Supplement of Saf. Nucl. Waste Disposal, 2, 41–41, 2023
https://doi.org/10.5194/sand-2-41-2023-supplement

Supplement of

The anaerobic corrosion of the carbon steel overpack under anoxic alkaline conditions representing the Belgian supercontainer concept

Roberto Gaggiano

Correspondence to: Roberto Gaggiano (r.gaggiano@nirond.be)

ONDRAF/NIRAS

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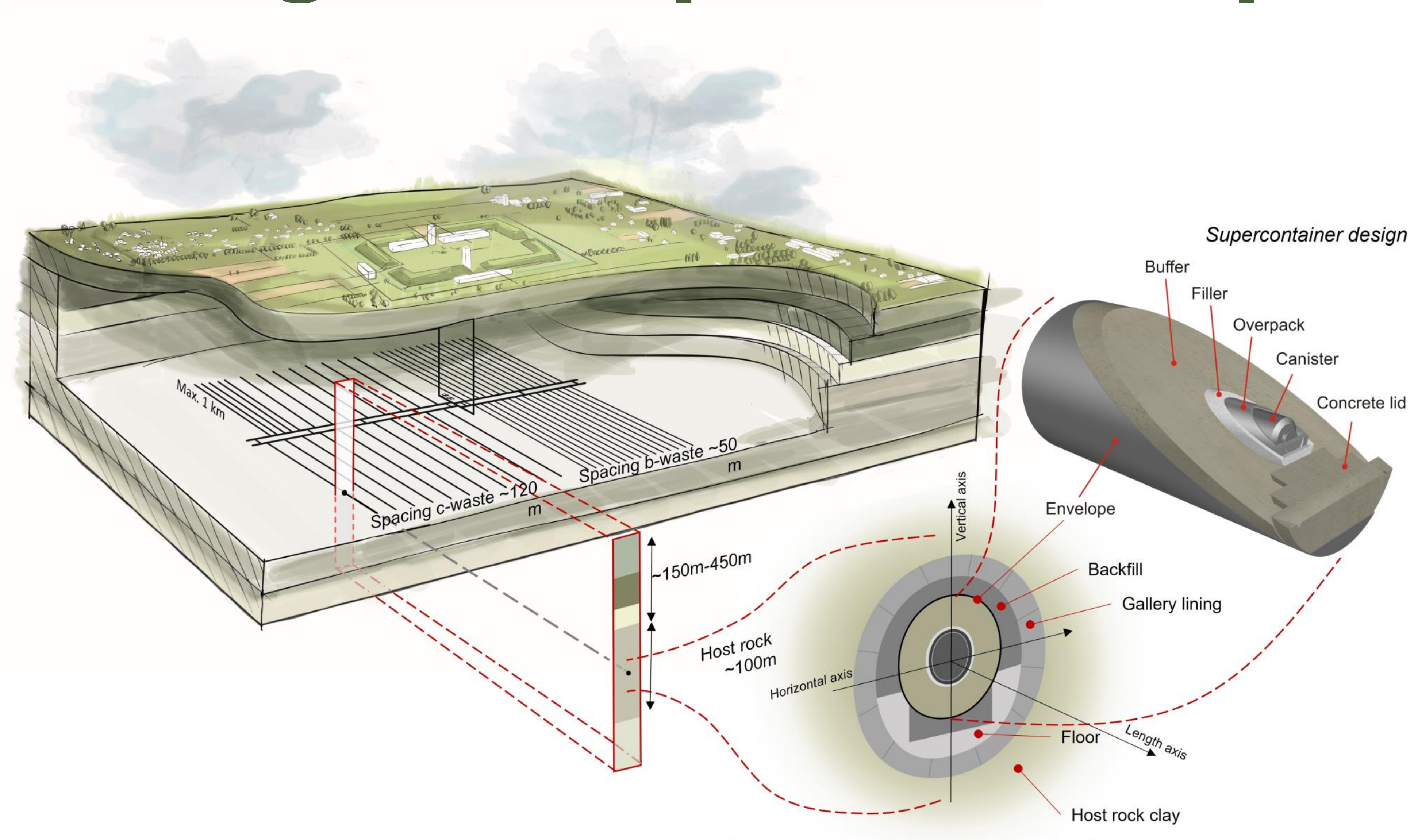
R. Gaggiano

