Overview

• **DOE NEUP**
  – *Advancement of Supercritical Carbon Dioxide Technology through Round Robin Testing and Fundamental Modeling*
  – 2015-2018
  – Nuclear Reactor Technology Program

• **Co-PIs & Collaborators:**
  – Julie Tucker (PI) & Líney Árnadóttir Oregon State University
  – Mark Anderson - University of Wisconsin, Madison
  – Bruce Pint - ORNL
  – Ömer Doğan - NETL
  – Henry Saari - Carleton University, Canada
  – Changheui Jang - KAIST
  – John Shingledecker - EPRI
NEUP Project Objectives

• Develop a sCO$_2$ materials working group
• Perform round robin test program
• Comparison of sCO$_2$ to SCW data
• Joint testing in sCO$_2$
• Empirical modeling
• Atomistic modeling of fundamental mechanisms
Round Robin Team Members

Round Robin Testing
• Oregon State University: Julie Tucker, Lucas Teeter, Benjamin Adam
• University of Wisconsin-Madison: Mark Anderson, Jacob Mahaffey*
• ORNL: Bruce Pint
• NETL: Omer Dogan, Gordon Holcomb, Casey Carney
• Carleton University: Henry Saari
• KAIST: Changheui Jang

Alternative Testing
• CSIRO Energy Center: Rene Olivares

Additional Support
• EPRI: Steven Kung & John Shingledecker

*Sandia National Lab
Round Robin Goals & Parameters

- Demonstrate comparable and reproducible results across organizations performing sCO₂ corrosion testing
- Environment: Research grade CO₂ (99.999% pure)
- Time of Exposure: 1500h in 500h increments
- Temperatures: 550°C and 700°C
- Pressure: 20 MPa
- Testing 5 alloys
  - 740H (700°C only)
  - 625
  - 316L
  - HR120
  - Grade 91 (550°C only)
**Characterization Plan**

- OSU performs AR characterization on all alloys
- Testing on 6 sample of each alloy at each temperature
- Weight change and SEM oxide thickness at each checkpoint
- Selected XRD, TEM and XPS as needed

<table>
<thead>
<tr>
<th>Characterization</th>
<th>500h</th>
<th>1000h</th>
<th>1500h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Change</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Mass Change Results – Grade 91 @ 550°C
Oxide Characterization – Grade 91

OSU exposure 1000h

Mounting Material
Copper
Iron Oxide
(Iron, Chromium) Oxide
Chromium Depleted Base Metal with Excess Oxygen
Base Metal

UW exposure 1500h

1.5kx
Mount
Copper
Fe₃O₄
Fe₃₋ₓCrₓO₄

Oxide Thickness
OSU 1000h ~23µm
UW 1500h ~40µm
KAIST 1500h ~39µm
Mass Change Results

Mass Gain of Alloy 316L Exposed to CO₂ at 550°C and 20 MPa

Mass Gain of Alloy 316L Exposed to CO₂ at 700°C and 20 MPa
Oxide Characterization – 316L @ 550°C

Oxide Thickness
OSU 1000h ~1.5µm
UW 1500h ~0.5µm continuous/ ~6µm (nodules)
KAIST 1500h ~6µm
Oxide Characterization – 316L @ 700°C

UW exposure 1500h

Oxide Thickness at 1500h
UW ~3µm continuous/ ~36µm (nodules)
Mass Change Results – HR 120

Mass Gain of Alloy HR 120 Exposed to CO$_2$ at 550°C and 20 MPa

Mass Gain of Alloy HR 120 Exposed to CO$_2$ at 700°C and 20 MPa
Oxide Characterization – HR120 @ 550°C

Oxide Thickness
OSU 1000h ~0.4µm
UW 1500h ~3µm continuous
KAIST 1500h ~0.1µm
Oxide Characterization – HR120 @ 700°C

UW exposure 1500h

Oxide Thickness
UW 1500h ~1.3µm continuous/3µm nodules
Mass Change Results - 625

Mass Gain of Alloy 625 Exposed to CO₂ at 550°C and 20 MPa

- KAIST
- NETL
- UW
- OSU

Mass Change [mg/cm²] vs Time [h]

Mass Gain of Alloy 625 Exposed to CO₂ at 700°C and 20 MPa

- KAIST
- NETL
- UW

Mass Change [mg/cm²] vs Time [h]
**Oxide Characterization – 625 @ 550°C**

OSU exposure 1000h

- Copper
- Chromium Oxide
- Base Metal
- 4µm

UW exposure 1500h

20kx

- 2µm
- Base 625

50kx

- 1µm
- Base 625

**Oxide Thickness**

- OSU 1000h ~0.2µm
- UW 1500h ~0.2µm continuous
- KAIST 1500h ~0.2µm
Oxide Characterization – 625 @ 700°C

