Dr. Ian de CURIERES

Secondary side corrosion of SG tube alloys in typical secondary side chemistries

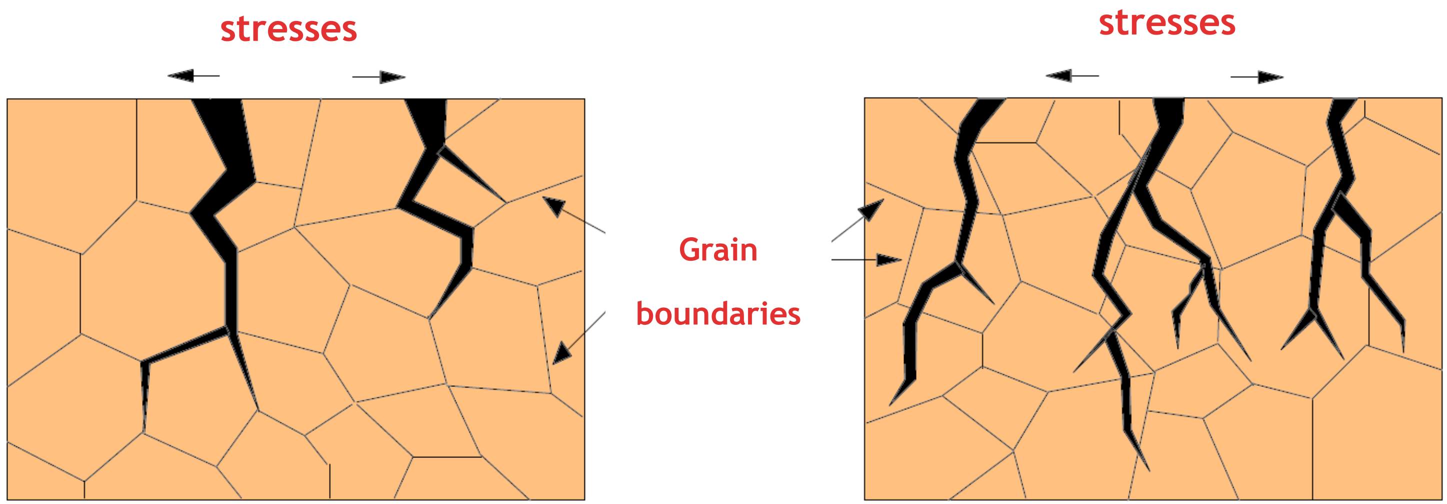
IRSN
INSTITUT
DE RADIOPROTECTION
ET DE SÛRETÉ NUCLÉAIRE

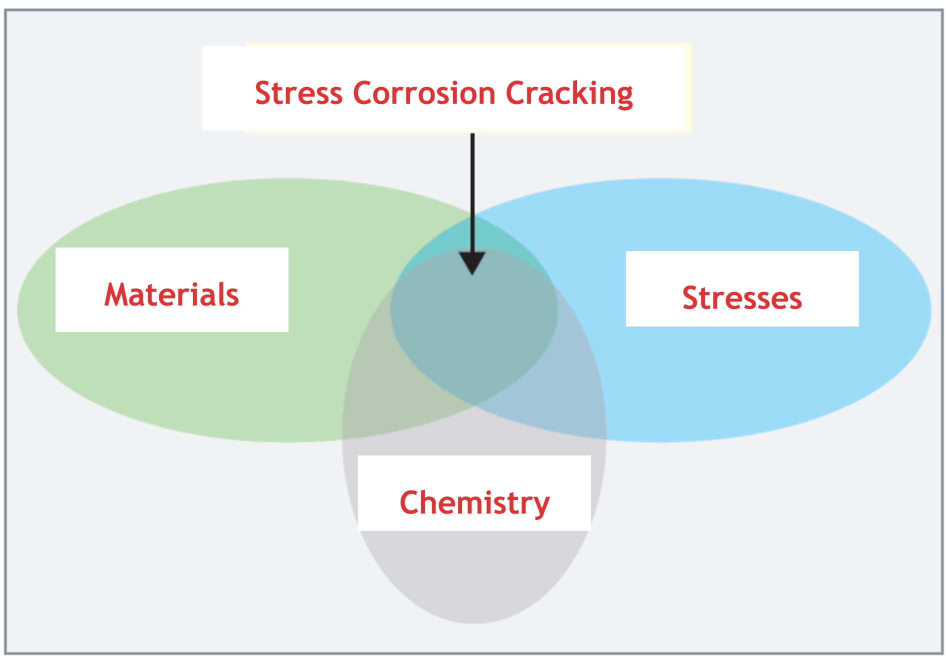
EUROSAFE 2016

OPEX of IGA/ODSCC (SG tube corrosion cracking)

- **600TT**
  - More than 200 tubes affected worldwide
  - Korea (1990+), USA (2002+), France (2012+)
    - Mostly at the top of tubesheet location
- **800NG**
  - About 200 tubes affected in 2010 (IAEA)
  - Sometimes after about 10 years of operation (4 years after TTS denting)
- **690TT**: nothing reported yet
  - But dented tubes exist
- Root cause analyses
  - Sometimes « non-optimized » microstructures
  - Sometimes denting (TTS)
  - Very often, Pb, S encountered. Also Al and Si

