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AN OVERVIEW OF CORROSION ISSUES IN SUPERCRITICAL FLUIDS

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Antibes – Juan-les-Pins, France
22-25 April 2018

SYNOPSIS

Introduction
Corrosion…

Supercritical water
Energy production (“pure” SCW)
Wastes treatment

Supercritical CO₂ & other SC Fluids
Pure SCF
Solubilities & Pollutants

Protection strategies
The annual cost of corrosion is 3-4% of the world’s Gross Domestic Product
One quarter of the steel annual production is destroyed by corrosion

Source: World Corrosion Organization (granted NGO by the United Nations)

Illustrations from the web

Corrosion cracking of the fuselage of airplane
(April 28, 1988 – 1 fatal over 95)

Mississippi Bridge, Minneapolis, August 1, 2007, 13 fatal
structural weakness caused by corrosion

Sculpture by
David E. Davis

ERIKA (1999) “result of structural
weakness caused by corrosion”

Pitting corrosion of an oil tank

Atmospheric corrosion in a chemical plant

Corrosion of pipes in SC CO₂ storage system
from G. Schmitt, White paper, WCO, 2009

Repair of stress corrosion cracking in an ultra- supercritical
(USC) power plant,
from Laborelec Suez, 2013,
http://www.laborelec.be/ENG/publicatio ns/newsletters/newsletter-2013-june-
power-generation/how-to-repair-
potential-cracks-in-t24-material/

Supercritical waterwall cracking,
from Steag, 2013,
**Material solicitations in a SCF**

- Mechanical (high pressures)
- Thermal (often high temperatures)
- Chemical
  - Variety of SCF
  - Density evolutions
  - Pollutants

- Corrosion behavior of structural materials
  - Localized / generalized corrosion
  - Kinetics

- Safety & economical issues
  - Material Choice
  - Design
  - Plant lifetime

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**Possible SC Fluids**

<table>
<thead>
<tr>
<th>Component</th>
<th>Boiling point°C</th>
<th>Critical temp°C</th>
<th>Critical pressure (atm)</th>
<th>Critical density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
<td>373</td>
<td>21.8</td>
<td>0.65</td>
</tr>
<tr>
<td>Carbon</td>
<td>78.5</td>
<td>316</td>
<td>72.8</td>
<td>0.46</td>
</tr>
<tr>
<td>Acetone</td>
<td>89.7</td>
<td>322</td>
<td>46.2</td>
<td>0.229</td>
</tr>
<tr>
<td>Methane</td>
<td>17.6</td>
<td>51.5</td>
<td>63.6</td>
<td>0.035</td>
</tr>
<tr>
<td>Propene</td>
<td>52.1</td>
<td>108</td>
<td>41.9</td>
<td>0.317</td>
</tr>
<tr>
<td>Acetone</td>
<td>133</td>
<td>223</td>
<td>110.3</td>
<td>0.263</td>
</tr>
<tr>
<td>Acetone</td>
<td>86.3</td>
<td>190</td>
<td>64.5</td>
<td>0.372</td>
</tr>
<tr>
<td>Methane</td>
<td>54.4</td>
<td>74.3</td>
<td>39.5</td>
<td>0.364</td>
</tr>
<tr>
<td>Ethane</td>
<td>69.7</td>
<td>84.2</td>
<td>40.5</td>
<td>0.206</td>
</tr>
</tbody>
</table>

---

**Schematic representation of microscopic behavior of pure fluid in the P-T phase diagram**

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**CHOICE OF MATERIAL**

**Main metallic materials used in SCF systems**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel</td>
<td>Bal.</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td>Some additives (Cr, Ni, Mo… &lt;1%)</td>
</tr>
<tr>
<td>Stainless steels</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>Bal.</td>
<td>18</td>
<td>10</td>
<td>&lt;0.03</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>Bal.</td>
<td>18</td>
<td>10</td>
<td>&lt;0.03</td>
<td>2% Mo</td>
</tr>
<tr>
<td>904L</td>
<td>Bal.</td>
<td>20</td>
<td>25</td>
<td>&lt;0.02</td>
<td>5% Mo</td>
</tr>
<tr>
<td>Nickel alloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 625</td>
<td>5</td>
<td>22</td>
<td>Bal.</td>
<td>&lt;0.03</td>
<td>10% Mo, 5% Nb</td>
</tr>
<tr>
<td>Alloy 690</td>
<td>10</td>
<td>32</td>
<td>Bal.</td>
<td>&lt;0.03</td>
<td>0.5% Si, 0.3% Al, 0.3% Ti….</td>
</tr>
</tbody>
</table>

... and also titanium, niobium or aluminum alloys

- Corrosion issues
  - Oxidation & dissolution: uniform and localized corrosion
  - Pitting and crevice corrosion
  - Intergranular corrosion and Stress corrosion cracking
  - Hydrogen embrittlement, carburization, nitridation
Corrosion issues in “pure” water

