

FROM RESEARCH TO INDUSTRY

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# AN OVERVIEW OF CORROSION ISSUES IN SUPERCRITICAL FLUIDS

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3 Innovation Fluides Supercritiques (Supercritical Fluids Innovation)  
IFS-Valence, France

12<sup>th</sup> International Symposium on Supercritical Fluids  
(ISSF 2018)

Antibes – Juan-les-Pins, France

22-25 April 2018

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## SYNOPSIS

### Introduction

Corrosion...

### Supercritical water

Energy production (“pure” SCW)

Wastes treatment

### Supercritical CO<sub>2</sub> & 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



ERIKA (1999) "result of structural weakness caused by corrosion"



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



Pitting corrosion of an oil tank



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



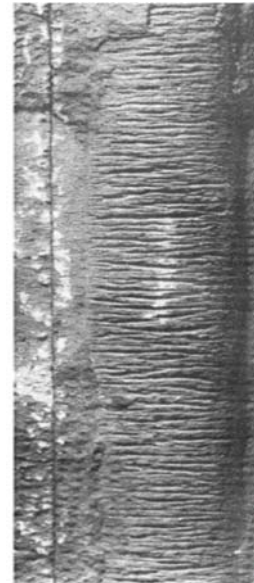
Sculpture by David E. Davis



Atmospheric corrosion in a chemical plant



Corrosion of pipes in SCCO<sub>2</sub> storage system from G. Schmitt, White paper, WCO, 2009



Supercritical waterwall cracking, from Steag, 2013, [http://www.eecpowerindia.com/codelibrar/y/ckeditor/ckfinder/userfiles/files/Water\\_Quality\\_for\\_Supercritical\\_Units\\_steag\\_for\\_mat.pdf](http://www.eecpowerindia.com/codelibrar/y/ckeditor/ckfinder/userfiles/files/Water_Quality_for_Supercritical_Units_steag_for_mat.pdf)



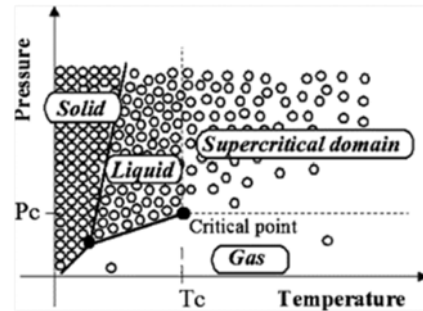
Repair of stress corrosion cracking in an ultra- supercritical (USC) power plant, from Laborelec Suez, 2013, <http://www.laborelec.be/ENG/publications/newsletters/newsletter-2013-june-power-generation/how-to-repair-potential-cracks-in-t24-material/>

## 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

Possible SC Fluids

| Compound         | Boiling point (°C) | Crit. temp. (°C) | Crit. pressure (atm) | Crit. density (g/cm <sup>3</sup> ) |
|------------------|--------------------|------------------|----------------------|------------------------------------|
| Ethylene         | -10.8              | 9.2              | 49.7                 | 0.218                              |
| Carbon dioxide   | -78.5              | 31.0             | 72.8                 | 0.468                              |
| Ethane           | -88.7              | 32.2             | 48.2                 | 0.203                              |
| Nitrous oxide    | -88.5              | 36.4             | 71.5                 | 0.452                              |
| Butane           | -17.8              | 91.8             | 45.6                 | 0.252                              |
| Propane          | -42.1              | 96.6             | 41.9                 | 0.217                              |
| Ammonia          | -33.5              | 132.5            | 111.3                | 0.235                              |
| Acetone          | 56.0               | 235.0            | 46.3                 | 0.277                              |
| Methanol         | 64.6               | 239.4            | 79.9                 | 0.272                              |
| Ethanol          | 78.3               | 243.0            | 63.0                 | 0.276                              |
| TiF <sub>4</sub> | 65.0               | 267.0            | 51.2                 | 0.321                              |
| Toluene          | 110.6              | 318.6            | 40.5                 | 0.291                              |
| Water            | 100.0              | 374.1            | 217.6                | 0.322                              |



