Corrosion of Heat Exchanger Alloys in sCO₂ Power Cycles

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Objectives

- **Corrosion database**
  - determine performance of structural alloys in laboratory high-temperature high-pressure supercritical CO$_2$ (sCO$_2$)

- **Computational model development**
  - build on an existing EPRI Oxide Exfoliation Model
    - includes laboratory data and configurations pertaining to sCO$_2$ heat exchangers and recuperators

**Materials selection to help DOE achieve Supercritical Transformational Electric Power (STEP) program**
Technology challenges for sCO$_2$ HX

- 4-10X heat duty compared to Rankin Cycle
- HX Expensive: ~40% of total plant cost
- Unique designs
  - small channels
  - large surface areas
- Materials considerations
  - Mechanical:
    - thermal fatigue, creep (thin-wall structures)
  - Manufacturing:
    - brazing/diffusion bonding
  - Corrosion:
    - oxidation, carburization, exfoliation, pluggage, etc.
Realistic sCO₂ conditions simulated in lab for Allam cycle

- **Survey of industry and literature data**
  - 700°C likely maximum temperature for heat exchangers

- **Evaluation of impurities for near-term ‘open/direct-fired cycle’ – Allam Cycle**
  - H₂O, O₂, N₂, Ar, NOₓ, SOₓ, HCl
  - thermodynamic and mass-balance calculations for methane (NG) and cooled coal syngas

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<table>
<thead>
<tr>
<th>Species</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methane</td>
</tr>
<tr>
<td>CH₄</td>
<td>100</td>
</tr>
<tr>
<td>CO</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>N₂+Ar</td>
<td>2.0</td>
</tr>
<tr>
<td>H₂S</td>
<td>2 ppm</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td></td>
</tr>
<tr>
<td>LHV</td>
<td>912 BTU/scf</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Fuel Stream</th>
<th>Methane</th>
<th>Cooled Raw Coal Syngas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Combustor Inlet</td>
<td>Turbine Inlet</td>
<td>Combustor Inlet</td>
</tr>
<tr>
<td>CO₂</td>
<td>95</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>H₂O</td>
<td>250 ppm</td>
<td>5.3</td>
<td>250 ppm</td>
</tr>
<tr>
<td>N₂+Ar</td>
<td>1</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>O₂</td>
<td>3.8</td>
<td>3.6</td>
<td>1</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td></td>
<td>20 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td></td>
<td>1,000 ppm</td>
</tr>
</tbody>
</table>

**3.6 mol% O₂, 5.3 mol% H₂O**
Scope of laboratory sCO$_2$ corrosion study

- **Alloys**
  - commercially available
  - code approved/industry relevant
  - focus on economics

- **Conditions**
  - 650-750°C, 200 bar
  - sCO$_2$
    - commercially pure CO$_2$
    - impure CO$_2$ (with O$_2$ + H$_2$O) - to simulate semi-open cycle in NG oxy combustion

- **Exposures**
  - 2 x 300-h shakedown tests in CO$_2$ ± impurities, 700°C, 200 bar (Gr91, TP304H, IN740H)
  - 3 x 1,000-h tests in CO$_2$ + impurities, 650, 700, 750°C, 200 bar (all 7 alloys)
  - 1 x 5,000-h test in CO$_2$ + impurities, 700°C, 200 bar (all 7 alloys)

<table>
<thead>
<tr>
<th>Material Class</th>
<th>Alloys Selected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferritic steels</td>
<td>Gr 91 (8-9Cr) VM12 (11-12Cr) Crofer 22H (20Cr)</td>
</tr>
<tr>
<td>Austenitic stainless</td>
<td>TP304H (18Cr) HR3C (25Cr)</td>
</tr>
<tr>
<td>Nickel-based</td>
<td>IN617 (20Cr, solid solution strengthened) IN740H (25Cr, ppt. strengthened)</td>
</tr>
</tbody>
</table>
Group 1
Ferritic steels: available mass-gain data in CO₂

- Pure CO₂
  - mass gains similar to those in steam at higher values of Larson-Miller parameter (P)
- Impure CO₂
  - significantly lower mass gains than in pure CO₂ at lower values of P
- Expect similar morphologies in sCO₂ and steam at higher T and/or longer time
Group 1
Typical scale morphologies formed on ferritic steels

T91, 64kh at 566°C & 138 bar steam (EPRI Atlas)

T91, 155kh at 538°C & 17 bar steam (EPRI Atlas)

T91, ≈300h at 550°C & 250 bar CO₂ (Rouillard, 2010)

Fe-9Cr, ≤9kh at 550°C & 40 bar (imp) CO₂ (Harrison, 1974)
Group 2
Austenitic stainless steels: available mass-gain data in sCO₂

