FIFTY YEARS OF NUCLEAR CORROSION: FROM THE PIONEER PERIOD TO A MATURE INDUSTRY AND SCIENCE

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WP4 50 Year Anniversary Workshop, EUROCORR'2017
September 4, 2017 - Prague, Czech Republic

SUMMARY

Nuclear corrosion Working Party (WP4)

Timeline
Evolution
Activities

Evolution of the concepts in corrosion (SCC of Alloy 600)

Historical perspectives
- The Copson Diagram
- The « Coriou effect »

Nuclear corrosion challenges

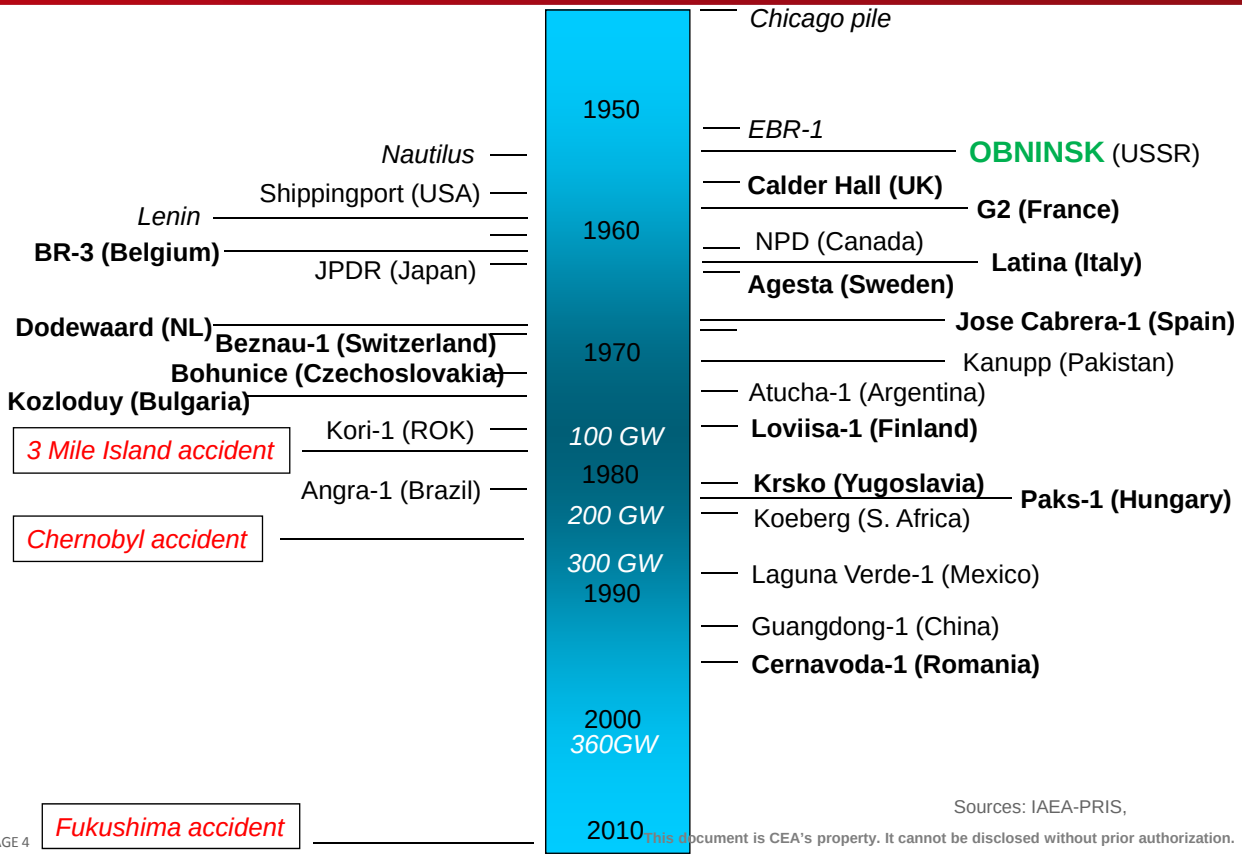
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THE NUCLEAR CORROSION WORKING PARTY OF THE EUROPEAN FEDERATION OF CORROSION