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

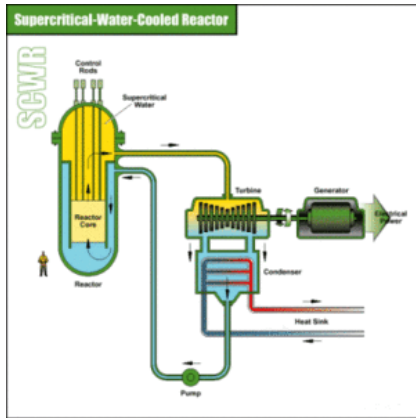
## Main metallic materials used in SCF systems

| Alloy                   | Fe   | Cr | Ni   | C     | Others                             |
|-------------------------|------|----|------|-------|------------------------------------|
| Carbon steel            | Bal. |    |      | <1    | Some additives (Cr, Ni, Mo... <1%) |
| <b>Stainless steels</b> |      |    |      |       |                                    |
| 304L                    | Bal. | 18 | 10   | <0.03 |                                    |
| 316L                    | Bal. | 18 | 10   | <0.03 | 2% Mo                              |
| 904L                    | Bal. | 20 | 25   | <0.02 | 5% Mo                              |
| <b>Nickel alloys</b>    |      |    |      |       |                                    |
| Alloy 625               | 5    | 22 | Bal. | <0.03 | 10% Mo, 5% Nb                      |
| Alloy 690               | 10   | 32 | Bal. | <0.03 | 0.5% Si, 0.3% Al, 0.3% Ti....      |

... 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 ...

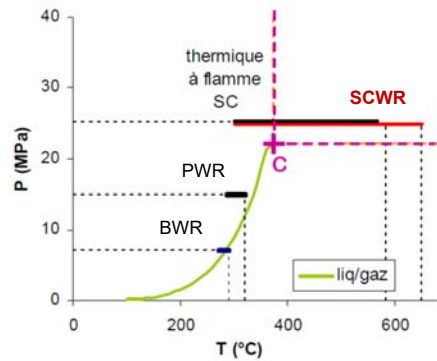
# SUPERCRITICAL WATER



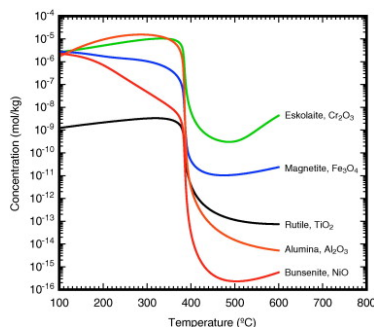
### ENERGY

#### 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...)



Pressure-temperature diagram of water showing the BWR, PWR and SCWR conditions



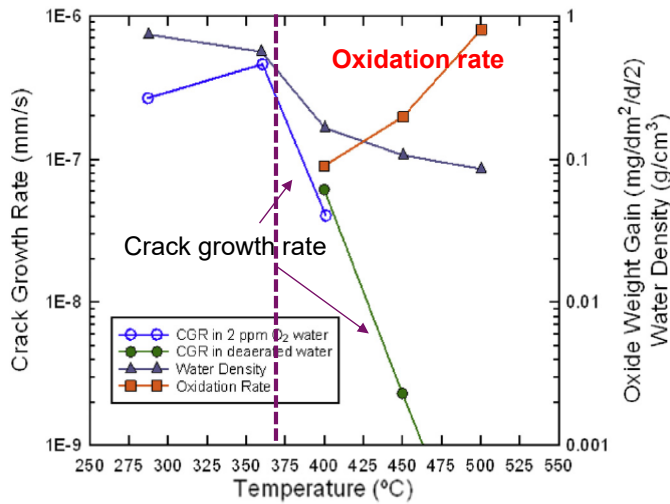
Evolution of the solubility of corrosion products, from Guzanos & Cook, Corrosion Science, 65, 2012, 48-66

- Boiling Water Reactor (BWR)**  
290°C, 8 MPa, pure water with hydrogen
- Pressurized Water Reactor (PWR)**  
330°C, 15 MPa, chemical conditioning with boron, lithium and hydrogen
- Supercritical Water Reactor (SCWR)**  
550°C-650°C, 25 MPa



