Effects of Oxygen, Temperature and Salinity on Carbon Steel Corrosion in Aqueous Solutions - Model Predictions versus Laboratory

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Brine Corrosion of Carbon Steel

- Water and saline solutions (brine) with oxygen can be found in essentially any industrial site
  - Cooling water ~0-300 ppm Cl(-)
    - Could include oxidizing biocides
  - Seawater ~ 3.4% NaCl
  - We all have this problem!

- Much of the pipe which contains these solutions is carbon steel
  - Waste headers, WWT operations, brine reffride systems, etc
  - Cost is a significant issue

- For example, a carbon steel waste header which needs to accept a new brine stream
  - Near neutral pH
  - Low concentration of NaCl

- Seems innocent enough, right?
Corrosivity of Brine

- **NaCl solutions are corrosive because**
  - Good electrolyte
  - Presence of chloride – forms metal chlorides
  - Affected by
    - pH
    - Temperature
    - Oxygen
    - Velocity

- **Metals that display lowest corrosion rates**
  - Copper alloys in the absence of oxygen (low strength is issue)
  - High Ni-Cr-Mo alloys to minimize SCC and crevice corrosion, Hastelloy C-276® ($$)
  - Titanium ($$)
  - Stainless steels suffer from pitting attack

- **Decision becomes financial**
Corrosion Modeling

- **Multi-disciplinary. Requires knowledge of**
  - Solution chemistry
  - Surface electrochemistry
  - Mass transport / Fluid flow
  - Metallurgy

- **Still an “infant” technology**
  - 1st comprehensive approach was Pourbaix (1950’s)
    - Purely thermodynamic

- **Some commercial products available**
  - Tend to be industry specific (i.e., Oil & Gas)
  - OLI CorrosionAnalyzer® (CA or CSP)
    - Most comprehensive
    - Solution based, broad chemistry coverage
Three Rules of Corrosion Modeling

1. “All models are wrong, but some are useful”
   - Prof George E.P. Box, Univ. of Wisconsin, 1979

2. Models are not completely predictive
   - Data are required to develop rate parameters
   - Need to incorporate BOTH thermodynamics and kinetics

3. Since data are always required, models will never replace laboratory and field corrosion testing!
Effect of pH on CS Corrosion in Brine

- Extremes of pH have profound effect on corrosion rate
  - Brines concerned primarily in pH 5-9 range

Reference:
Kirby, G.N., Chemical Engineering, March 12, 1979
Pg 72-84
Effect of pH on CS Corrosion in Brine

Slow moving H₂O or 3.5 wt% Brine; 3.9 ppmw O₂

Graph showing the effect of pH on corrosion rate in various conditions.
Corrosion Rate as a Function of Temperature

- **Temperature will affect corrosion rate**
- **Effect is multi-faceted**
  - **Kinetics**
    - Corrosion rate (kinetics) increase with temperature
    - Usually follows Arrhenius kinetics
    - Temperature can affect equilibrium composition of solution
  - **O₂ solubility**
    - O₂ solubility decreases with temperature
    - Increases rate of diffusion through layers of Fe(OH)ₓ
  - **pH**
    - Not significant through reasonable temperature ranges
  - **Mass transfer will also increase with temperature**
- **Difficult to experimentally keep all other variables constant**
O₂ Solubility vs Temperature

\[ p(O₂) = 0.2094 \text{ atm}; \text{NaCl conc} \sim 0.34 \text{ g/kg soln} \]

O₂ Solub Reference:


**pH vs Temperature**

\[
p(O_2) = 0.2094 \text{ atm} \\
\text{NaCl conc} \approx 0.34 \text{ g/kg soln}
\]
Equilibrium Concentration of O₂ in Brine

- Brines exposed to air will absorb O₂
- Amount of O₂ absorbed will depend on
  - p(O₂)
  - Salt concentration
  - Temperature
  - Brine / gas surface area
- For example, splash zones in seawater exposures up to 10x higher corrosion rates than subsurface exposure
  - High surface area for O₂ transfer
  - Concentration of NaCl due to evaporation of splash
Comparison of OLI Predictions to Data

\[ p(O_2) = 0.2094 \text{ atm; } 37^\circ C \]

