Corrosion Resistant Alloys in CO₂ Injection Wells for CCS and CCUS Projects

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What is CCS and CCUS?

• Carbon capture and sequestration (CCS)
• Carbon capture utilization and storage (CCUS)
• This presentation will focus on CO₂ injection well metallurgy for storage wells

Source: https://netl.doe.gov/carbon-management/carbon-storage/faqs/carbon-storage-faqs
So What’s the Problem?

- CO₂ pipelines have been successfully developed for many years without corrosion
- Pipelines are typically carbon steel
- No water → No corrosion
  - Carbon and low alloy steel okay
- Free water → Severe corrosion
  - CRAs needed
- Possible sources of water
  - Condensation
  - Formation water
  - Flowback
Corrosion Assessment

• Major challenge → Limited data for many CRAs in SC-CO₂
• Can lean on related experience for guidance with significant limitations
  ▪ Oil and gas production – No oxygen
  ▪ Acid gas injection – Lower temperature, No oxygen
  ▪ Seawater injection – Near neutral pH
  ▪ CO₂ EOR
    – CCS wells are often deeper and hotter
    – CCS utilizes continuous injection, no WAG
    – CCS wells typically have longer design lives
    – CCS injectate may have additional contaminants
Factors that Impact Corrosion in SC-CO₂

- **Injectate composition and impurities in the SC-CO₂ stream**
  - H₂S, O₂, SOₓ, NOₓ, H₂

- **Water / water chemistry**
  - No water → No corrosion
  - Fresh condensate → No buffering, no chlorides
  - Formation water → Buffering, chlorides

- **Temperature**
  - Important, but impact substantially dependent on other factors
  - Generally, higher temperature → higher corrosion rates to CRAs

- **pH**
  - Directly related to CO₂ pressure / fugacity
  - Generally, lower pH → higher corrosion rates
SC-CO₂ Stream Impurities

- Impurity contents vary substantially by source
- H₂S, O₂, SOₓ, NOₓ of utmost interest for material selection
- Examples shown below, but many other sources and compositions exist
- These ranges are too broad for material selection criteria
  ▪ Actual project stream specification needs to be considered

<table>
<thead>
<tr>
<th>Data Source</th>
<th>Industries</th>
<th>Typical Impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPCC Special Report</td>
<td>Power Generation – Coal Fired Plants</td>
<td>0-0.5% SO₂, 0-0.01% NO, 0-0.6% H₂S, 0.01-3.7% N₂/Ar/O₂</td>
</tr>
<tr>
<td>IPCC Special Report</td>
<td>Power Generation – Gas Fired Plants</td>
<td>&lt; 0.01% SO₂, &lt; 0.01% NO, &lt; 0.01% H₂S, 0.01-4.1% N₂/Ar/O₂</td>
</tr>
<tr>
<td>Industry Experience</td>
<td>Natural Gas Processing</td>
<td>&lt; 1% H₂S, &lt; 10 ppm O₂</td>
</tr>
<tr>
<td>Industry Experience</td>
<td>Ethanol plants</td>
<td>&lt; 10 ppm H₂S, &lt; 2% O₂</td>
</tr>
</tbody>
</table>
Effect of SC-CO₂ Stream Impurities

- **SOx and NOx**
  - Sulfuric acid and/or nitric acid formation in water phase
    - pH reduction
  - When present together, NO₂ catalyzes oxidation of SO₂

- **H₂S**
  - Can promote cracking susceptibility
  - Has not been rigorously studied in SC-CO₂
  - ISO 15156 best available guideline
    - Based on experience in oxygen-free oilfield environments

- **O₂**
  - Dissolved oxygen in the water phase promotes susceptibility to pitting and crevice corrosion
  - Perhaps most significant difference between CCS and oil and gas production environments
  - PREN helpful tool for ranking stainless steels
    - \( \text{PREN} = \%\text{Cr} + 3.3 \times (\%\text{Mo} + 0.5\%\text{W}) + 16 \times \%\text{N} \)
    - Relationship has not been established between PREN and corrosion resistance in SC-CO₂ environments