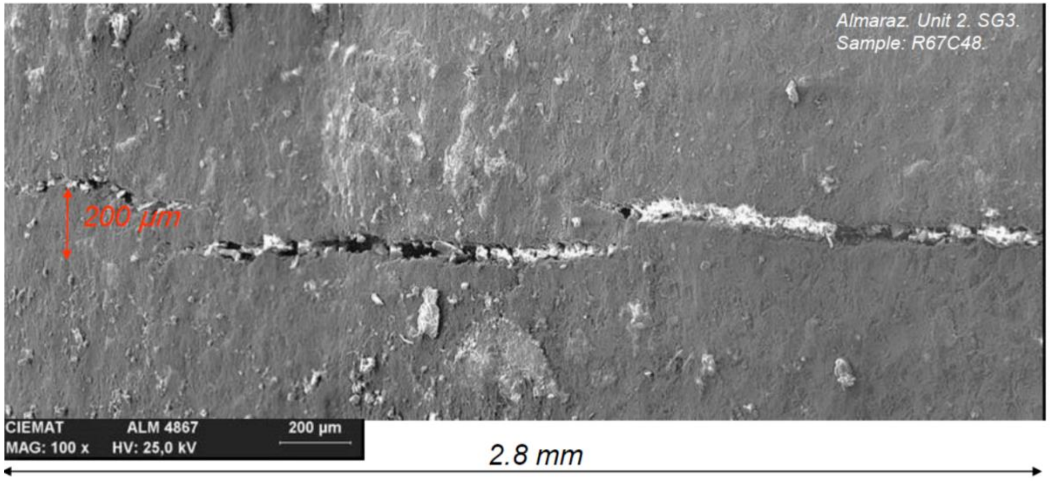
Insights on stress corrosion cracking





From CEA

Some recent ODSCC cracks

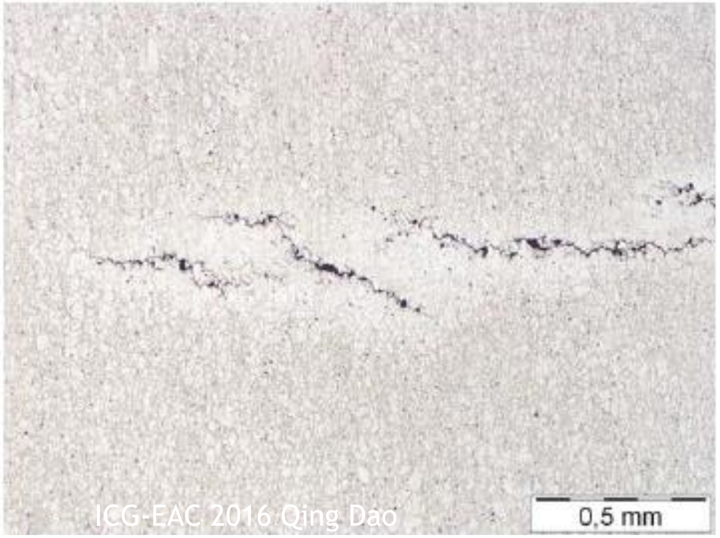


ODSCC in alloy 800NG tubes

Circumferential cracks network

12 years of operation

From Gonzalo, Fontevraud 8



ODSCC in alloy 600TT tubes

Circumferential cracks network

From Boccanfuso, 17th E. Deg

EUROSAFE 2016

Safety stakes of IGA/ODSCC

↗ SGTR (steam generator tube rupture)

- Is one potential cause for core melting
  - Probability of 10^{-8}/reactor.year for a 1-2 tubes « small » SGTR
  - In addition high risk of radioactive product release to the atmosphere
- IGA/ODSCC
  - Affects thousands of tubes worldwide
  - Many instances of circumferential cracking
- Tougher detection by NDE than primary side cracks
  - Deposits, copper, TSP intersections…

↗ IGA/ODSCC, although limited on modern SG tubes alloys, remains a crucial safety issue