12/09/2023

Geological disposal concept



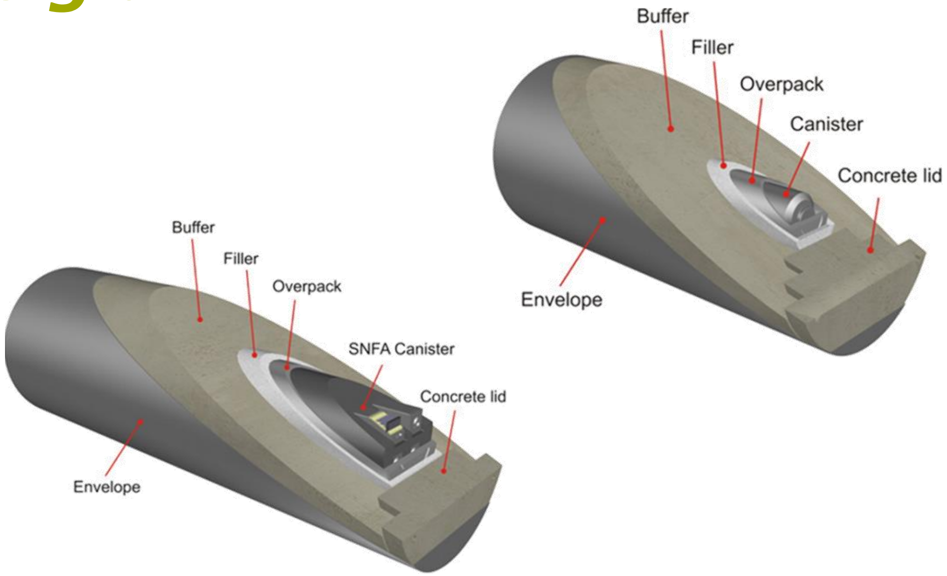
Vertical cross-section of the disposal gallery for C-waste

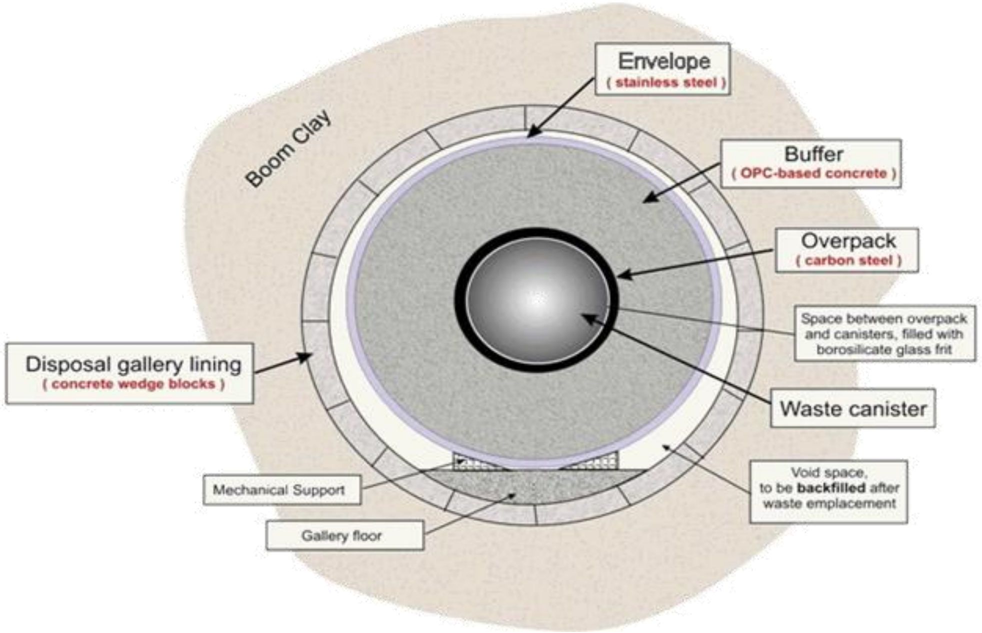
Design 2020 – ONDRAF/NIRAS ©

The ‘Supercontainer’ design

Reference disposal concept in Belgium

- Carbon steel **overpack** containing either vitrified HLW canisters or spent fuel assemblies
- The overpack is surrounded by a OPC-based concrete **buffer**



