Damage Occurring in FCC Hexmesh Systems

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Damage Occurring in FCC Hexmesh Systems

• Reactor Hexmesh Damage
  o Hexmesh that separated from the vessel wall
  o Brittle fracture of the welds
  o Corrosion and cracking of the hexmesh steel at the attachment welds

• Regenerator Hexmesh Damage
  o Examples of failures
  o Sigma embrittlement of FCC Regenerator welds
  o Carburization of hexmesh steel and welds
  o Test sample cut from FCC cyclone crossover piping
  o Damage found at the interface
Hexmesh that Separated from the Reactor Wall

Reactor Operating Temperature
960-990°F  510-530°C

Welds that Held Hexmesh to the Vessel Wall
Why the Welds Holding the Hexmesh Failed

Something happened along the weld metal to 1Cr-½Mo interface.

Extra E309 Weld Metal?

E309 Weld

Corrosion of Sensitized Hexmesh with minor cracking

1Cr-½Mo Vessel Wall Was Here

Bakelite
Carbon from the 1Cr-½Mo diffused into the stainless steel forming chromium carbides and lowering the fracture toughness of the weld metal. Refer to NACE Paper 626 from NACE Corrosion 1993 for examples of this phenomenon.
Example of Regenerator Hexmesh Failures
Inside of a cyclone

Black Sulfide Deposits
Behind the Hexmesh
Pushed the Hexmesh Out
Hexmesh Metal Completely Corroded Away

Hexmesh Metal Corroded Away Leaving Deposits Mixture of Sulfides and Oxides
Results of Corrosion Deposit Analysis

Metal sulfides convert to oxides when exposed to air, so while in-service the deposits contained more sulfur.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Weight %</th>
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</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>35.6</td>
<td>16.6</td>
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<tr>
<td>Iron</td>
<td>23.0</td>
<td>37.3</td>
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<tr>
<td>Chromium</td>
<td>14.4</td>
<td>21.8</td>
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<tr>
<td>Sulfur</td>
<td>10.9</td>
<td>10.2</td>
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<tr>
<td>Carbon</td>
<td>8.3</td>
<td>2.9</td>
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<tr>
<td>Nickel</td>
<td>4.2</td>
<td>7.2</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>Other Elements</td>
<td>2.62</td>
<td>1.54</td>
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</tbody>
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Table A1-2: Results of the Analysis of the Corrosion Product from Hexmesh Steel
Areas Where Welds Fractured and Hex Corroded

Red arrows point to fractured welds. White arrows point to corrosion damage.
Close-up of the Weld Fracture and Corroded Hex

Fractured Weld

Corroded 304H Hexmesh
What’s Happening to the Stainless Steel?

Fractured Weld

Carburized Stainless
Carburization of 304H Stainless Steel

Failed Weld

Hexmesh 304H

Carburized Stainless - Brittle

0.40 mm
Carburized Stainless at Higher Magnifications

Corrosion occurred around the chromium carbides.

Oxides & Sulfides

Chromium Carbides

Spectrum 1

Electron Image 1

40μm
The exact formula for pure chromium carbide is Cr$_{23}$C$_6$, but the composition of metal carbides typically varies with some Fe, Mn, and Ni in place of Cr atoms. When chromium carbides form, the surrounding stainless becomes non-stainless.

<table>
<thead>
<tr>
<th>Elements Present in Order of Descending Atomic %</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>47.94</td>
<td>61.03</td>
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<td>Carbon</td>
<td>27.00</td>
<td>7.94</td>
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<td>Iron</td>
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<td>Nickel</td>
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<td>2.90</td>
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<td>Oxygen</td>
<td>2.00</td>
<td>0.79</td>
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<tr>
<td>Sulfur</td>
<td>1.39</td>
<td>1.09</td>
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<td>Manganese</td>
<td>1.06</td>
<td>1.42</td>
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<tr>
<td>Silicon</td>
<td>0.82</td>
<td>0.57</td>
</tr>
<tr>
<td>Other</td>
<td>0.17</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Sigma Formation in Weld Metal Causing Brittle Weld Fractures

The dark phase is sigma in E309 weld metal – it creates aligned weak interfaces.
Fracture toughness this low could cause brittle fracture while in-service or during shut-downs.
CITGO’s 2015 Investigation of Hexmesh Damage in a Regenerator after 5 Years of Service

- Test sample cut from FCC Regen crossover duct
- Early in the degradation so mechanisms can be seen
- Specimens dry cut from the sample to avoid contamination
- The interface between refractory and steel was inspected and damage was found at the interface
- Analysis of corrosion deposits and phases present to identify the corrosion mechanism
Process Temperature During the 5 Year Run

Process Pressure: 25-33 psig  172-228 kPa
Regenerator Was Running Partial Burn

2010 Turnaround

1100 1150 1200 1250 1300 1350 1400
Temperature °F

600 650 700 750 800
Temperature °C

10 12:00:00 AM  7/12/2018 12:00:00 AM

1826.00 days

RGN DLT PHASE NE
2015 Sample Cut from the Lemont Regenerator
Specimens Cut from the Sample
Close-up of the Refractory-Steel Interface

AA-22 Refractory

Typical Interface - Tight

Some Areas Not Tight
Damage Found at the Refractory-Steel Interface

Corrosion Penetrating the 304H Beneath the Surface Pit.
A Closer Look at the Corrosion Damage

Mixture of Oxides and Sulfides with Steel Fragments

Oxides in Grain Boundaries with Some Sulfur

Sulfides in Grain Boundaries
X-Ray Analysis Results for Light Grey Deposits

No Oxygen Peak
Chromium Oxide Prevents Stainless Corrosion

Etched with Oxalic Acid     Original - 100X

Chromium Oxide Protective Layer

0.004 in

0.003 in

0.009 in
Conclusions

• Hexmesh failures in FCC Reactors at the vessel wall can be significantly reduced or eliminated with cold wall reactor design.
• Cold wall design prevents diffusion of carbon into the weld metal and avoids brittle fracture of welds.
• Polythionic stress corrosion cracking occurs in the hexmesh steel due to sensitization at the welds holding the hexmesh to the wall.
• Hexmesh failures in FCC regenerators are caused by carburization of the 304H hexmesh and carburization of E308 or E309 weld metal.
• Corrosion in FCC regenerators occurs due to both oxidation and sulfidation. Carburization of the stainless promotes the corrosion.
• Going to full burn operation in the Regenerator should reduce the sulfidation corrosion and that could also reduce oxidation.
• Sigma formation in FCC Regenerator welds causes the weld metal to become brittle, and easily fracture in service or during turnarounds.
• The chromium oxide protective layer on the stainless is very thin and damage of that thin layer by refractory movement could occur.