EFC WP4

HTTP://EFCWEB.ORG/WP4.HTML

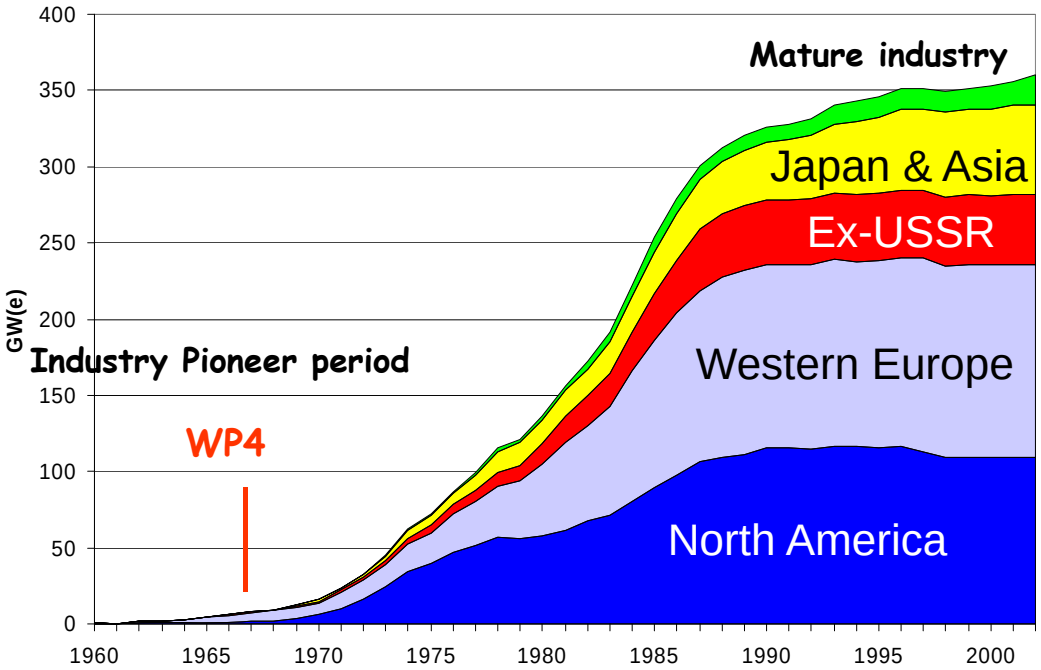
TIMELINE OF THE FIRST INDUSTRIAL NUCLEAR POWER REACTORS



Sources: IAEA-PRIS,

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EVOLUTION OF THE NUCLEAR CAPACITY (1960-2000)



Sources: IAEA-PRIS,

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TIMELINE OF THE EFC WP4 « NUCLEAR CORROSION »

EFC (1955)

Preliminary Period (55-67)

WP4 (1967)

First Period (67-85)
"Club" organization
No minutes – debates in French

Second Period (86-00)
Organization based on 9 topics
Eurocorr'87: Expert talks
Eurocorr'92: First nuclear corrosion session
Transition (00-02)

Third Period (02-)
Organization based on working groups (workshops, books, …)
One or two meeting each year
Several sessions during Eurocorrs

1950
1960
1970
1980
1990
2000
2010

H. CORIOU, Chairman
12 countries : Austria, Belgium, Denmark, France, Germany (Federal R.), Hungry, Italy, Nederland, United Kingdom, Spain, Sweden, Switzerland and Euratom
34 members