## Corrosion issues in "pure" water

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

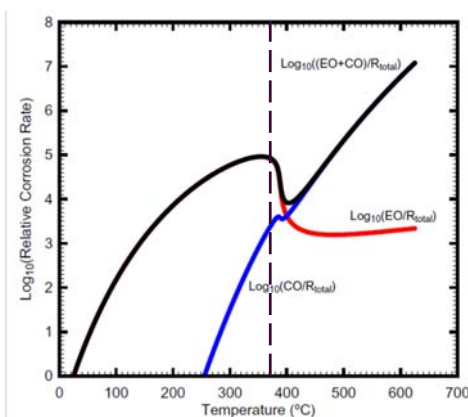


Crack growth and oxidation rates versus temperature across the subcritical-supercritical conditions (unsensitized 316L stainless steel)

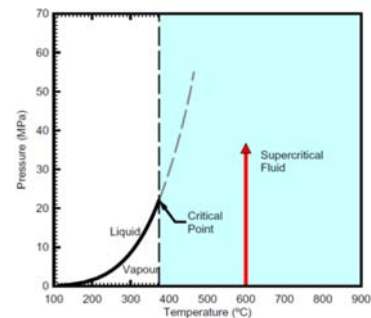
from Peng & Al., Corrosion, 63 (11), 2007, 1033-1041

## Corrosion current understanding is linked to the water density

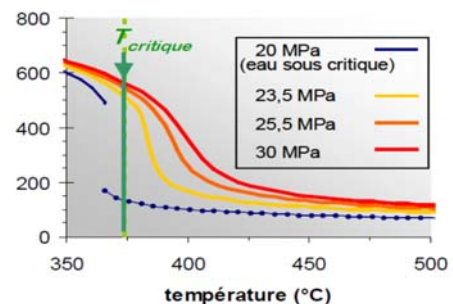
- Low water densities: "chemical oxidation" like in gas (CO)
- Higher water densities: "electrochemical oxidation" like in liquid (EO)



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

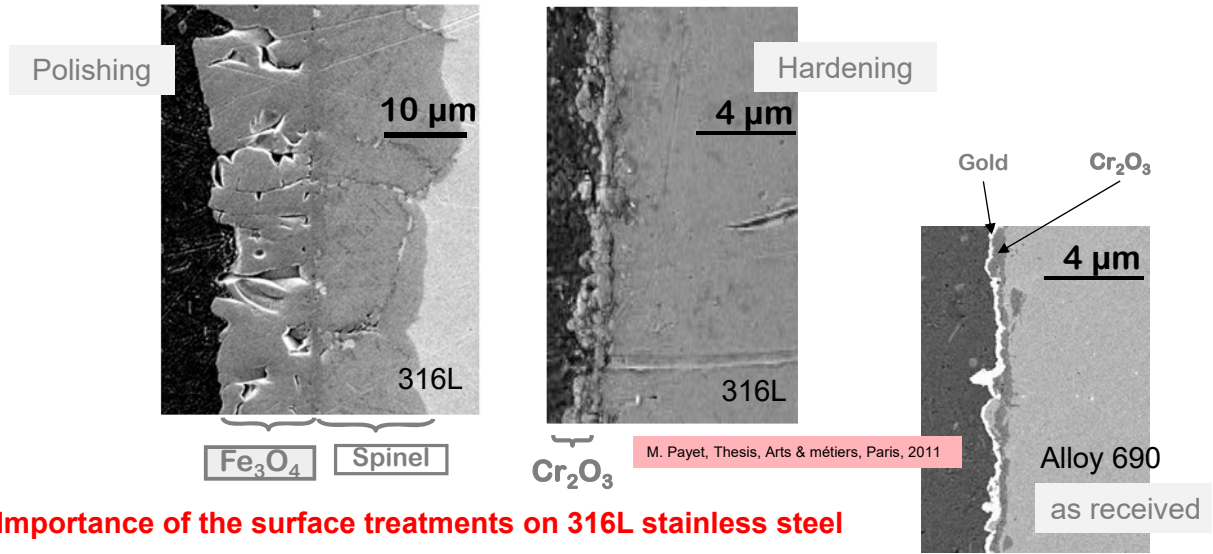


Phase diagram for water showing the region of supercritical fluid  
from: Guzonas & Cook, Corrosion science, 65 (2012) 48-66



Evolution of water density with pressure and temperature,  
from: M. Payet, Thesis, Arts & métiers, Paris, 2011

