USAGE OF CORROSION RESISTANT ALLOYS – CRA – FOR OIL AND GAS PRODUCTION (OCTG)

Daniel Guerra - Vallourec
Agenda

- Critical parameters for downhole Corrosion
- Main challenges of corrosive environments
  - CO₂ corrosion, H₂S cracking
  - Geographic overview
- Material Selection
  - From the challenges to the consequences on OCTG
  - Material Selection decision matrix
  - Testing
- Conclusions

- Open discussion – questions
Critical parameters for downhole Corrosion

- $O_2$, $CO_2$ and $H_2S$ concentration
- Water chemistry (Water cut / Water breakthrough)
- pH
- Temperature (min and max)
- Pressure (BHP)
- $Cl^-$ concentration
- Flow rate / particles
- Service (e.g. change from oil/water to water or production to injection)
- Addition of “new” chemicals e.g. corrosion inhibitor, biocides, etc.
- Presence of elemental sulphur (S), Mercury (Hg) or other corrosive elements.
### Main challenges of corrosive environments

<table>
<thead>
<tr>
<th><strong>H₂S</strong></th>
<th><strong>H₂S + CO₂</strong></th>
<th><strong>CO₂</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sour Gas</strong></td>
<td><strong>Highly corrosive Gas</strong></td>
<td><strong>Sweet Gas</strong></td>
</tr>
<tr>
<td><strong>FAST</strong></td>
<td><strong>FAST</strong></td>
<td><strong>SLOW</strong></td>
</tr>
<tr>
<td><strong>Cracking</strong></td>
<td><strong>Cracking + Metal Loss</strong></td>
<td><strong>Metal Loss</strong></td>
</tr>
<tr>
<td><strong>SSC</strong></td>
<td><strong>SSC: Sulfide Stress Cracking</strong>&lt;br&gt;&lt;br&gt;<strong>SCC: Stress Corrosion Cracking</strong></td>
<td><strong>Mass loss corrosion</strong>&lt;br&gt;&lt;br&gt;<strong>Pitting – Crevice</strong></td>
</tr>
<tr>
<td><strong>To be avoided</strong>&lt;br&gt;&lt;br&gt;<strong>Zero Risk approach</strong></td>
<td><strong>To be avoided</strong>&lt;br&gt;&lt;br&gt;<strong>Zero Risk approach</strong></td>
<td><strong>Can be controlled</strong>&lt;br&gt;&lt;br&gt;<strong>Life Cycle Cost approach</strong></td>
</tr>
<tr>
<td><strong>Severe at low T°C</strong></td>
<td><strong>Severe at low &amp; High T°C</strong></td>
<td><strong>Severe at high T°C</strong></td>
</tr>
</tbody>
</table>

**COMPLEX**
Main challenges of corrosive environments

H$_2$S corrosion

- **Sour gas** is natural gas or any other gas containing significant amounts of **hydrogen sulfide** (H$_2$S)

- Due to their small sizes, the hydrogen atoms penetrate the material and interact with the steel which **becomes brittle** ➔ risk of crack under stress

- Corrosive phenomenon is **Sulphide Stress Cracking (SSC)**, due to stress concentrations

- Failures can be **catastrophic** and **unpredictable** (as fast as few minutes)

- **Tubing and Production Casing** (as 2$^{nd}$ barrier) and **on case by case** **Intermediate Casing** shall be H$_2$S resistant

- **Lower temperature and high stresses** emphasize risk of SSC
Main challenges of corrosive environments

CO₂ corrosion

- Referred to as “Sweet” Gas – CO₂ is a carbonic acid when dissolved in water
- CO₂ leads to general metal loss & local pitting (+ Stress Corrosion Cracking – SCC, when H₂S is also present)
- CO₂ corrosion becomes more severe at higher temperatures
- A minimum of 12% Chromium is required to resist CO₂

Uniform Corrosion affects tubing / liner
Main challenges of corrosive environments