P. BERGE (86-94)
13 countries

1989 - First EFC book

F. DE KEROULAS (94-99)

J. DARET, (00-02)

D. FERON, (02-16)

2004- EFC event

14 countries

2011 – AWARDS
2015 -Summer school

S. RITTER (17-)

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OBJECTIVES OF THE WP4 « NUCLEAR CORROSION »

- To provide links between European teams in nuclear corrosion field, with an opening on to the world.
- To initiate and stimulate opportunities of exchanges on scientific & technical subjects related to nuclear corrosion, *particularly on today main nuclear research areas: waste systems, water reactors, generation IV and fusion reactors*
- To promote corrosion science and technical developments by events such as seminars, workshops, publications, …

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SESSIONS, SEMINARS AND WORKSHOPS (EFC EVENTS)

- Nuclear corrosion session during Eurocorrs, each year since 1996
- Specific sessions or workshops in conjunction with Eurocorr

Corrosion issues in future nuclear systems (2005), in reprocessing plant (2006), nuclear corrosion monitoring (2007, 2011), simulation, modelling and life time prediction (2009), Corrosion in future nuclear systems (2009), Environmental-assisted cracking (2012), Radiation and corrosion in NPP(2013), …

- Workshops & conferences (EFC events)

"High temperature electrochemistry in light water reactor's, 2004, Leuven (EFC 279, Belgium)

"International Workshop on Sulphur-Assisted Corrosion in Nuclear Waste Disposal Systems", SACNUC 2008, Brussels (EFC 311)

Jubilee Day: 'Stress Corrosion Cracking of Nickel-Base Alloys at CEA - Coriou Effect', Saclay, 2010 (EFC 333)

International Workshop on 'Coupling Mechanisms to Improve Lifetime Prediction of LWRs, Les Renardières, 2010 (EFC 331)

Conference on Flow Accelerated Corrosion - FAC 2016, Lille (EFC 406)

NUCPERF 2006, 2009 and 2012 (Cadarache), 2010 (Toronto) / (Cementitious barriers and reinforced concrete in nuclear facilities)

" Long-term prediction of corrosion damage in nuclear waste systems" 2001 (Cadarache-EFC 256), 2004 (Nice), 2007 (Penn. State U.), Bruges (2010), 2013 (Asahikawa), 2016 (Toronto)

The 7th workshop- **LTC2019 or LongTermCor'2019**- is planned in 2019 at Nancy (France)

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EFC WP4 SUMMER SCHOOLS & EFC WP4 AWARDS (2011)

- "Summer schools" (one week)
  - Modelling of Corrosion for Nuclear Reactors (Saclay, 2012 & 2014)
  - **NuCoSS-15: Nuclear Corrosion Summer School (Bled, Slovenia, 2015)**



- Poster Award

2013 - Monica M. Schvartzman (Brasil), 2014-Renato de Mendonça (Belgium), 2015-Zuzana Skoumalova (Czech R.)

- Oral presentation award (young scientist-engineer below 35)

2014-Jacqueline Caballero Hinostroza (France), 2015- Alice Laferrere (UK), 2016-Juxing Bai (Switzerland) & Cristian Pérez-Brokate (France)

- EFC WP4 Honorary Medal - "Henri Coriou award"





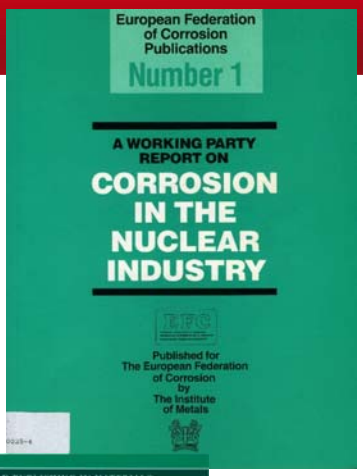
2016 – David Tice (UK)