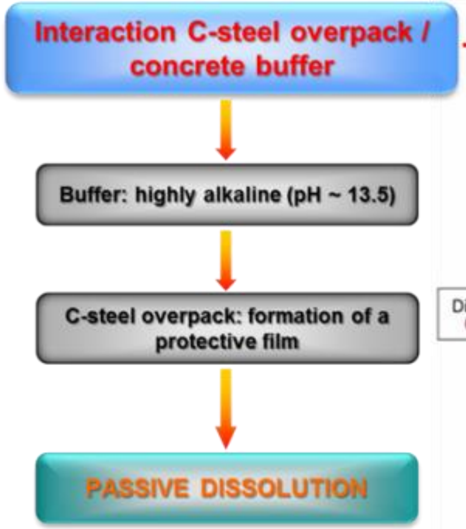


- The cylindrical cavity between the overpack and the concrete buffer is filled with a cementitious filler
- The concrete buffer is enterily encased in a stainless steel **envelope.**

Corrosion programme: RD&D methodology and research activities

Contained Environment Concept

- Aim: to fix and preserve a favourable chemical environment in the immediate vicinity of the overpack for a long time, at least for the duration of the thermal phase

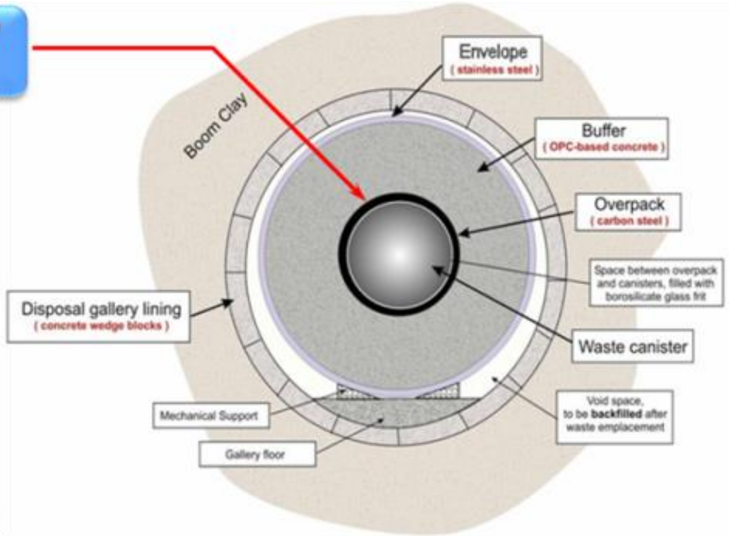


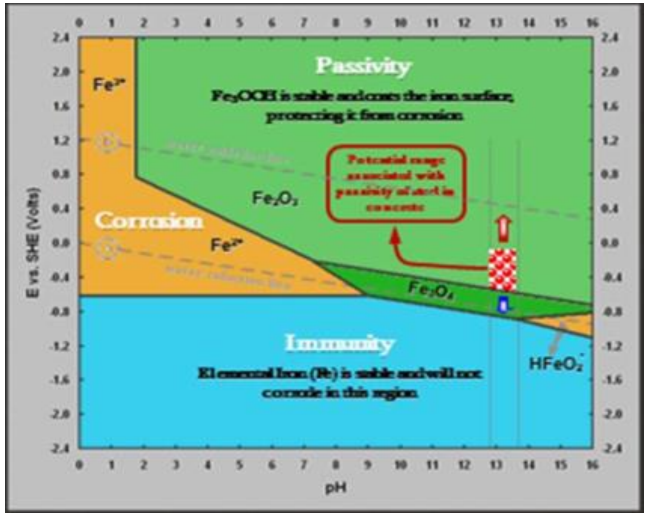
Interaction C-steel overpack / concrete buffer

Buffer: highly alkaline (pH ~ 13.5)

