Lessons Learned from Sour Service Product Development

Roxanne Stankievech, Research Engineer, E.I.T.
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Outline

- Industry Specifications for Sour Service
- Test Methods
  - HIC
  - SSC
- Development of ERW L80 for Critical Sour Service
- Development of Sour Service X65
- Moving Forward – Regina Upgrades
Industry Specifications for Sour Service

- **NACE MR0175/ISO 15156**: Petroleum, petrochemical, and natural gas industries – Material for use in H₂S-containing environments in oil and gas production
  - Defines sour service as a H₂S partial pressure over 0.3 kPa (0.05 psi)
  - A large number of industry specifications have requirements that come from this document

- **Casing**:
  - **API 5CT**: Specification for Casing and Tubing is the base specification
  - **AER Directive 010**: Minimum Casing Design Requirements adds additional requirements for grades used in wells over 0.05 psi H₂S in Alberta
  - **Industry Recommend Practice Volume 1**: Critical Sour Drilling for the Canadian Oil and Gas Industry adds additional requirements for “critical sour wells” in Alberta

- **Line Pipe**:
  - **API 5L**: Specification of Line Pipe is the American base specification. Annex H includes sour service requirements
  - **CSA Z245.1**: Steel Pipe is the Canadian base specification. Clause 16 includes sour service requirements
Corrosion Test Methods – HIC

- Examines the effect of hydrogen on *unloaded* specimens

- **NACE TM0284 Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking**
  - Exposed to an acidic solution and \( \text{H}_2\text{S} \) gas for the test duration and then sectioned and cracks are measured
  - Three different standard solutions, including a Fit-for-purpose solution
  - Typically 4 day test duration, however if \( \text{H}_2\text{S} \leq 10\% \) the duration increases
Corrosion Test Methods - SSC

- Examines the effect of hydrogen on a specimen under load

- NACE TM0177 Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking
  - 4 test methods
    - Method A - Tensile test
    - Method B - Bent beam test (rarely used)
    - Method C - C-ring test
    - Method D - Double cantilever beam test
  - Four standard test solutions, not necessarily the same as the HIC solutions
  - Typically 30 day test duration

- NACE TM0316 Four-Point Bend Testing of Materials for Oil and Gas Applications
  - Specifies the procedure for loading, exposure and failure appraisal. Can be used with any environment.
Corrosion Test Methods - SSC

- Method D tests a material's susceptibility to crack propagation after a crack is already formed.
  - Fatigue cracked, wedge inserted and exposed to environment
  - After exposure, crack growth is measured and K1SSC is calculated
  - The further the crack propagated, the worse the material performance
Development of ERW L80 for Critical Sour Service

- Q&T grade with SMYS of 80 ksi. Often used for sour service applications as it is the lowest strength Q&T grade in API 5CT.

<table>
<thead>
<tr>
<th></th>
<th>API 5CT</th>
<th>D 010</th>
<th>IRP Vol 1</th>
<th>Other</th>
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<tbody>
<tr>
<td>Min Tempering Temp.</td>
<td></td>
<td>621°C</td>
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<tr>
<td>Hardenability*</td>
<td>50% Martensite</td>
<td>90% Martensite</td>
<td>90% Martensite 4 quadrants</td>
<td>90% Martensite 1 quadrant</td>
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<tr>
<td></td>
<td>90% Martensite (Annex H)</td>
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<td></td>
<td></td>
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<tr>
<td>Prior γ Grain Size</td>
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<td></td>
<td>7 or finer</td>
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<tr>
<td>Tensile (MPa)</td>
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<td></td>
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<tr>
<td>YS (0.5% EUL)</td>
<td>552-655</td>
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<td></td>
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<tr>
<td>UTS</td>
<td>655 min</td>
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<tr>
<td>Y/T</td>
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<td>Hardness, max (HRC)</td>
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<td>Reading, max</td>
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<td>Variation, max</td>
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<td>3HRC</td>
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<td>Micro Hardness</td>
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<td>248 HV (500gf)</td>
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<tr>
<td>LPA</td>
<td>27-47 J @ 0ºC</td>
<td>min 80J @ 0ºC</td>
<td>SR16 -40ºC, % shear reported, transition curve on new MIP</td>
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<tr>
<td>TPA</td>
<td>14-23 J @ 0ºC</td>
<td>min 55J @ 0ºC</td>
<td>SR16 -40ºC, % shear reported, transition curve on new MIP</td>
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</tr>
<tr>
<td>SSC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method A</td>
<td></td>
<td></td>
<td>If requested</td>
<td>90% Actual YS</td>
</tr>
<tr>
<td>Method C</td>
<td></td>
<td></td>
<td>If requested</td>
<td>About ERW seam, 90% Actual YS</td>
</tr>
<tr>
<td>Method D</td>
<td></td>
<td></td>
<td>K_{1SSC}, ave = 33.0 Mpa√m (K_{1SSC} specimen = 29.7 Mpa√m)</td>
<td></td>
</tr>
<tr>
<td>HIC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%CLR, max</td>
<td></td>
<td></td>
<td></td>
<td>10.00%</td>
</tr>
<tr>
<td>%CTR, max</td>
<td></td>
<td></td>
<td></td>
<td>2.00%</td>
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</tbody>
</table>
Development of ERW L80 for Critical Sour Service

