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

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Supercritical CO$_2$ is moving towards commercialization

11/17/2021: NetPower 25MW component demonstration plant in Laporte, TX
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…
Impurities differ in indirect- & direct-fired sCO₂ cycles (i.e. closed vs. open)

Closed cycle:
“pure” CO₂ 100-300 bar

Open cycle:
sCO₂ + impurities (O₂, H₂O…)

Fossil: 2013-2015 general study
Solar: 2015-2018 700°-800°C
Fossil: 2019-21 Cermets 1000+°C
Fossil: 2015-2018 750°C
Fossil: 2020-2022 steel project

ARPA-E: 2019-22: ≥800°C HX
**CO₂ compatibility evaluated three ways at 400°-1200°C**

- **Autoclave**: 300 bar sCO₂, 500-h cycles (400°-800°C)
  - Correct temperature and pressure
  - 4-5 cm² alloy coupons

- **Tube furnace**: 1 bar CO₂, 500-h cycles
  - Same cycle frequency as autoclave

- **“Keiser” rig**: above 800°C, 500-h cycles, 1-43 bar CO₂

- **Box furnace**: Lab. Air, 500-h cycles (baseline)
  - Studies at 1-43 bar

Baseline of research grade (RG) CO₂: ≤ 5 ppm H₂O and ≤ 5 ppm O₂

Industrial grade (IG) CO₂: 18±16 ppm H₂O and ≤ 32 ppm O₂
sCO₂ compatibility: broad range of conditions considered

**400°-650°C: concern about steel carburization**
- Well-known issue from CO₂-cooled reactors
  - Grade 9 steel current issue
- 550°-600°C transition temperature for normal austenitic steels

**650°-800°C: Ni-based alloys**
- No issues for Ni-based alloys
  - Low C solubility, protective Cr₂O₃ formation
- Similar rates for air, CO₂ and sCO₂
  - **no P effect**

**>800°C: challenging for superalloys/cermets/FeCrAl**
- Initial results at 0.1 & 2 MPa
  - *Subcritical P effect observed*
- Mo/W cermets need coating
- Accelerated attack of Ni-based superalloys
- SiC promising, but not MoSi₂
- FeCrAl attacked at 1200°C
  - Al₂O₃ supposed protective?

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![Graph showing specimen mass change vs. exposure time](image)

**Legend**
- 0.1 MPa CO₂
- 2 MPa CO₂
Initial test matrix is complete

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RG sCO₂</th>
<th>+1%O₂+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

<table>
<thead>
<tr>
<th>Alloy</th>
<th>UNS</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr.91</td>
<td>K90901</td>
<td>8.6</td>
<td>0.3</td>
<td>0.5</td>
<td>0.4</td>
<td>.10</td>
<td>.05</td>
<td>0.9Mo,0.2V</td>
</tr>
<tr>
<td>VM12</td>
<td>12CrCoW</td>
<td>11.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>.12</td>
<td>.04</td>
<td>1.6W,1.5Co</td>
</tr>
<tr>
<td>316H</td>
<td>S31609</td>
<td>16.3</td>
<td>10.0</td>
<td>0.8</td>
<td>0.5</td>
<td>.04</td>
<td>.04</td>
<td>2.0Mo,0.3Co</td>
</tr>
<tr>
<td>NF709</td>
<td>S31025</td>
<td>20.1</td>
<td>25.2</td>
<td>0.9</td>
<td>0.4</td>
<td>.06</td>
<td>.15</td>
<td>1.5Mo,0.2Nb</td>
</tr>
</tbody>
</table>
Pure sCO₂: Cr₂O₃ scale prevents C ingress

- 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
Adding impurities caused accelerated attack in SS:

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

650°C, 300 bar

- Open box: RG sCO$_2$
- Shaded box: 1%O$_2$+0.1%H$_2$O

Minor changes for 9-12Cr steels: Thick scales in all cases

Increase for 709

Spallation for 316H
Matrix complete: Acceleration evident for 316H and 709

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
- What about 600°C?
- What about coatings?
- Can we do better than $k_p$ metric assessment?
Increased C ingress with impurities

Determined by combustion analysis (bulk measurements)

Need to repeat 709 measurement
25°C tensile properties with impurities: similar effect on all

All steels show loss in ductility after 650°C sCO₂+imp compared to 650°C Ar anneal.
**sCO₂ 600°C: one more RG sCO₂ experiment**

- Previously 450, 550 and 650°C
  - 30 MPa, RG CO₂
  - Fill in gap + add new materials
    - 825: industry interest
    - 253MA: suggestion at NACE 2021
    - CF8C-Plus: code case in progress

- Mass change: 1ˢᵗ indications
  - 4-6 specimens of each alloy
  - Box plot: median value shown
  - Higher mass gain: Fe-rich oxide
  - 709+825 showed low mass gain
  - 253MA+CF8C-Plus: accelerating mass gain = FeOₓ nodules...

