Sour Corrosion Modeling

Yannick Beauregard
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Sour Gas Pipeline Incidents


Sour gas defined as containing 1 mol% $\text{H}_2\text{S}$ or more

Figure 1.2 Sour Gas Pipeline Incidents by Cause

All Other Causes includes: Earth Movement (2), Girth Weld Failure (3), Mechanical Joint Failure (1), Miscellaneous (3), Operator Error (3), Overpressure Failure (3), Unknown (1).

Sour gas incidents represented 3% of all incidents in Alberta in 2008.
The corrosion rate is influenced by many parameters, including:

- Acid gas composition, i.e., CO$_2$, H$_2$S
- Brine chemistry
- Flow rates
- Liquid hydrocarbons
- Inhibitor use
- Sand, solids
- Temperature
- Pressure.
General Mechanism and Appearance

Rapid Film Formation (semi-protective)

Film breakdown caused by presence of solids, chlorides, methanol, elemental Sulphur, high velocities...


Guidelines for Managing Internal (Sour) Corrosion

Referenced in CSA Z662-15 Section 16 – Sour Service Pipeline

Methodology:
Step 1: Pre-assessment
Step 2: Indirect Inspection
Step 3: Detailed Examination
Step 4: Post-assessment
Modeling Sour Corrosion

- Modeling is part of the NACE ICDA Indirect Inspection Step
  - 16 models listed in NACE WG-ICDA (SP0110-2010) Appendix B
  - Not all models listed are intended for H2S
- Guidance for selecting models is provided in NACE publication 21410 (Selection of Pipeline Flow and Internal Corrosion Models)

The predictive models are used to answer the following questions:

- Does internal corrosion pose a threat?
- Where in the pipeline is the internal corrosion likely to occur?
- When during operation is the internal corrosion likely to occur?
- What is the corrosion mechanism likely to be?
- Which operating parameters need to be monitored to predict the corrosion?
Model Approaches

Mechanistic
Based on fundamental equations that represent the physical and chemical phenomenon

Empirical
Based on correlations observed in experimental or field data
Highlighted Models


Freecorp incorporation expected soon, available at www.corrosioncenter.ohiou.edu/

Zheng et al. 2016 – Model Overview

1. Chemical reactions in the bulk solution
2. Mass transport of aqueous species through the liquid boundary layer and porous surface layer
3. Electrochemical reactions at the steel surface
4. Formation of porous corrosion product layers that may or may not be protective

$\mathbf{N_{w,j}} = \pm \frac{j_{j}}{n_{j} F}$

Flux due to electrochemical reaction at the steel surface

$\mathbf{C_{scale,j}}$: concentration of different species at the scale surface

$\mathbf{C_{bulk,j}}$: concentration of different species in the bulk solution

$\mathbf{C_{surface,j}}$: concentration of different species at the steel surface
Zheng et al. (2016) – Validation

- Validated against experimental data from glass cell tests, flow loop tests, open literature and other model
- Surface Layer Conditions: no corrosion product layer, iron carbonate corrosion layer and iron sulfide corrosion layer
- Effect of $\text{pH}_2\text{S}$, pH, flow, temperature
Zheng et al. (2016) – Validation – Good fit under certain conditions

FIGURE 6. Comparisons between model predictions and experiment results for 30°C, 1 bar (100 kPa) total pressure, and various H$_2$S concentrations, velocities, and pH.
Zheng et al. (2016) – Validation – certain conditions still need refinement

**FIGURE 12.** Corrosion rate changing with time. Points: experimental data, lines: model predictions. Conditions: 0.054 bar (5.4 kPa) pH$_2$S, balance nitrogen, $T=80^\circ$C, stirring rate: 600 rpm for pH 4 and pH 5, and 400 rpm for pH 6.
Localized corrosion in sour environment remains an area of active research and has not yet been incorporated into this model. Examples of ongoing research:


Possible approaches for incorporating localized corrosion:

- Stochastic approach based on empirical relationships of the initial corrosion rate and scaling tendency (currently used in JIP software MultiCorp for sweet corrosion)
- Probability of localized attack based on pH, ionic strength, concentrations of carbonate and sulfide species\(^1\)

