



## Overview on corrosion in supercritical fluids

D. Feron

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# OVERVIEW OF CORROSION IN SUPERCRITICAL FLUIDS

Institut of Metal Research, Chinese Academy of Sciences  
Shenyang  
November, 2016

| Damien Féron

Service de la corrosion et du comportement des matériaux dans leur environnement  
Commissariat à l'énergie atomique et aux énergies alternatives  
*French atomic energy and alternatives energies Commission*  
Saclay, France

## 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



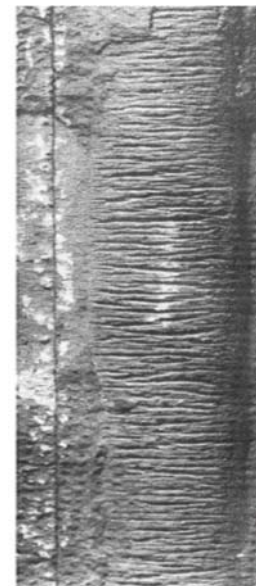
Atmospheric corrosion in a chemical plant



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



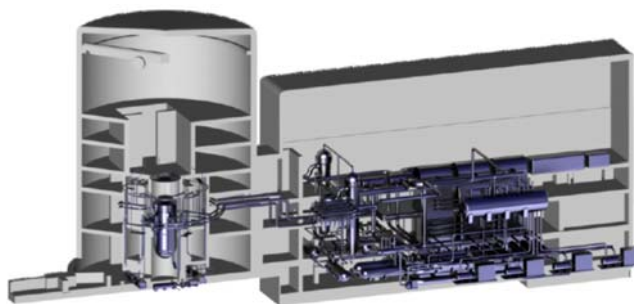
Repair of stress corrosion cracking in an ultra-supercritical (USC) power plant, from Laborelec Suez, 2013, <http://www.laborelec.be/ENG/publications/newsletters/newsletter-2013-june-power-generation/how-to-repair-potential-cracks-in-t24-material/>



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

## Supercritical fluids have wide fields of applications

- Extraction of chemicals, dyeing of fibers, **destruction of hazard chemicals**, decontamination of soils, production of (sub)micron powders....
- And also in energy production
  - **Fossil energies**: CO<sub>2</sub> capture
  - **Electricity production**: Supercritical CO<sub>2</sub> Brayton cycle (solar thermal, geothermal & nuclear powers, shipboard propulsion, ...)
  - **Nuclear energy**: generation IV reactors
    - Supercritical water reactors



Conceptual design of a supercritical-water-cooled nuclear reactor of 1000 MWe

from: Gen VI Roadmap, OCDE, January 2014

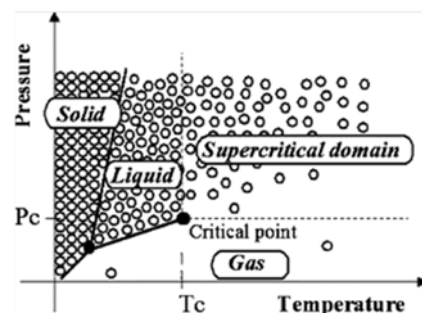
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## Material solicitations in a SCF

- 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	0.232
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
TiBF	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

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## Main metallic materials used in SCF systems

Alloy	Fe	Cr	Ni	C	Others
Carbon steel	Bal.			<1	Some additives (Cr, Ni, Mo... <1%)
Stainless steels					
304L	Bal.	18	10	<0.03	
316L	Bal.	18	10	<0.03	2% Mo
904L	Bal.	20	25	<0.02	5% Mo
Nickel alloys					
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....

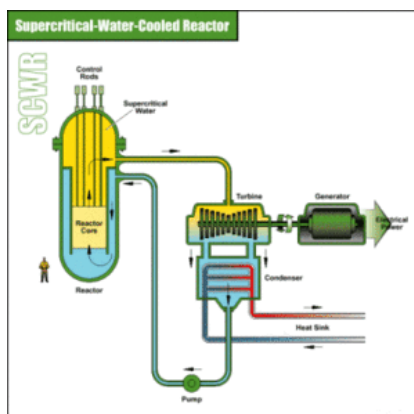
... and also titanium, niobium or aluminum alloys

### Corrosion issues

- Oxidation & dissolution: uniform and localized corrosion
- Pitting and crevice corrosion
- Intergranular corrosion and Stress corrosion cracking
- Hydrogen embrittlement, carburization, nitridation ...

