caustic addition, have severe operational and/or corrosion problems. One of the immediate difficulties with caustic addition is higher solution viscosity which can lead to less efficient absorption and stripping.

One thing that Bosen and Beddel overlooked (also not addressed in our calculations) is that the decrease in FeS solubility attributed to Na^+ or K^+ by their calculation, was of approximately equal magnitude to the increase in FeS solubility that would be caused by the change in activity coefficients caused by the increase in ionic strength upon addition to the solution of the respective amounts of Na^+ or K^+ . The net effect is no reduction in FeS solubility. Thus, addition of caustic to bicine laden solutions will have no beneficial effect.

Plant experience with Amino Acids

A Texas gas plant identified bicine as the root cause of amine system corrosion, correlated dissolved iron increases and decreases with bicine increases and decreases, found no reduction in corrosion attack upon 'neutralization' by caustic addition, and demonstrated effective online removal of bicine (and sodium) and greatly reduced corrosivity and dissolved iron using MPR's mobile HSSX® process.¹¹

A Gulf Coast Refinery added caustic to the amine solution to control escalating bicine levels. No impact on measured corrosion rates was observed, but unit performance continued to deteriorate, until they reduced the contaminants by purging out a significant portion of the amine and replacing with new amine.

A Gulf Coast gas plant encountered escalated corrosion rates and high bicine levels. Sodium was added in an effort to control the corrosion. Minimal impact was observed.

Three large Latin American gas plants belonging to the same operating company all experienced severe aggressive corrosion (pitting/etching) in stripper tower and reboiler. Bicine concentrations ranged from 7000 – 18000 ppm.

In all of these plant amine solutions, some amino acids other than bicine were detected. In many, HES could be identified, but some other amino acids were detected that have not yet been identified. All these would be expected to enhance corrosion in the same

manner as bicine. In amine solutions that we have analysed, the unidentified amino acids often appear to be more concentrated than the bicine.

A western U. S. natural gas producer was concerned about corrosion in the amine system due to bicine. The amine contained about 5,200 ppm amino acids, including 1,825 ppm Bicine. During a turn-around, the amine system was taken offline, and the entire system circulated through mobile ion exchange unit. The Bicine content was reduced to less than 25 ppm (0.0025 wt %).

WHAT CAN BE DONE TO PREVENT OR MITIGATE CORROSION?

Friedman² recently reviewed the various types of corrosion and detailed industry practices and recommended materials. Once the metallurgy and design of a plant has been chosen, the corrosion to be experienced will depend on the gas to be treated – the acid gases and the contaminants – and the mitigation methods applied. Metallurgy upgrade is usually a very expensive, thus infrequently used, method of corrosion reduction. Nielsen, et al,¹ with a long bibliography, reviewed various types of corrosion and detailed several prevention or mitigation methods that were common at the time, relating to wet CO₂ corrosion, NH₃, HCN, acid gas loading, temperature, H₂S/CO₂ ratio, heat stable salts, degradation products, erosion, and cracking. They also noted that the more basic amine solutions seem to be the more corrosive (e.g., MEA more than MDEA), and suggest the alkanolammonium ion to be the culprit. More probably responsible is the higher lean loading of acid gas, that is, the higher bisulfide and/or bicarbonate ion concentration in the more basic amines.

Erosion corrosion due to suspended solids can be mitigated by effective filtration. Unfortunately, filtration may not capture all the solids, because of pore size selection (e.g., larger pore size to reduce filter change out frequency), and solids may continue to circulate, or accumulate in low velocity areas to plug, block, or be picked up later. The beneficial filtration will remove large and small particles and keep the average particle size very small. Such a filtration process is MPR's SSX™ process.

Diamines, resulting from degradation of primary and secondary amines (e.g, MEA, DEA, DIPA), can be strong chelators of iron and thus promote corrosion by the acid gases. Diamines typically result from side reactions with CO₂, and rarely reach significant levels in amine systems, except in a few extreme situations. The only sure way to eliminate diamines in such extreme situations is to change to a tertiary amine (like MDEA or TEA). Systems which experience slow accumulation of diamines seem to also typically run with high heat stable salt content. Perhaps average stripper and reboiler temperatures are elevated because of the salt content, and the diamines form. If so, then reducing the salt content, should result in reduced formation rate of diamines and thus reduced accumulation. While it is too early to make firm conclusions, preliminary evidence indicates such a synergy. Two refinery DEA systems that had been accumulating the diamine THEED (tris-hydroxyethoxyethylenediamine), have for the past year been operating at lower than normal HSS concentrations and have not seen an increase in THEED concentration. The salts have been reduced by continuous ion exchange installations (MPR HSSX® process), which does not directly remove THEED.

