

Predicting corrosion rates in amine and sour water systems

A chemistry-based predictive model predicts corrosion rates in specific processing conditions

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Corrosion is a ubiquitous problem in gas treating in the petroleum and natural gas industries, in syngas plants, in processing unconventional gases such as shale and coal seam gas, and in numerous other treating applications. The primary impurities removed in the treating process are the acid gases carbon dioxide and hydrogen sulphide. The corrosion of equipment and piping is an inevitable consequence of removing these very gases with amines, and of handling sour water. There are other corrosive impurities that either enter in small amounts with the gas, such as HCN and oxygen, or that are produced in the amine system itself, mostly heat stable salts (HSS) derived from HCN. Corrosion rates are affected by the nature of the corrosive agent, temperature, fluid velocity, the presence of solids, and the metallurgy involved.¹ To prevent equipment failures, mitigate risk and select optimal materials, one must be able to predict corrosion rates pertinent to the particular processing conditions. This article describes the underpinnings of a chemistry-based predictive corrosion model built on both public and much proprietary corrosion rate data. The model includes dependence on ionic solution composition (speciation), fluid velocity, temperature, HSSs, and metallurgy.

Corrosion in alkaline systems

Although the concepts presented here apply equally to pH-neutral and acidic systems, these systems are not addressed because the amount of corrosion data available

for modelling is not as extensive. The corrosive action of H₂S is inherently different from that of CO₂ in that H₂S can and does form a relatively robust, protective iron sulphide layer on the metal surface. On the other hand, iron carbonate forms a more fragile layer, so it offers much less protection. There are several tenets embedded in the model:

- The corrosive agents are acids
- In and of itself, the amine (or ammonia) is not corrosive

Corrosion rates are affected by the nature of the corrosive agent, temperature, fluid velocity, the presence of solids, and the metallurgy involved

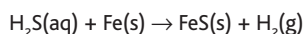
- The iron sulphide film can protect against further corrosion
- Iron carbonate also offers protection but to a lesser degree
- High fluid velocities physically increase corrosion rates
- Higher temperature increases corrosion rates
- Heat stable salts chemically exacerbate corrosion.

Although technically incorrect, the industry continues to bandy about such terms as 'amine corrosion' and 'alkaline stress corrosion cracking' to describe corrosion that, at the root level of chemistry, is really caused by dissolved acid

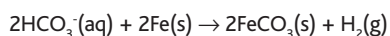
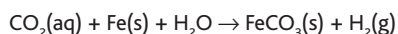
gases in various forms. For example, nearly 60 years ago, Polderman² reported that 20 wt% MEA without acid gas was actually less corrosive to steel than pure water. As far as the corrosive agents themselves are concerned, the important parameter is the chemical activity of the dissolved acid gas species responsible for corrosion. The activity (vs concentration) changes with the amine type, amine concentration, acid gas loadings, the concentrations and identities of HSSs, and temperature. This may make some amine systems appear to be more susceptible to corrosion than others; however, the essential point is that it is the activity of the corrosive species that is of direct importance, not the type of amine *per se*.

The chemical species of interest are: bisulphide ion (HS⁻), free physically dissolved H₂S, bicarbonate ion (HCO₃⁻), and free physically dissolved CO₂, all of which are oxidising agents. These species are called protonic acids because they can give up a hydrogen ion.³ Sulphide (S⁼) and carbonate (CO₃⁼) ions are also present; however, they themselves are final reaction products and are unable to provide the hydrogen ion necessary for the oxidation of iron. Molecular hydrogen sulphide and carbon dioxide react with iron only in the presence of water. The final distribution of molecular and ionic species is found by solving the equations of chemical reaction equilibria, atom balances, and a charge balance. The resulting set of species concentrations is termed the solution's speciation.

In their simplest stoichiometric forms, the basic corrosion reactions of dissolved H₂S species with iron are:



For CO₂, the relevant reactions are:



The oxidation reaction with hydrogen sulphide is faster than the reaction with bisulphide; however, the alkalinity of the amine (and ammonia) solutions means that the dissolved H₂S is predominantly in the bisulphide form, with very little remaining as free molecular hydrogen sulphide. This is also true of dissolved carbon dioxide. The concentrations of free H₂S and CO₂ are pH dependent and pH is a function of amine strength, total dissolved acid gas, temperature, and to a lesser extent HSS concentrations. However, heat stable salt species and their concentrations do affect the speciation of the solution, especially in lean solvents.