- Considerable data scattering
- No real trend for pure vs. impure CO₂
  - or for HP vs. 1 atm.
  - or vs. HP steam (not shown)
- Expect similar morphologies in sCO₂ ± most impurities, and HP steam
Group 2
Typical scale morphologies on austenitic stainless steels

Main features of scale in HP steam (Wright & Dooley, 2011)

TP347HFG, 11kh at 670°C & 251 bar steam (EPRI Atlas)

TP347HFG, 500h at 700°C & 200 bar CO₂ (Pint & Keiser, 2014)
Group 3
HT Ni-base alloys (Cr$_2$O$_3$ formers): available data in sCO$_2$

$P = T(^{°}K)[20+\log t(hr)] \times 10^{-3}$
Group 3

Thickness measurements on HT alloys are challenging

- Maximum power of optical microscopy produced marginal resolution

- New SEM/BSE/EDS/EBSD techniques used
  - Non-uniform scale clearly evident on 740H surface

- FIB-STEM can offer better resolution but is time consuming and limited in area coverage
Carburization: Concern for surface hardening and Cr depletion

Current Understanding

- **Ferritic steels**
  - UK research (1970s) identified breakaway oxidation phenomenon under AGR conditions

- **Austenitic steels**
  - C pick-up observed only in initial stages, or when duplex scales present (or after exfoliation)

- **Cr$_2$O$_3$ scales are known to be excellent barriers to C ingress**
  - confirmed by recent observations at 550-750°C, 200 bar (Pint, ORNL)

- **High total Ni+Cr content in alloys is beneficial**

- **High-Cr Ni-based (HT) alloys are likely to resist carburization**
  - maybe equally applicable to solid solution and precipitation-strengthened Ni-based alloys
Ferritic steels showed different degrees of surface hardening after 1000h at 700°C in CO₂ -3.6% O₂-5.3% H₂O at 200 bar
Overall observations on carburization (this study)

- Ferritic steels
  - expect continuous C uptake until alloy saturation
  - oxidizing impurities retard hardening

- Conventional austenitic steel
  - TP304H showed initial hardening (after 300h) in sCO₂ with oxidizing impurities
    - after 1,000h, possibly small increase in overall alloy hardness, but no gradient (consistent with UK AGR results)

- Reliable Cr₂O₃-forming alloys:
  - high-Cr austenitic (HR3C): hardening of surface to 150-200 µm
  - Ni-base alloys: no evidence of hardening (as expected)
Modeling: Thickness-based oxide growth kinetics for sCO₂ corrosion

**Focus on three potential failure modes:**
1. Reduction of flow area in channels from oxide growth
2. Cr depletion due to oxide formation
3. Time to scale failure (oxide exfoliation/blockage)

**Arrhenius constants used to modify EPRI Oxide Exfoliation Model**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>T°C</th>
<th>A (μm²/h)</th>
<th>Q (kJ/mole)</th>
<th>R²</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr91</td>
<td>650-750</td>
<td>2.3 x 10¹⁹</td>
<td>374</td>
<td>0.88</td>
<td>This work</td>
</tr>
<tr>
<td>VM12</td>
<td>650, 750</td>
<td>4.1 x 10⁷</td>
<td>162</td>
<td>1*</td>
<td>This work</td>
</tr>
<tr>
<td>Crofer 22H</td>
<td>650-750</td>
<td>1.2</td>
<td>14**</td>
<td>1*</td>
<td>This work</td>
</tr>
<tr>
<td>TP304H</td>
<td>650-750</td>
<td>7.6 x 10⁵</td>
<td>148</td>
<td>0.99</td>
<td>This work</td>
</tr>
<tr>
<td>HR3C</td>
<td>650-750</td>
<td>NA</td>
<td>NA</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>IN617</td>
<td>650-750</td>
<td>NA</td>
<td>NA</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>IN740</td>
<td>650-750</td>
<td>NA</td>
<td>NA</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>IN740</td>
<td>650-800</td>
<td>1.4 x 10⁵</td>
<td>166</td>
<td>0.97</td>
<td>17 bar steam</td>
</tr>
<tr>
<td>310HCbN</td>
<td>650-800</td>
<td>2.3 x 10²</td>
<td>112</td>
<td>0.98</td>
<td>17 bar steam</td>
</tr>
</tbody>
</table>

*Two data points only, at 650 and 750°C

**Very unusual T-dependence, possibly associated with a change in the type of scale formed due to rapidly increasing Cr diffusion at the higher temperatures.
Oxide growth in sCO₂ predicted by modified EPRI Oxide Exfoliation Model (isothermal)
Growth of scale thickness along a compact HX channel

- Local T along a channel dictates the rate of scale growth
  - hottest end will attain \( d_{\text{crit}} \) first
  - length of channel (for a given \( \Delta T \)) influences blockage considerations