**316L stainless steel** exposed 335h at 600°C, 25 MPa in ultra pure water with H<sub>2</sub>



**Importance of the surface treatments on 316L stainless steel**

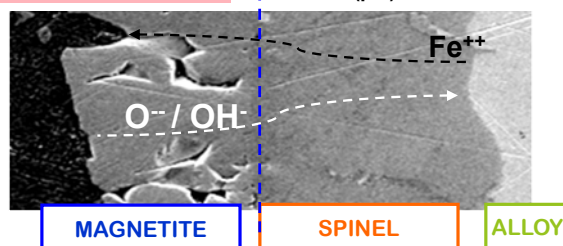
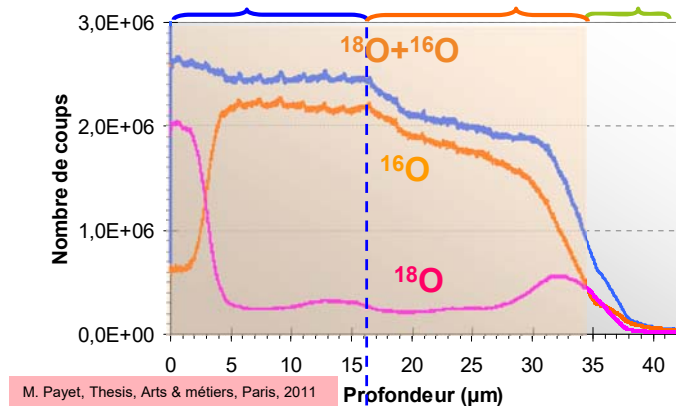
- High corrosion rates with duplex oxide layer on polished surfaces
- Formation of a protective chromium oxide layer on hardened or cold rolled surfaces linked to the preferential diffusion of chromium via internal defects due to the hardening.

**Good behavior of 690 nickel base alloy (higher chromium content)**

**Alloy 690**, 840h

Experimental procedure: use of tracers, <sup>18</sup>O

- First oxidation  
760h, 600°C, 25 MPa, H<sub>2</sub><sup>16</sup>O
- Second oxidation  
305h, H<sub>2</sub><sup>18</sup>O, idem
- SIMS analyses to locate <sup>18</sup>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



**WASTES**

**In SCWO, corrosion is linked to impurities**

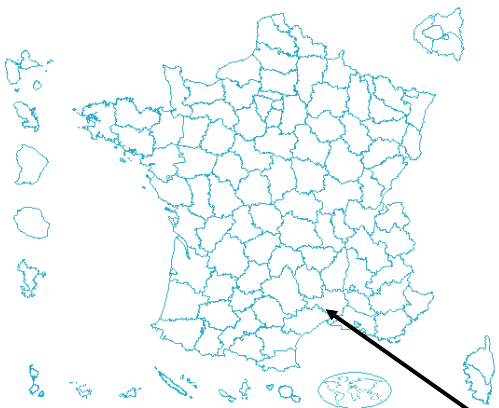
- Supercritical Water Oxidation (SCWO), or Hydrothermal Oxidation (HTO), is thermal oxidation process of hazardous and non-hazardous wastes
- Oxidation of halogenated or sulfur-bearing compounds results in the formation of hydrochloric acid and sulfuric acid
- High corrosion rates and failures are reported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

| Alloy                 | Corrosion rate |
|-----------------------|----------------|
| 316L stainless steel  | 39 mm/y        |
| Alloy Ni/20Cr         | 29 mm/y        |
| 625 nickel base alloy | 18 mm/y        |
| Niobium alloy         | <1 mm/y        |

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

from E. Asselin et al. / Corrosion Science 52 (2010) 118–124.