As discussed by Cummings *et al*¹, the sequence of physico-chemical steps in the process of oxidising iron consists of transporting the acid from the bulk solution to the metal surface, adsorption of the acid onto the surface, reaction with iron, and transport of reaction products back into the bulk solution. The steps are similar to what occurs in heterogeneous catalysis. The reaction of H₂S with the iron component of various iron-based metallurgies forms solid iron sulphide and hydrogen gas, and as the reaction proceeds, the surface of the iron is changed to a mosaic of iron and sulphide ions. The surface expands by addition of sulphide, and the liberation of hydrogen gas exacerbates the expansion. The surface layer is somewhat porous, and it adheres to the surface of the free metal. The iron-H₂S and iron-HS⁻ reactions form reaction products in completely different phases, as do

the reactions with carbon dioxide and bicarbonate. Thus, because reaction products are continually 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 that the passivating film leaves available at the metal surface. A secondary factor is the concentrations of dissolved reactant gases, H₂S and CO₂, which are other parameters. Thus, H₂S, HS⁻, CO₂ and HCO₃⁻ all react with unprotected iron. To control the concentration of dissolved gas in their various forms, most practitioners adopt a rich amine acid gas loading, upper limit of <0.4 to 0.5 moles of total acid gas per mole of molecular amine.

Passivation

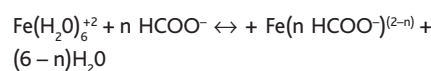
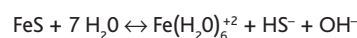
In a new amine unit or in one that has just been cleaned, during the period immediately following introduction of H₂S, for example, the corrosion rate climbs exponentially. Measurements by Cummings *et al*.³ using a bench-scale mini-amine plant with relatively lean amine indicated in some cases over 600 mpy corrosion rate during this phase of operation. Eventually, the corrosion rate levels off and begins to fall as the iron sulphide layer increasingly occludes contact between H₂S and iron (passivation). Finally, once the iron sulphide layer is established, the system settles down to a nominal (and hopefully low) residual corrosion rate. The time over which the final steady corrosion rate is attained is on the order of hours or even days. During these three phases of passivation, the solution first becomes nearly black, and then it changes to dark green, lighter green, and finally slightly amber. Chelated iron (which results from complexation) scatters light and turns otherwise contaminant-free solution to amber. The coloration depends on the size of the iron sulphide particles. The results of experiments on the time dependence of iron passivation by carbon dioxide are sparse. In one

test, CO₂ was added to an amine solution that already contained H₂S. The corrosion rate quickly rose and in less than one hour a new higher steady corrosion rate was established. The precipitated layer of iron carbonate is very fragile, so it is unlikely to adhere as tenaciously to metal surfaces as iron sulphide does. Different abilities to adhere are contained within the framework of the present model.

Managing corrosion begins primarily with protecting the iron sulphide film on the metal. Fluid velocity creates sheer stress on solid surfaces — the sheer stress can be enough to rip off the imperfect iron sulphide layer, and even a low velocity seems very likely to dislodge and remove iron carbonate deposits. When this happens, fresh iron is exposed and corrosion increases in the region of high shear stress. Subsequently, the dislodged iron sulphide and iron carbonate particles can act as scouring agents and increase corrosion in other areas of the plant via that mechanism. 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/s while rich amine velocities are commonly held below 3–5 ft/s.

Even a little flashing can greatly increase the velocity in a pipe, and the high velocity flow from the passing biphasic scours the iron sulphide layer. This results in drastically shorter piping life. Although less accurately than for single-phase flows, it is still possible to provide reasonable estimates of corrosion rates in two-phase flows, and this is done in the present model.