- Critical oxide thickness (\( d_{\text{crit}} \)) is dictated by considerations of:
  - acceptable reduction in flow area (i.e., pressure drop)
  - exhaustion of Cr reservoir (breakaway oxidation)
  - scale exfoliation/failure and channel blockage
Failure mode 1:
Reduction in flow area from oxide growth (RFA\textsubscript{ox})

- Favored designs of sCO\textsubscript{2} recuperators employ small flow channels
  - $\Delta P$ is thus a critical consideration

- Rate of oxide growth drives RFA\textsubscript{ox}
- If RFA\textsubscript{ox} values of $\geq 5\%$ cannot be tolerated, the resulting $d_{\text{crit}}$ is very small

<table>
<thead>
<tr>
<th>Tube ID (mm)</th>
<th>Critical Oxide Thickness, $d_{\text{crit (µm)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$RFA_{\text{ox}}$:</td>
<td>1%</td>
</tr>
<tr>
<td>0.3</td>
<td>0.75</td>
</tr>
<tr>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>0.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>

• shown for laminar flow
  • lower $\Delta P$ for turbulent flow
  • RFA of 2-5% typically considered acceptable

Oxide thicknesses 1-10\(\mu\text{m}\) may also impact heat transfer even if scale remains intact
Failure mode 1: Reduction in flow area by oxide growth occurs rapidly.

In terms of lifetime:
- 0.3 mm channels are problematic for all alloys
- 1% $RFA_{ox}$ problematic (except for IN740H with 0.9 mm channel ID)
Failure mode 2:
Depletion of Cr reservoir leading to breakaway oxidation

- Model approach validated for conditions where there is no depletion gradient in Cr
  - for alumina-forming ferritic steels at $T > 1000^\circ C$
- Where a Cr-depletion gradient exists, critical Cr content ($C_b$) may be significantly reduced
  - if, for instance, Cr gradient results in 1.25x assumed $C_b$, calculated lives would be reduced by a factor of 40-70%
- New modeling based on this scenario (Duan, et al. 2016) should provide guidance
  - Overall, it appears that this scenario is likely to be life-limiting only for TP304H

<table>
<thead>
<tr>
<th>Alloy</th>
<th>T°C</th>
<th>Lifetime, kh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness, mm:</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>TP304H</td>
<td>650</td>
<td>19</td>
</tr>
<tr>
<td>HR3C</td>
<td>700</td>
<td>739</td>
</tr>
<tr>
<td>IN740H</td>
<td>700</td>
<td>1,070</td>
</tr>
</tbody>
</table>

**NOTE**
$C_b$ values estimated from general knowledge.
Failure mode 3:
Time to reach critical scale strain for exfoliation

Assumptions:

- **Unit is shut down every 3 months**
  - \( \Delta T (\Delta P) \) in shut down provides stress peak/scale failure and exfoliation
  - *tubes cleaned out*

- **Length of accumulated exfoliant = 10x channel diameter**

- **Blockage (RFA\(_B\)) is a discrete event**
  - \( RFA_{ox} \) is a function of time

### Table: Alloy vs. Lifetime (kh)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( T°C )</th>
<th>Channel length, m:</th>
<th>Lifetime, kh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Channel diam, mm:</td>
<td></td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>TP304H</td>
<td>550-700</td>
<td>33.9</td>
<td>&gt;&gt;40</td>
</tr>
<tr>
<td></td>
<td>600-750</td>
<td>13.2</td>
<td>17.5</td>
</tr>
<tr>
<td>IN740H</td>
<td>600-750</td>
<td>22.4</td>
<td>&gt;40</td>
</tr>
</tbody>
</table>

‘Fate of debris’ for thermally grown oxides is not understood for small-channel HX
Summary

- First project to address oxidation in direct-fired sCO$_2$ Allam cycles (with impurities)

- Oxide growth rates in sCO$_2$
  - appear consistent with (and similar to) those in HP steam
  - possibly slower when oxidizing impurities are present in sCO$_2$
  - no systematic effect from pressure

- Scale morphologies
  - nominally follow expectations for steam oxidation, with some potential influences from C

- Surface hardening
  - identified in Gr 91 and VM12; more pronounced in ‘pure’ sCO$_2$
  - also found in TP304H & HR3C
  - none apparent in Ni-base alloys

- Existing EPRI Oxide Exfoliation Model modified

- Impact of three lifetime-limiting scenarios from scale growth in sCO$_2$ evaluated
  - Degree of concern: RFA > exfoliation/blockage > Cr depletion
  - Model available for corrosion researchers and system designers to use in component design
Acknowledgements

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- NETL project manager: Vito Cedro
Together...Shaping the Future of Electricity
Group 4
HT Ni-base alloys (Al₂O₃ formers): available data in sCO₂

- Considerable scattering
- Less protective γ-Al₂O₃ is formed at low T
- Similar growth rates as Cr₂O₃ formers