<table>
<thead>
<tr>
<th>H₂S</th>
<th>H₂S + CO₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mitigate even if short exposure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Casing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermediate Casing  case by case</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production casing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production Liners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Completion Tubing</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Long exposure possible
- Surface Casing
- Intermediate Casing
- Production casing
- Production Liners
- Completion Tubing

Material Selection OCTG - May/2016
Main challenges of corrosive environments
Geographic overview

- Main « H₂S » areas
- Main « CO₂ » areas
- Main « H₂S + CO₂ » areas
Material Selection
Simplified Material Selection Chart

- Usage domain of standard Carbon Steel and Sour Service Grades
  - Low ppCO_2 (<2psi)
  - Strong influence of the H_2S content
- Usage domain of Chrome and Nickel Alloys
  - Higher CO_2 content (>2psi)
  - ppH_2S and temperature dependant
- Other parameters like chloride content and pH, will also influence
Material Selection
Definition & normative requirements

- **Corrosion Resistant Alloys (C.R.A.)**
  - Materials with ability to resist corrosion in presence of water & corrosive species
  - Products governed by:
    - API 5CRA / ISO 13680 specifications
      - 4 groups defined by their composition and mechanical properties
      - 2 Product Specification Levels (PSL) : PSL 1 is basis of API 5CRA
      - PSL 2 : restricted chemical composition & mechanical properties (in some cases)
    - NACE MR0175 / ISO 15156 :
      - Guideline for selection and qualification of metallic materials used in Oil & Gas
      - Part 3 of this specifications focuses on CRA :
        - Environmental limits for any equipment
        - Chemical composition per material type

*Note:* 13CR grade L80 is still included into API 5CT specification and not API 5CRA
### Material Selection
NACE MR0175 / ISO 15156 - usage domains

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Material Group</th>
<th>Table – NACE Part 3</th>
<th>H2S Limit (psi)</th>
<th>Temp Limit (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13Cr Grade L80</td>
<td>Martensitic Stainless Steel</td>
<td>A.19</td>
<td>1.5</td>
<td>None (*)</td>
</tr>
<tr>
<td>Super 13Cr</td>
<td>Super Martensitic Stainless Steel</td>
<td>A.19</td>
<td>1.5</td>
<td>None (*)</td>
</tr>
<tr>
<td>25CR PREN&gt;40</td>
<td>Super Duplex</td>
<td>A.25</td>
<td>3</td>
<td>None (*)</td>
</tr>
<tr>
<td>825, 28CR</td>
<td>Nickel Base (4C)</td>
<td>A.14</td>
<td>200</td>
<td>350</td>
</tr>
<tr>
<td>Alloy G3</td>
<td>Nickel Base (4D)</td>
<td>A.14</td>
<td>300</td>
<td>425</td>
</tr>
<tr>
<td>C-276</td>
<td>Nickel Base (4E)</td>
<td>A.14</td>
<td>1000</td>
<td>450</td>
</tr>
</tbody>
</table>

- (*) Temp limit was not necessarily determined but mechanical properties will suffer too much at very high temperatures
Material Selection
SSC and SCC Domain

- Usage domain based on NACE MR0175 recommendations
- Usage domain also dependent on CO2 and Chloride level
# Material Selection

## Simplified decision matrix

<table>
<thead>
<tr>
<th></th>
<th>Hydrocarbon production</th>
<th>Gas Injection</th>
<th>Water injection (*)</th>
<th>Turnaround well</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel</td>
<td></td>
<td></td>
<td>Avoid!</td>
<td>Avoid!</td>
</tr>
<tr>
<td>3%Cr Alloyed Steel</td>
<td></td>
<td></td>
<td>Avoid!</td>
<td>Avoid!</td>
</tr>
<tr>
<td>Martensitic 13Cr</td>
<td></td>
<td></td>
<td>Avoid!</td>
<td>Avoid!</td>
</tr>
<tr>
<td>Supermartensitic 13Cr-5 Ni-2Mo</td>
<td></td>
<td></td>
<td>Avoid!</td>
<td>Avoid!</td>
</tr>
<tr>
<td>Super Duplex 25Cr-7Ni-2Mo (PREN&gt;40)</td>
<td></td>
<td></td>
<td>Not normally considered</td>
<td>Not normally considered</td>
</tr>
<tr>
<td>Nickel-base alloy</td>
<td></td>
<td></td>
<td>Not normally considered</td>
<td>Not normally considered</td>
</tr>
<tr>
<td>Titanium alloys</td>
<td>Not normally considered</td>
<td>Not normally considered</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GRE lined steel</td>
<td>Not normally considered</td>
<td>Not normally considered</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- (*) depending on the quantity of Oxygen dissolved in water
Material Selection Testing