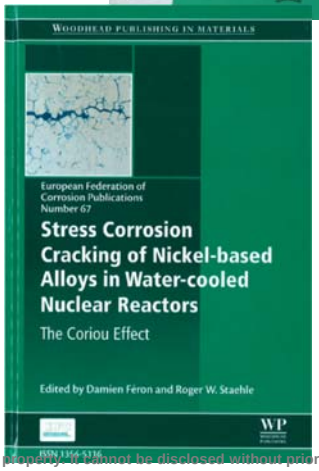
2017 – Hannu Hänninen (Finland)

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PUBLICATIONS

- **EFC series (9 « green books »)**
  - N°1 Corrosion in the Nuclear Industry (1989)
  - N°7 Corrosion problems related to nuclear waste disposal
  - N°36 Prediction of long term corrosion behaviour in nuclear waste systems
  - N°48 Corrosion of metallic heritage artefacts
  - N°49 Electrochemistry in light water reactors: refrence electrodes, measurements, corrosion and tribocorrosion
  - N°51 Corrosion issues in light water reactors: stress corrosion cracking
  - N°56 Corrosion monitoring in nuclear systems
  - N°59 Sulphur-assisted corrosion in nuclear disposal systems
  - N°67 Stress corrosion cracking of nickel base alloys in water cooled nuclear reactors: the Coriou effect (2016)
- **Two other books**
  - **published by Andra & Rilem**
- **Special issues**
  - JNM (1)
  - CEST (4)





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FIRST CORROSION CHALLENGES IN NUCLEAR POWER REACTORS

Pioneer period

Selection of appropriate materials

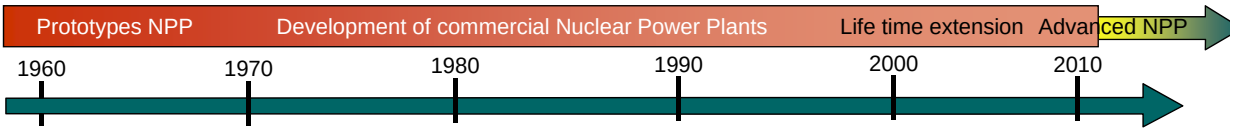
Stress corrosion cracking
BWR
Stainless steels in recirculation loops (70s) and vessel weldings
PWR
Alloys 600 tubing (80s) & Vessel head penetrations (90s)

Flow accelerated Corrosion
BWR, Magnox, PWR, VVER, ….
All components and tubing where two phases (liquid and vapor) are together

- Shippingport
- Dresden, Fermi I
- Magnox

- LWR-PWR, BWR
- CANDU
- VVER/RBMK

- ABWR
- EPR
- AP600

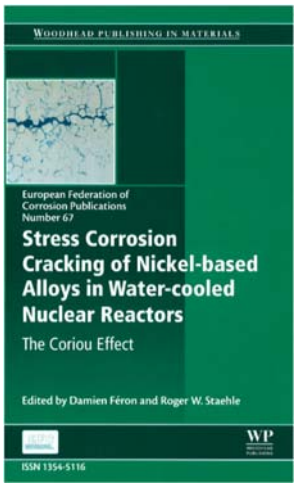


During the last 50 years, large evolutions of
- the alloys
- the chemistry
- the prediction / modelling
- the concepts

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Evolution of corrosion concepts

The "Coriou effect"



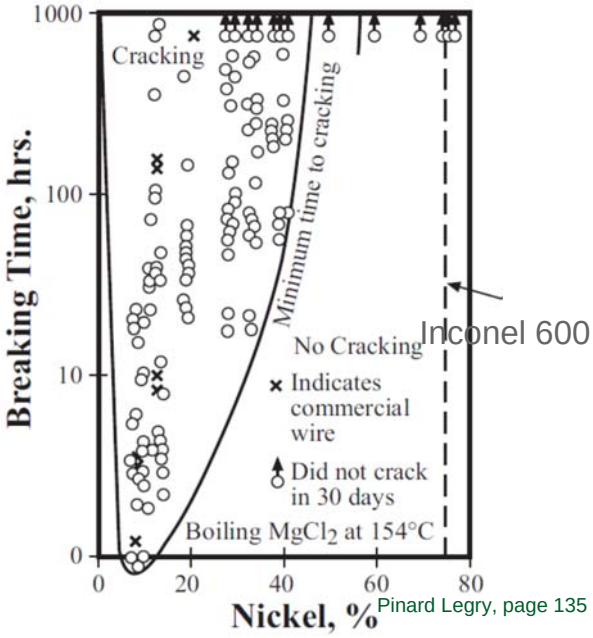
Ref: first author of the chapter, page 000