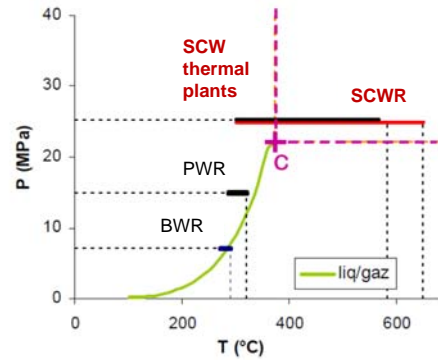
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## SUPERCritical WATER

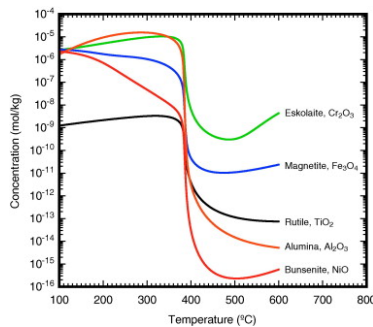


## Corrosion issues in "pure" water

- 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

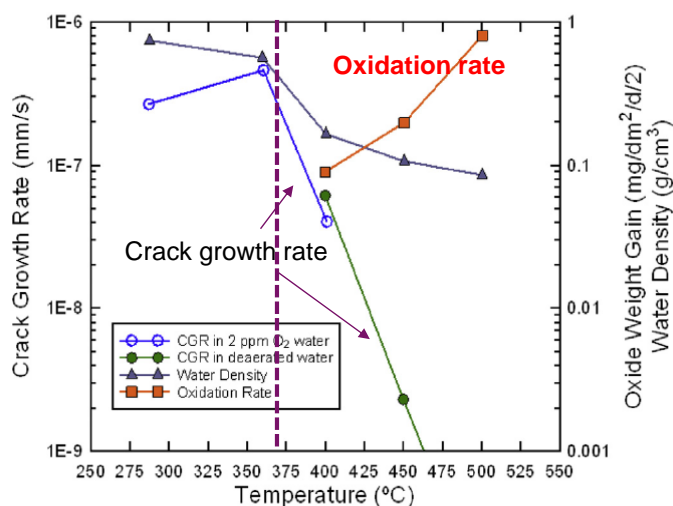


Evolution of the solubility of corrosion products, from Guzanos & Cook, Corrosion Science, 65, 2012, 48-66

- ☐ **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)



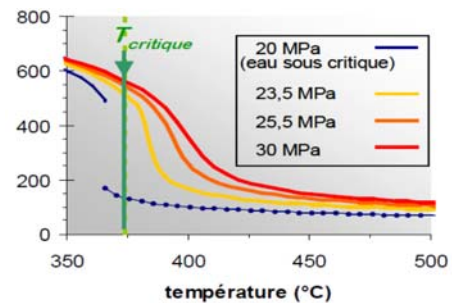
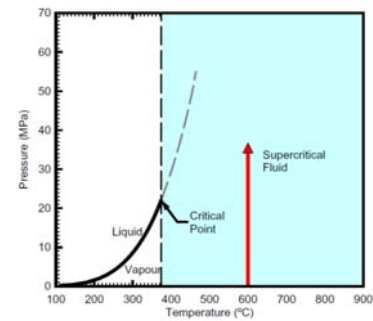
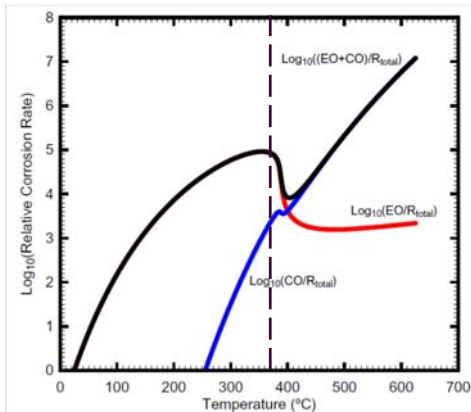
**Crack growth** and **oxidation** rates versus temperature across the subcritical-supercritical conditions (unsensitized 316L stainless steel)