- Continuity
- Metallic materials and alloys are not thermodynamically stable under sub- and super-critical water conditions (Pourbaix diagrams)
- Large evolution of water properties around the critical point (density, solubility…)

Corrosion issues in “pure” water

- Main issues in reactor conditions
  - Stress corrosion cracking (subcritical water)
  - Generalized corrosion (supercritical water)

Crack growth and oxidation rates versus temperature across the subcritical-supercritical conditions (unsensitized 316L stainless steel)

Crack growth rate

Oxidation rate

Corrosion current understanding is linked to the water density

- Low water densities: “chemical oxidation” like in gas (CO)
- Higher water densities: “electrochemical oxidation” like in liquid (EO)

Modelling of relative corrosion rate including electrochemical oxidation (EO) and chemical oxidation (CO) from Guzanos & Cook, Corrosion Science, 65, 2012, 48–66

Phase diagram for water showing the region of supercritical fluid from: Guzonas & Cook, Corrosion Science, 65 (2012) 48-66

**PASSIVE ALLOYS BEHAVIOUR IN SUPERCRITICAL WATER**

316L stainless steel exposed 335h at 600°C, 25 MPa in ultra pure water with H₂

- **Importance of the surface treatments on 316L stainless steel**
  - High corrosion rates with duplex oxide layer on polished surfaces
  - Formation of a protective chromium oxide layer on hardened or cold rolled surfaces linked to the preferential diffusion of chromium via internal defects due to the hardening.
  - **Good behavior of 690 nickel base alloy (higher chromium content)**

**MECHANISM OF THE FORMATION OF THE TWO LAYERS ON 316L STAINLESS STEEL IN SCW**

Experimental procedure: use of tracers, $^{18}$O

- **First oxidation**
  760h, 600°C, 25 MPa, $\text{H}_2^{16}$O
- **Second oxidation**
  305h, $\text{H}_2^{18}$O, idem
- **SIMS analyses to locate $^{18}$O which is found at two locations**
  - Magnetite/SCW
  - Spinel/alloy
- **Growth of the oxide layers at the two interfaces**
  - Magnetite/SCW
  - Spinel/alloy
  - Modelling
In SCWO, corrosion is linked to impurities

- Supercritical Water Oxidation (SCWO), or Hydrothermal Oxidation (HTO), is a thermal oxidation process of hazardous and non-hazardous wastes.
- Oxidation of halogenated or sulfur-bearing compounds results in the formation of hydrochloric acid and sulfuric acid.
- High corrosion rates and failures are reported as a function of temperature, density and pollutants (uniform/pitting/SCC).

### Coupon corrosion rates after exposure to ammoniacal sulfate solutions at 380–390 °C, 20-25 MPa

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Corrosion rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L stainless steel</td>
<td>39 mm/y</td>
</tr>
<tr>
<td>Alloy Ni/20Cr</td>
<td>29 mm/y</td>
</tr>
<tr>
<td>625 nickel base alloy</td>
<td>18 mm/y</td>
</tr>
<tr>
<td>Niobium alloy</td>
<td>&lt;1 mm/y</td>
</tr>
</tbody>
</table>


---

### CEA Marcoule Center

CEA Marcoule Center dedicated to:
- research on the nuclear fuel cycle
- decontamination and dismantling of nuclear research facilities
Before 2014: No industrial process → DELOS Process:
- Treatment of spent fuel contaminated organic liquids
- C.H.O.N., TBP/alcane, amines, aromatics...

ATALANTE / DELOS
DESTRUCTION OF CONTAMINATED ORGANIC LIQUID WASTES

Processing cell

WASHING

EVAPORATION

SuperCritical
Water Oxidation

Aqueous wastes processing

Ventilation shaft

Aqueous wastes processing

Drums

Industrial Incineration

Facilities under decommissioning

Solvents Storage

HLLW organics

LLLW organics

Aqueous (α, βγ)

CO₂

Blanketing

HLLW aqueous

LLLW aqueous

900 l

450 l

450 l

420 l

1.2 m³

300 l

WASTE (+ H₂O)

H₂O + O₂/N₂

Effluents

Outlet

Stirrer

Confinement Tube

Magnetic HP drive

Corrosion and plugging management using an internal stirred Sheath in a continuous supercritical water oxidation autoclave

Combustion of dodecane/tributylphosphate/dichloromethane (94.9995/5/0.0005 %vol)

Material: Ti Grade 2

Welding design

Massive design

TiP₂O₇, Ti(OH)PO₄

Synergistic effects: mechanical and chemical

Final Scale up

100 h → 300 h → 1000 h

Corrosion < 5 μm/h
Corrosion < 5 μm/h
Industrial Conditions
Mechanical Strength
6 months Batch
1 hour maintenance

SUPER-CRITICAL CO₂
AND OTHER S.-C. FLUIDS
Corrosion issues in Supercritical CO$_2$

- Extraction and CO$_2$ capture and storage
  - Low temperature (<150°C)
  - Corrosion is linked to the impurities (water condensation and other pollutants)

- Energy conversion (CO$_2$ Brayton cycles / solar, nuclear, fossil...)
  - High temperatures (450°C – 650°C) / 20 MPa
  - Oxidation by CO$_2$
  - Carburization by CO$_2$

“The interest in supercritical CO$_2$ Brayton cycles stems from its improved economics, system simplification, and high power conversion efficiencies.”

