OIL & GAS

Modeling Localized Corrosion and Cracking in Severe Oil & Gas Well Environments

OLI Simulation Conference

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CRA Performance in Oil & Gas Productions

- CRA is essential for increasingly severe O&G production conditions
  - HPHT: 23,000 psi, 300°C, at >10,000 m (32,800 ft) well depth
  - chloride (2,000~200,000 ppm), H₂S & CO₂, S⁰, organic acid, trace Hg, extremely low O₂.
  - Composition of water changes with life of well.
- CRAs exhibit excellent resistance to general corrosion, but suffer from localized corrosion & stress corrosion cracking (SCC) in downhole environment
Motivations

- Material specifications for sour environment scatter around: standard (ISO15156/NACE MR0175), guidance (EFC NO.17), company spec., operator experience, fit-for-purpose testing, etc.

- Current standards and guidelines are inadequate: static testing, uncertainties at boundaries (especially for lower grade), empiricism, lack of adequate basis for more aggressive environments, long test time for qualification.
Challenges for SCC Modeling

- Too many different SCC mechanisms depending on combinations of environment and alloy
- Difficult to consider all crack tip and external processes in one integrated model
  – Chemistry
  – Electrochemistry
  – Metallurgy
  – Mechanics
- Difficult to consider a wide range of chemistry

Approach

Focus on a sub-set of environmentally assisted cracking and break the problem down to manageable pieces:

CRA in chloride-H₂S containing environment
Concept: SCC Prediction in Sour Environments

- 3 parameters drive SCC.
- Similar critical chemistry at bottom of a localized corrosion site and active SCC crack tip.
- A mechanistic model based on alloy composition and environment (Cl-, H2S, T) to predict $E_{rp}$ & $E_{corr}$ from limited measurements is possible.
JIP: Performance Assessment of CRA’s in Aggressive Oil & Gas Wells

- **Objective:**
  - Establish the limits of CRA in terms of localized corrosion and SCC using a combination of experimental data and mechanistic models.
  - Enable the extrapolation from a limited number of tested environments and alloys to a broader range.
  - Establish a sound basis for accelerated SCC test methods in order to reduce test time and number of tests.
  - Develop CRA selection guidelines and performance assessment.

- **Participants:** DNV GL, OLI Systems Inc., Chevron, ConocoPhillips, Petrobras, JFE, Nippon Steel & Sumitomo Metal, Sandvik, and Vallourec-Manesmann.

- **Status**
  - Phase I kicked off with 4 members in October 2011
  - Extensive experiments and testing started in October 2012
  - Phase I completed in August 2015
  - Phase II kicked off in March 2016
Scope of Work

1. Generate $E_{rp}$ data for OLI Systems to develop $E_{rp}$ model for a variety of CRAs in chloride and $H_2S$ containing environments.

2. Generate $E_{corr}$ data for OLI Systems to develop $E_{corr}$ model for a variety of CRAs in chloride and $H_2S$ containing environments.

3. Development and verification of OLI models.

4. Conduct SCC tests to validate concept: SCC occurs when $E_{corr} > E_{rp}$ and local strain rate permits.
Approaches

Corrosion/Electrochemical Testing
- Cylindrical coupon and crevice sample assembly
- Corrosion potential long-term monitoring
- Potentiodynamic-Potentiostatic-Potentiodynamic (PD-PS-PD) as alternative Cyclic Potentiodynamic Polarization (CPP)
- Tsujikawa-Hisamatsu Electrochemical Test (THE)

SCC Testing
- Slow Strain Rate Test (SSRT)
- Ripple SSRT (RSSRT) and/or cyclic SSRT (CSSRT)
- Crack Growth Rate Test (CGR)
CRA Materials and Environments

<table>
<thead>
<tr>
<th>Alloy</th>
<th>UNS No.</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Mo</th>
<th>N</th>
<th>C</th>
<th>Other</th>
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</thead>
<tbody>
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<td>S41425</td>
<td>5.9</td>
<td>bal.</td>
<td>12.1</td>
<td>1.9</td>
<td>0</td>
<td>0.01</td>
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<td>bal.</td>
<td>14.6</td>
<td>1.9</td>
<td>0</td>
<td>0.03</td>
<td>Cu 0.97, Mn 0.28, Si 0.36</td>
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<tr>
<td>2507</td>
<td>S32750</td>
<td>6.93</td>
<td>bal.</td>
<td>25.17</td>
<td>3.87</td>
<td>0.27</td>
<td>0.017</td>
<td>Cu 0.40, Mn 0.8, Si 0.28</td>
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<tr>
<td>2535</td>
<td>N08535</td>
<td>30.6</td>
<td>bal.</td>
<td>24.7</td>
<td>2.78</td>
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<td>0.02</td>
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<td>bal.</td>
<td>27.0</td>
<td>4.4</td>
<td>0</td>
<td>≤0.02</td>
<td>Cu 1.0, Mn≤2.5, Si ≤1.0</td>
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<tr>
<td>28</td>
<td>N08028</td>
<td>31.0</td>
<td>bal.</td>
<td>27.0</td>
<td>3.5</td>
<td>0</td>
<td>≤0.02</td>
<td>Cu 1.0, Mn≤2.0, Si ≤0.6</td>
<td>39</td>
</tr>
</tbody>
</table>

\[ \text{PREN, } F_{\text{PREN}} = \text{Cr} + 3.3\cdot(\text{Mo} + 0.5\cdot \text{W}) + 16\cdot\text{N}, \text{ pitting resistance equivalent number is calculated by Equation (1) in ISO 15156 – part 3.} \]