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

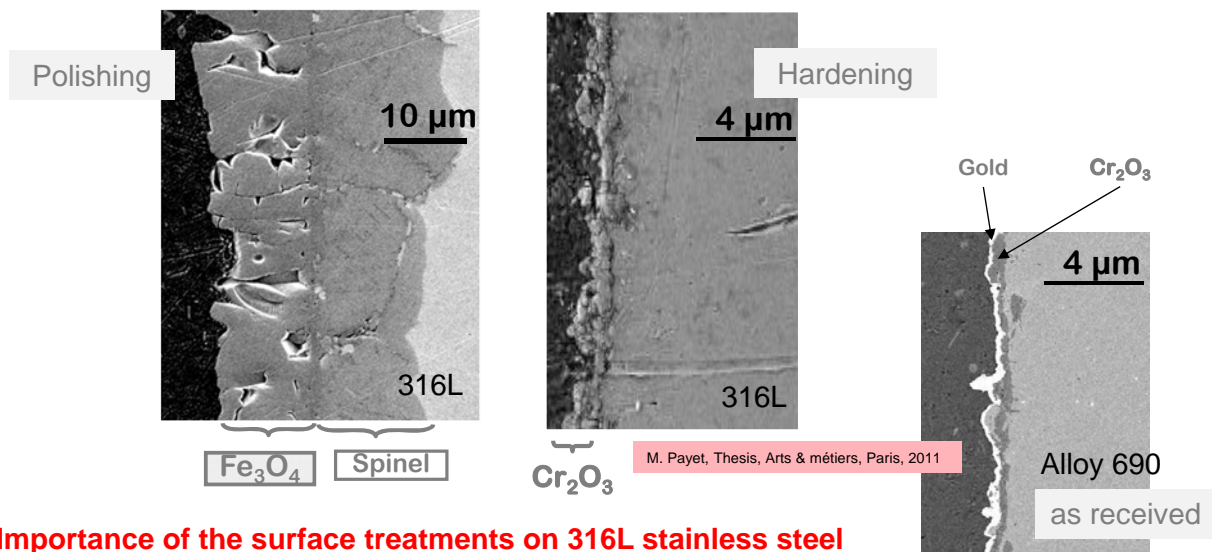


## Corrosion current understanding is linked to the water density

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



**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

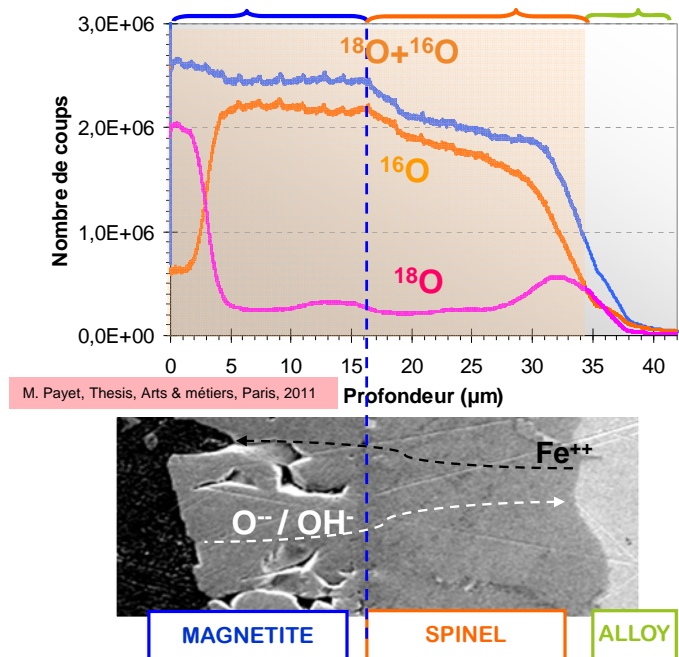
- High corrosion rates with duplex oxide layer on polished surfaces
- Formation of a protective chromium oxide layer on hardened or cold rolled surfaces linked to the preferential diffusion of chromium via internal defects due to the hardening.
- Good behavior of 690 nickel base alloy (higher chromium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

**Alloy 690**, 840h

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

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

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



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## SUPERCritical WATER OXIDATION

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)

