An overview of corrosion issues in supercritical fluids

D. Feron, S. Sarrade, F. Rouillard, S. Perrin, R. Robin, Ha. Turc

FROM RESEARCH TO INDUSTRY

AN OVERVIEW OF CORROSION ISSUES IN SUPERCRITICAL FLUIDS

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SYNOPSIS

Introduction

Corrosion…

Supercritical water

Energy production (“pure” SCW)
Wastes treatment

Supercritical CO_2 & other SC Fluids

Pure SCF
Solubilities & Pollutants

Protection strategies

CORROSION …

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

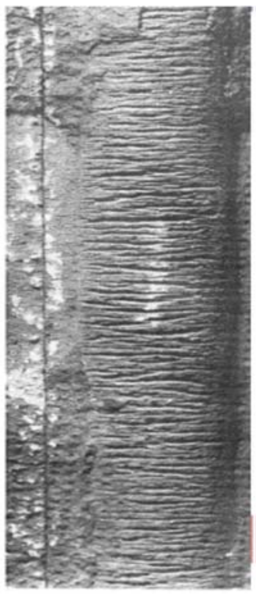
Corrosion cracking of the fuselage of airplane (April 28, 1988 – 1 fatal over 95)

Sculpture by David E. Davis

Atmospheric corrosion in a chemical plant

CORROSION IN SUPERCRITICAL FLUIDS

Corrosion of pipes in $SCCO_2$ storage system
from G. Schmitt, White paper, WCO, 2009



Supercritical waterwall cracking,
from Steag, 2013,
http://www.eecpowerindia.com/codelibrary/ckeditor/ckfinder/userfiles/files/Water_Quality_for_Supercritical_Units_steag_format.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/

CORROSION AND SUPERCRITICAL FLUIDS

Material solicitations in a SCF

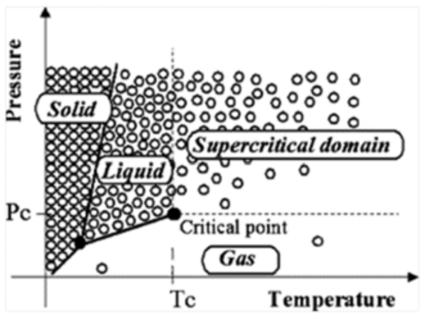
- Mechanical (high pressures)
- Thermal (often high temperatures)
- Chemical
  - Variety of SCF
  - Density evolutions
  - Pollutants

➢ **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/cm³)
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
THF	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

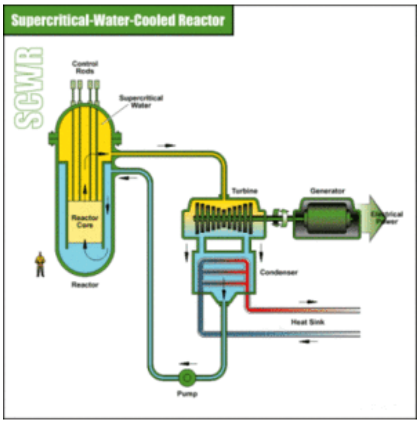
CHOICE OF MATERIAL

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 …



SUPERCRITICAL WATER

SUB- & SUPERCRITICAL WATER

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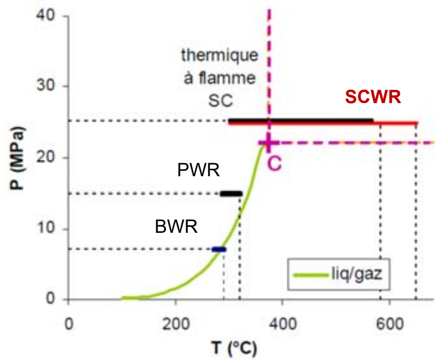
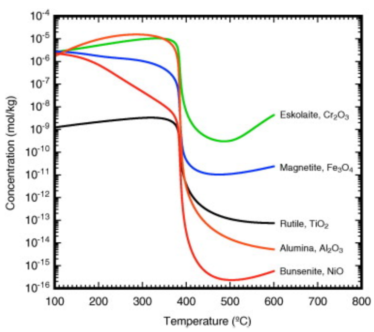
ENERGY