**WASTES**



**CEA Marcoule Center**

dedicated to:

- research on the nuclear fuel cycle
- decontamination and dismantling of nuclear research facilities

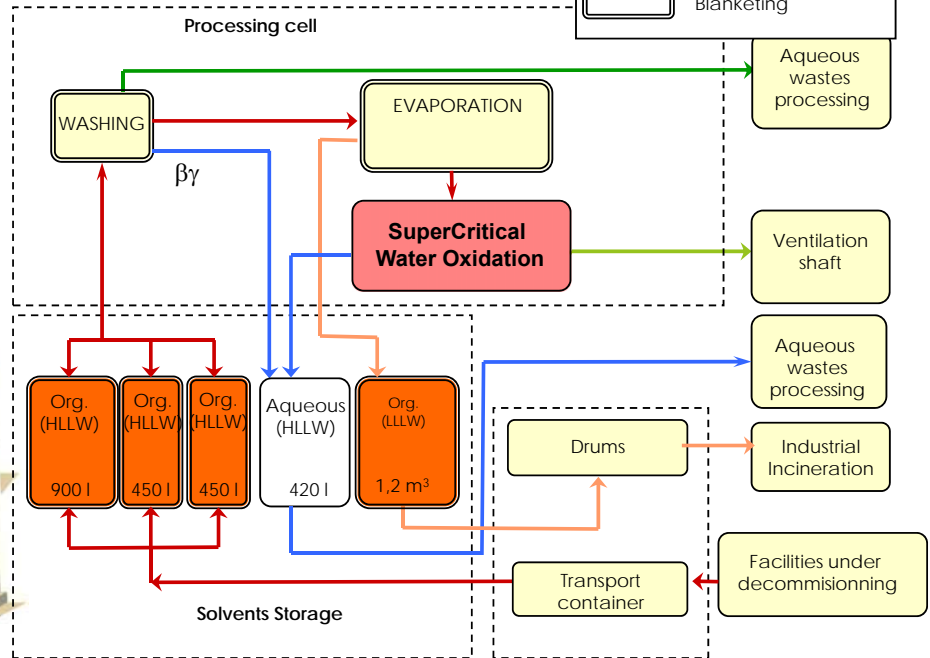
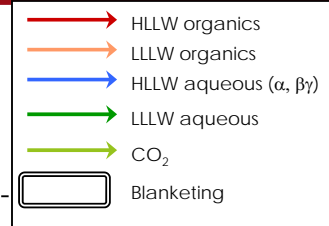




WASTES

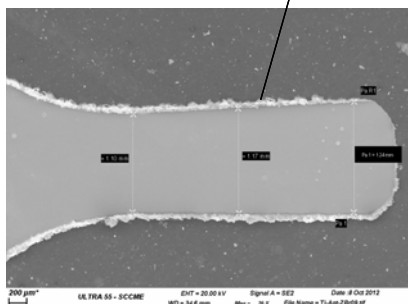
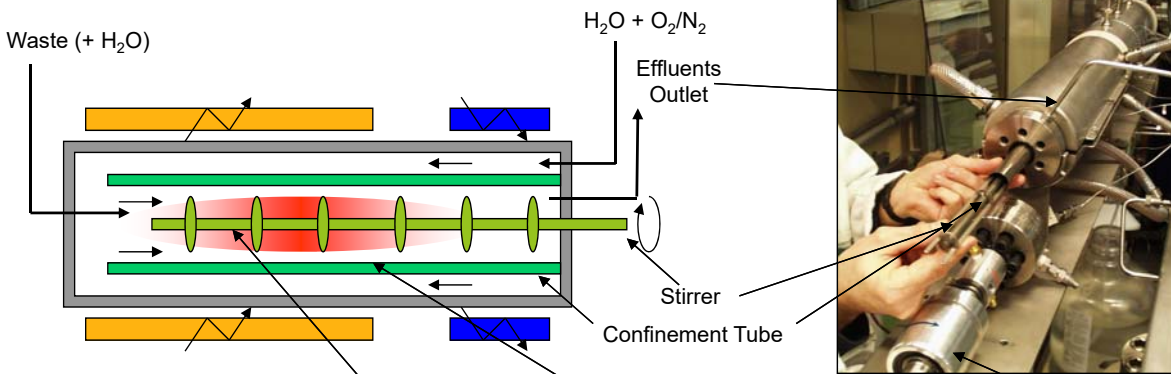
Before 2014: No industrial process → DELOS Process :

- Treatment of spent fuel contaminated organic liquids
- C.H.O.N., **TBP/alcane**, amines, aromatics...



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

Jousot-Dubien C., Turc H.A., Didier, G., Brevet FR 2814967, 2000.