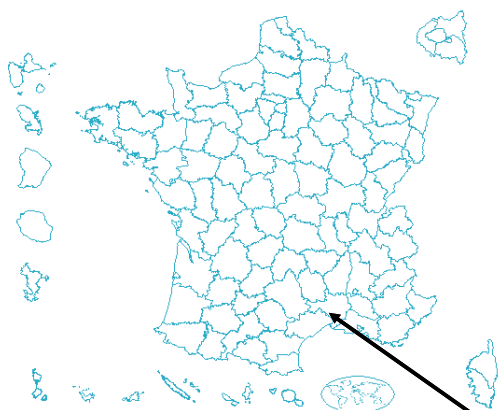
Alloy	Corrosion rate
316L stainless steel	39 mm/y
Alloy Ni/20Cr	29 mm/y
625 nickel base alloy	18 mm/y
Niobium alloy	<1 mm/y

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.

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## CEA Marcoule Center

dedicated to:

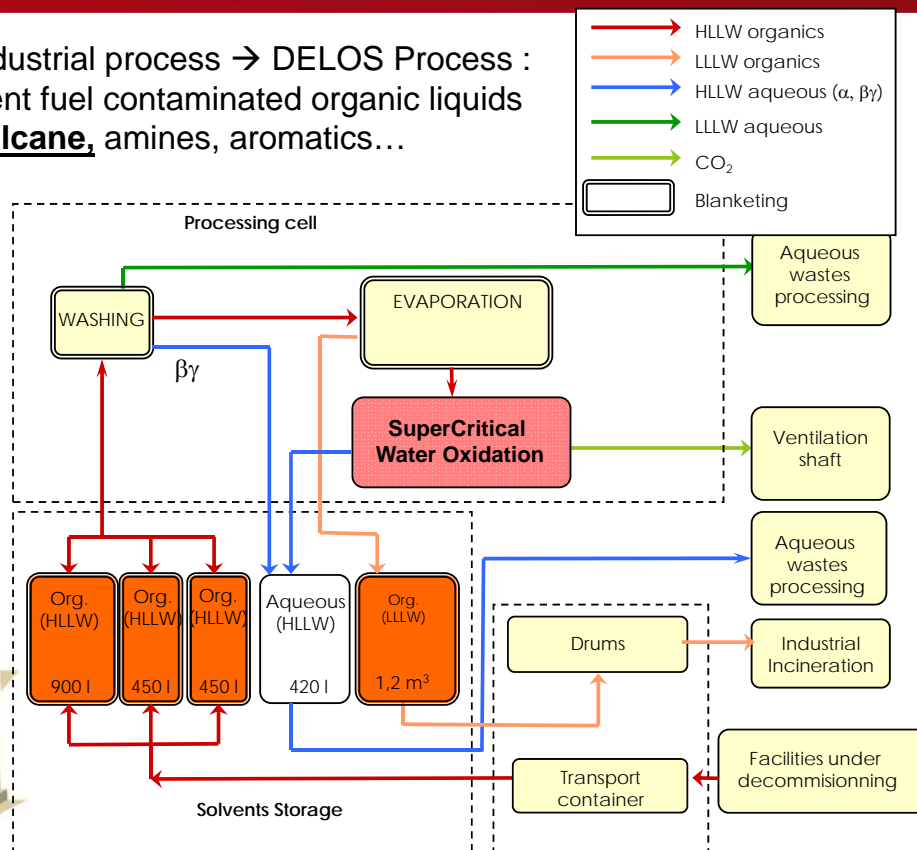
- research on the nuclear fuel cycle
- decontamination and dismantling of nuclear research facilities