- **Nitrogen (N₂) and Hydrocarbons** not expected to influence material selection
  - Possible effects of Hydrogen (H₂) in CCS streams has not been explored and may warrant review
Formation Water

- For CRA selection, chloride is the critical constituent
- Chloride can vary substantially from formation to formation
  - Also sample to sample and test to test
- Ideally, material selection based on water analyses from several samples
- Sometimes preliminary recommendations are needed based only on estimated TDS
  - Conservative assumption is that TDS is entirely NaCl
- Formation water pH shown is *BEFORE* injection

### Table: Fossil Fuel Formation Water Analysis

<table>
<thead>
<tr>
<th>Species</th>
<th>Compiled by Zerai [CWRU, 2006]</th>
<th>For Reference*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rose Run</td>
<td>Clinton</td>
</tr>
<tr>
<td>Na⁺</td>
<td>mg/kg</td>
<td>mg/kg</td>
</tr>
<tr>
<td>K⁺</td>
<td>3,354</td>
<td>850</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>37,600</td>
<td>23,200</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>5,881</td>
<td>1,840</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>122</td>
<td>200</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>191,203</td>
<td>160,400</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>326</td>
<td>523</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>456</td>
<td>753</td>
</tr>
<tr>
<td>pH</td>
<td>6.4</td>
<td>6.5</td>
</tr>
<tr>
<td>TDS</td>
<td>277,571</td>
<td>250,000</td>
</tr>
</tbody>
</table>

*Source: NACE Corrosion Engineer’s Reference Book
pH Considerations

• As CO₂ pressure increases, the pH of present freshwater approaches 3
  ▪ Can be demonstrated by modeling

• Adding as little as 100 ppm SO₂ can drop pH to 2.5
  ▪ Recall that streams from coal-fired plants may have up to 5000 ppm SO₂

• These pH values are lower than most available corrosion data from oil and gas wells

pH Considerations (cont.)

- Injection plume models have predicted that the pH near the wellbore will remain low even after many years.
- pH increases with distance from the wellbore due to dilution and buffering.
- Monitoring wells may therefore see higher pH, and different metallurgy may be suitable.
Candidate Alloys – Many Options Available

• Casing and Tubing
  ▪ Carbon and Low-alloy Steel
  ▪ 13Cr/S13Cr
  ▪ 15Cr/17Cr
  ▪ 22Cr
  ▪ 25Cr
  ▪ Higher Cr options
  ▪ Nickel-base (G3/2550/C22)
  ▪ Titanium

• Packers and Tubing Hangers
  ▪ Carbon and Low-alloy Steel
  ▪ 22Cr and 25Cr – limited strength
  ▪ PH Ni-base alloys
  ▪ Titanium

• Wellheads/Trees
  ▪ Low alloy steel – No water drop out
  ▪ Class CC – Limited acceptable options
  ▪ Class HH
How to Select? Material Selection Philosophy

• Can exposure to water be reliably avoided over the life of the well?
  ▪ If so, then carbon steel may be acceptable
  ▪ Applies to non-wetted portions of the tree/wellhead and properly cemented casing above the packer

• Intermittent water warrants a risk assessment
  ▪ Very corrosive when present
  ▪ Balance equipment integrity against workover schedule

• Frequent or continuous water exposure requires CRA
  ▪ Which CRA to choose?
  ▪ Water from condensation or formation?
  ▪ Cost typically increases substantially with corrosion resistance
  ▪ Consultation with a Subject Matter Expert (SME) is needed
Martensitic Stainless Steels

- 13Cr, S13Cr, 15Cr, 17Cr
  - Strengthened by heat treatment, quenched and tempered
- 13Cr is commonly used in oil and gas production
  - AISI 420, L80 Type 13Cr
  - Available test data suggests that it is questionable for SC-CO₂, even without the presence of oxygen
- S13Cr
  - Alloyed with Mo for improved corrosion and cracking resistance
  - Better pitting resistance than 13Cr, but still limited in CCS environments
- 15Cr and 17Cr
  - No publicly available data in SC-CO₂
  - May be suitable in low O₂ – testing recommended
- Cracking resistance of these alloys has not been established at low pH expected in CCS when H₂S is present
- Possible application in monitoring wells, but Subject Matter Expert review is recommended
Duplex Stainless Steels