<table>
<thead>
<tr>
<th>T</th>
<th>NaCl</th>
<th>H$_2$S</th>
<th># Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>85°C</td>
<td>0.0003 m</td>
<td>0%</td>
<td>Total 196</td>
</tr>
<tr>
<td>150°C</td>
<td>0.003 m</td>
<td>1%</td>
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</tr>
<tr>
<td>200°C</td>
<td>0.03 m</td>
<td>71%</td>
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</tr>
<tr>
<td>232°C</td>
<td>0.3 m</td>
<td>100%</td>
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<tr>
<td></td>
<td>3.0 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.65 or 2.5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25%</td>
<td></td>
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Repassivation Potential Modelling

Cracking appears to be associated with localized corrosion
- Similar critical local chemistry at pit bottom and crack tip.
- Micro process that lead to stabilization of pits or cracks appear to be similar.
- $E_{rp}$ represents the driving for stabilization/repassivation of localized process.

The $E_{rp}$ model simulates electrochemical processes in a pit or crevice in the limit of repassivation $\rightarrow$ conservative $E_{rp}$ values.
Repassivation Potential Modelling with Presence of H$_2$S

- Competitive adsorption and formation at interface
- Aggressive species (Cl$^-$, H$_2$S) promotes metal dissolution
- Inhibitive species (oxyanions, H$_2$O) promotes oxide formation

Potential drop across interfaces

\[ E = \Delta \Phi_{MX(1,2)} + \Delta \Phi_{MX(2,3)} + \Delta \Phi_{MX/S(3,4)} + \Delta \Phi_{S(4,5)} \]

Passive current density: 1×10$^{-6}$ A/cm$^2$
Surface coverage: \(1 = \sum \theta_i + \theta_{MS} + \theta_{MO}\)
Continuity of species flux at interfaces
At steady state, equilibrium between formation and dissolution
Steady-state limit for surface coverage fraction rate

Metal – Metal Halide – Occluded Solution
MO: protective oxide
MS: metal sulfide
MX: non-protective hydrous halide layer, or salt layer

Potential drop across interfaces

Repassivation Potential Modelling

Input: Alloy composition, concentration of chloride and H$_2$S in solution.

A few thermodynamic parameters were determined from literature $E_{rp}$ data of stainless steel and Ni-based alloys, and some H$_2$S related ones were from a small set of recent published S13Cr $E_{rp}$ data.
S15Cr Blind Test

Independent experimental data measurement and $E_{rp}$ model prediction, by using parameters optimized from S13Cr

- Presence of $H_2S$ substantially reduces $E_{rp}$ and enhances susceptibility to localized corrosion and/or SCC, except low $H_2S$ and chloride condition.
- Based on limited experimental data, the model is capable of generalizing the experimental database and extrapolating to a wide range of conditions.
Experimental data of 2535 were used to develop temperature dependence of thermodynamic parameters in the $E_{rp}$.

Elevated temperature diminishes the effect of $H_2S$ on the reduction of the repassivation potential.
Corrosion Potential Modelling with Presence of H$_2$S

- Based on mixed-potential theory
- Individual partial electrochemical reactions on the metal surface
- Incorporates transport processes for the reacting species
- Zero net current: $\sum_{j} i_{a,j} = \sum_{k} i_{c,k}$

Metal – Metal Oxide – Solution
- MO: protective oxide
- MS: metal sulfide

Cathodic:
- Reduction of water
- Reduction of adsorbed H$_2$S molecules

Anodic:
- Passive dissolution of oxide and/or sulfide
Without $H_2S$, $E_{corr}$ is controlled by $H_2O$ reduction
- Strong dependence on salt concentration due to dependence of water activity on salt concentration

With $H_2S$, $E_{corr}$ is controlled by $H_2O$ reduction and $H_2S$ reduction
- pH dependent $H_2O$ reduction, weak salt concentration dependence
- Temperature and salinity dependent $H_2S$ solubility
- Crossover at low temperature
Concept Validation by SSR/RSSR Test

S13Cr, 0.3 m NaCl, 85°C, N₂
Concept Validation by CGR Test

S13Cr, 0.3 m NaCl, 85°C

11.5 days

-300 mV vs. Ref

-250 mV vs. Ref

1wt% H₂S

10wt% H₂S

20wt% H₂S

20% O₂ N₂

0.9% O₂ N₂

S13Cr, 0.3 m NaCl, 85°C
References

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SAFER, SMARTER, GREENER