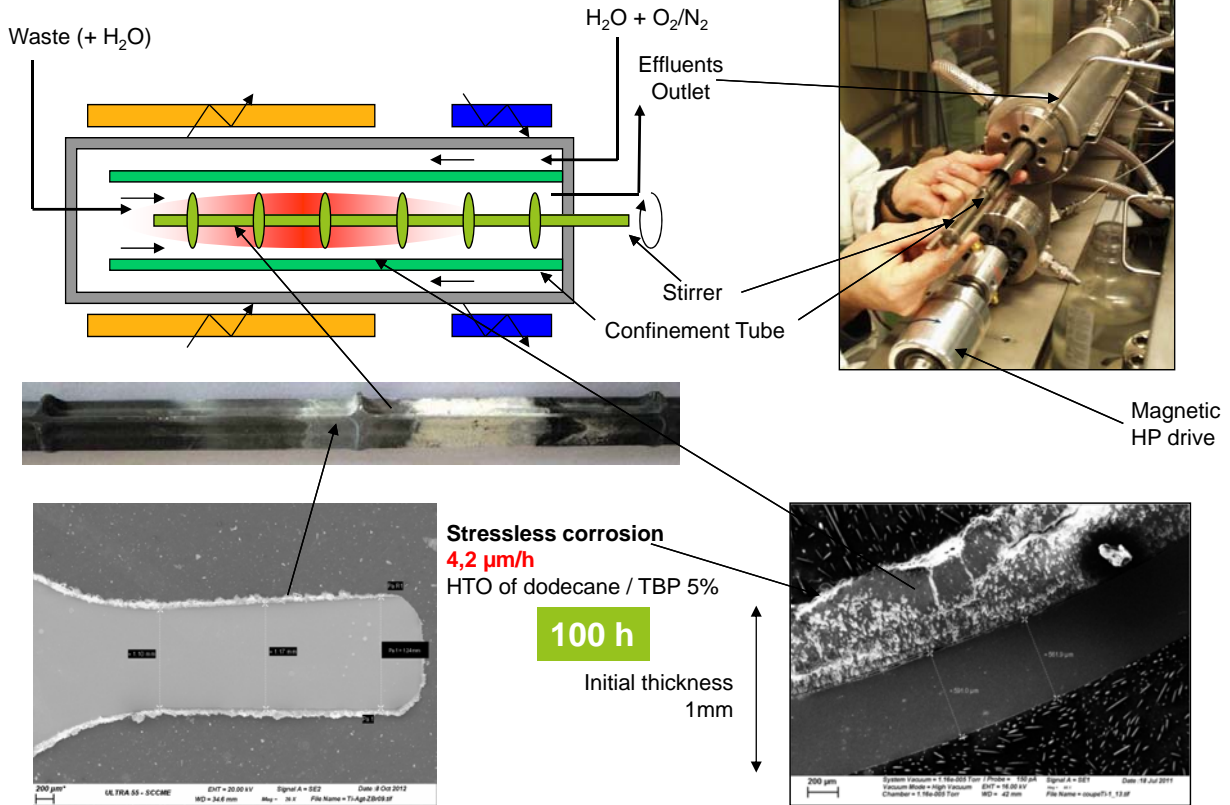
## ATALANTE / DELOS DESTRUCTION OF CONTAMINATED ORGANIC LIQUID WASTES

Before 2014: No industrial process → DELOS Process :

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

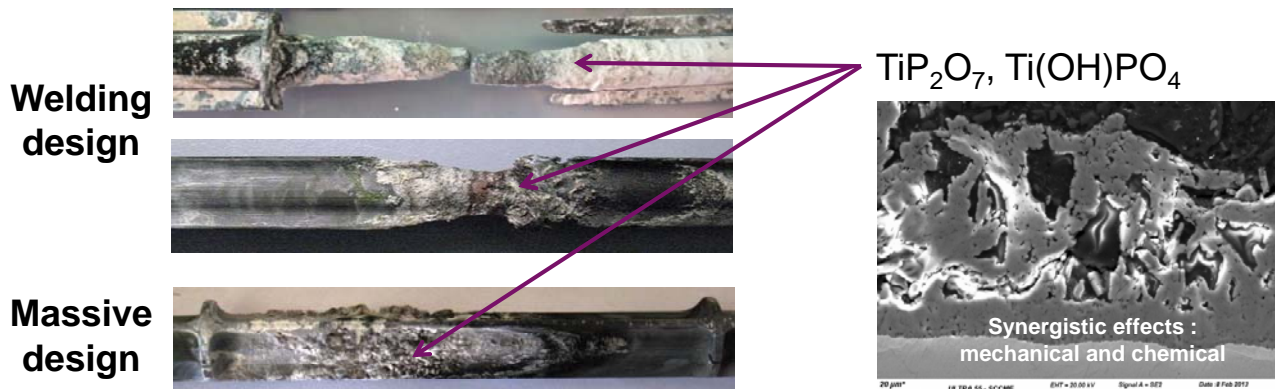


Jousset-Dubien C., Turc H.A., Didier, G., Brevet FR 2814967, 2000.