Heat stable salts can be removed by ion exchange, distillation and electro dialysis. The best long term affects on corrosion are realized when HSS are continually kept low – 5000 to 8000 ppm or lower.

Amino acids, such as bicine, are best kept continually at very low concentrations – recommendations vary from 2000 ppm to less than 250 ppm. Depending on accumulation rate, this may require continual removal or occasional removal. Bicine and other amino acids have been removed from operating amine systems by ion exchange. Ion exchange is the only economical means of maintaining the recommended low concentrations of amino acids, if operated skillfully.

SUMMARY

Corrosion in amine systems is primarily caused by the acid gases which the amine is intended to absorb. Several factors enhance the acid gas corrosion rate directly or indirectly by interaction with corrosion limiting corrosion products. In this paper, we have reviewed the fundamental chemistry of acid gas corrosion and corrosion enhancement, and focused primarily on the chemical corrosion enhancers Heat Stable Salt, diamines, and amino acids. In recent years, amino acids (primarily bicine) have been shown to exist in a very large number of refinery and gas plant amine systems, and have been the focus of much attention and concern. Caustic ‘neutralization’ has been proposed as a means of reducing bicine’s corrosive effects, yet theory and plant experience shows it to be not the case. Plant experience has shown effective reduction of bicine by ion exchange.

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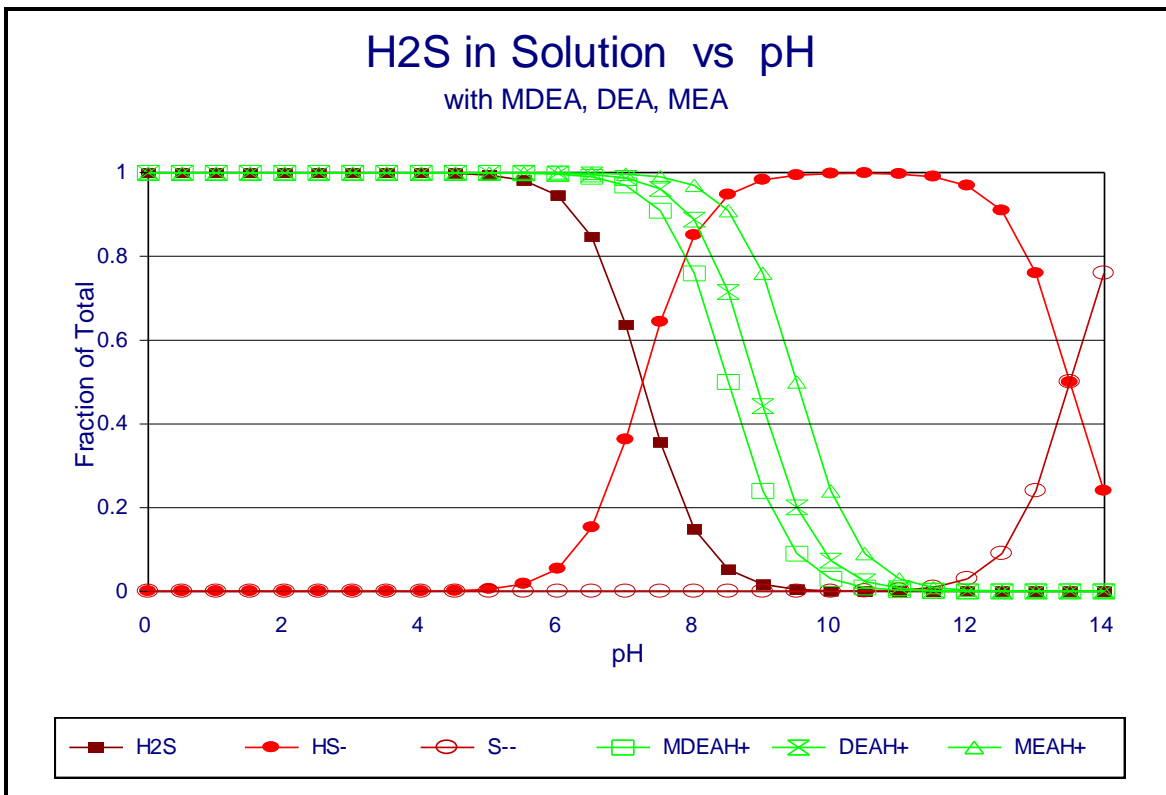