### Experimental Conditions

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Minimum Condition</th>
<th>Maximum Condition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Production</td>
<td>No Solids Present</td>
<td>Solids are Present</td>
<td>n.a</td>
</tr>
<tr>
<td>Temperature</td>
<td>5</td>
<td>65</td>
<td>°C</td>
</tr>
<tr>
<td>Total Pressure</td>
<td>0</td>
<td>750</td>
<td>psi</td>
</tr>
<tr>
<td>H₂S Partial Pressure</td>
<td>0</td>
<td>50</td>
<td>psi</td>
</tr>
<tr>
<td>CO₂ Partial Pressure</td>
<td>0</td>
<td>100</td>
<td>psi</td>
</tr>
<tr>
<td>Bicarbonate Concentration</td>
<td>0</td>
<td>4000</td>
<td>ppm</td>
</tr>
<tr>
<td>Sulphate Concentration</td>
<td>0</td>
<td>2500</td>
<td>ppm</td>
</tr>
<tr>
<td>Chloride Concentration</td>
<td>0</td>
<td>120000</td>
<td>ppm</td>
</tr>
<tr>
<td>Flow</td>
<td>0</td>
<td>5</td>
<td>m/s</td>
</tr>
</tbody>
</table>

**FIGURE 3 – Photos of Rotating Cage Coupons (after cleaning the sample after 100 h of experiment) – Effect of Temperature**

Model developed primarily based on linear fit of rotating cage corrosion experiments carried out in the laboratory at high temperature and pressure.
Overall Pitting Corrosion Rate is calculated as the average of individual localized pitting corrosion rates (PCR)
The uncertainty in the corrosion rate is treated as the standard deviation of PCRs
Pipe cutout after MFL detected metal loss defects 72% w.t. 1 km pipe section received water flood for 23-24 months. Majority of pits discovered penetrated <50% of wall thickness, one pit penetrated 75% wall thickness.

### FIELD CONDITIONS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Production Rate (m³/d)</td>
<td>27</td>
</tr>
<tr>
<td>Pipe OD (mm)</td>
<td>168.30</td>
</tr>
<tr>
<td>Water Production Rate (m³/d)</td>
<td>50</td>
</tr>
<tr>
<td>Pipe ID (mm)</td>
<td>161.94</td>
</tr>
<tr>
<td>Gas production Rate (m³/d)</td>
<td>N/A</td>
</tr>
<tr>
<td>Chloride Ion Concentration (ppm)</td>
<td>6000</td>
</tr>
<tr>
<td>Sand Production</td>
<td>Yes</td>
</tr>
<tr>
<td>Sulphate Ion Concentration (ppm)</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>13</td>
</tr>
<tr>
<td>Bicarbonate Ion Concentration (ppm)</td>
<td>2330</td>
</tr>
<tr>
<td>Pressure (psi)</td>
<td>300</td>
</tr>
<tr>
<td>H₂S Partial Pressure (psi)</td>
<td>60</td>
</tr>
<tr>
<td>CO₂ Partial Pressure (psi)</td>
<td>6</td>
</tr>
</tbody>
</table>
Papavinasam et al. – Case Study

Summary of Models

Zheng et al. (2016)

*Mechanistic* CO$_2$/H$_2$S Model
Considers protective film formation
Does not consider pitting corrosion
Will be incorporated into Freecorp shortly and will be available free of charge

Papavinasam et al.

*Empirical* pitting corrosion model for the oil and gas industry
Based on linear fit of high temperature and pressure experimental data
Equation is simple to apply but must be done within model boundaries

**Engineer’s Note**

It is useful to apply multiple models for one assessment to obtain range of predictions based on different approaches
Modeling should be used as part of sour corrosion management

Guidelines are available for model selection. Applying multiple models to one scenario can be beneficial.
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AER Failure Statistics

Figure 8b. Pipeline failures by cause for all years combined
All pipeline failures from January 1, 1990, to December 31, 2012 (leaks and ruptures only)

Figure 15a. All “other product” pipeline incidents by cause for all years combined
January 1, 1990, to December 31, 2012 (hits, leaks, and ruptures, excludes pressure tests)

All Pipelines

Pipelines carrying “Other Products”
  e.g., ethane


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Guidelines defining sour corrosion environment

- CAPP:
  - H₂S concentration in the gas phase is greater than 500 ppm and H₂S is dissolved in water general statement in report
  - For reporting failures: 1% H₂S by volume

- CSA Z662-15:
  - for pipeline systems containing a gas phase, service in which the H₂S partial pressure exceed 0.3 kPa at the design absolute pressure
  - For pipeline systems not containing a gas phase (gas-free liquid pipeline systems), service in which the effective H₂S partial pressure exceeds 0.3 kPa at the bubble point absolute pressure

- NACE
  - Molar gas ratio of 500, theoretically 1400. CO₂/H₂S ratio > 500, corrosion dominated by CO₂ corrosion process, between 20-500 FeCO₃ and FeS coexist and research is still progressing in this field, ratio < 20, dominated by FeS, very low corrosion rate unless there is breakdown of the film caused by Cl (>10000 ppm, elemental S, O₂, sludge, flow regime slug or stagnat…Fes can breakdown locally resulting in very severe pitting corrosion rates several times higher than the CO₂ corrosion rate
Species considered in bulk chemical reactions:
- $\text{H}_2\text{S}$, $\text{HS}^-$, $\text{S}^{2-}$
- $\text{CO}_2$, $\text{H}_2\text{CO}_3^-$, $\text{CO}_3^{2-}$
- $\text{OH}^-$, $\text{H}^+$

$N_{w,j} = \pm \frac{j_j}{n_j F}$

Flux due to electrochemical reaction at the steel surface

$N_{e,j}$, flux from bulk to the steel

$C_{\text{surface},j}$: concentration of different species at the steel surface.