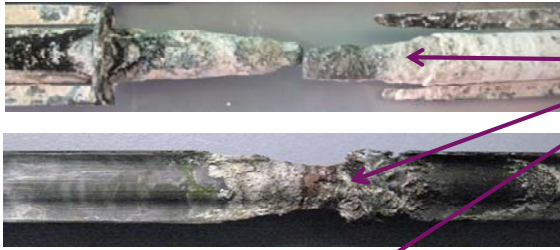
Stressless corrosion  
 4,2 μm/h  
 HTO of dodecane / TBP 5%  
 100 h  
 Initial thickness 1mm



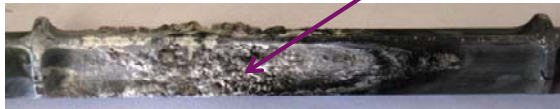
WASTES

Combustion of dodecane/tributylphosphate/dichloromethane (94,9995/5/0,0005 %vol)  
Material : Ti Grade 2

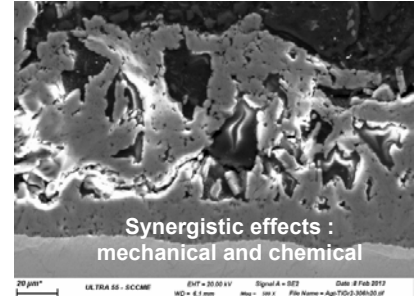
Welding design



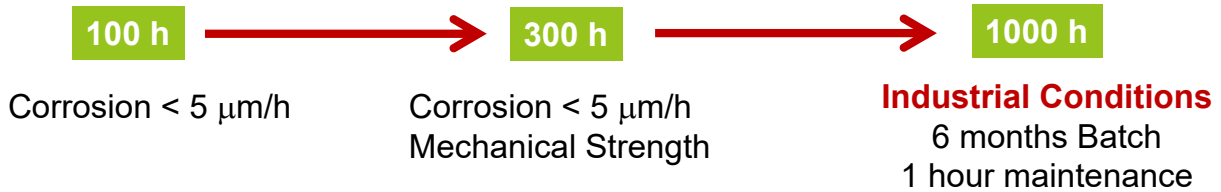
Massive design



$TiP_2O_7$ ,  $Ti(OH)PO_4$



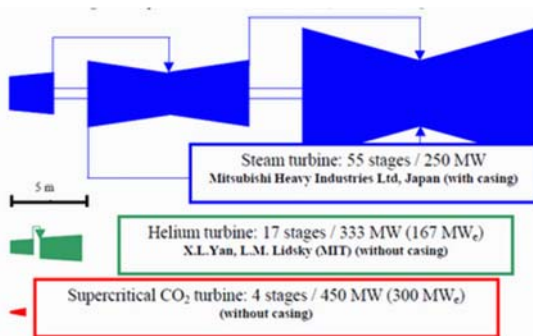
Final Scale up



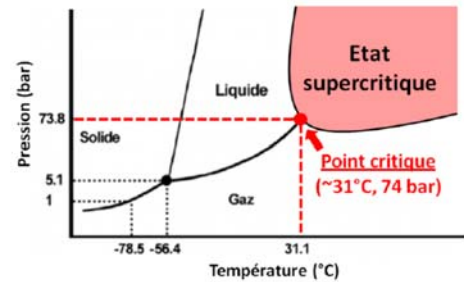
SUPER-CRITICAL CO<sub>2</sub>  
AND OTHER S.-C. FLUIDS

## Corrosion issues in Supercritical CO<sub>2</sub>

- **Extraction and CO<sub>2</sub> capture and storage**
  - Low temperature (<150°C)
  - Corrosion is linked to the impurities (water condensation and other pollutants)
- **Energy conversion** (CO<sub>2</sub> Brayton cycles / solar, nuclear, fossil...)
  - High temperatures (450°C – 650°C) / 20 MPa
  - **Oxidation** by CO<sub>2</sub>
  - **Carburization** by CO<sub>2</sub>



from Sandia lab.