Heat stable salts (HSS) affect corrosion rates by altering solution speciation, and they chemically exacerbate corrosion by chelating iron and destroying the passivating iron sulphide layer:



There are very few quantitative measurements of the effect of HSSs

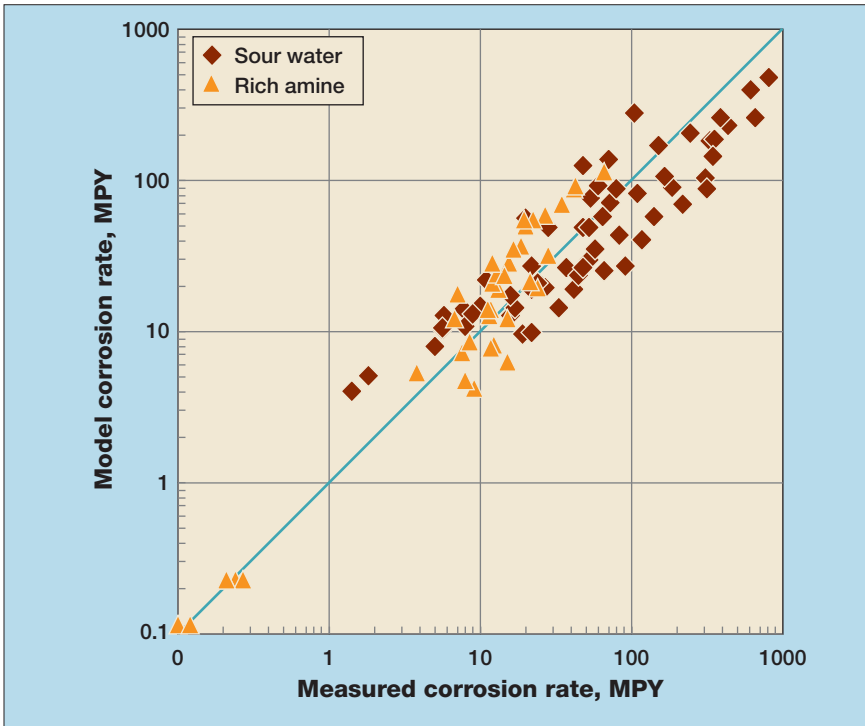


Figure 1 Parity plot of measured vs model corrosion rates in rich amine and sour water systems containing H₂S only

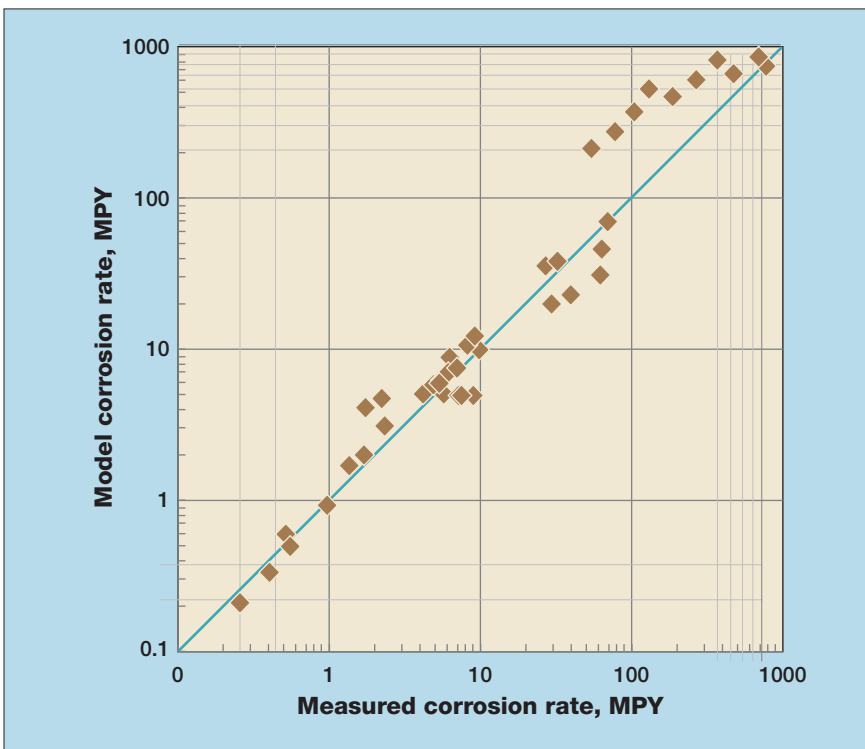


Figure 2 Parity plot of measured vs model corrosion rates in amines containing CO₂ only

on corrosion and, although data on certain HSSs are included in the current model, more data over a broader range of species and conditions would be very welcome.