Stakes of IGA/ODSCC

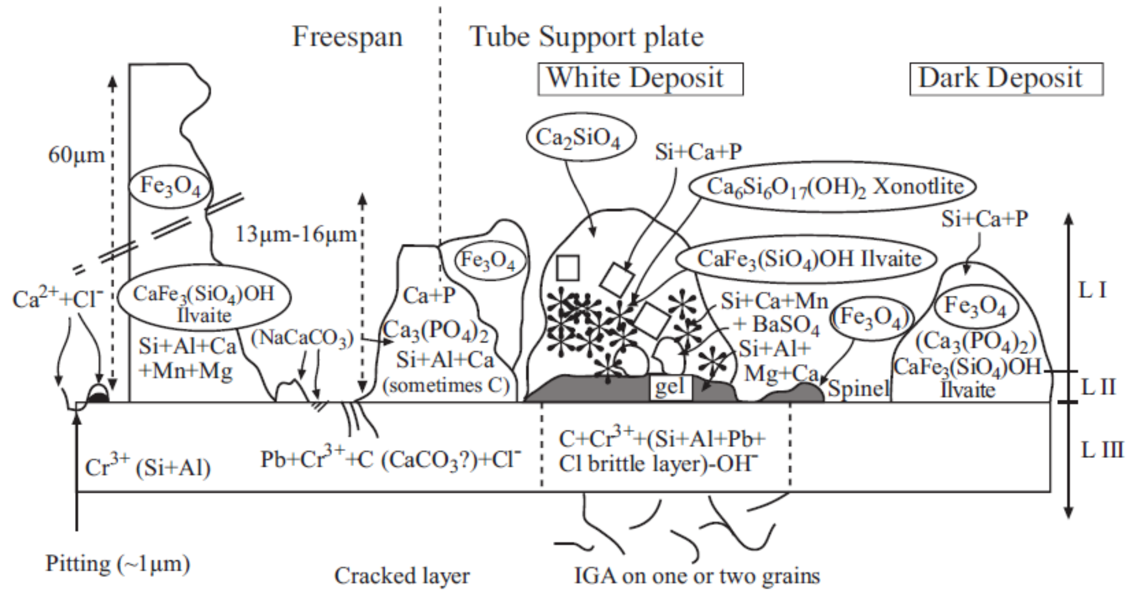
- R&D: risks of ODSCC exist
  - Even for corrosion resistant alloys
- OPEX for 600TT and 800NG
  - When ODSCC occurs, a few dozen tubes may be affected per SG
  - 2-3 affected tubes may be enough for a severe safety problem if SGTR
- Complexity of chemistries
  - No predictive modeling likely to be available
- Need for assessment tools
  - **Allowing plant chemists to specifically act**
  - Based on **« easy-to-access » data for utilities**
    - Actual chemistry: HOR (hide-out-return), sludge lancing analyses

➚ **Necessity of a domains of vulnerability approach**

Secondary side chemistry - insights

Secondary Water Chemistry

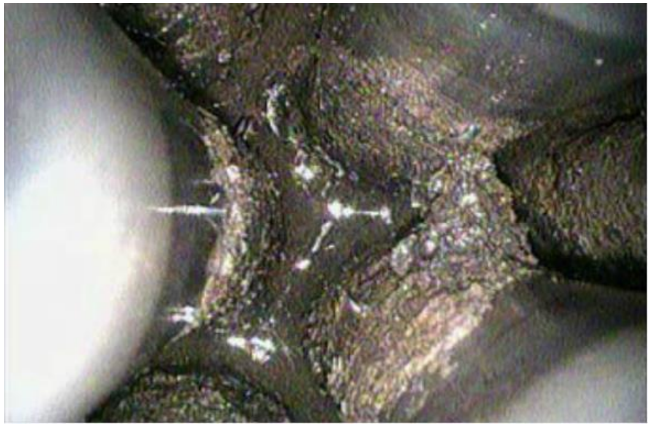
Role	Species	Conc., ppb
pH control	NH_3	X
O_2 decrease	N_2H_2	$\leq 8xO_2$
Leaks	O_2	< 10
Boil off remnant	H_2	1
Corrosion product	Cu	< 1
	Fe	< 5
Contaminant	Na	< 5
	Cl_2	< 10
	SO_4	< 10



- What is specified
- What is actually encountered on SG tubes
- Very complex local chemistries despite good operating procedures

What is a typical local secondary side chemistry?

- Analysis of OPEX over 25 years
  - Sludge lancing, HOR data…
- Many deposits/sludge at the TTS location, with a typical composition
  - Magnetite (Fe_3O_4) as balance
  - 2-10% **aluminosilicates**
  - <5 % of **calcium** species
  - 0.1 to 0.2%wt of **Pb** in sludge at the tube contact
    - Up to 1,4% of Pb in sludge collars (if pollution)
  - Presence of **S** (up to 10 000 ppm soluble from HOR)
    - Cu sometimes



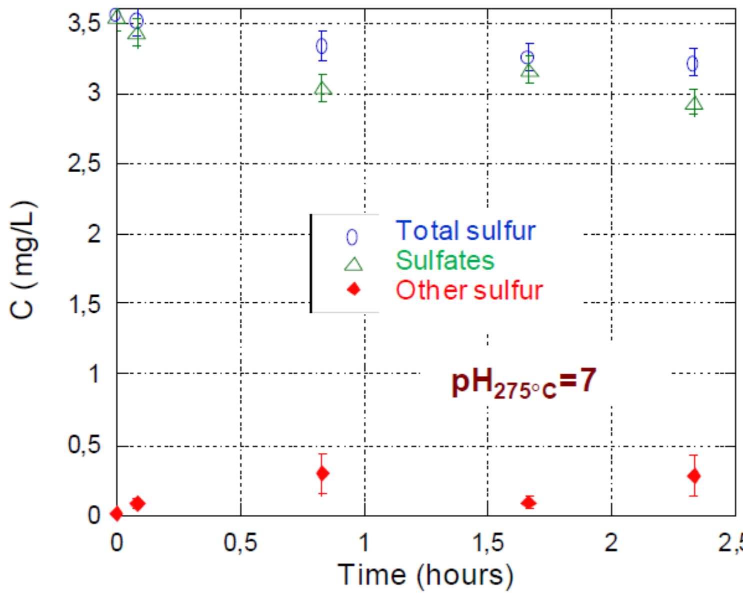
From Brechun, 2015

- Crevice pH_T estimated by utilities
  - Multeq, OLI, MRI…
  - Ranging from **4 to 9** **(range where test data are often missing)**