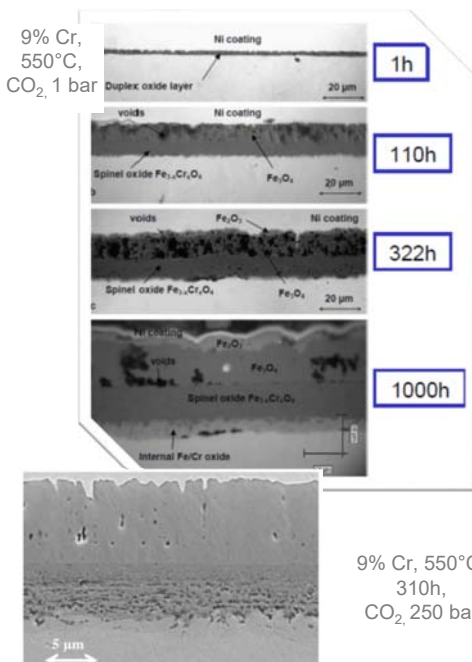
“The interest in supercritical CO<sub>2</sub> Brayton cycles stems from its improved economics, system simplification, and high power conversion efficiencies.”

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ENERGY

## Oxidation of ferritic-martensitic steels

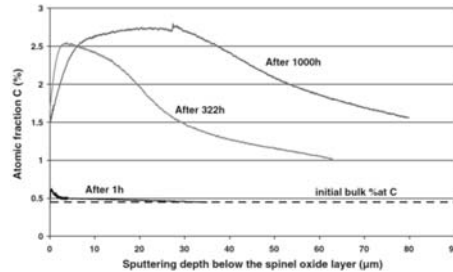
- 9% Cr and 12% Cr steels are good candidates (low thermal expansion and high thermal conductivity)



- **Formation of a complex oxide layer** (spinel/magnetite/hematite)
- Experiments with C<sup>16</sup>O<sub>2</sub> and C<sup>18</sup>O<sub>2</sub> showed gas/oxide and oxide/metal interfaces enriched in <sup>18</sup>O
- **Oxidation due to CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>)
  - Evolution of the alloy with addition of minor elements (Mo, Si,...)

Carburization of ferritic-martensitic steels

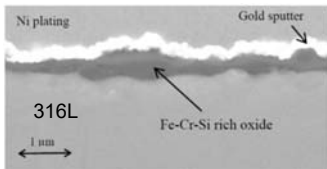
- In parallel to the formation of the oxidation, alloys may suffer also **carburization** (increase of carbon content in the alloy which may become brittle)
- With 9%Cr, carburization increases with time. In supercritical CO<sub>2</sub>, carbon deposition is also observed in the inner oxide layer ⇒ **carburization is linked to oxidation**



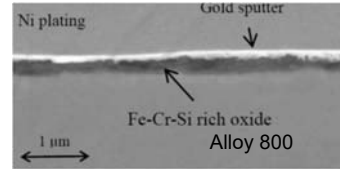
Carbon profile in 9% Cr exposed at 550°C in 1 bar of CO<sub>2</sub>

F. Rouillard & al., Oxid. Met. 2012, 77, 57-70

Better oxidation resistance of austenitic alloys



- Oxide layers after 310h in supercritical CO<sub>2</sub> at 550°C and 250 bars
- Breakaway after long exposure times?

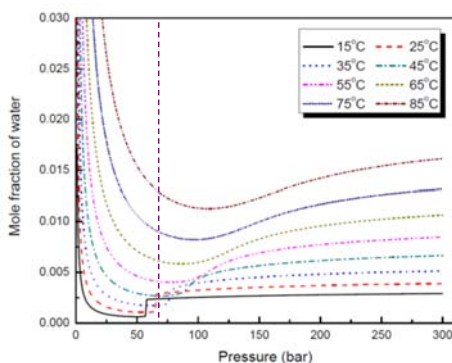


F. Rouillard & al., Proceedings of SCCO<sub>2</sub> power cycle symposium, 2009

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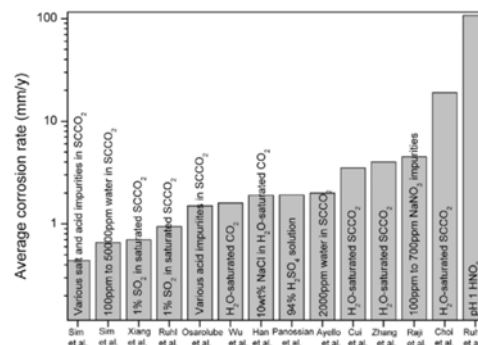
Corrosion issues in supercritical CO<sub>2</sub> – water environments