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



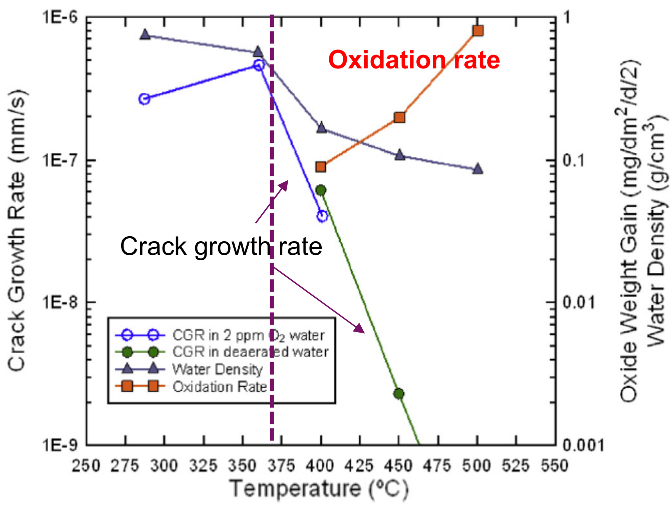
Evolution of the **solubility of corrosion products**, from Guzanos & Cook, Corrosion Science, 65, 2012, 48–66

- **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

SUB- & SUPERCRITICAL WATER

Corrosion issues in “pure” water

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



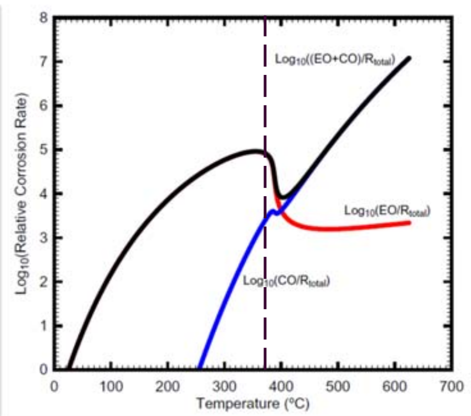
Crack growth and oxidation rates versus temperature across the subcritical-supercritical conditions (unsensitized 316L stainless steel)

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

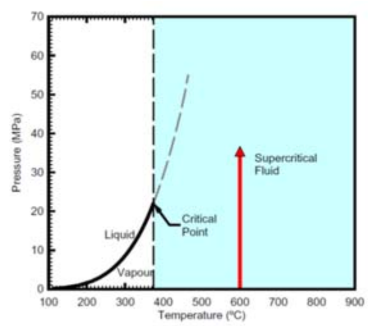
SUPERCRITICAL WATER

Corrosion current understanding is linked to the water density

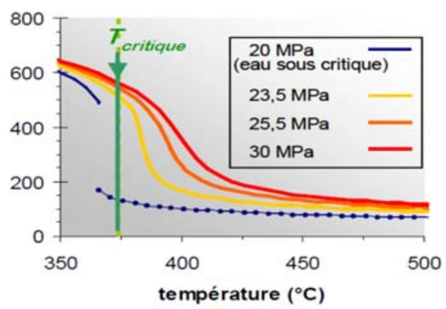
- Low water densities: “chemical oxidation” like in gas (CO)
- Higher water densities : “electrochemical oxidation” like in liquid (EO)



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



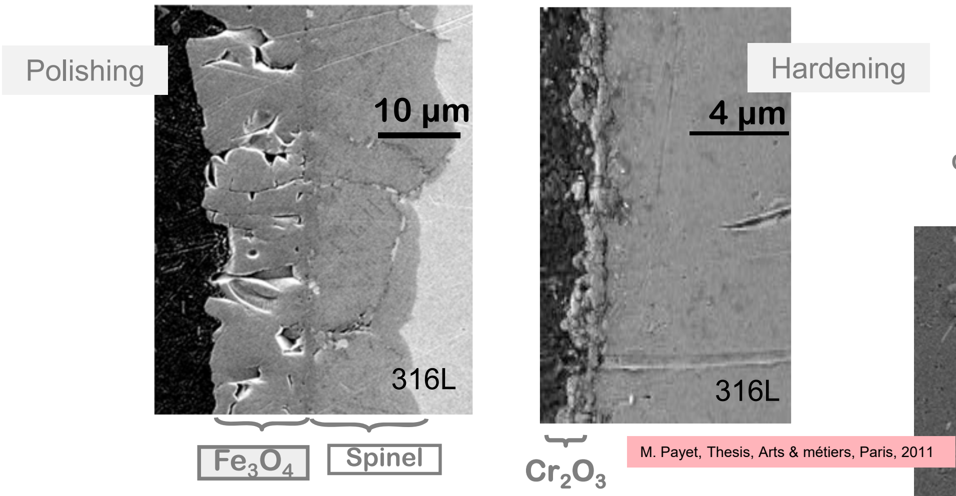
Phase diagram for water showing the region of supercritical fluid
from: Guzonas & Cook, Corrosion science, 65 (2012) 48-66