UW exposure 1500h

Oxide Thickness at 1500h
UW ~1.3µm
Mass Change Results – 740H

Mass Gain of Alloy 740H Exposed to CO₂ at 700°C and 20 MPa

Mass Change [mg/cm²]

Time [h]

KAIST
NETL
UW
Oxide Characterization – 740H @ 700°C

UW exposure 1500h

Oxide Thickness at 1500h
UW ~1µm

Oregon State University
College of Engineering
Comparison to Literature Results

**Gr91 316SS**

- **Mass Gain, mg/cm²**
  - Trend for RG & CG CO₂
  - Trend for CO₂+impurities

- **Graphs**
  - 9Cr Ferritic Steels
  - TP316 Austenitic Steel

- **Equation**
  \[ P = T(°K)[20+\log_{10}(hr)] \times 10^{-3} \]
Comparison to Literature Results

HR120

Mass Gain, mg/cm²

$P = T(°K)[20+\log(t/hr)]*10^{-3}$
Comparison to Literature Results

$P = T(\circ K)[20+\log_{10}(hr)] \times 10^{-3}$
Calculation of Rate Constants

Mass Gain of Alloy 625 Exposed to CO₂ at 700°C and 20 MPa

- KAIST
- NETL
- UW

Mass Change [mg/cm²]

Time [h]

Mass Gain of Alloy 625 Exposed to CO₂ at 700°C and 20 MPa

- KAIST
- NETL
- UW

Mass Change [mg/cm²]

Time¹/² [s¹/²]
## Parabolic rate constant $K_p \text{ (mg}^2/\text{cm}^4\text{-s)}$

<table>
<thead>
<tr>
<th>Institution</th>
<th>550°C</th>
<th>700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G91</td>
<td>316L</td>
</tr>
<tr>
<td>KAIST</td>
<td>6.3E-06</td>
<td>7.8E-10</td>
</tr>
<tr>
<td>NETL</td>
<td>1.7E-06</td>
<td>9.0E-10</td>
</tr>
<tr>
<td>UW</td>
<td>2.6E-06</td>
<td>2.9E-10</td>
</tr>
<tr>
<td>OSU</td>
<td>1.4E-06</td>
<td>8.4E-10</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>3.0E-06</strong></td>
<td><strong>7.0E-10</strong></td>
</tr>
<tr>
<td><strong>Std. Dev.</strong></td>
<td><strong>2.2E-06</strong></td>
<td><strong>2.8E-10</strong></td>
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</tbody>
</table>
Summary

• Mass change data available to date has shown reasonable agreement among teams and with existing literature data.
  – some discrepancies between data sets on alloys with higher corrosion rates
    • G91 at 550°C and 316L at 700°C
• Oxide thickness similar for G91
• Higher mass change shown for 316L is more consistent with data generated under similar conditions
• Additional data from more round robin teams and future oxide analysis will help to clarify sources of discrepancies
Acknowledgements

• Materials donated by Special Metals, Haynes & EPRI
• Machined, polished and shipped by EPRI
• Ian Wright and the EPRI-DOE University Turbine Systems Research (UTSR) Project for assistance in gathering data for the Larson-Miller plots.
• Financial support from DOE NEUP DE-NE0008424 (Project 15-8495) “Advancement of Supercritical Carbon Dioxide Technology through Round Robin Testing and Fundamental Modeling”
Materials Degradation in CO₂ Environments

Symposium at the...

Abstracts due this Saturday, March 31
Questions?

Thank you!

Julie.Tucker@oregonstate.edu
Round Robin Test Samples

- Materials donated by Special Metals, Haynes & EPRI
- Independent chemical analysis performed
- Machined, polished and shipped by EPRI