$C_{\text{scale},j}$: concentration of different species at the scale surface

$C_{\text{bulk},j}$: concentration of different species in the bulk solution
Electrochemical reactions at steel surface (modeled using Tafel Equation, surface concentration of species):

\[ \text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^- \]

\[ 2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_2_{(g)} \]

\[ 2\text{H}_2\text{CO}_3_{(aq)} + 2e^- \rightarrow \text{H}_2_{(g)} + 2\text{HCO}_3^{-}_{(aq)} \]

\[ 2\text{H}_2\text{S}_{(aq)} + 2e^- \rightarrow \text{H}_2_{(g)} + 2\text{HS}^-_{(aq)} \]

\[ 2\text{H}_2\text{O}_{(l)} + 2e^- \rightarrow \text{H}_2_{(g)} + 2\text{OH}^-_{(aq)} \]

\[ i = i_0 10^{\frac{E-E_o}{b}} \]

\( C_{\text{surface},j} \): concentration of different species at the steel surface.

\( C_{\text{bulk},j} \): concentration of different species in the bulk solution.
Corrosion Product Heterogeneous Equations:

\[ \text{Fe}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightleftharpoons \text{FeCO}_3_{(s)} \]

\[ R_{\text{FeCO}_3_{(s)}} = e^{28.20 - \frac{64.85}{RT}} \frac{S}{V} K_{sp\text{FeCO}_3} (S_{\text{FeCO}_3} - 1) \]

\[ \log K_{sp\text{FeCO}_3} = -59.3498 - 0.041377T - \frac{2.1963}{T} + 24.5724 \log T + 2.5181^{0.5} - 0.6571 \]

\[ \text{Fe}^{2+}_{(aq)} + \text{S}^{2-}_{(aq)} \rightleftharpoons \text{FeS}_{(s)} \]

\[ R_{\text{FeS}_{(s)}} = e^{48 - \frac{40.000}{RT}} \frac{S}{V} K_{sp\text{S}_2^{-}} (S_{\text{FeS}} - 1) \]

\[ K_{sp\text{S}_2^{-}} = 10^{\frac{2.848.779}{T} - 6.347 K_{hs} K_{bs}} \]

\[ N_{w,j} = \pm \frac{i_j}{\eta_j F} \]

Flux due to electrochemical reaction at the steel surface

\( C_{\text{surface,}j} \): concentration of different species at the steel surface.
Corrosion Product affects:

Electrochemical reaction rate – by reducing the available surface area

\[ i = \varepsilon i_0 \exp \left( \frac{E - E_0}{b} \right) \]

Mass transfer of species to the surface:

\[ k_{s,j} = \frac{\varepsilon \tau D_j}{\delta_s} \]

Porosity and thickness of layer change with time

\[ \frac{\partial \varepsilon}{\partial t} = - \frac{M_{FeS}}{\rho_{FeS}} R_{FeS} - CR \frac{\partial \varepsilon}{\partial x} \]

\[ \Delta \delta_s = \frac{\Delta x R_{FeS(s)} M_{FeS} \Delta t}{\rho_{FeS}(1 - \varepsilon)} \]

\[ N_{w,j} = \pm \frac{j_j}{n_j F} \]

Flux due to electrochemical reaction at the steel surface

\[ C_{\text{surface,j}} \]: concentration of different species at the steel surface.
Dual effect of H2S

Accelerates the corrosion by enhancing the cathodic reaction rate. H2S promotes the rate of iron sulfide precipitation that decreases the general corrosion rate.

Figure 8 illustrates the predicted effect of pH2S on the corrosion rate calculated by the present model. The initial corrosion rate increases with increasing pH2S; because no corrosion product layer protectiveness is accounted for at the initial time (time zero), the system is overwhelmed by the accelerating role of H2S reduction. However, during longer reaction times, such as 1 d, the formation of a protective iron sulfide layer is promoted by pH2S. The best example of the dual roles of H2S is that at 10 bar (1,000 kPa) pH2S, the initial corrosion rate is the highest, but the corrosion rate after 1 d is the lowest.