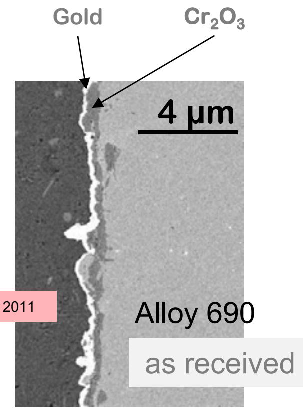


Evolution of water density with pressure and temperature,
from: M. Payet, Thesis, Arts & métiers, Paris, 2011

PASSIVE ALLOYS BEHAVIOUR IN SUPERCRITICAL WATER

316L stainless steel exposed 335h at 600°C, 25 MPa in ultra pure water with H_2





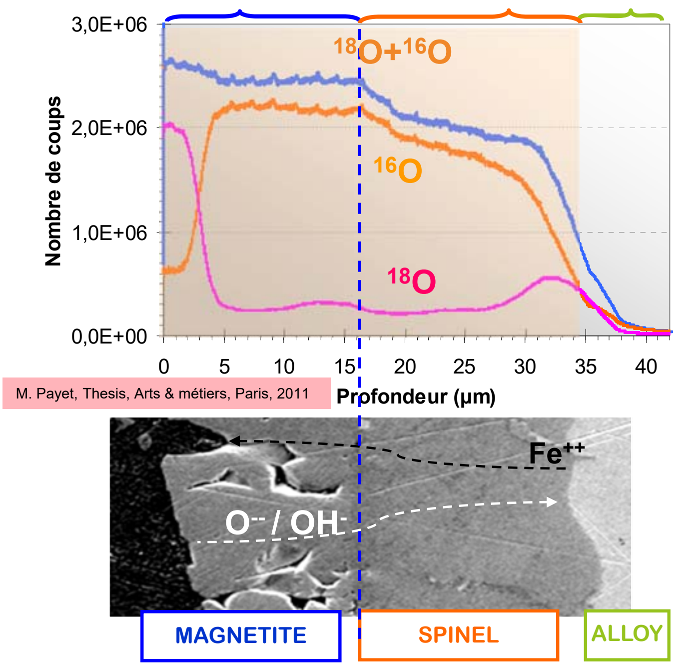
Alloy 690, 840h

- **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, **$H_2{}^{16}O$**
- Second oxidation
  305h, **$H_2{}^{18}O$**, 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