SCC of Fe-Cr-Ni alloys — 1957

1953: Stress Corrosion Cracking occurred in the stainless steel tubing of the steam generator of the prototype for the Nautilus. SCC failures occurred on the secondary surfaces of the tubes.

By 1957, H. Copson at INCO had demonstrated that the Stress corrosion cracking of Fe-Cr-Ni alloys would stop above about 40% Ni, when exposed to boiling $MgCl_2$.

This work continued with additional data in 1959 and 1963.



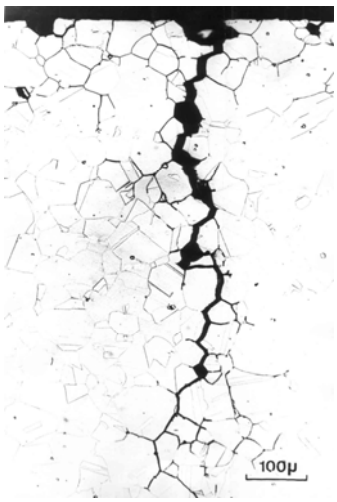
Pinard Legry, page 135

Time to failure of laboratory alloys (1963)

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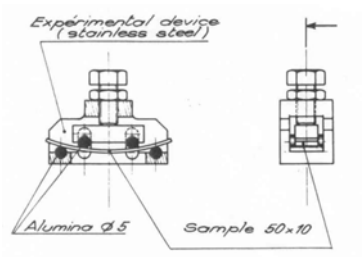
The "Coriou effect" — 1959

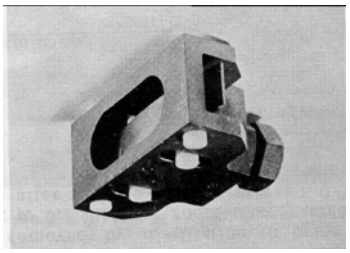
1959: *Coriou et al.* published that Alloy 600 (75% Ni & 15% Cr) is sensitive to SCC in "pure" water at 350°C.



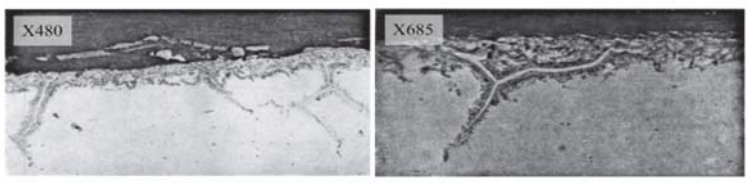
Pinard Legry, page 136

Intergranular SCC of Alloy 600 (350°C, pure deoxygenated water) – 3 months





Staehle, page 14



Intergranular oxidation on Alloy 600 (350°C, pure deoxygenated water, 3 months)

« Pure water » more corrosive than polluted water (boiling $MgCl_2$) ?

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Copson and Dean, 1965, announce Pb contaminant produces SCC of Alloy 600, not pure water

Effect of Contaminants on Resistance To Stress Corrosion Cracking Of Ni-Cr Alloy 600 in Pressurized Water

By H. R. COPSON* and S. W. DEAN**

National Association of Corrosion Engineers

Vol. 21 No. 1 January, 1965

described in other publications.[3-11] These investigations showed conclusively that applied stress (up to and exceeding the room temperature yield strength), crevices, galvanic coupling, alternate wetting and drying, and exposure to the vapor phase did not promote stress corrosion cracking or intergranular attack in Alloy 600 in simulated primary and secondary reactor waters at temperatures between 300 F (149 C) and 680 F (360 C). It

These observations prompted the present investigation to define the cause of the unexpected results. Tests were run both in uncontaminated water, and in water containing some contaminants normally extraneous to the system. Contaminants included sodium fluoride, air, lead or lead compounds, and air in conjunction with stresses in a crevice area.