<table>
<thead>
<tr>
<th>wt.%</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Nb</th>
<th>Mn</th>
<th>Mo</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>Cu</th>
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<tbody>
<tr>
<td>Gr 91</td>
<td>89.27</td>
<td>0.13</td>
<td>8.234</td>
<td>0.018</td>
<td>0.063</td>
<td>0.45</td>
<td>0.93</td>
<td>0.010</td>
<td>0.279</td>
<td>0.003</td>
<td>0.091</td>
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<tr>
<td>316L</td>
<td>68.29</td>
<td>9.93</td>
<td>16.844</td>
<td>0.214</td>
<td>0.009</td>
<td>1.58</td>
<td>1.98</td>
<td>&lt;0.002</td>
<td>0.360</td>
<td>0.010</td>
<td>0.492</td>
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<tr>
<td>HR120</td>
<td>34.48</td>
<td>37.44</td>
<td>24.936</td>
<td>0.248</td>
<td>0.561</td>
<td>0.80</td>
<td>0.47</td>
<td>0.069</td>
<td>0.483</td>
<td>0.015</td>
<td>0.065</td>
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<tr>
<td>625</td>
<td>3.66</td>
<td>61.65</td>
<td>21.168</td>
<td>0.178</td>
<td>3.422</td>
<td>0.28</td>
<td>8.70</td>
<td>0.204</td>
<td>0.168</td>
<td>0.210</td>
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<tr>
<td>740H</td>
<td>0.11</td>
<td>50.42</td>
<td>24.144</td>
<td>20.421</td>
<td>1.559</td>
<td>0.23</td>
<td>0.31</td>
<td>1.312</td>
<td>0.153</td>
<td>1.374</td>
<td>0.002</td>
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</table>
# Sample Summary

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Supplier</th>
<th>Material Supplied</th>
<th>Material Area</th>
<th># Samples Total</th>
<th># Samples per Lab</th>
<th>Material Need (Sheet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>740H</td>
<td>Special Metals</td>
<td>4.5”x11.5” sheet 1/8” thick</td>
<td>51.75 in²</td>
<td>42</td>
<td>6</td>
<td>26 in²</td>
</tr>
<tr>
<td>625</td>
<td>Haynes</td>
<td>2*(8”x8” sheet)</td>
<td>96 in²</td>
<td>84</td>
<td>12</td>
<td>52 in²</td>
</tr>
<tr>
<td>316L</td>
<td>Rolled Alloys</td>
<td>12x12 sheet 1/16” thick</td>
<td>144 in²</td>
<td>84</td>
<td>12</td>
<td>52 in²</td>
</tr>
<tr>
<td>HR 120</td>
<td>Haynes</td>
<td>2*(8”x8” sheet)</td>
<td>96 in²</td>
<td>84</td>
<td>12</td>
<td>52 in²</td>
</tr>
<tr>
<td>Grade 91</td>
<td>EPRI</td>
<td>Stock</td>
<td></td>
<td>42</td>
<td>6</td>
<td>26 in²</td>
</tr>
</tbody>
</table>
## Round Robin Capabilities

<table>
<thead>
<tr>
<th>Organization</th>
<th>Maximum Temperature</th>
<th>Maximum Pressure</th>
<th>Chamber Volume</th>
<th>Flow rate (mL/min)</th>
<th>Autoclave Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSU</td>
<td>800°C</td>
<td>26 MPa</td>
<td>1235 cm³</td>
<td>0-24</td>
<td>Haynes 230</td>
</tr>
<tr>
<td>UW (2 systems)</td>
<td>750°C</td>
<td>25 MPa</td>
<td>900 cm³ (combined)</td>
<td>0-24</td>
<td>Inconel 625</td>
</tr>
<tr>
<td></td>
<td>760°C</td>
<td>38 MPa</td>
<td></td>
<td>0-24</td>
<td>Haynes 282</td>
</tr>
<tr>
<td>ORNL</td>
<td>850°C</td>
<td>30 MPa</td>
<td>1400 cm³</td>
<td>0-24</td>
<td>Haynes 282</td>
</tr>
<tr>
<td>NETL</td>
<td>800°C</td>
<td>28 MPa</td>
<td>1040 cm³</td>
<td>0-24</td>
<td>Haynes 230</td>
</tr>
<tr>
<td>Carleton</td>
<td>750°C</td>
<td>25 MPa</td>
<td>1150 cm³</td>
<td>0-250</td>
<td>Inconel 625</td>
</tr>
<tr>
<td>KAIST (2 systems)</td>
<td>700°C</td>
<td>25 MPa</td>
<td>1077 cm³ (each)</td>
<td>0-24</td>
<td>Inconel 625</td>
</tr>
<tr>
<td>CSIRO</td>
<td>1000°C</td>
<td>25 MPa</td>
<td>68 cm³</td>
<td></td>
<td>Variable Tube</td>
</tr>
</tbody>
</table>
Pre-Exposure Sample Preparation

- Cut to size with EDM, water jet cutting or other low heat process
- Drill sample holes
- Polish the larger area surfaces to a 30 micron grit finish, which is equivalent to a 600-grit finish or 20-40 Mesh
- Hand polish the sides up to 600-grit.
- Rinse, Ultrasonic bath with Ammonium Hydroxide based solution, Rinse
- Ultrasonic bath with propanol remove oils and surface particles.
- Store in a desiccator until testing
Post-Exposure Sample Preparation

• 10-15nm gold sputter deposition layer
• Copper electroplating
• Sample mounting
• Polishing