References:

NOTE: MSE framework does not yet include Setchenov-type correlations.
Corrosion Rate as a Function of $O_2$ Concentration

- $O_2$ provides the cathodic reaction for corrosion

  $\text{Metal} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Metal}^{(2+)} + 2 \text{OH}^(-)$

- Higher $O_2$ conc $\rightarrow$ higher corrosion rates

- …but as we have discussed, the variables are interdependent. So what happens in real experiments?
Lab Data vs OLI Predictions

CorrosionAnalyzer assumptions:
- Static flow conditions
- Liquid saturated with O₂
- p(O₂) = 0.21 atm
- p(O₂) = 0 for N₂ purge cases
Corrosion Rate as a Function of Velocity

- Limiting current density is a function of species movement to/from the surface

\[ i_{i,\text{lim}} = n_i \cdot F \cdot k_{m,i} \cdot (a_{i,\text{bulk}}) \]

- Role of velocity and flow conditions is to define mass transfer coefficient, \( k_m \)

- Velocity also affects adherency of passive films
  - Higher velocity can remove films, leaving base metal
  - It can also cause erosion or mechanical removal of metal
Different Flow Conditions

- Flow conditions available in Corrosion Analyzer
  - Static
    - \( k_m \sim 0 \)
  - Rotating Disk
    - \( k_m = 0.6211 \frac{D^{2/3} \omega^{1/2}}{\nu^{1/6}} \)
  - Rotating Cylinder
    - \( k_m \frac{d}{D} = 0.0791 \text{Re}^{0.70} \text{Sc}^{0.356} \)
  - Pipe Flow
    - \( k_m \frac{d}{D} = 0.0165 \text{Re}^{0.86} \text{Sc}^{0.33} \)
  - Complete Agitation
    - \( k_m = \text{very large number} (\rightarrow \text{infinity}) \)
### Compare Predictions, Similar Conditions

#### Flow Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Water 1018 CS</th>
<th>Water 1018 CS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Static</td>
<td>4</td>
<td>0.44</td>
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<tr>
<td>Pipe flow (d = 2 m; v = 0.0127 m/s)</td>
<td>10.3</td>
<td>0.44</td>
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<tr>
<td>Rotating Disk (d = 10 cm; 2.5 cycle/min)</td>
<td>8.7</td>
<td>0.44</td>
</tr>
<tr>
<td>Rotating Cylinder (d = 10 cm; 2.5 cycle/min)</td>
<td>9.5</td>
<td>0.44</td>
</tr>
<tr>
<td>Pipe flow (d = 2 m; v = 6.1 m/s)</td>
<td>229</td>
<td>0.81</td>
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<tr>
<td>Rotating Disk (d = 10 cm; 1165 cycle/min)</td>
<td>195</td>
<td>0.52</td>
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<tr>
<td>Rotating Cylinder (d = 10 cm; 1165 cycle/min)</td>
<td>515</td>
<td>0.77</td>
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<tr>
<td>Completely Agitated</td>
<td>211</td>
<td>3.9</td>
</tr>
</tbody>
</table>
CorrosionAnalyzer Velocity vs Data at 23°C

T = 23°C, Mild Steel
Assume p(O₂) = 0.2094 atm and 3.5% NaCl brine
References:
Summary

- Velocity and oxygen concentration appear to have most significant impact on corrosion in near neutral brines
  - Both in experimental and OLI prediction
- Temperature is secondary effect
- pH is not a significant factor between 5 and 9
- OLI CorrosionAnalyzer® predictions
  - Very good for static conditions
  - Velocity effect needs further development
Summary

- **Corrosion modeling is multi-faceted and interdisciplinary**
  - Use all your resources
  - Study all the variables

- **Modeling and experimental programs are interactive**
  - Model suggests experiment conditions
  - Experimental data validate and/or feed model
  - Improve the model
  - Suggest new experiments
  - Etc…

- **Did not discuss MIC and microbiological, including impact of oxidizing biocides**
  - Very important considerations for water corrosivity!