- Authors observed that **no corrosion occurs at low temperature in pure SC CO<sub>2</sub>**
- Solubility of water** in SC CO<sub>2</sub> decreases with temperature and **condensation** may occur in SC CO<sub>2</sub> systems
- The **corrosion rates of carbon steel** in SC saturated water are very high (**several mm/y**)
- Presence of pollutants** like SO<sub>2</sub> or Cl<sup>-</sup> increases corrosion rates of carbon steels



Y.-S. Choi & S. Nescic, Corrosion 2009, paper 09256

**Solubility of water in supercritical CO<sub>2</sub>** as function of the pressure and of the temperature



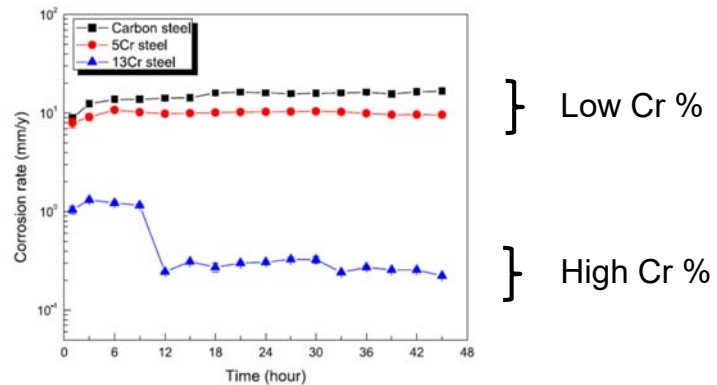
S. Sim & al., Int. J. Greenhouse Gas Control, 29, 2014, 185-199

**Comparison of corrosion rates** of carbon steels in various SCCO<sub>2</sub> conditions

## CO<sub>2</sub> Capture and storage

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

Corrosion rate of steels in SCCO<sub>2</sub> at 30 bar, 60°C and in presence of brine



S. Assani & al., Int. J. Greenhouse Gas Control, 23, 2014, 30-43

## Processes with SCCO<sub>2</sub> and cosolvents

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

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## High temperatures (450°C-650°C)

- Oxidation and carburization by CO<sub>2</sub>**
- Beneficial effect of chromium** : stainless steels and nickel alloys / surface finishing

## Low temperatures (<150°C)

- No corrosion in pure CO<sub>2</sub>**
- 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)

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### 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 CO<sub>2</sub>)
- **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 CO<sub>2</sub> 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.

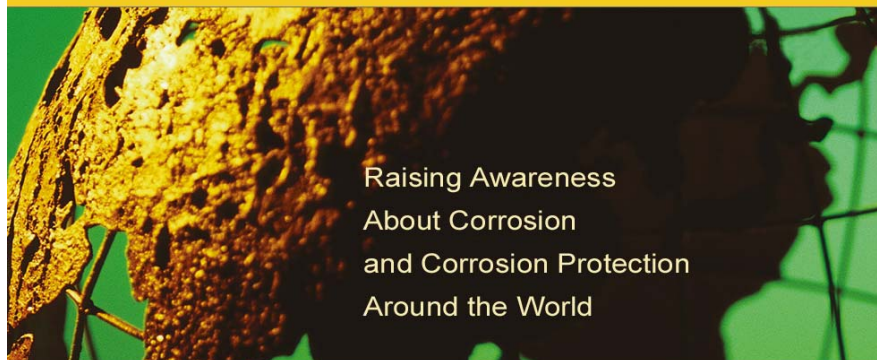
**Future trends: Material development, Surface coating, Chemical inhibitors, ...**

EUROPÄISCHE FÖDERATION KORROSION  
EUROPEAN FEDERATION OF CORROSION  
FEDERATION EUROPEENNE DE LA CORROSION



THE WORLD  
CORROSION  
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Raising Awareness  
About Corrosion  
and Corrosion Protection  
Around the World

Welcome to WCO – The World Corrosion Organization  
a non-governmental organization (NGO) of the United Nations (UN)  
April 24<sup>th</sup> is Corrosion Awareness Day



**Thank You for your attention**

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