WASTES

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

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

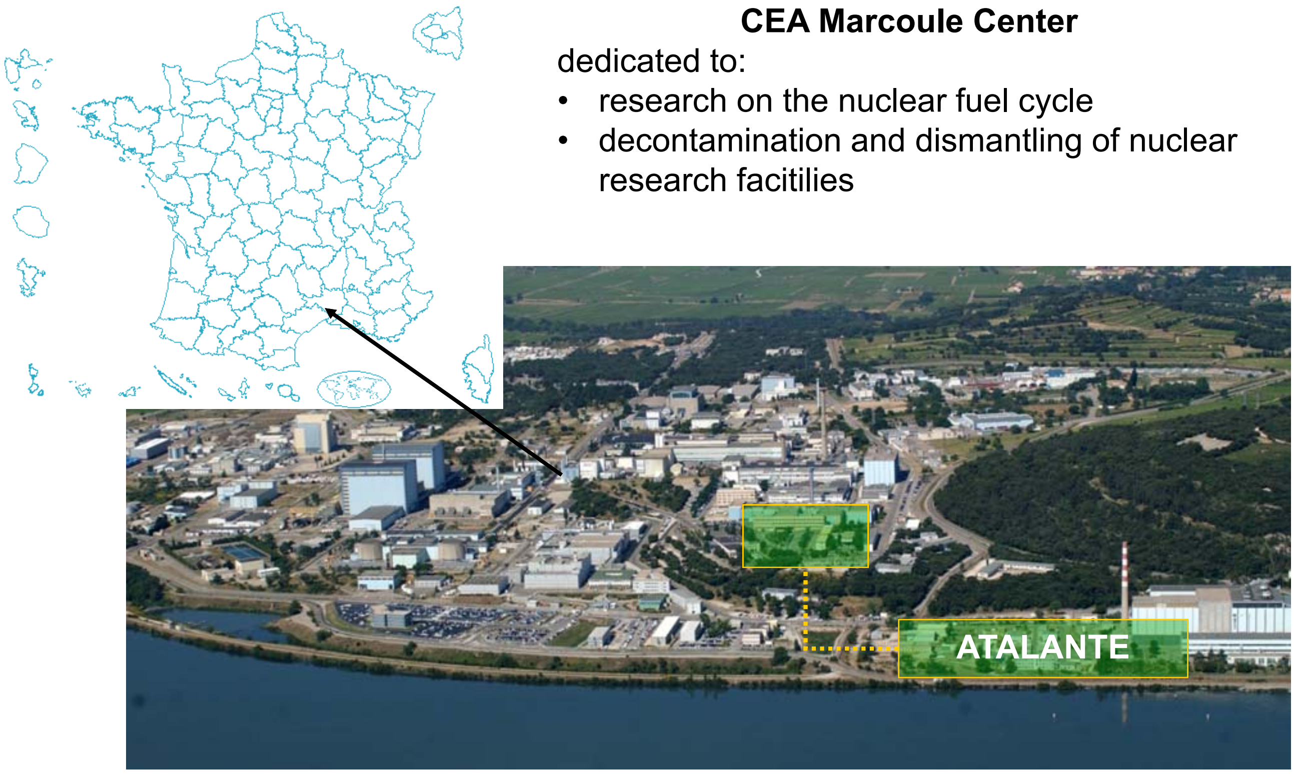
WASTES

SUPERCRITICAL WATER OXIDATION IN CEA
HTO: HYDROTHERMAL OXIDATION OF WASTES

CEA Marcoule Center

dedicated to:

