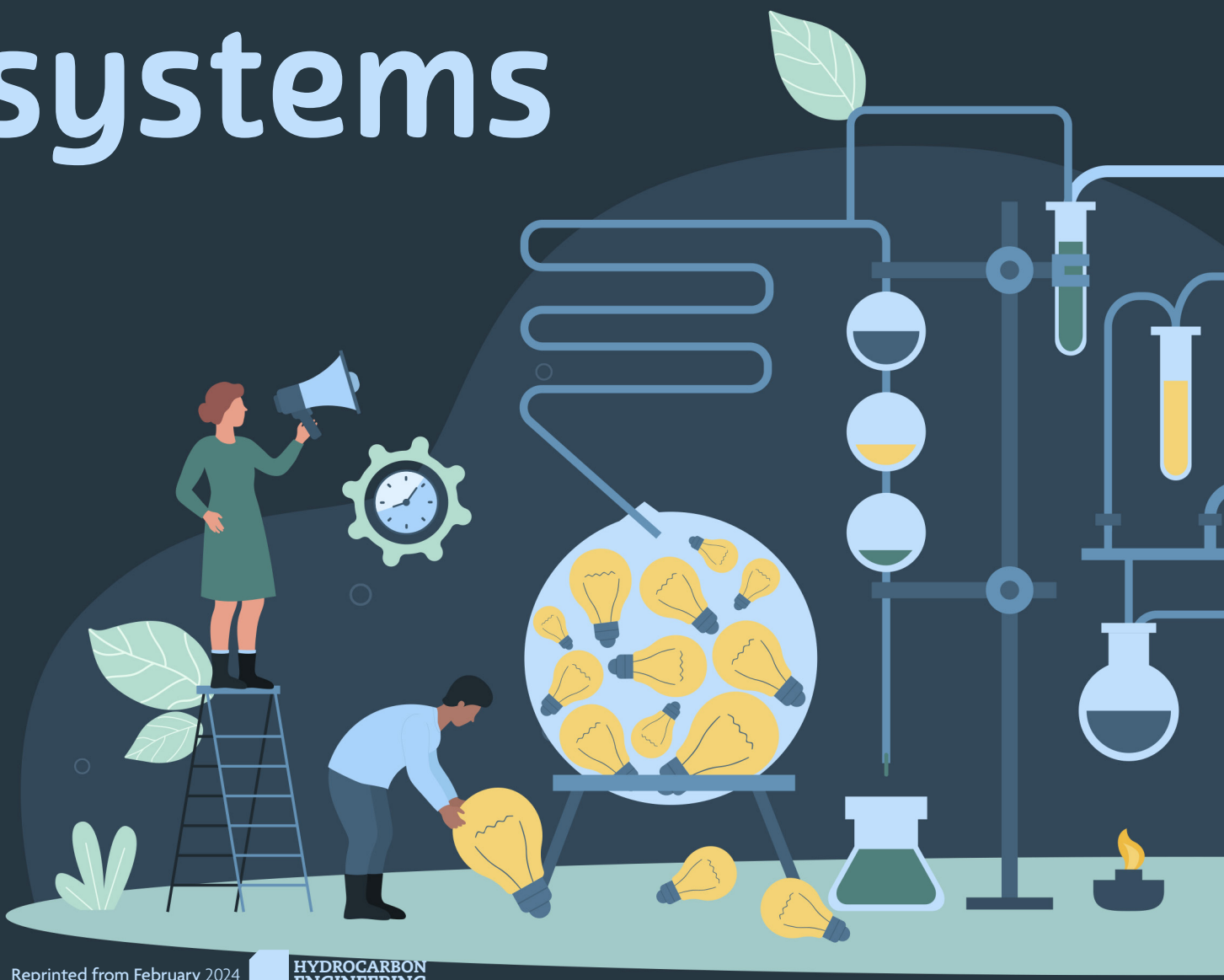
Understanding corrosion in amine and sour water systems



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Ralph H. Weiland, Optimized Gas Treating Inc. (OGT), reveals how acid gas corrosion can be understood from the perspective of chemistry.

The focus of this article is on understanding acid gas corrosion in alkaline amine and sour water systems from the perspective of basic chemistry. Some underlying tenets are presented and developed to explain observations and common symptoms seen in operating plants. The discussion is simplified as follows:

- Carbon steel: stainless steels (austenitic in particular) are much more resistant to this type of corrosion, and it is recognised that they can be used, albeit at a higher investment cost. The primary issue however, is to understand when carbon steel may be a poor metallurgical choice.
- Alkaline environments: many of the concepts apply equally to pH-neutral and acidic systems. However, the level of corrosion data for modelling is much sparser and these areas exist primarily in the regenerator overhead acid gas circuit. Acidic systems are outside of the scope of this article.

Tenet 1: the amine (or NH_3) is not corrosive

Despite being completely incorrect, the industry continues throwing around such terms as 'amine corrosion' and 'alkaline stress corrosion cracking' to describe corrosion that, at the root level, is really caused by dissolved acid gases, not the amine.