➚ **No precise knowledge of what may happen in these conditions**

The sulfur case

- Sulfates are measured at the SG blowdown
  - Sulfates in crevices may be 50 000x that measured during HOR
- In the operating SG, sulfates may be reduced
  - Magnetite, hydrazine…
  - Up to 10% of sulfur species in a « reduced » condition
    - According to pH_T



From Delaunay, 2012

Need to consider some reduced sulfur species in tests

Test protocol

Materials

Industrial SG tubes
690TT, 600TT, 600MA

Specimens

RUB (1/6 SG tube)

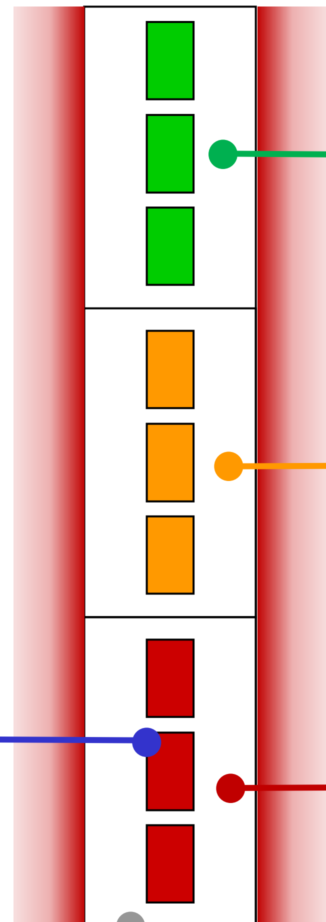
- Pre oxidized in nominal AVT environment

σ~550MPa, ε^p~9-10%
9 specimens per capsule

Experimental setup

Capsule test

- Exposure 7000 h at 320°C
- Hydrogen removal
- Heat flux OD → ID



Wet Steam

Resulting from the other conditions

Crevice simulating solution

- Nominal AVT environment
- Addition of NaCl essentially
- 4 < pH_T< 9

Polluted sludge

Sludges « typical » from opex

- Al , Si, Ca
- Addition of Pb and/or S pollutions

Not too accelerated tests in representative secondary side chemistries

Material and test specimens

Chemical compositions

Material	Heat	C (%)	Si (%)	S (%)	P (%)	Mn (%)	Ni (%)	Cr (%)	Cu (%)	Co (%)	Ti (%)	Al (%)	Fe (%)
600TT	WF489	0.027	0.27	0.001	0.012	0.83	73.1	16.2	0.02	0.018	0.24	0.16	8.9
690TT	116201	0.017	0.173	<0.001	<0.015	0.33	58.0	29.84	<0.01	<0.035	0.37	0.048	11

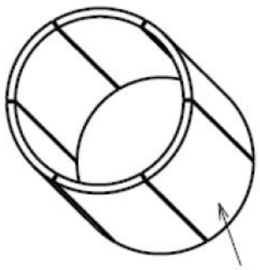
Fullfill the RCC-M requirements

Test specimens : Reversed U Bend

RUB (1/6 SG tube)
Pre oxidized in nominal AVT environment

σ~550MPa, ε^{p}~9-10%

9 specimens per capsule



6 sections per tube

Test matrix

- Type of environment

Sludges : Fe_3O_4 + 0,8% CaO + 5% of Al_2O_3/SiO_2 with Si/Al=4

Liquid phase: H_2O + 3ppm ETA + 1 ppmNH_3 + 3M NaCl + N_2H_4

- pH_T and type of pollution

	pH_T = 4	pH_T = 7.5	pH_T = 9
2000 ppm of Pb in sludge as **PbO**	✓	✓	✓
2000 ppm of Pb in sludge as (**91% $PbSO_4$ 9% PbS**)	✓	✓	✓
8000 ppm of soluble SO_4^{2-} as (**91% Na_2SO_4 and 9% Na_2S**)	✓	✓	✓
Pb/S free sludge	✓	✓	✓

pH_T adjusted by NaOH or HCl/H_2SO_4 based on thermodynamical simulations

Global preliminary results

		pH_T= 4			pH_T= 7,5		
		WF422 600MA	WF489 600TT	116201 690TT	WF422 600MA	WF489 600TT	116201 690TT
Pb (PbO)	Solid	c	c		c		
	Liquid	-		C	-	-	-
	Steam	-		C	-	-	-
Pb and S ($PbSO_4$/PbS)	Solid	C	C		C	C	
	Liquid	-	C	C	-	C	
	Steam	-	C	C	-	C	
S (Na_2SO_4/Na_2S)	Solid	C					
	Liquid	-	C	C	-		
	Steam	-	C		C	C	-