Figure 1
DISTRIBUTION OF H₂S FORMS IN AMINE SOLUTIONS
 pH is set by fraction of amine in bound (AmH⁺) form
 for example, pH of 0.5 mol/mol loaded MDEA is 8.5, so about 95% of H₂S is in HS⁻ form

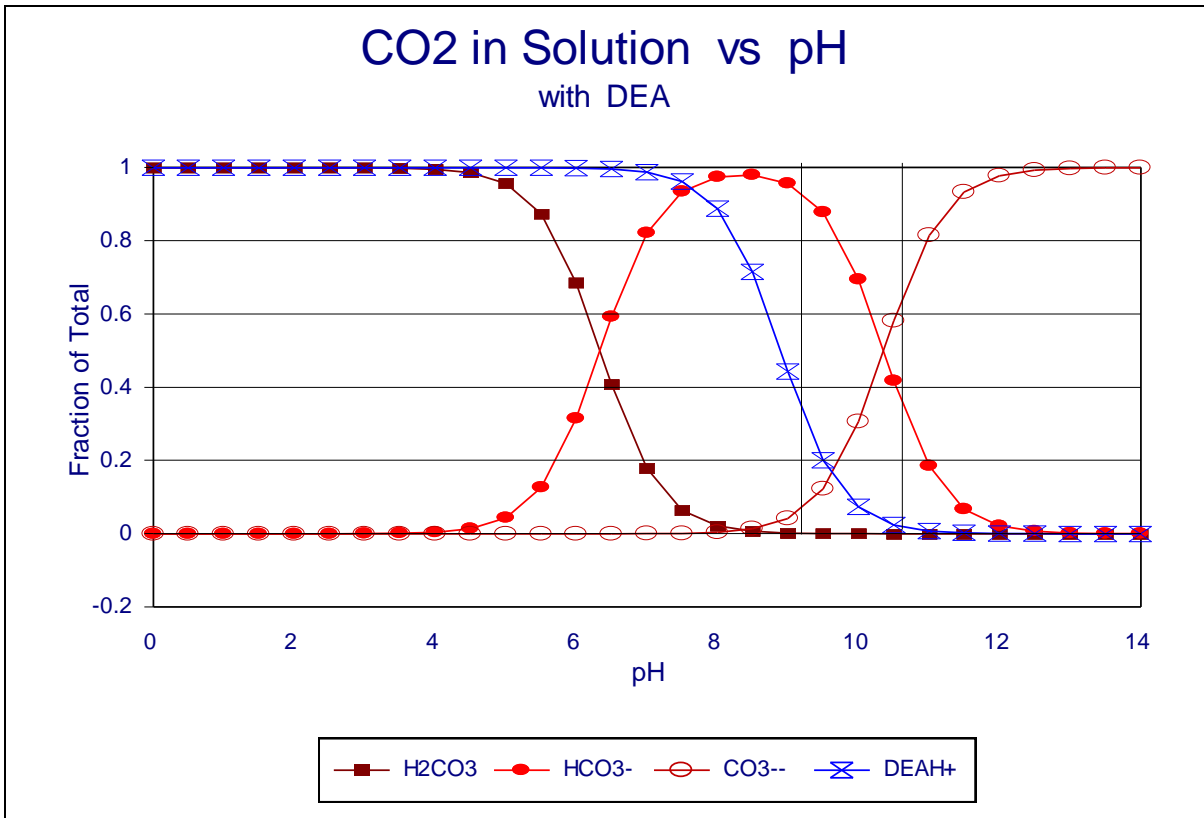


Figure 2
DISTRIBUTION OF CO₂ FORMS IN DEA SOLUTION
 pH is set by fraction of DEA in bound (DEAH⁺) form

For example, in 0.4 mol/mol loaded DEA about 95% of dissolved CO₂ is in HCO₃⁻ form, but in 0.02 mol/mol lean DEA it's about 40% HCO₃⁻, 60% CO₃²⁻.

