Predicting Corrosion Rates in Amine and Sour Water Systems

This issue of The Contactor discusses the basis for a semi-empirical, mechanistic model for H_2S-induced corrosion of various metallurgies in alkaline systems. This model is being offered commercially for the first time in ProTreat® Version 5.3. Although the concepts presented her apply equally to pH-neutral and acidic systems, the amount of corrosion data available for modeling is much smaller, so these systems are not addressed.

Several tenets are embedded in the model, and we will discuss each one briefly:

- The amine (or ammonia) is *not* corrosive
- The iron sulfide film can protect against further corrosion
- Fluid velocity physically increases corrosion
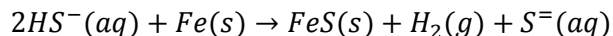- Heat stable salts chemically exacerbate corrosion

Although completely <u>in</u>correct, the industry continues to bandy about 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. For example, more than 55 years ago, Polderman[†] reported that 20 wt% MEA without acid gas was actually *less* corrosive to steel than pure water. The *activity of the dissolved acid gas species* changes with the amine type, concentration, acid gas loading, and temperature—this may make some amine systems <u>appear</u> more susceptible to corrosion than others. The species of interest are: bisulfide ion (HS^-), free physically dissolved H_2S, bicarbonate ion (HCO_3^-) and free physically dissolved CO_2[‡].

In their simplest stoichiometric form, the basic corrosion reactions of dissolved H_2S species with iron are as follows:
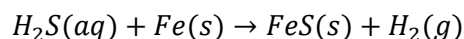
$$H_2S(aq) + Fe(s) \rightarrow FeS(s) + H_2(g)$$

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

The reaction of H_2S with the iron component of various steel metallurgies forms solid iron sulfide precipitate and hydrogen gas. Both reactions create reaction products in completely different phases. Thus, because reaction products are removed from the reacting solution, it follows from Le Chatelier's principle that there is a *strong thermodynamic driving force powering continued corrosion*. What limits the corrosion reactions is primarily the amount of bare unreacted iron at the metal surface. A secondary factor is the concentration of dissolved reactant gas, i.e., H_2S, which is another parameter. To control the concentration of dissolved gas, most practitioners adopt upper limits[§] to rich-amine acid-gas loading.

In a new amine unit or in one that has just been cleaned, during the period immediately following introduction of H_2S, the corrosion rate climbs exponentially. Measurements by Cummings et al.[**] using a bench-scale mini-amine-plant with relatively lean amine indicated in some cases over 600 mpy corrosion rate during this phase of operation. Eventually the corrosion rate levels off and begins to fall as the iron sulfide layer increasingly occludes contact between H_2S and iron (passivation). Finally, once the iron sulfide layer is established, the system settles down to a nominal (and hopefully low) residual corrosion rate. During these three phases, in succession, the solution will first become nearly black, and then change to dark green, lighter green, and finally slightly amber[††]. The coloration depends on the size of the iron sulfide particles.
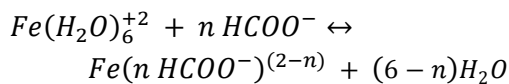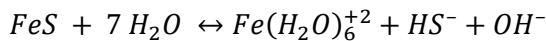

[†] Polderman, L.D., Dillon, C.P., Steel, A.B., Oil & Gas J., May 16, 1955, p. 180.
[‡] Carbonate ($CO_3^=$) and sulfide ($S^=$) are themselves oxidation products that cannot donate the necessary proton for reaction with iron.

[§] The loading of H_2S and CO_2 in the rich amine is limited to < 0.4–0.5 moles of *total* acid gas per mole of amine in solution.
[**] Cummings, A.L., Veatch, F.C., Keller, A.E., *Corrosion and Corrosion Control Methods in Amine Systems Containing H_2S,* NACE Corrosion 1997 Conference, Paper No, 341
[††] Chelated iron (which results from complexation) scatters light and will otherwise turn contaminant-free solution amber.

Managing corrosion begins with protecting the iron sulfide film on the metal. Fluid velocity creates sheer stress on solid surfaces—the shear force can be enough to rip off the imperfect iron sulfide layer. When this happens, fresh iron is exposed and corrosion increases in the area of high velocity. Subsequently, the dislodged iron sulfide particles can act as a scouring agent and increase corrosion in other areas of the plant. 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 below 7–10 ft/sec while rich amine velocities are commonly held below 3–5 ft/sec. Note: the two-phase flows that result from even a little flashing can cause extremely high velocities.

Heat stable salts (HSSs) chemically exacerbate corrosion by chelating iron:

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

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

Our model framework can be extended to cover heat stable salts and OGT is looking for data

Our semi-empirical, chemistry-based kinetic expression was developed on the basis of about 130 corrosion measurements taken in well-controlled bench-scale equipment using rich amine systems and sour water. Although the quantitative model is proprietary to Optimized Gas Treating, Inc., it follows the general form below. It contains many of the elements that comprise the tenets discussed earlier:
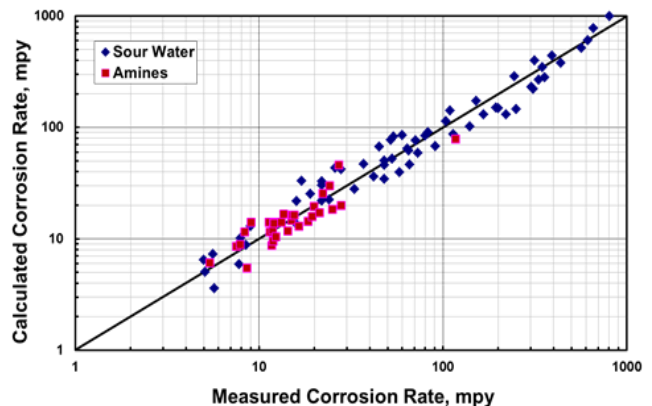
$$Corrosion\ Rate\ (mpy) =$$
$$K_o e^{[-(aV+b)/RT]}\left[a_{H_2S}^n a_{HS^-}^p + c\right]$$

Here: K_o = Arrhenius pre-exponential factor
a, b, n, c and p are regression parameters
a_{H_2S} = activity of dissolved H_2S
a_{HS^-} = activity of dissolved bisulfide ion
R = ideal gas constant
T = absolute temperature
V = fluid velocity in pipe at lab conditions

Data were correlated over the range of conditions shown in Table 1. Figure 1 shows that this model fits the measurements over nearly three orders of magnitude to within a remarkable ±30%.

Table 1   Data Ranges Correlated

Parameter	Range of Data
Lab velocity	0 – 80 ft/s
Temperature	130 - 250°F
Sour water	1-30%wt NH_4HS equivalent 50-150 psia H_2S partial pressure
Amines	MEA (18-30%wt) DEA (30%wt) MDEA (45%wt) 0.1 – 0.8 mole H_2S/mole amine
Calculated pH	6.0 – 9.5

Figure 1 Measured vs. Calculated Corrosion Rate

In correlating the corrosion rates, an Arrhenius form in temperature was found to fit the data well. The constant *c* was selected to force the model to asymptote to the corrosion rate of carbon steel in pure water under the limit of zero acid gas concentration. Additionally, as velocity approaches zero, the correlating equation approaches the measured corrosion rate in a static equilibrium cell. Note that *amine strength and ammonia strength do not appear explicitly*, although their concentration does affect the activity of the dissolved species.

This model's mechanistic underpinning lends it to confident interpolation and extrapolation to conditions well outside the measured ranges.

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