No analyzis	-
GC and/or IGA	
No indications	
C	Cracks observed from the surface

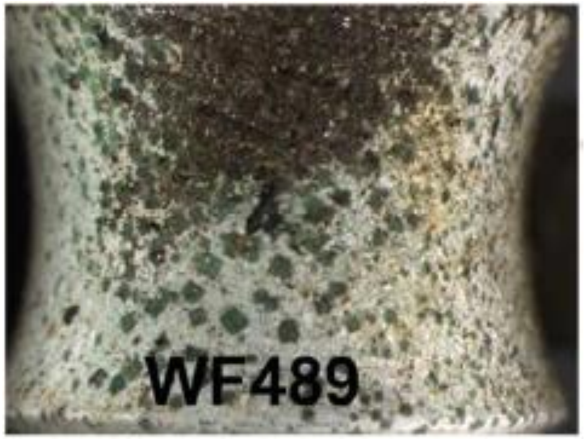
Test at pH_T 9 not yet finished December 2016

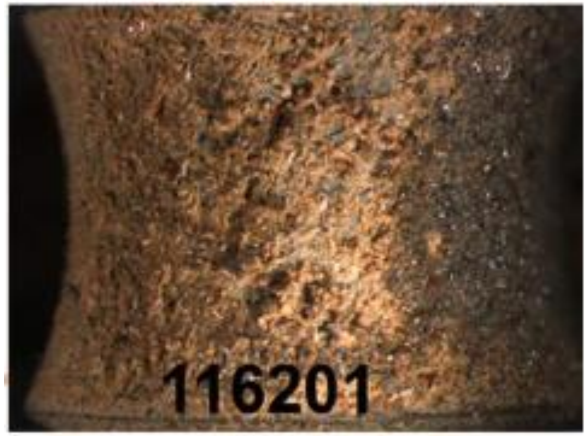
Examination of specimen

Optical examination – pH_T = 4 – liquid phase

No observable sign apart from oxidation

PbO





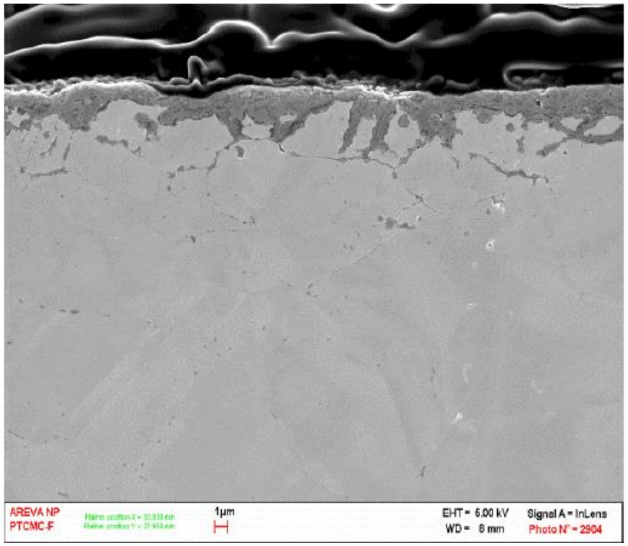
$PbSO_4$

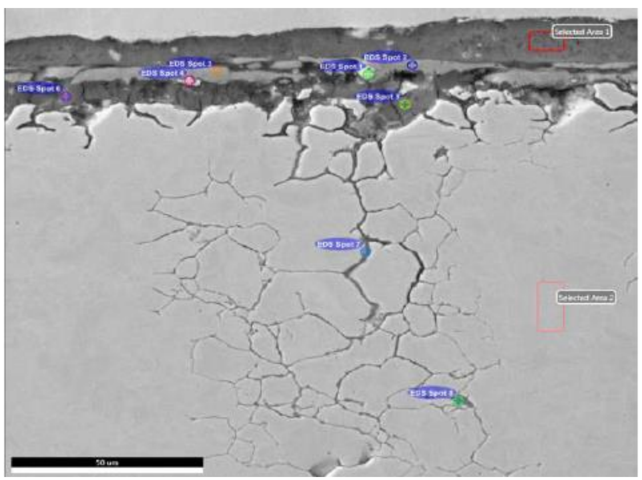
600TT

690TT

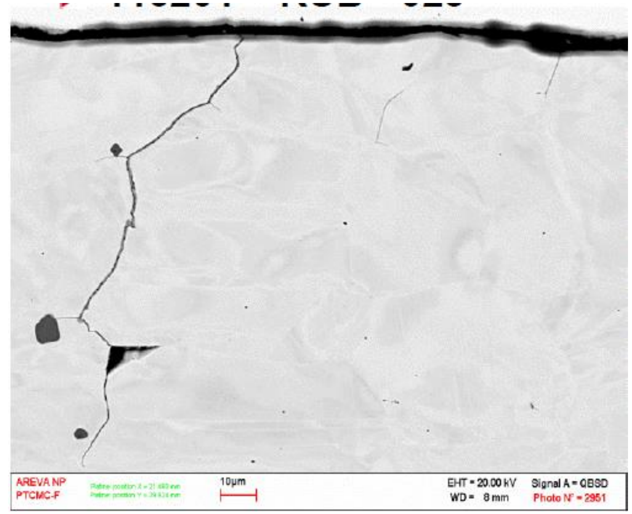
SEM cross sections – pH_T = 4 – liquid phase