Also, Copson indicates PbSCC is TGSCC, erroneously based on his sensitized specimens.



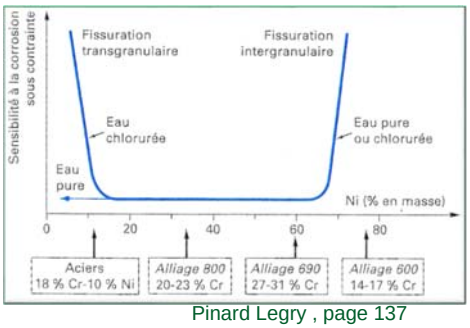
Alloy No.	Type of U-bend	Time to Cracking, weeks			
		Pb powder + hydrocarbon (5)**	Pb powder (6)**	PbO (7)**	Fractional Pb + hydrocarbon (8)**
9A	Single	8	8	4	OK
11A	Single	8	8	6	6
9A	Double, outer	8	8	6	OK
9A	Double, crevice	8	8	6	6

* Air-saturated distilled water, pH 10 at start-up, 316°C
** Author's test number
OK = No cracking at end of test, which lasted 1,350 hours in Tests 5, 6 and 8 and 100 hours in Test 7.

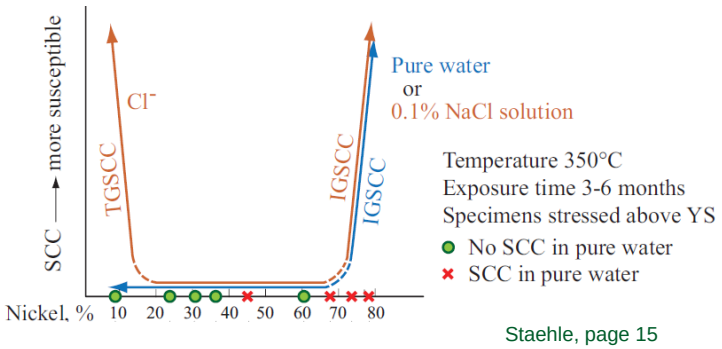
From R. Staehle, *Jubilee day, January 26, 2010, CEA-Saclay*

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"COPSON diagram" by CORIOU



Pinard Legry , page 137



Staehle, page 15

SCC susceptibility as function of the nickel content (Coriou's work – summary 1967)

Work done with a series of laboratory alloys Fe-18%Cr-Ni with various Ni content
Pure water and solution with 0.1% NaCl / 350°C / 6 months / 1.2 and 1.7 $E_{0.2}$

TABLE I - Lead Content of Experimental Materials.

Description	Lead Content ppm
Sintered alumina rods	7
Autoclave 18/10 steel	39 ± 8
Stress apparatus 18/10 steel	39 ± 8
Inconel 600-rod	30 ± 6
Inconel 600-sheet	55 ± 10
Inconel 600 Type alloy (ARC 7915) sheet	52 ± 10

Lead is controlled not only in water but also in all experimental materials

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"Coriou effect"

1960-67: *Publications of Copson & Berry in primary and secondary conditions: no cracking while Coriou and his coworkers reported cracking of Inconel 600*

Conclusions

The results of this study indicate that, from a corrosion standpoint, Inconel is an excellent construction material for primary and secondary waters of pressurized water reactors.

Inconel forms tightly adherent tarnish films in the waters studied. It contributes a relatively small amount of corrosion product to a high velocity stream of primary water. It corrodes at rates comparable with those of Type 347 stainless steel.