- Two main alloy strategies for L80:

- Cr-Mo
  - Improve hardenability and create carbides which reduce temper softening
  - Carbides are believed to be benign H traps

- Ti-B
  - Greatly increases hardenability. Required for larger diameter, heavier WT casing.
  - Ti is added to scavenge N and ensure B is effective. This leads to TiN inclusions

- Mn is used in both strategies. It is inexpensive and improves hardenability, however is strongly segregates to the centerline.

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Mo</th>
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<tr>
<td>0.26</td>
<td>1.15</td>
<td>&lt;0.0015</td>
<td>&lt;0.010</td>
<td>0.35</td>
<td>0.12</td>
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</table>
Development of ERW L80 for Critical Sour Service

- Morphology of inclusions
Development of ERW L80 for Critical Sour Service

Aim for < 0.0015 wt% S

Aim for Ca:S ratio between 1.5 - 3.5
Development of ERW L80 for Critical Sour Service

- Hard areas over 248 HV are detrimental

450 HV (500gf)
Development of ERW L80 for Critical Sour Service
Development of ERW L80 for Critical Sour Service

- Confirmation Trial:
  - Good centerline
  - Steel with 0.0003 - 0.0006 wt% S
  - Treated with Ca and had Ca:S ratios of 1.0 - 3.3
  - Had excessive HIC cracking due to numerous small MnS inclusions
Development of ERW L80 for Critical Sour Service

Previous trial with no HIC cracks
S = 0.0010 wt%    Ca = 0.002 wt%
Ca:S = 2.0

Recent trial with large HIC cracks
S = 0.0003 wt%    Ca = 0.001 wt%
Ca:S = 3.3
Development of Sour Service X65

- API 5L Annex H
  - Stricter chemistry requirements for a large number of alloy elements
  - S restricted to 0.002 wt% and a requirement for Ca/S ≥ 1.5 if S > 0.0015
  - Hardness restricted to 22 HRC or 250 HV\textsubscript{10kg}
  - HIC testing in Solution A max %CLR = 15, %CTR = 5, %CSR = 2
  - Optional four point bend SSC test

- CSA Z245.1 Clause 16: Sour Service
  - Ni content in weld or body shall not exceed 1.0%
  - UTS restricted to 650 MPa
  - Hardness restricted to 22 HRC and 248 HV\textsubscript{500gf}
  - Optional HIC testing
Sour Service Linepipe Considerations

- Have Sour Service X52 & X60 products, the increased strength and increased alloy content in X65 steel has made it difficult to get good HIC results
- Restrict chemistry that meets the API requirements
- Max S of 0.0015 wt%

- Casting issues that may increase inclusion content and lead to poor HIC results include:
  - Sudden changes in cast speed
  - Low tundish weight between heats
  - Clogged tundish nozzle
  - First and last slabs of a sequence
Development of Sour Service X65

Ca/S > 10
Sour Service Linepipe Considerations

- Segregation
- Mannesmann Rating: Scale from 1 - 5
Regina Steel Upgrades

- **Soft Reduction**
  - Squeeze out Non-metallic inclusions and improve centerline

- **Increased reduction capability of the rolling mill and increased laminar flow cooling rate**
  - Achieve strength with reduced alloy content which will reduce alloy concentration at the centerline

- **Vacuum Degasser**
  - Lower H & N content decrease number of size of nitride inclusions

### Mannesmann Rating Table

<table>
<thead>
<tr>
<th>Mannesmann Rating</th>
<th># of Slabs Before</th>
<th># of Slabs After</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>58</td>
<td>71</td>
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<tr>
<td>2</td>
<td>132</td>
<td>170</td>
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<td>3</td>
<td>49</td>
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<td>5</td>
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