IGA, IGSCC and GC (600TT) vs IGSCC (690TT) confirmed

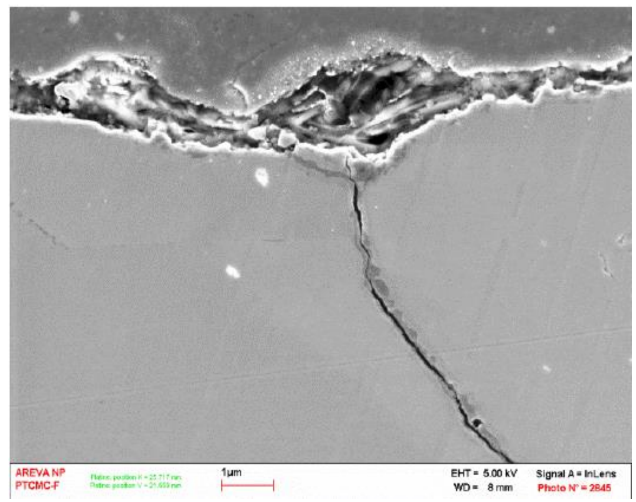




600TT



PbO



$PbSO_4$

690TT

SEM cross sections – $pH_T = 4$

Summary

		600TT		690TT	
		Max. depth	Crack density* (/ mm)	Max. depth	Crack density* (/ mm)
PbO	Liquid	180 µm	2	110 µm	0.9
	Wet steam	20 µm (IGA)	/	63 µm	0.5
$PbSO_4$	Liquid	180 µm	~3	60 µm	0.7
	Wet steam	78 µm	1	45 µm	0.32
Na_2SO_4	Liquid	79 µm	0.7	92 µm	0.2
	Wet steam	31 µm	0.3	/	/