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

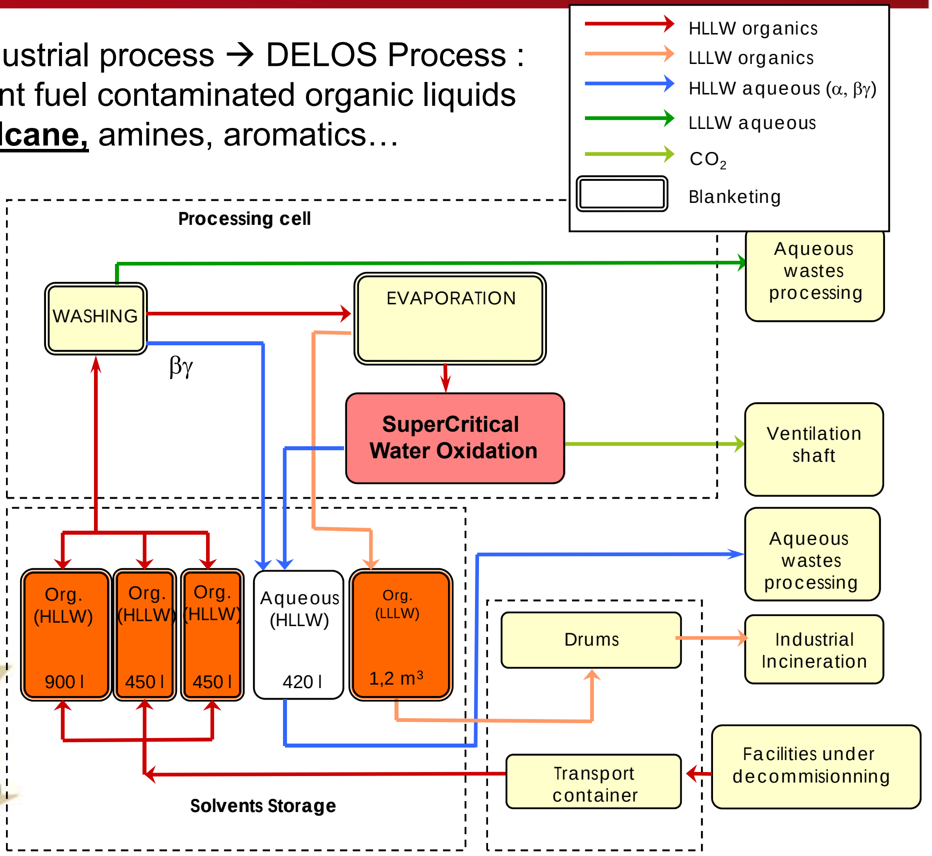


ATALANTE / DELOS
DESTRUCTION OF CONTAMINATED ORGANIC LIQUID WASTES

WASTES

Before 2014: No industrial process → DELOS Process :

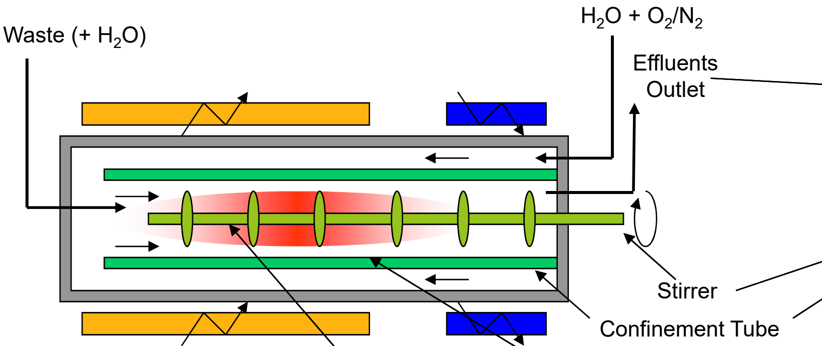
- Treatment of spent fuel contaminated organic liquids
- C.H.O.N., **TBP/alcane,** amines, aromatics…

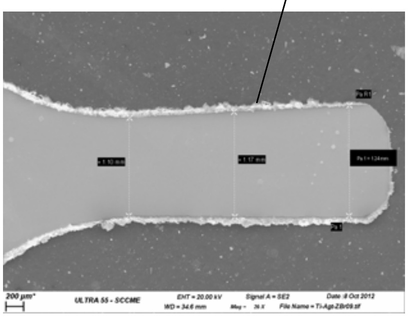


Corrosion and plugging management using an internal stirred Sheath in a continuous supercritical water oxidation autoclave

WASTES

Joussot-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

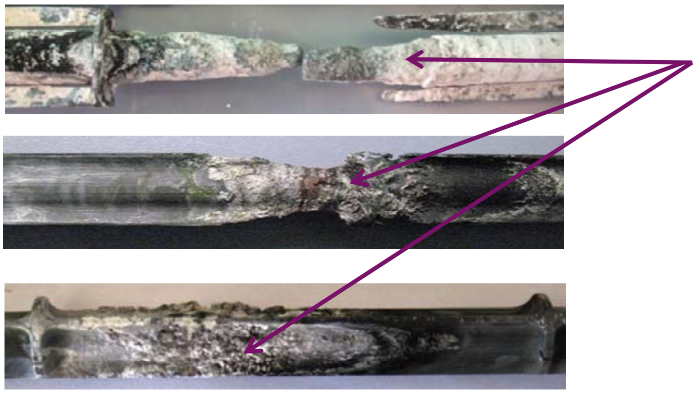
DAMAGE MANAGEMENT & FINAL PROCESS

Combustion of dodecane/tributylphosphate/dichloromethane (94,9995/5/0,0005 %vol)