As early as 1955, Polderman et al reported that 20%wt monoethanolamine (MEA) solution without acid gas was less corrosive to steel than pure water.[1]

It is true that some amine systems appear to be more susceptible to corrosion than others. The reason for this is that the activity of the dissolved acid gas species changes with the amine type, its concentration, the acid gas loading, and the temperature. The amine type itself, however, is not directly responsible. The dissolved acid gas species of interest are: bisulfide ion (HS^-), free physically dissolved hydrogen sulfide (H_2S), bicarbonate ion (HCO_3^-) and free physically dissolved carbon dioxide (CO_2). Carbonate ($CO_3^=$) and sulfide ($S^=$) are themselves oxidation products that cannot donate the proton necessary for reaction with the iron in carbon steel and, therefore, are inherently noncorrosive. The corrosivity of CO_2, H_2S, bicarbonate and bisulfide depend on the activity of these species, not their concentration.

In their simplest stoichiometric form, the basic corrosion reactions of dissolved H_2S and CO_2 species with iron are as follows:

$$H_2S(aq) + Fe(s) \rightarrow FeS(s) + H_2(g) \quad (1)$$

$$2HS^-(aq) + Fe(s) \rightarrow FeS(s) + H_2(g) + S^=(aq) \quad (2)$$

$$CO_2(aq) + Fe(s) + H_2O + FeCO_3(s) + H_2(g) \quad (3)$$

$$2HCO_3^-(aq) + 2Fe(s) \rightarrow 2Fe(s)CO_3(s) + H_2(g) \quad (4)$$

The oxidation reaction with H_2S is faster than with bisulfide; however, the alkalinity of the amine (and ammonia) solutions means that the dissolved H_2S is predominantly in the bisulfide form, with very little remaining as free molecular H_2S. This is also true of dissolved CO_2. The concentrations of free acid gases are pH dependent, and pH is a function of amine strength, total dissolved acid gas, temperature and, to a lesser extent, heat stable salt (HSS) concentrations. However, HSSs and their concentrations do affect the speciation of the solution, especially in lean solvents. As discussed later, certain HSSs, notably bicine, can chelate iron and thereby significantly accelerate corrosion.

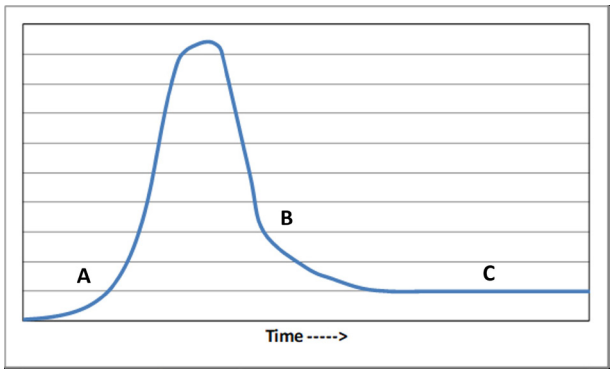

Figure 1. Corrosion vs time for steel passivation.

When H_2S reacts with the iron in carbon steel, solid iron sulfide precipitate is formed, along with hydrogen gas. Since both reactions transcend phase boundaries and create reaction products in completely different phases (for example, hydrogen is generated into a separate phase), it follows from Le Chetalier's principle that there is a powerful thermodynamic driving force causing corrosion to occur. What limits the reaction is primarily the presence and the amount of bare unreacted iron at the steel surface. A secondary factor is the concentration of dissolved acid gas reactant, i.e., H_2S. The dissolved H_2S concentration can be regarded as another parameter. In an attempt to control the concentration of dissolved acid gas, many practitioners have adopted upper limits on the acid gas loading of the rich amine.

Tenet 2: iron sulfides can protect against further corrosion

If in a new amine unit (one that had never previously been exposed to H_2S) one were to plot corrosion rate as a function of time, the plot qualitatively would look similar to the one shown in Figure 1. This is for the period immediately following H_2S introduction. There is an initial period (Region A) during which the corrosion rate climbs almost exponentially as the fresh iron is exposed to dissolved acid gas. This is followed by a period during which the corrosion rate levels off and then falls (Region B) as the iron sulfide film begins to block or occlude contact of fresh H_2S with the iron. Eventually, once the iron sulfide layer is established, the system settles down to the nominal and, hopefully, low residual corrosion rate shown in Region C.

If one were to examine the steel surface with an electron microscope, the iron sulfide protective layer would appear to be imperfect. This is primarily the result of evolution of hydrogen gas that is formed as a product of the corrosion reaction itself. Because of this, a residual nominal corrosion rate is expected and observed in operation. It is the quality of the iron sulfide protective layer or film that dictates the final, residual corrosion level for the system.