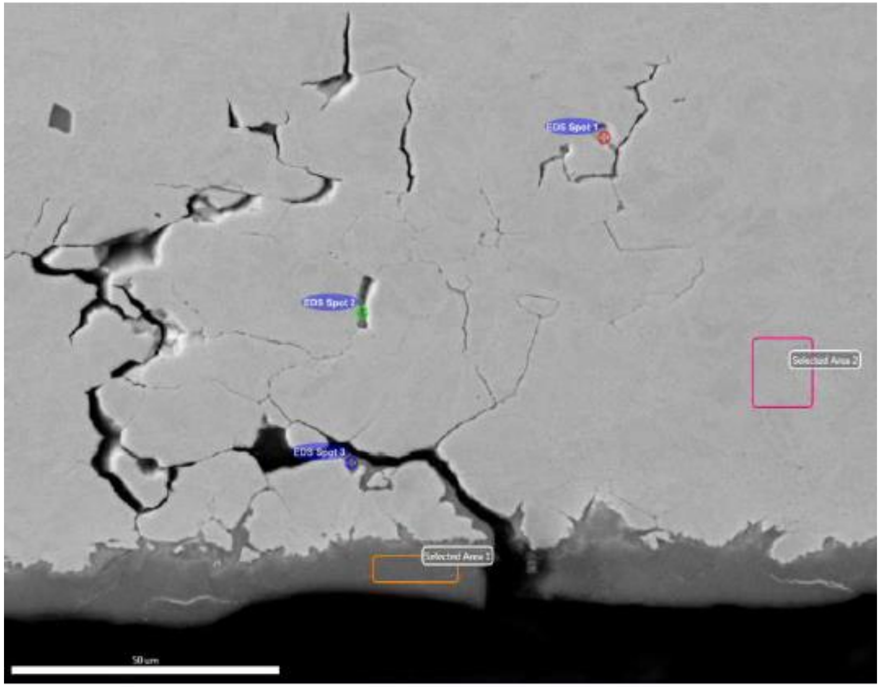
* Depth > 15 µm, specimen width ~10 mm

SEM chemical analyses – $pH_T = 4$

IGA, IGSCC and GC (600TT) vs IGSCC (690TT) confirmed

- SEM - EDS
  - No Pb or S apart from traces
  - Al, Si clearly detected

600TT
$PbSO_4$
sludge

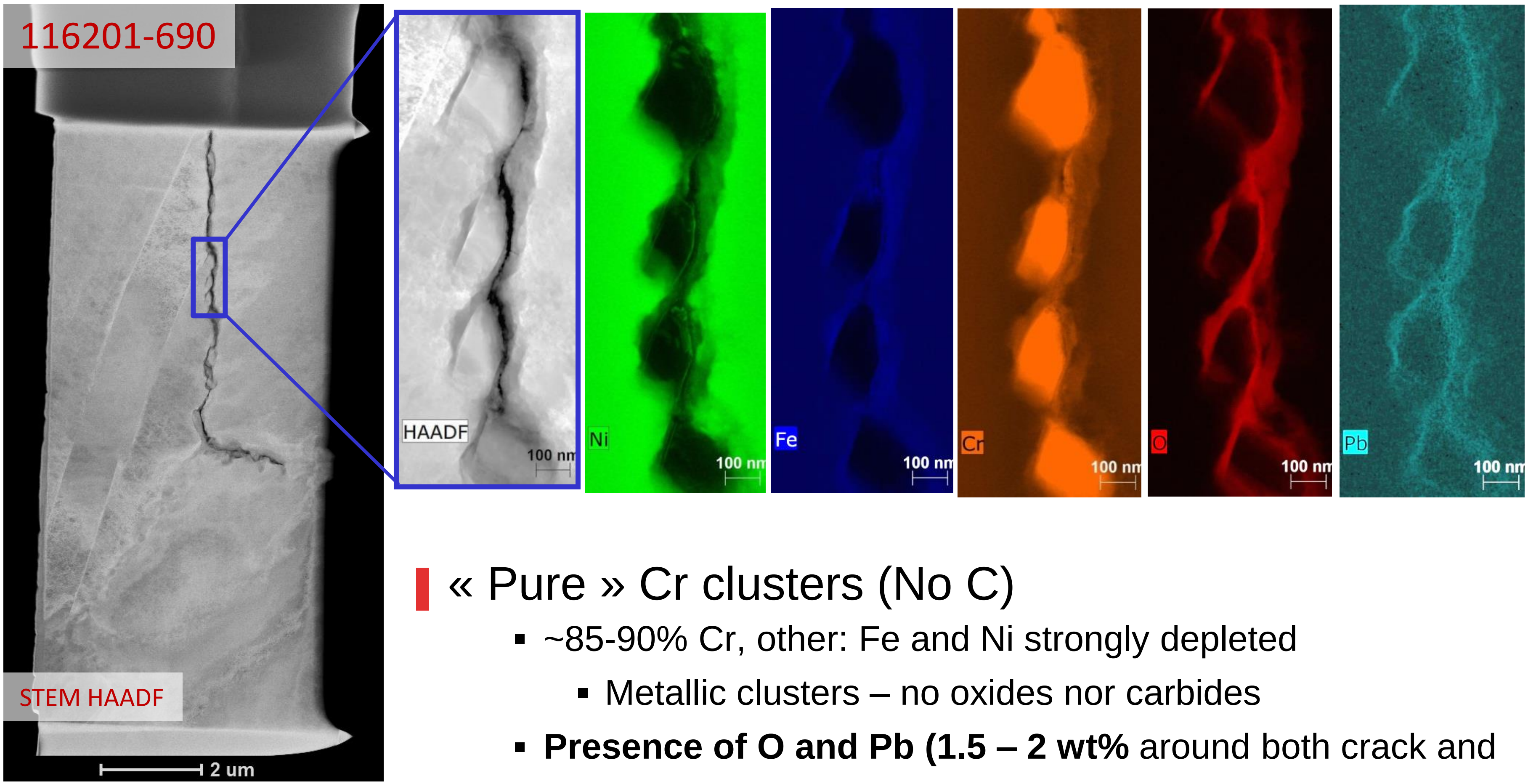


	O	Mg	Al	Si	S	Ca	Ti	Cr	Fe	Ni	Pb
WF489-027 | Area 1 | EDS Spot 1				0,7				16,8	9,6	72,9	
WF489-027 | Area 1 | EDS Spot 2	2,7	1,7	1,1					17,6	9	67,9	
WF489-027 | Area 1 | EDS Spot 3	1,6		1,4	0,6				16,6	9,3	70,5	
WF489-027 | Area 1 | Selected Area 1	21,8		0,6	1,3		0,5	0,5	27,1	15,8	31,5	0,7
WF489-027 | Area 1 | Selected Area 2	1,5			0,7				16,8	9,3	71,7	