C-steel overpack: formation of a protective film

PASSIVE DISSOLUTION





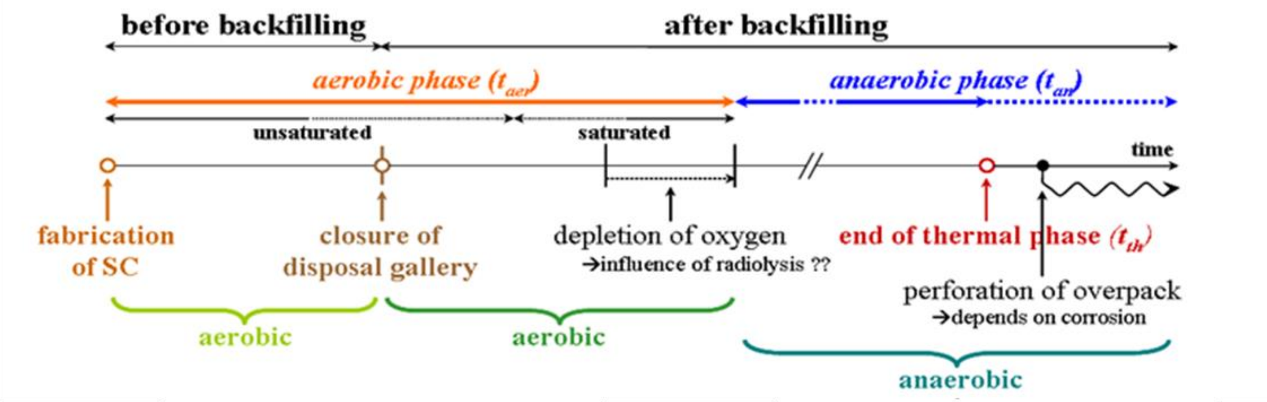
- The main goal of the ongoing RD&D corrosion studies is to **provide confidence that the integrity of the carbon steel overpack will not be jeopardized at least for the duration of the thermal phase.**

Long-term safety function C-steel overpack

RD&D methodology

Integrated 3-step approach

1. Development of the Corrosion Evolutionary Path



2. Determining reliable uniform corrosion rate data

- Reliable estimate of the uniform corrosion rate for the different phases of the CEP
- Lifetime predictions (i.e., the reduction in wall thickness in µm/year)

$$d_{overpack} = \sum v_i \cdot t_i$$

- Evolution of the passive film with time

3. Proving the validity of the 'exclusion principle'

- Any other form of corrosion cannot occur
  - ⇨ Pitting corrosion
  - ⇨ Stress corrosion cracking

Research activities

Uniform corrosion

- **Measurement of H_2 generated during the anoxic corrosion of carbon steel** $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$
- 4 independent techniques:
    - Barometric glass gas cells
    - Autoclaves equipped with pressure transducers
    - Solid-state hydrogen sensor
    - Electrochemical measurements

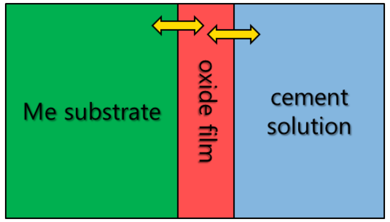
Pitting corrosion

- **Study of chloride pitting of carbon steel**
    - Potentiodynamic polarization measurements
    - Modelling of the results and long-term prediction by means of the Point Defect Model and the Mixed Potential Model.

Passive oxide film

- **Study of the characteristics and evolution of the passive film**

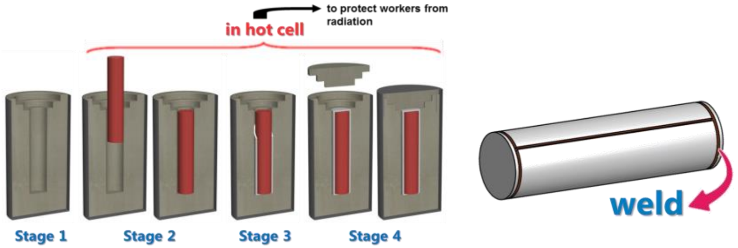
  → electrochemical techniques and surface analysis



Stress corrosion cracking

- **Study the SCC susceptibility of plain and welded C-steel** exposed to alkaline media (YCW, pH ~13.5) under anoxic conditions

  → Slow Strain Rate Tests



Radiolysis of the buffer

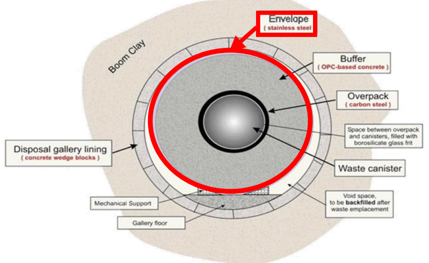
- Modellling of the radiolysis of water in the concrete buffer

→ Equilibria in solution

→ Hydrogen produced by radyolisis

Envelope

- Electrochemical screening of possible construction materials exposed to highly alkaline media.