Case	[Bicine]	[Na]	Log K _{Na}	Dow		MPR		
				[FeS] solubility	Ratio to case A	[FeS] solubility	Ratio to case A	Ratio to Case 0
0	0	0.00				1.4E-07		1
A	0.097	0.00	0.1	9.8E-05	1.00	6.2E-05	1.00	443
B	0.097	0.10	0.1	8.8E-05	0.90	5.5E-05	0.89	393
C	0.097	0.30	0.1	7.3E-05	0.74	4.6E-05	0.74	329
D	0.097	0.54	0.1	6.1E-05	0.62	3.8E-05	0.61	271
F	0.097	0.10	0.5	7.8E-05	0.80	4.9E-05	0.79	350
G	0.097	0.30	0.5	5.5E-05	0.56	3.4E-05	0.55	243
H	0.097	0.54	0.5	4.0E-05	0.41	2.5E-05	0.40	179

Table 1
Solubility of Iron Sulfide in H₂S Service at a pH of 10. The units of concentration are Moles/Liter

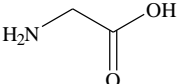
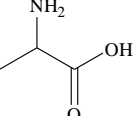
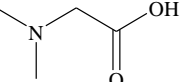
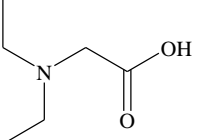
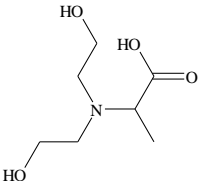
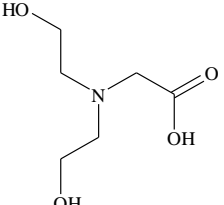
Ligand	Structure	Log K								
		Na ⁺ L	Mg ⁺² L	Mg ⁺² L ₂	Fe ⁺² L	Fe ⁺² L ₂	Cu ⁺² L	Cu ⁺² L ₂	Ni ⁺² L	Ni ⁺² L ₂
Glycine		-0.5	1.4	2.3	4.3	7.6	8.2	15.2	6.2	10.5
Alanine		0.3 ?	2.0		3.5		8.3	15.3	5.6	9.8
Dimethylglycine									4.8	8.6
Diethylglycine							6.9	12.6	4.2	
bis-Hydroxyethylalanine							8.3		6.0	
Bicine			1.2		4.3	7.4	8.2	13.4	6.4	10.8

Table 2. Comparison of Formation Constants for Bicine and Other Ligands. Formation constants were taken from reference 17, except the formation constant for alanine-Na was taken from reference 19.

Case	[Bicine]	[Na]	Log K_{Na}	MPR		
				[FeS] solubility	Ratio to case A	Ratio to Case 0
0	0	0.00		1.4E-07		1
L	0.097	0.10	-0.1	5.7E-05	0.92	409
M	0.097	0.30	-0.1	5.0E-05	0.81	359
N	0.097	0.54	-0.1	4.4E-05	0.71	313
O	0.097	0.10	-0.5	6.0E-05	0.96	426
P	0.097	0.30	-0.5	5.6E-05	0.91	402
Q	0.097	0.54	-0.5	5.3E-05	0.85	377

Table 3
Solubility of Iron Sulfide in H₂S Service at a pH of 10. The units of concentration are Moles/Liter.

Case	[Bicine]	[Na]	Log K_{Na}	2.5 M Amine, 0.3 M/M CO ₂			2.5 M Amine, 0.01 M/M CO ₂			Lean/Rich Ratio
				[FeCO ₃] solubility	Ratio to case A	Ratio to Case 0	[FeCO ₃] solubility	Ratio to case A	Ratio to Case 0	
0	0	0.00		1.5E-10		1	4.5E-09		1	30
A	0.097	0.00		2.9E-05	1.00	1.9E+05	8.6E-04	1.00	1.9E+05	30
B	0.097	0.10	-0.5	2.7E-05	0.94	1.8E+05	8.1E-04	0.94	1.8E+05	30
C	0.097	0.30	-0.5	2.4E-05	0.84	1.6E+05	7.1E-04	0.83	1.6E+05	30
D	0.097	0.54	-0.5	2.0E-05	0.70	1.3E+05	6.0E-04	0.70	1.3E+05	30
F	0.097	0.10	-0.1	2.5E-05	0.87	1.7E+05	7.4E-04	0.86	1.6E+05	30
G	0.097	0.30	-0.1	1.7E-05	0.59	1.1E+05	5.2E-04	0.60	1.2E+05	31
H	0.097	0.54	-0.1	1.0E-05	0.35	6.7E+04	3.1E-04	0.36	6.9E+04	31

Table 4. Solubility of Iron Carbonate in CO₂ Service at a pH of 10. The units of concentration are Moles/Liter. Rich conditions are 0.3 M/M [CO₂]/[amine]. Lean conditions are 0.01 M/M [CO₂]/[amine].