The corrosion rates in Region A are commonly observed during initial startup or following a turnaround after a chemical cleaning (especially acidising types) has been conducted. The amine will typically appear black from the macroscopic iron sulfide particles that are suspended in solution and absorbing light. A period of hours to weeks can pass, during which particle filters will plug and require change-out almost immediately after being placed in service. Measurements by Cummings et al on a bench-scale mini-amine plant with relatively lean amine, indicated in some cases over 600 mils per year (mpy) corrosion rate during this phase of operation.[2]

As the steel begins to passivate (Region B), solid iron sulfide particles will grow and begin to find homes either in a filter element (desired), or by settling out on trays or equipment and piping low points (undesired). As the solution clears of iron sulfide particles, the colour will change from black to dark green, and then paler green (microscopic iron sulfide particles). Ultimately the solvent

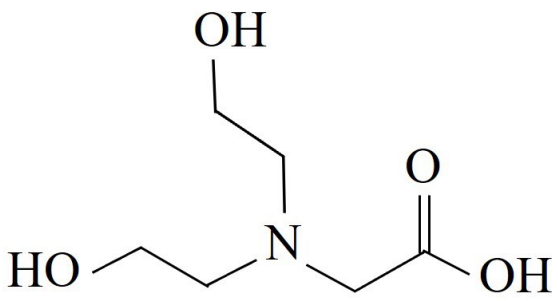

Figure 2. Structure of bicine.

should return to clear and either colourless, or with a slight amber colouration.

Managing corrosion begins with preservation of the protective iron sulfide film. Velocity creates sheer stress on the pipe surface and the sheer force can be sufficient to rip off the imperfect iron sulfide layer. This exposes fresh steel, and corrosion locally increases in the area of this high velocity and high shear rate. The iron sulfide particles that are dislodged can subsequently act as a scouring agent to increase corrosion in other areas of the plant. Furthermore, wherever velocity is reduced, the particles can settle out in unwanted places.

For these reasons, the gas treating industry has generally adopted velocity limits for carbon steel piping in amine service. Lean amine velocities are typically held to 7 - 10 ft/s while rich amine velocities are commonly held to 3 - 5 ft/s. Special care should be taken in areas of the plant where two-phase flow (flashing) can occur as this can result in extraordinarily high velocities, slug flow, and very high corrosion rates, certainly reaching more than 10 mpy. Rich amine level control valves, pressure letdown valves and the heated rich amine outlet from the lean-rich exchanger are special problem areas and are often constructed using austenitic stainless steel (304L or 316L SS).

Just as sheer stress can physically accelerate corrosion, reactions can accelerate corrosion by chemical means. Through chelation, insoluble iron sulfide can be converted into an ionic complex that is dissolved in solution. The equilibration between the iron sulfide present on the steel surface (FeS) and the complexed iron can be expressed as a solubility product through the following chemistry[2] exemplifying iron chelation by formate ion ($HCOO^-$):

$$FeS + 7\,H_2O \rightleftharpoons Fe(H_2O)_6^{+2} + HS^- + OH^- \quad (5)$$

$$Fe(H_2O)_6^{+2} + nHCOO^- \rightleftharpoons Fe(n\,HCOO^-)^{(2-n)} + (6-n)\,H_2O \quad (6)$$

Metallic iron is insoluble in water, even at high temperatures. However, reaction (6) provides a sink for iron. Complexed iron is in a different phase than the iron sulfide reactant, so the driving force can be significant. This chemistry leads to an impressive transport mechanism for accelerating corrosion that works as follows:

- Equation (5) shows that the presence of H_2S loading as bisulfide ion (HS^-) drives the system towards the left. Therefore, H_2S loading tends to promote a stable iron sulfide protective film.
- HSSs are stripping promoters and reduce the lean loading, tipping the equilibrium of (5) towards the right.
- Additionally, the complex provided by the HSS anion – formate ion in Equation (6) – further pushes the reactions towards destabilisation of the iron sulfide film.
- The complexed iron is not filterable and travels in a form that appears to the naked eye as yellow-tinted amine to an absorber where the H_2S concentration is higher.
- At the higher H_2S concentrations in a typical absorber, the equilibrium is shifted away from complexation and back to making iron sulfide corrosion product. This time, however, instead of being on the pipe surface, the iron sulfide is present as variously sized particles inside the contactor. It leaves with the rich amine and travels to other points in the treating plant.

Bicine

Bicine (Figure 2) has received considerable attention as a pernicious bane for corrosion in amine systems.[3,4] As an amino acid, bicine is a zwitterion, but although it is an ion, it is close to being a neutrally charged molecule under the pH conditions extant in amine systems. Typical of all amino acids, bicine has both an amino functional group and an acidic (HSS) group. By all indications, the zwitterionic or hermaphroditic nature of this molecule appears to give it the characteristics of a very strong iron chelator. In many cases, the concentrations at which serious corrosion has been reported seem to be higher (several weight percent in solution) than those typically encountered with HSSs. There is insufficient exisiting data to allow modelling corrosion by HSSs.

Bicine appears to show up in DEA and secondary amine systems subject to oxygen contamination when treating CO_2 only, or with systems containing very low H_2S concentrations in the feed. When H_2S is present at significant concentrations in the feed gas, oxygen is expected to be scavenged effectively by reaction with the residual H_2S present as lean loading to make the HSS, thiosulfate. Bosen and Bedell ran corrosion simulations which suggested that the presence of H_2S in the amine at as little as 10 ppm could eliminate the chelation concerns of bicine.[5]

References

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