→ **TEM**

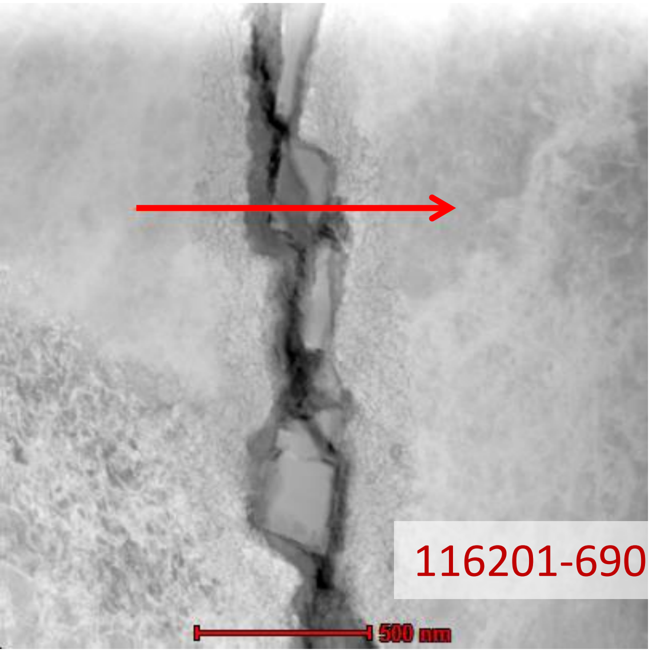
TEM – 690TT – PbO – pH_T 4 – liquid phase

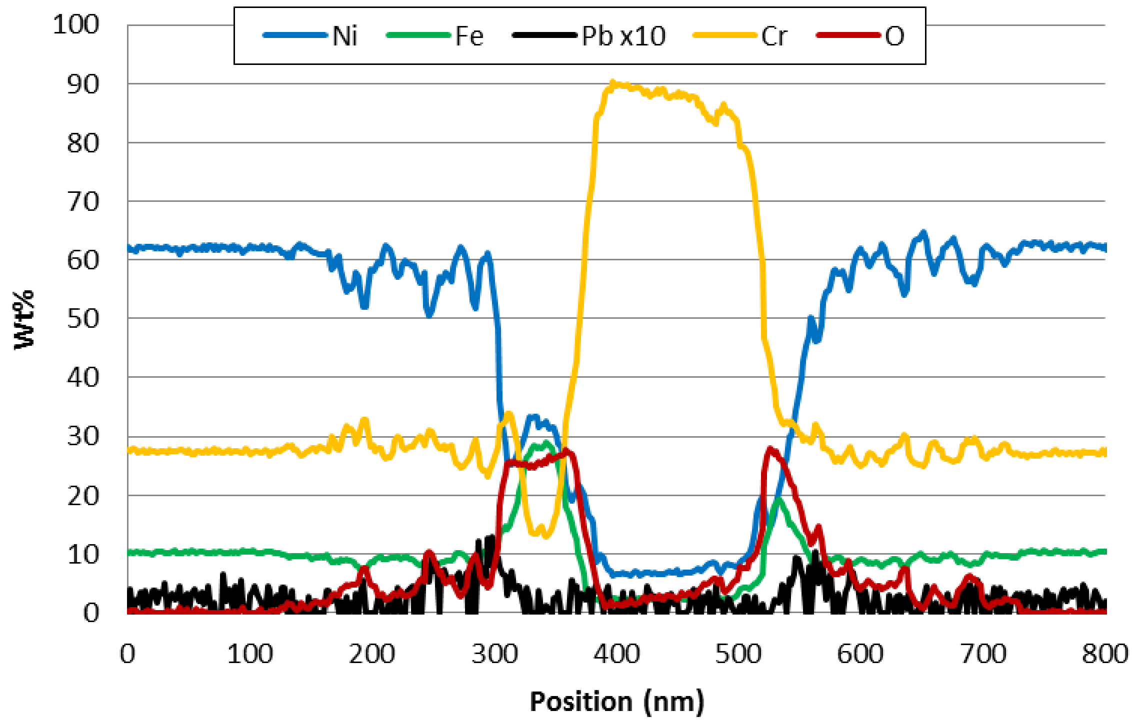
- EDX – ChemiSTEM of the crack



- « Pure » Cr clusters (No C)
  - ~85-90% Cr, other: Fe and Ni strongly depleted
    - Metallic clusters – no oxides nor carbides
  - **Presence of O and Pb (1.5 – 2 wt%** around both crack and Cr rich clusters)

TEM – 690TT – $PbSO_4$ – pH_T 4 – liquid phase





- « Pure » Cr clusters
  - Surrounded by oxides
  - Alloy disturbances prior to oxidation

- Pb at the metal/oxide interface
  - ~1% wt of Pb

Conclusions (1/2)

↗ IRSN performed corrosion tests on SG tube alloys

- In typical local secondary side environments
  - Based on opex from 20 years of sludge analysis
  - pH_T in the range quoted by utilities, 4, 7 and 9
- Two goals
  - Identifying domains of vulnerabilities in « typical » chemistries
  - Understanding potential damage mechanisms
- pH_T 4
  - All alloys suffer from corrosion
  - **GC, IGA and IGSCC** (IGSCC only for 690TT)
  - Alloy 690TT is not immune and IGSCC (no TG) could be encountered, even with S alone (no Pb)
- pH_T 7.5 and 9
  - Pending results - Already 600MA and 600TT susceptible at pH_T 7.5

Conclusions (2/2)

- Examinations confirm the involvment of Pb and S in the currently observed damage
  - 2 potential mechanims currently assumed
    - Research work going on

- Tests performed identify potential risks
  - Confirmed by OPEX (600TT)
  - Increase the available knowledge for assessing the risk of currently operating components