**Figure 8:** The predicted effect of pH2S on the corrosion rate from present model for pH 5.0, T = 80°C, and V = 1 m/s.
Add comparison to other model

PCR = \left\{ \sum (-0.54P_{\text{H}_2\text{S}}+67) + (0.85[S]+9.7) + (-0.63P_{\text{CO}_2}+74) + (-0.08 \ p_{\text{Total}}+88) + (0.57T+20) + (0.19W_{\text{ss}}+64) + (0.51\%W+12.13) + (-0.339+55) + (-0.013\text{[Sulfate]}+57) + (-0.014\text{[Bicarbonate]}+81) + (0.0007\text{[Chloride]}+9.2) + (25\text{[Solid]}+50)/12 \right\} \\
(17)

Model Philosophy including Pitting:
Based on experiments carried out in the laboratory at high temperature and pressure, field tests carried over a period of four years, analysis of field data
Multiple parameters considered
The effect of each parameter is taken into account based on a linear fit of the experimental data. Some parameters reduce the corrosion rate, others increase the corrosion rate.
The Pitting corrosion rate is calculated as the average of PCRs for all factors
The uncertainty in the corrosion rate is treated as the standard deviation of the individual localized pitting corrosion rates.

Model Development:

Model Range of Applicability:

Model validation:
Partial pressure of $\text{H}_2\text{S}$

$$PCR_{H_2S} = -0.54 p_{H_2S} + 67$$

### EFFECT of $\text{H}_2\text{S}$

<table>
<thead>
<tr>
<th>Partial Pressure $\text{H}_2\text{S}$, psi</th>
<th>Pit growth rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;2.5</td>
<td>85</td>
</tr>
<tr>
<td>2.5 to &lt;10</td>
<td>50</td>
</tr>
<tr>
<td>10 to &lt;50</td>
<td>45</td>
</tr>
<tr>
<td>$\geq 50$</td>
<td>40</td>
</tr>
</tbody>
</table>
Model Constraints Based on Test Conditions

<table>
<thead>
<tr>
<th>EXPERIMENTAL CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental Parameter</strong></td>
</tr>
<tr>
<td>Solid Production</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Total Pressure</td>
</tr>
<tr>
<td>H$_2$S Partial Pressure</td>
</tr>
<tr>
<td>CO$_2$ Partial Pressure</td>
</tr>
<tr>
<td>Bicarbonate Concentration</td>
</tr>
<tr>
<td>Sulphate Concentration</td>
</tr>
<tr>
<td>Chloride Concentration</td>
</tr>
<tr>
<td>Flow</td>
</tr>
</tbody>
</table>

**Correction needed above 65°C**

**FIGURE 2 – Variation of Mass Loss as a Function of Temperature**

**FIGURE 3 – Photos of Rotating Cup Corrosion after stirring the sample after 100 h of experiment – Effect of Temperature**
Papavinasam et al. – Model Overview

Concentration of chloride ion.

\[
PCR_{\text{chloride}} = -0.0007 C_{\text{chloride}} + 9.2
\]

EFFECT OF CHLORIDE

<table>
<thead>
<tr>
<th>Concentration Chloride, ppm</th>
<th>Pit growth rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>60000 to &lt;80000</td>
<td>55</td>
</tr>
<tr>
<td>80000 to &lt;100000</td>
<td>60</td>
</tr>
<tr>
<td>100000 to &lt;120000</td>
<td>95</td>
</tr>
<tr>
<td>≥120000</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Partial Pressure H₂S, psi</th>
<th>Pit growth rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;2.5</td>
<td>85</td>
</tr>
<tr>
<td>2.5 to &lt;10</td>
<td>50</td>
</tr>
<tr>
<td>10 to &lt;50</td>
<td>45</td>
</tr>
<tr>
<td>≥50</td>
<td>40</td>
</tr>
</tbody>
</table>
Partial pressure of $H_2S$  \[ PCR_{H_2S} = -0.54 p_{H_2S} + 67 \]

<table>
<thead>
<tr>
<th>Partial Pressure $H_2S$, psi</th>
<th>Pit growth rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;2.5</td>
<td>85</td>
</tr>
<tr>
<td>2.5 to &lt;10</td>
<td>50</td>
</tr>
<tr>
<td>10 to &lt;50</td>
<td>45</td>
</tr>
<tr>
<td>≥50</td>
<td>40</td>
</tr>
</tbody>
</table>
Key takeaways

1. The mechanisms and parameters controlling sour corrosion are complex
2. Modeling is part of the mitigation strategies for internal sour corrosion
3. Multiple models have been developed to predict sour corrosion rate
   • Models are developed using different approaches
   • Users should understand the capabilities and boundaries of each model prior to application