Variations in composition and heat treatment have little effect on the corrosion behavior of Inconel in primary and secondary waters. Applied stress, crevices, or welding do not cause selective or intergranular attack. Galvanic coupling of Inconel to steel or to stainless steel does not accelerate the attack on either member of these couples.

Copson, corrosion, 16, 1960, 79-85

The tests were conducted in autoclaves for up to 3000 hours. The composition of the gas phase and the pH were controlled. The materials tested included Alloys 600, 625, 800, stainless steels Type 304, 304L, 347, and some experimental laboratory compositions. In these tests no attack was observed in specimens stressed at 90 percent of the room temperature yield strength. No attack was

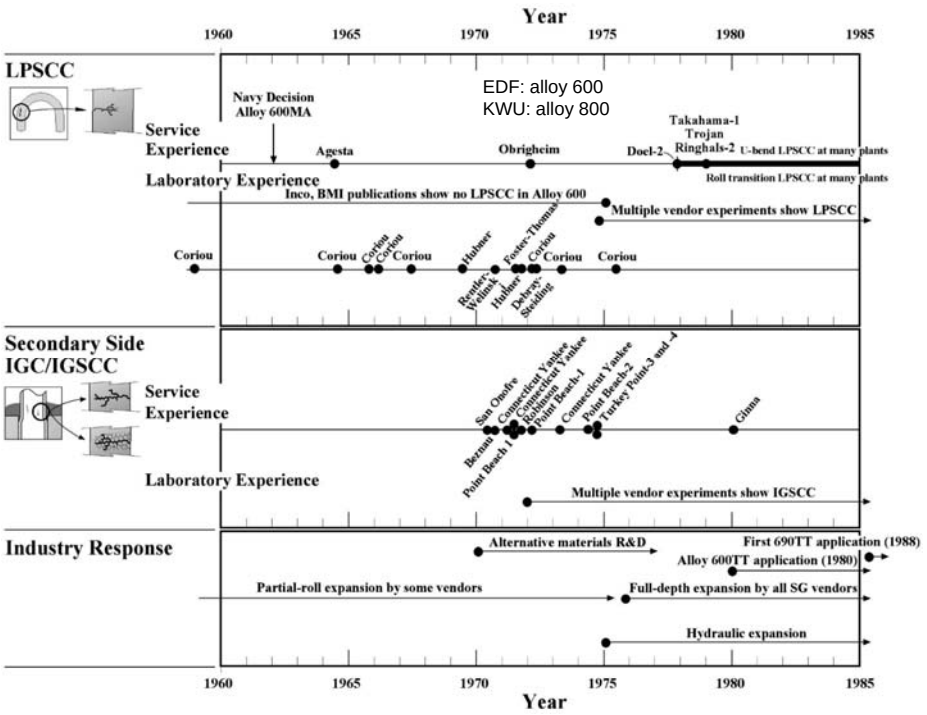
Copson, discussion at the Ohio state University meeting on stress corrosion cracking (September 11-15, 1967)

Comments

- In CEA tests, the stress are higher than the yield strength and the test durations are very often over 8000h. Good behavior of stainless steels including Alloy 800.
- Reproducibility of results not evocated in these articles
- Important experimental parameters not known and poor characterization of the alloy