Model

Our mechanistic, chemistry-based corrosion rate model was

developed on the basis of the sequence of steps outlined earlier, namely, diffusion of the corrosive agent to the surface, adsorption, reaction with iron, and either deposition or diffusion of products away from the surface. The parameters in the model have been regressed to a large number of corrosion

measurements taken in well-controlled bench scale flow apparatuses and static equipment using both H₂S and CO₂ rich amine systems and sour water. Although the details of the quantitative model are proprietary to Optimized Gas Treating, Inc., the corrosion rate in the model is a function of the important factors:

$$\text{Corrosion rate} = f(a_{\text{H}_2\text{S}}, a_{\text{HS}^-}, a_{\text{CO}_2}, a_{\text{HCO}_3^-}, v, T)$$

Here: $a_{\text{H}_2\text{S}}$ = activity of dissolved H₂S
 a_{HS^-} = activity of bisulphide ion in solution

a_{CO_2} = activity of dissolved CO₂

$a_{\text{HCO}_3^-}$ = activity of bicarbonate ion in solution

T = absolute temperature

v = superficial fluid velocity in pipe.

The model contains many of the elements that comprise the tenets discussed earlier and in a form consistent with the various steps occurring during corrosion, including adsorption isotherms and the temperature dependence of both reaction kinetics and turbulent diffusion. The model even includes corrosion by water alone as a limiting case in highly dilute solutions. Data for corrosion by H₂S were correlated over the range of conditions shown in Table 1. Although scatter in the data is sizeable, if for no other reason than that repeatable corrosion rate measurements are hard to make, especially by weighing coupons, Figure 1 shows that this model fits the measurements over nearly three orders of magnitude. Data for corrosion by CO₂ were taken in both a static cell and in a flow apparatus. Parameter ranges and a parity plot comparing the model with measurements of corrosion in CO₂-only amine systems are shown in Table 2 and Figure 2, respectively.

In correlating the model, Arrhenius kinetics was found to fit the data well. This is in agreement with the proposal of Cummings *et al.*³ These authors assumed a power law kinetics expression in terms of molecular and ionic concentrations; however, we found a better fit using activities rather than concen-

Parameter ranges for corrosion by H ₂ S	
Parameter	Range
Lab velocity	0–25 m/s
Temperature	55–120°C
Sour water	1–30 wt% NH ₄ HS equivalent 3.5–10 bar H ₂ S partial pressure
Amines	MEA (18–30 mass %) DEA (30 mass %) MDEA (45 mass %)
Calculated pH	0.1–0.8 mole H ₂ S/mole amine 6.0–9.5

Table 1

trations. Note that neither amine strength, nor amine type, nor ammonia content appears explicitly, although these parameters have significant effects on the activity of the corrosive species in solution because speciation depends on the amine type, its concentration, and the temperature. Corrosion of other metallurgies is included in the model's capabilities, as is the corrosion of common pipe fittings. The model's mechanistic

Parameter ranges for corrosion by CO ₂	
Parameter	Range
Lab velocity	0–13.5 m/s
Temperature	20–160°C
Amines	MEA (6–30 mass %) DEA (10–40 mass %) AMP (9–35 mass %) MDEA (35 mass %)
Calculated pH	0.0–0.4 mole CO ₂ /mole amine 8.4–11.36

Table 2

underpinning lends it not only to confident interpolation, but also to reliable extrapolation to conditions well outside measured ranges.

References

- 1 Cummings A L, Waite S W, Nelsen D K, Corrosion and corrosion enhancers in amine systems, Brimstone Sulfur Conference, Banff, Alberta, April 2005.
- 2 Polderman L D, Dillon C P, Steel A B, *Oil & Gas J.*, 16 May 1955, 180.

3 Cummings A L, Veatch F C, Keller A E, Corrosion and corrosion control methods in amine systems containing H₂S, NACE Corrosion 1997 Conference, Paper No, 341.

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