MATERIALS FOR CO$_2$ BRAYTON CYCLES

Oxidation of ferritic-martensitic steels

- 9% Cr and 12% Cr steels are good candidates (low thermal expansion and high thermal conductivity)

  - Formation of a complex oxide layer (spinel/magnetite/hematite)
  - Experiments with C$_{16}$O$_2$ and C$_{18}$O$_2$ showed gas/oxide and oxide/metal interfaces enriched in $^{18}$O
  - Oxidation due to CO$_2$ and not to impurities (oxygen or water)
  - Better behavior of 12% Cr, but nevertheless corrosion rates too high for industrial use
  - No major influence of the CO$_2$ pressure

  - Evolutions:
    - Impurities play a major role regarding the formation of the initial oxide which may be protective under very pure conditions (few vppm of O$_2$)
    - Evolution of the alloy with addition of minor elements (Mo, Si, ...)

Carburization of ferritic-martensitic steels

- In parallel to the formation of the oxidation, alloys may suffer also carburization (increase of carbon content in the alloy which may become brittle)
- With 9%Cr, carburization increases with time. In supercritical CO$_2$, carbon deposition is also observed in the inner oxide layer ⇒ carburization is linked to oxidation

Better oxidation resistance of austenitic alloys

- Oxide layers after 310h in supercritical CO$_2$ at 550°C and 250 bars
- Breakaway after long exposure times?

Corrosion issues in supercritical CO$_2$ – water environments

- Authors observed that no corrosion occurs at low temperature in pure SC CO$_2$
- Solubility of water in SC CO$_2$ decreases with temperature and condensation may occur in SC CO$_2$ systems
- The corrosion rates of carbon steel in SC saturated water are very high (several mm/y)
- Presence of pollutants like SO$_2$ or Cl$^-$ increases corrosion rates of carbon steels
**CO₂ Capture and storage**

- Beneficial effect of chromium in steels is observed with chloride and sulfate water pollutants

![Graph showing corrosion rate of steels in SCCO₂ at 30 bar, 60°C and in presence of brine](image)

**Processes with SCCO₂ and cosolvents**

- Stainless steels and nickel base alloys are compatible, while carbon steel, aluminum and copper alloys suffer corrosion in water-saturated conditions

**Summary of Materials Behavior in Supercritical CO₂**

**High temperatures (450°C-650°C)**

- Oxidation and carburization by CO₂
- Beneficial effect of chromium: stainless steels and nickel alloys / surface finishing

**Low temperatures (<150°C)**

- No corrosion in pure CO₂
- Electrochemical phenomena linked to condensate water
  - Importance of impurities (chloride, sulfate,…)
- Material choice in relation with aqueous corrosion behavior
  - **Carbon steels**: uniform corrosion rates highest than in aqueous solution, but also linked to the pollutants
  - **Passive alloys** (stainless steels or nickel base alloys) are often suitable
    - Take care of pollutants
      - For instance, stainless steels 304L is suitable without chloride, but 316L is preferable with some chlorides (more alloyed steels are preferable if high chloride concentrations are expected, and a nickel base alloy or a titanium alloy have to be used if large amounts of chlorine are foreseen)

Same material behavior in other supercritical fluids used at low temperatures (<150°C)
CONCLUSIVE REMARKS

General trends of the corrosion in supercritical fluids

- Corrosion of metals and alloys in supercritical fluids is primary function of the temperature and of the water content.
- At high temperatures, the SCF may react itself with the metals and alloys (supercritical water and CO₂).
- Supercritical water (SCW) is a very aggressive environment, even “pure SCW” like for energy production.
  - High temperature (above 374°C)
  - Corrosion rates increase with temperature, pressure (water density) and more often with pollutants.
  - Uniform or localized phenomena are function of the pollutants.
  - For some specific applications (SCWO, HTO), alloys are “consumable” and/or titanium or niobium are needed.
- At low temperatures (below around 150°C), water condensation is the major parameter.
  - Carbon steels, used for CO₂ capture and storage, suffer mainly uniform corrosion.
  - Passive alloys are mainly used for extraction purposes. The material choice has to take into account water condensation and expected pollutants.

Future trends: Material development, Surface coating, Chemical inhibitors, …
Thank You for your attention