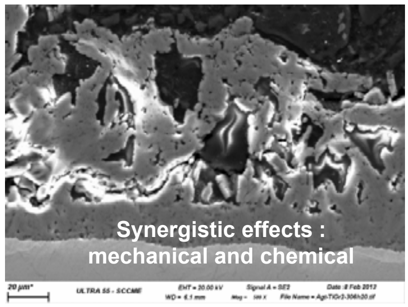
Material : Ti Grade 2

Welding design

Massive design



TiP_2O_7, $Ti(OH)PO_4$



Final Scale up

100 h → 300 h → 1000 h

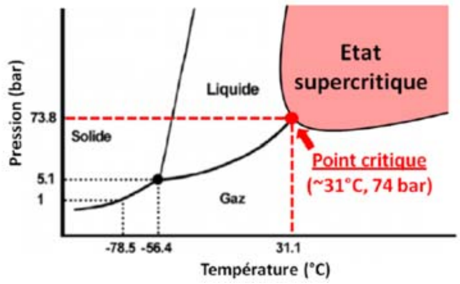
100 h	300 h	1000 h
Corrosion < 5 µm/h	Corrosion < 5 µm/h Mechanical Strength	**Industrial Conditions** 6 months Batch 1 hour maintenance

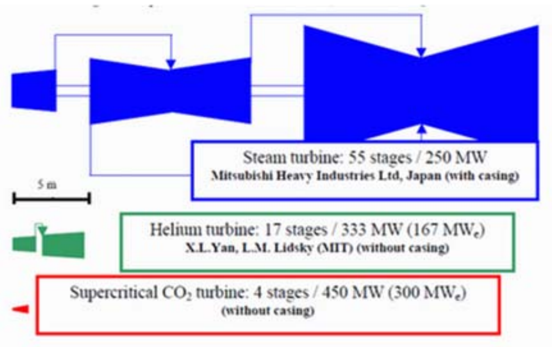
SUPER-CRITICAL CO_2 AND OTHER S.-C. FLUIDS

SUPERCRITICAL CO_2

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."

from Sandia lab.

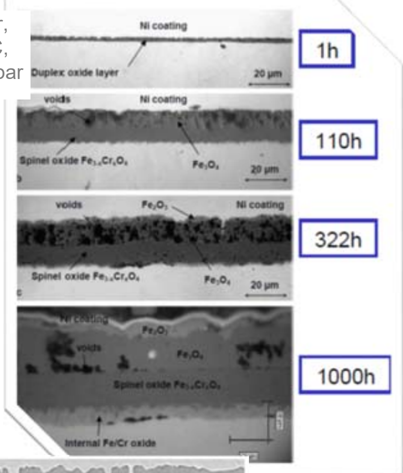
MATERIALS FOR CO_2 BRAYTON CYCLES

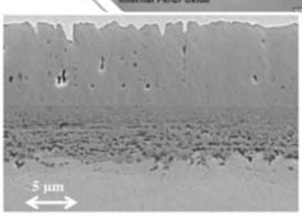
ENERGY

Oxidation of ferritic-martensitic steels

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

9% Cr, 550°C, CO_2, 1 bar





9% Cr, 550°C, 310h, CO_2, 250 bar

- **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,…)

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

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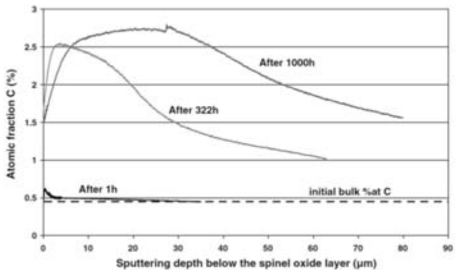
ENERGY

MATERIALS FOR CO_2 BRAYTON CYCLES

Carburization of ferritic-martensitic steels

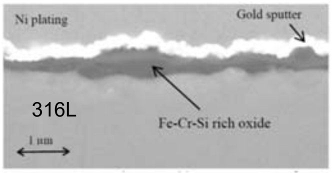
- In parallel to the formation of the oxidation, alloys may suffer also **carburization** (increase of carbon content in the alloy which may become brittle)
- With 9%Cr, carburation increases with time. In supercritical CO_2, carbon deposition is also observed in the inner oxide layer ⇨ **carburization is linked to oxidation**



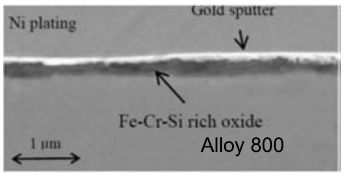
Carbon profile in 9% Cr exposed at 550°C in 1 bar of CO_2

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

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?