- Qualification testing to assess corrosion resistance of various materials in a specific well conditions.
- Fit For Purpose (FFP) tests can be performed, to evaluate the material susceptibility in a specific environment.
  
  o Tests in autoclave:
    - Metal loss
    - Pitting
    - Crevice
    - SCC
  
  o NACE testing according to all 4 methods (A/B/C/D) of NACE TM0177 – 2005

<table>
<thead>
<tr>
<th>Test method</th>
<th>NACE A</th>
<th>NACE B</th>
<th>NACE C</th>
<th>NACE D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress application</td>
<td>Tensile % of SMYS</td>
<td>3 points bent</td>
<td>C ring</td>
<td>Wedge</td>
</tr>
<tr>
<td>Duration</td>
<td>720 hours</td>
<td></td>
<td>360 hours</td>
<td></td>
</tr>
<tr>
<td>Results</td>
<td>Rupture / No rupture</td>
<td>S_c</td>
<td>Rupture / No rupture</td>
<td>Stress Intensity Factor</td>
</tr>
</tbody>
</table>
Material Selection
Focus on CRA

- **Corrosion can be mitigated by**
  - Regular tubing replacement (Work-over)
  - Use of down hole inhibitors (or internally coated tubings)
  - Use of corrosion resistant alloys (CRA)

- **Ferritic-austenitic & Austenitic grades are the most reliable & economical solution when:**
  - Costs and frequency of work-overs are high
  - There is a high cost of lost production
  - Harsh conditions – acid gas fields (CO2+H2S), high temperature

- **Decision to go for CRA materials is technical vs cost based**
  - Depends on well environment and life, company policy etc.
Material Selection
Focus on CRA

- CRA prices are very sensitive to Cr, Ni and Mo price variation

<table>
<thead>
<tr>
<th>Steel or Alloy</th>
<th>Alloy low price</th>
<th>Alloy high price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel for SS</td>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>Martensitic 13Cr</td>
<td>2</td>
<td>2.2</td>
</tr>
<tr>
<td>Martensitic Super 13 Cr</td>
<td>3.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Austenitic – Ferritic</td>
<td>4.6</td>
<td>5.4</td>
</tr>
<tr>
<td>Super Austenitic – Ferritic</td>
<td>5.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Austenitic (Ni &lt; 50%)</td>
<td>10.0</td>
<td>12.5</td>
</tr>
<tr>
<td>Austenitic Ni-based (Ni &gt; 50%)</td>
<td>16 / 25</td>
<td>21 / 32</td>
</tr>
</tbody>
</table>
Material Selection OCTG – Conclusions

- **Complex process with a lot of uncertainties**
  - Consider complete well life and potential scenarios

- **Reservoirs containing H₂S (SSC)**
  - Even at low levels of H₂S, the material can be susceptible to SSC phenomenon
    - Zero Risk approach!

- **Reservoirs containing CO₂ (Metal Loss)**
  - Well Strategy will be decisive for Material Selection:
    - Price of the metallurgy vs workover / well stoppage

- **Reservoirs containing CO₂ + H₂S (SCC + SSC)**
  - SCC and SSC criticity will vary as function of the temperature
    - Zero Risk approach!

- **CRA metallurgy**
  - Combine SCC and SSC resistance