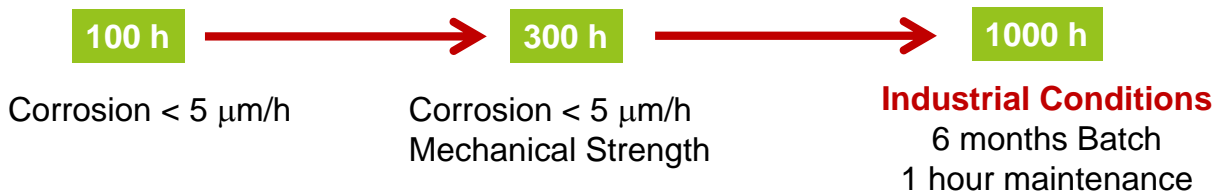


## DAMAGE MANAGEMENT & FINAL PROCESS

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



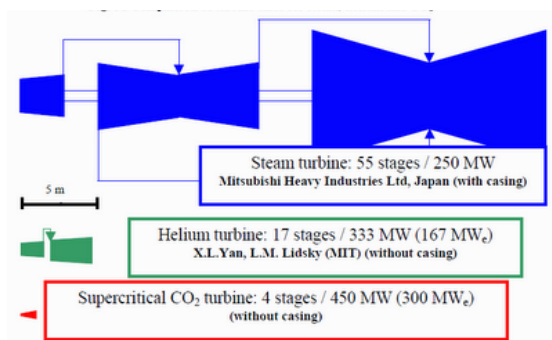
### Final Scale up



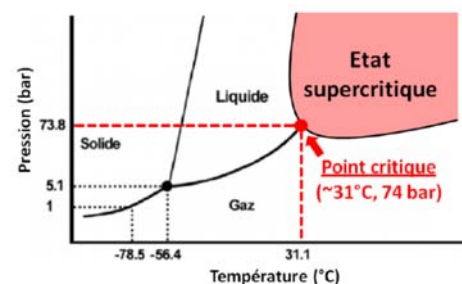
# SUPER-CRITICAL CO<sub>2</sub> AND OTHER S.-C. FLUIDS

### 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>



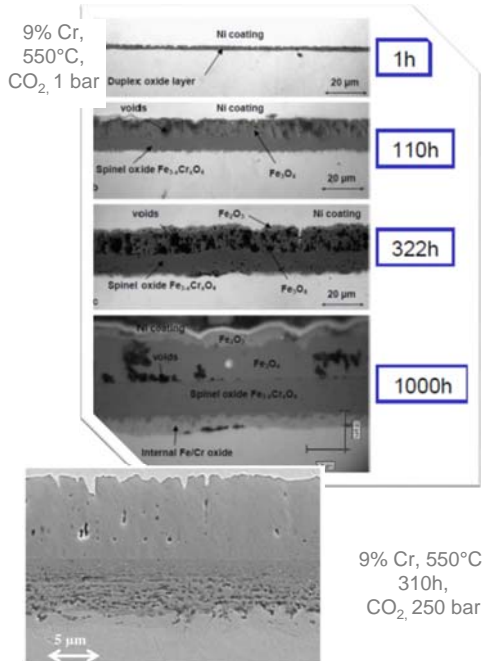
from Sandia lab.



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

## Oxidation of ferritic-martensitic steels

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



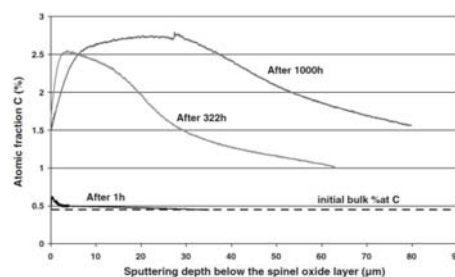
- Formation of a complex oxide layer (spinel/magnetite/hematite)
- Experiments with C<sup>16</sup>O<sub>2</sub> and C<sup>18</sup>O<sub>2</sub> showed gas/oxide and oxide/metal interfaces enriched in <sup>18</sup>O
- Oxidation due to CO<sub>2</sub> and not to impurities (oxygen or water)
- Better behavior 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,...)