- **22Cr** (e.g. SAF 2205, SM22CR, VM 22)
  - Good experience in oil and gas
  - Limited in H₂S and O₂ bearing streams
- **25Cr** (e.g. SAF 2507, SM25CR/CRW, VM 25S)
  - Exhibits some pitting resistance in dissolved oxygen
    - Demonstrated by good industry experience in offshore equipment and seawater injection
  - Critical pitting and crevice corrosion temperatures well established in saturated seawater and acidified ferric chloride
    - CCS limits not established

- Very limited CCS data available for 22Cr and 25Cr
- No public data for higher Cr DSS such as 3207

- Strengthened by cold-work, so may not be suitable for high strength hangers and packers with thick sections

### CPT and CCT for Select CRAs in Seawater

<table>
<thead>
<tr>
<th>Alloy</th>
<th>CPT, °C</th>
<th>CCT, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 SS</td>
<td>2</td>
<td>-15</td>
</tr>
<tr>
<td>316 SS</td>
<td>10</td>
<td>-10</td>
</tr>
<tr>
<td>22Cr DSS</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>25Cr SDSS</td>
<td>80</td>
<td>70</td>
</tr>
</tbody>
</table>
Nickel Alloys

- Solid solution and cold-worked alloys for tubing and casing
  - Alloys 2535, G3, 2550, C276, C22
  - Tubulars may be offered in grades up to 125 ksi SMYS

- Precipitation-hardened (PH) alloys
  - Alloys 925, 718, 725, 625 Plus
  - Strengthened by heat treatment
  - PH nickel alloys may be needed for higher strength packers and hangers

- Almost no publicly available CCS data
  - Some CCS combinations of low pH, high T, and high O₂ may still be pitting risk
Common Questions

• Will galvanic corrosion be a concern?
• Will this new alloy that my supplier is suggesting work for my well?
• What thread should we use for our downhole connections?
• What material requirements should we specify to the mill?

• Classic metallurgist response: “It Depends!” 

• These are all good questions that need to be carefully considered on a project-by-project basis with the input from subject matter experts from several disciplines
Other Considerations

- Injection rates
  - Consideration of critical erosional velocities
- Threaded connections
  - Gas-tight premium connections
  - Risk of low temperature event?
- Annular fluids
  - Typically halide brines with additive package including oxygen scavengers
  - Need to be compatible with CRA
  - Can become aggressive if comingled with CO₂ stream
- Acid jobs
  - Possible damage to equipment if not quickly circulated out
- Elastomers
  - Sealing elements used for production equipment may not be compatible in SC-CO₂
- Cements
  - Portland cement is not compatible with CO₂
  - Need CO₂-resistant cement for exposed portions of well
Final Thoughts on CO₂ Injection Well Metallurgy

- The information presented here is intended to bring attention to the parameters that need to be considered in material selection.
- It is always recommended that material selection and procurement specifications be reviewed by a Subject Matter Expert prior to ordering equipment.
- Free water is the most critical factor in a corrosion assessment, and standard steel construction is suitable so long as the water stays completely soluble in the supercritical CO₂ for the life of the well.
- When free water is determined to be present, material selection should be reviewed by a Subject Matter Expert and should carefully consider the following:
  - The composition of the injectate and maximum allowable impurities in the stream.
  - The composition of water in the injection zone, such as a saline formation.
  - Maximum injection pressures and bottomhole temperatures.
Industry Needs as CCS Continues to Grow

- More corrosion data in SC-CO\textsubscript{2} environments
  - 2023 is expected to yield a large volume of new tests data
  - Temperature and impurity limits will need to be established for many CRAs
- Material selection guidelines
  - Currently, only a couple papers have been published touching on material selection guidelines for CCS injection wells
  - The PCOR Partnership and Stress Engineering have recently developed more comprehensive guidelines for CCS injections wells
    - Publication is in progress
- More field experience and case studies
Thank You!