- 825: 40Ni-31Fe-23Cr-3Mo-1.7Cu-1Ti-0.5Mn-0.3Si
- CF8C-Plus: Fe-12.5Ni-19.5Cr-4Mn-0.7Nb-0.7Si-0.5Cu-0.3Mo-0.25N (ASTM spec.)
- 253MA: 65Fe-11Ni-21Cr-1.5Si-0.7Mn-0.3Mo0.15N-0.03Ce-0.01La
sCO₂ 600°C: 2021 explored some additional candidates

- **550°-600°C critical temperature**
  - 30 MPa, RG CO₂
  - 4-6 specimens of each alloy

- **Ni-based alloy 825 (Ni-31Fe-23Cr)**
  - Small mass change (as expected)
  - Similar to advanced austenitic 709 (Fe-20Cr-25Ni)

- **253MA: higher Cr, Si + Ce/La**
  - accelerating mass gain = FeOₓ nodules...

- **CF8C-Plus (cast 347): high Mn**
  - Higher strength version of CF8C
  - Also accelerating mass gain

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**Figure**: Graph showing specimen mass change vs. exposure time for different alloys at 600°C and 300 bar. Key points:

- **825**: 40Ni-31Fe-23Cr-3Mo-1.7Cu-1Ti-0.5Mn-0.3Si
- **CF8C-Plus**: Fe-12.5Ni-19.5Cr-4Mn-0.7Nb-0.7Si-0.5Cu-0.3Mo-0.25N (ASTM spec.)
- **253MA**: 65Fe-11Ni-21Cr-1.5Si-0.7Mn-0.3Mo0.15N-0.03Ce-0.01La
Rate from 2 data points provides a comparison

- T91: in line with $sCO_2 + sH_2O$
- 316H: faster than literature
  - Due to heating in $sCO_2$?
- 709: low as measurable
  - 20Cr/25Ni: value of higher Ni
    - 310SS: 25Cr/20Ni, much weaker
- 253MA/CF8C+: some benefit
  - Looking for cheaper than 709
- 825: 0.01mg/cm$^2$ mass loss
  - Average of 3-4 specimens
EPMA: measurements of C ingress for modeling

- Massive C uptake at 650°C for both alloys
- Very little uptake at 450°C for both alloys
- Collecting more EPMA data to feed modeling task
- GDOES now operational: beginning measurements
Initial steel modeling (Pillai): Calculated average C profiles and carbide fraction

Goal: predict 100,000 kh C ingress as a function of temperature for T91 and 316H
Collecting C profiles using GDOES at 450°-650°C

GDOES: Glow discharge optical emission spectroscopy

GDOES C profiles (in progress)
- Effect of temperature
- Effect of impurities
- 316H/709 comparison

Last task is to complete modeling work
Summary: sCO\textsubscript{2} is a challenging environment for steels

- At 650\textdegree-800\textdegree C, Ni-based alloys appear compatible
- Steels have problem forming protective scales:
  - 9-12\%Cr may be limited to ~500\textdegree C
  - Fe-rich oxide formation observed in sCO\textsubscript{2}
  - 316H at 600\textdegree-650\textdegree C in RG sCO\textsubscript{2}
    - Carbon ingress + embrittlement
  - 709 formed Cr-rich oxide in all cases
    - Longer times at 650\textdegree C?
    - 310HCbN/alloy 25: no C ingress at 750\textdegree C
    - Accelerated attack at 650\textdegree C with impurities
- All of these steels are affected by impurities!
Backups

RG sCO₂ + 1%O₂ + 0.25%H₂O or +0.25%H₂O or +1%O₂

750°C
1,000 h

Carbon activity (ac)

550 600 650 700 750 800

Temperature °C

Cr₂O₃ Pₜₙₙ = 1 bar

Fe₃O₄ Pₜₙₙ = 1 bar

metal dusting criteria

Fe₂O₃ Pₜₙₙ = 1 bar

All 650°C, 500 h, sCO₂

Cr-rich scale

Cr-coated T91

>100μm Fe-rich duplex scale

bare T91 50μm

bared T91 10μm

Cr-coated T91