S. Bouhieda thesis, ENS Mines Saint-Etienne, 2012  
F. Rouillard & al., Oxid. Met. 2012, 77, 27-55

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## Carburization of ferritic-martensitic steels

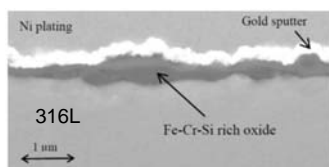
- In parallel to the formation of the oxidation, alloys may suffer also **carburization** (increase of carbon content in the alloy which may become brittle)
- With 9%Cr, carburization increases with time. In supercritical CO<sub>2</sub>, carbon deposition is also observed in the inner oxide layer ⇒ **carburization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



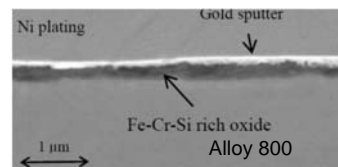
F. Rouillard & al., Oxid. Met. 2012, 77, 57-70

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

## 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

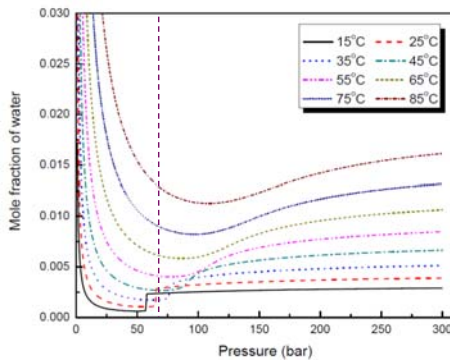
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# EXTRACTION AND CO<sub>2</sub> CAPTURE AND STORAGE

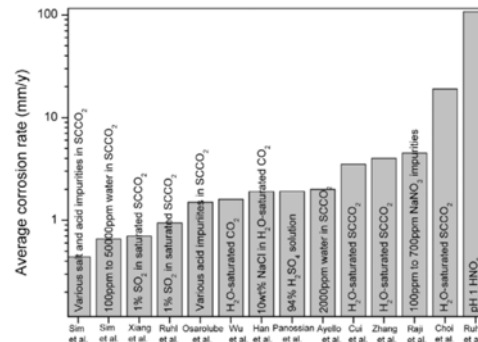
## Corrosion issues in supercritical CO<sub>2</sub> – water environments

- 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. Netic, 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

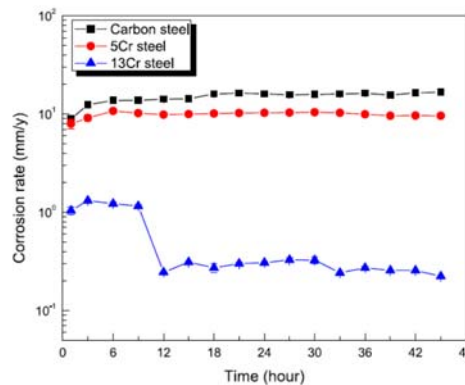
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# MATERIAL BEHAVIOR IN SCCO<sub>2</sub> WITH POLLUTANTS

## 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

} Low Cr %

} High Cr %

## 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

- **Suitable materials choice:**
- **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, ...**

Yes ...

**Louisville Waterfront Park:**  
a 72-acre (290,000 m<sup>2</sup>) municipal park  
with water reservoirs...



## Thank You for your attention



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Centre de Saclay | 91191 Gif-sur-Yvette Cedex

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## 11th International Symposium on Supercritical Fluids

October 11-14, 2015

Seoul, Republic of Korea

# CORROSION IN SUPERCritical FLUIDS

Damien Féron<sup>1</sup>, Stéphane Perrin<sup>1</sup>, Raphael Robin<sup>1</sup>, Fabien Rouillard<sup>1</sup> Hubert-Alexandre Turc<sup>2</sup>  
& Stéphane Sarrade<sup>1&3</sup>

<sup>1</sup>- Département de Physico-Chimie (*Department of Physics and Chemistry*)

**CEA-Saclay, France**

<sup>2</sup>- Département de Traitement et Comportement des Déchets

**CEA-Marcoule, France**

<sup>3</sup> Innovation Fluides Supercritiques (Supercritical Fluids Innovation)

**IFS-Valence, France**

|

*Incorporating with Supergreen 2015*