From R. Staehle, *Jubilee day, January 26, 2010, CEA-Saclay*

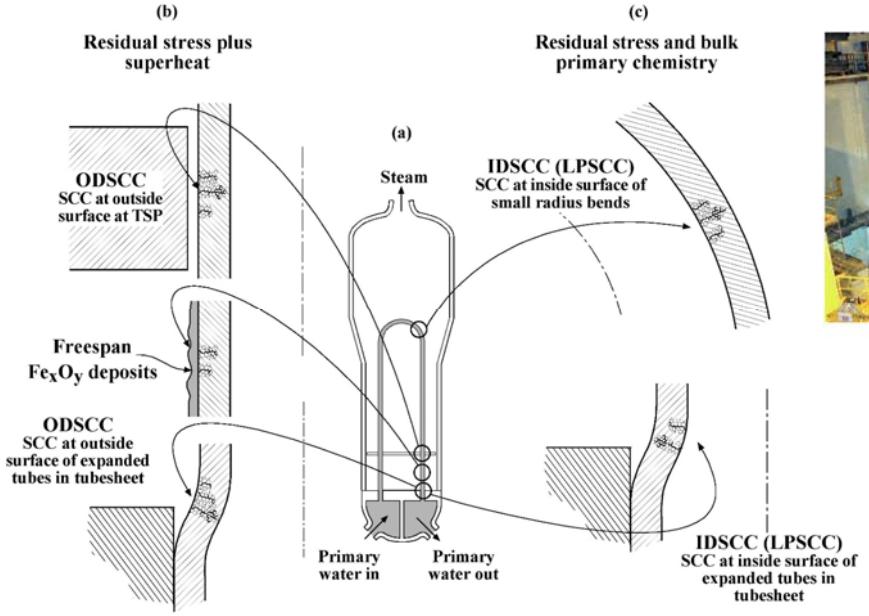
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Staehle, page 106

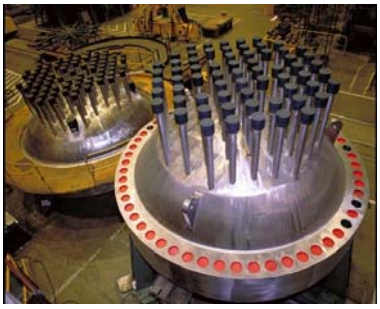
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Some additional comments





Remplacement d'un générateur de vapeur



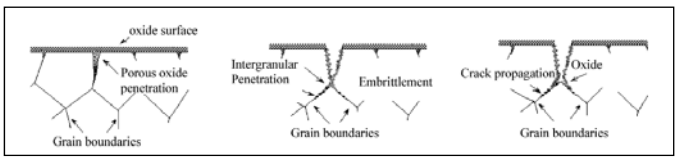
Complementary works

- Copson & Al. / Secondary side (pollutants)
- Coriou & Al. / Primary side (no pollutants)

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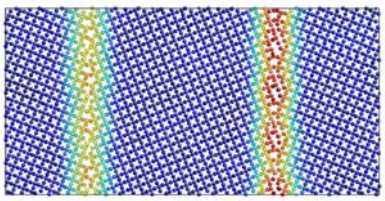
ADDITIONNAL COMMENTS « CORIOU EFFECT »

- Large progress on mechanisms



Internal oxidation model with an eventual influence of the cathodic hydrogen in grain bound

- Multi-scale modelling



Grain boundary structure
$(Ni,Fe)Cr_2O_4$

A. Chartier et al, JCP 139 (2013) 134702
L. Van Brutzel et al, NIMB 278 (2014) 278

- Good behavior of Alloy 690 and Alloy 800 linked to the higher chromium content

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NUCLEAR CORROSION: from yesterday to tomorrow



Reprocessing

First facilities



Power plants

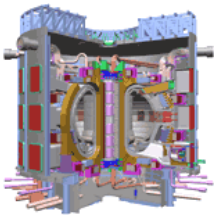


New facilities



Generation IV and Fusion



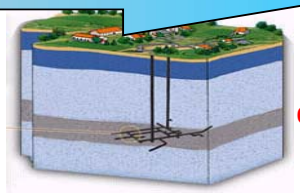


1950 1970 1990 2010 2030 2050 2070 2090

Source : CEA

Material selection

Failures investigations
Performance increases



Nuclear Waste disposal

MATERIALS & CORROSION

Exploitation time (Power & other plants, …)
Long term prediction (HLNW disposal)
High temperatures (innovative materials)

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Thank you for your attention

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