F. Rouillard & al., Proceedings of $SCCO_2$ power cycle symposium, 2009

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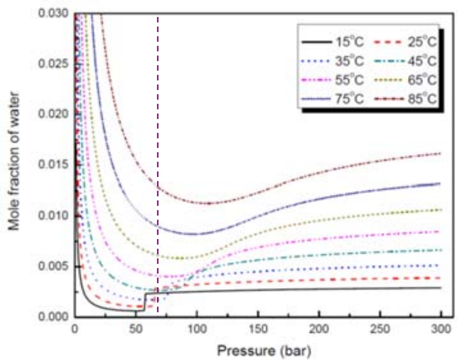
PROCESS

EXTRACTION AND CO_2 CAPTURE AND STORAGE

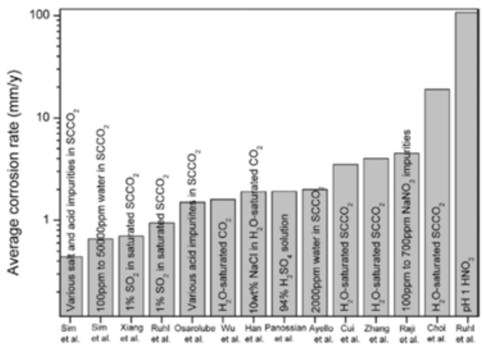
Corrosion issues in supercritical CO_2 – water environments

- 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



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

Solubility of water in supercritical CO_2 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 $SCCO_2$ conditions

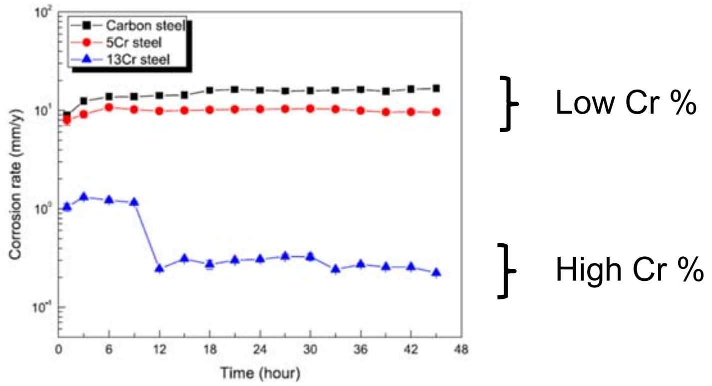
MATERIAL BEHAVIOR IN SCCO$_2$ WITH POLLUTANTS

PROCESS

CO_2 Capture and storage

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

Corrosion rate of steels in SCCO$_2$ 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$_2$ 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 CO$_2$

High temperatures (450°C-650°C)

- **Oxidation and carburization by CO_2**
- **Beneficial effect of chromium** : stainless steels and nickel alloys / surface finishing

Low temperatures (<150°C)

- **No corrosion in pure CO_2**
- **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 CO_2)
- **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_2 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, …

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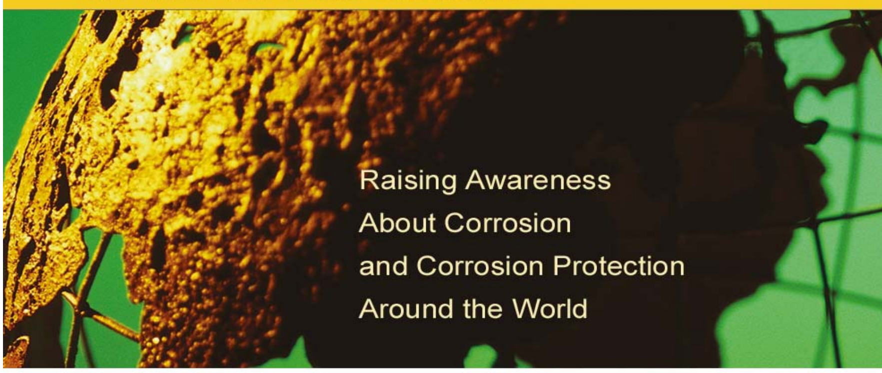

Welcome to WCO – The World Corrosion Organization

a non-governmental organization (NGO) of the United Nations (UN)

April 24th is Corrosion Awareness Day

Thank You for your attention

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