Effect of Impurities on Supercritical Carbon Dioxide (Steels at 450°-650°C)

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Supercritical CO$_2$ is moving towards commercialization

8 Rivers Unveils 560 MW of Allam Cycle Gas-Fired Projects for Colorado, Illinois

8 Rivers Capital, inventor of a novel supercritical carbon dioxide (CO$_2$) cycle, plans to begin operating a 280-MW NET Power natural gas-fired plant within the Southern Ute Indian Reservation in southwest Colorado by 2025. The company on April 15 also said it will team with agricultural and processing firm Archer-Daniels-Midlands Co. (ADM) to locate a 280-MW NET Power facility in Decatur, Illinois.

The first clean fossil energy: integrated CO$_2$ capture

BUT, burning natural gas in sCO$_2$ creates impurities...
Without impurities, there is a carburization concern in sCO₂

- Low critical point (31°C/7.4 MPa)
- High, liquid-like density
- Flexible, small turbomachinery

Ni-based alloys: OK in sCO₂
But cost is a concern:
Where can steels be used?
New metrics focus on internal carburization

Factsage calculations

Young et al., 2011
Initial test matrix is complete

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RG sCO₂</th>
<th>+1%H₂O+0.1%H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C (842°F)</td>
<td>2000 h</td>
<td>1000 h</td>
</tr>
<tr>
<td>550°C (1022°F)</td>
<td>2000 h</td>
<td>1000 h</td>
</tr>
<tr>
<td>650°C (1202°F)</td>
<td>1000 h</td>
<td>1000 h</td>
</tr>
</tbody>
</table>

Focus on four steels

- Four primary alloys in test matrix
  - T91 (9Cr-1Mo)
  - VM12 (~11Cr)
  - 316H (conventional stainless steel)
  - NF709 (advanced austenitic, 20Cr-25Ni+Nb)

- 10 specimens of each alloy
- With & without impurities (open vs. closed cycle)

Baseline of research grade (RG) CO₂: ≤ 5 ppm H₂O and ≤ 5 ppm O₂
Mass change of 5-6 specimens in RG sCO$_2$ plotted

- One specimen of each alloy removed at 500 h for metallography
- High mass gains for 9-12%Cr steels in all cases
- Low mass gains for FCC steels except 316H at 650°C
Measured rates in sCO$_2$ consistent with the literature

- Metric developed for Solar CSP
  - Slow rate = OK for 100kh life
- Ni-based alloys all “good”
  - Lifetime model: ≤ 800°C = 100kh
- Steel limitations
  - Ferritic-martensitic alloys <500°C
  - Austenitic alloys <600°C
    - Obvious jump in kinetics
    - Advanced austenititics, better
      - Value in 20-25%Cr, 20-25%Ni

9-12Cr steels have similar rates in 276 bar steam
New metric #1: post-exposure room temperature ductility

- 25mm long dogbone specimens
- 316H (16Cr-10Ni)
  - Cr-rich oxides = low mass gain + good ductility
  - Fe-rich oxides = high mass gain + embrittlement
- 709 (20Cr-25Ni):
  - no loss in ductility in this experiment

Pint, 2021, ECS Interfaces, in press
Adding impurities caused accelerated attack in SS:

- $\text{sCO}_2 + 1\% \text{O}_2 - 0.1\% \text{H}_2\text{O}$ per NetPower

**Diagram:**
- 650°C, 300 bar
- Specimen Mass Change (mg/cm²)
- Exposure Time (hr)
- Open box: RG sCO₂
- Shaded box: 1%O₂ + 0.1%H₂O

**Legend:**
- T91
- VM12
- 316H
- 709

**Notes:**
- Minor changes for 9-12Cr steels
- Increase for 709
- Spallation for 316H
Acceleration evident for 316H and 709 (20Cr-25Ni)

316H and 709 rates above the metric at 550°C

→ Longer exposures may be needed to obtain more accurate steady-state rates in this environment
New metric #2: Bulk C measurements after exposure

C increase detectable mainly at 650°C

650°C: most materials showed higher C uptake with impurities in sCO$_2$ : less protective scales
Light microscopy: just getting started on characterization

(a) 450°C sCO$_2$+imp  (b) 550°C sCO$_2$+imp  (c) 650°C sCO$_2$+imp  (d) 650°C RG sCO$_2$

sCO$_2$+1%O$_2$-0.1%H$_2$O per NetPower
Summary: sCO$_2$ is a challenging environment for steels

- At $650^\circ$-$800^\circ$C, Ni-based alloys appear compatible

- Steels have problem forming protective scales:
  - 9-12%Cr may be limited to $\sim500^\circ$C
    - Fe-rich oxide formation observed in sCO$_2$
  - 316H at $650^\circ$C in RG sCO$_2$
    - Carbon ingress + embrittlement
    - **What about 600$^\circ$C?**
  - 709 formed Cr-rich oxide in all cases
    - Longer times at 650$^\circ$C?
    - 310HCbN/alloy 25: no C ingress at 750$^\circ$C
    - Accelerated attack at 650$^\circ$C with impurities

- All of these steels are affected by impurities!