Current status Belgian RD&D corrosion programme

Uniform corrosion

Results - volumetric method

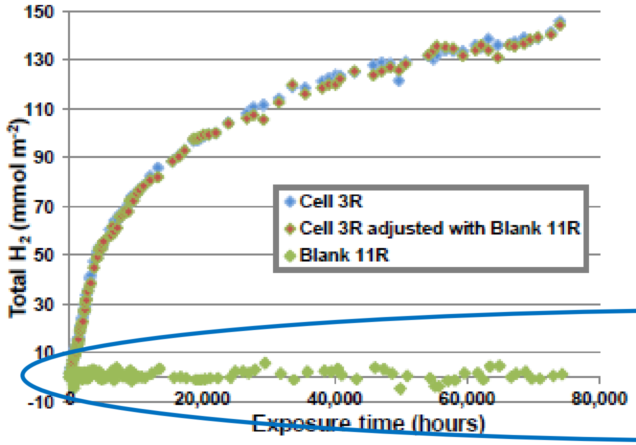
(Limit of detection: ~100 nm/y)

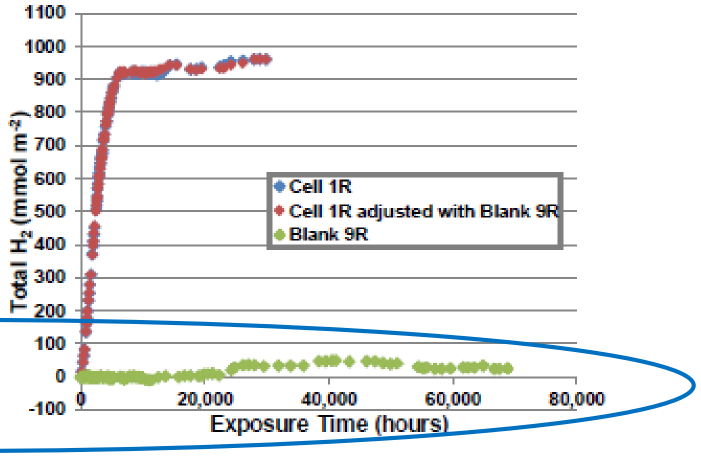
Boundary conditions:
[Cl^-]: 100 mg/L
[S^{2-}]: 500 mg/L
[$S_2O_3^{2-}$]: 100 mg/L
T = 25°C, 50°C, 80°C
γ = 25 Gy/h

25°C

80°C

unirradiated

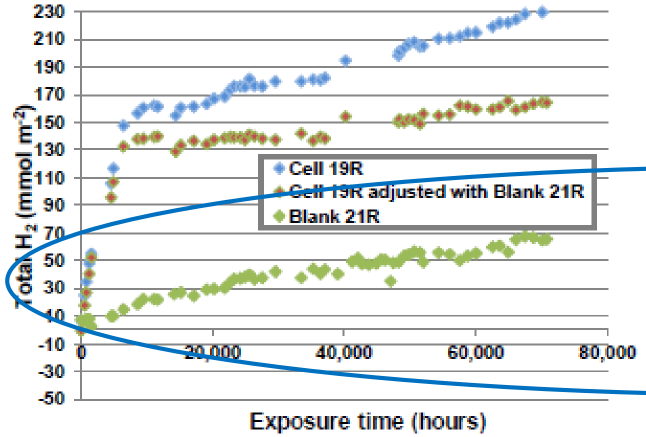


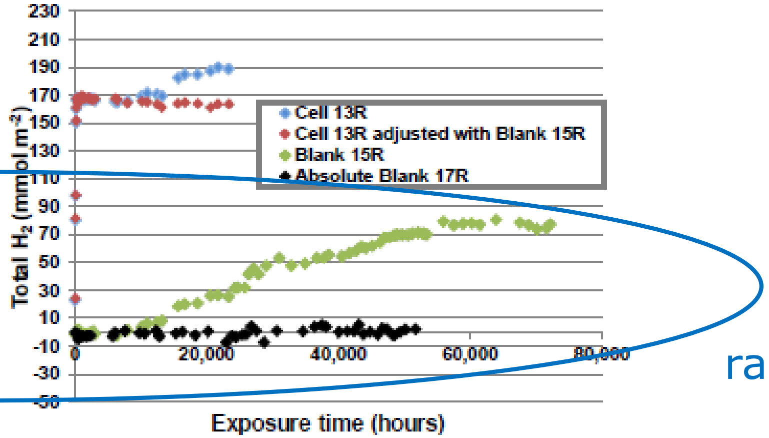


Increase in gas generation steeper in irradiated cells over initial period

no radiolysis or other degassing process

irradiated





radiolysis

Uniform corrosion

Results - volumetric method

Boundary conditions:
[Cl^-]: 100 mg/L
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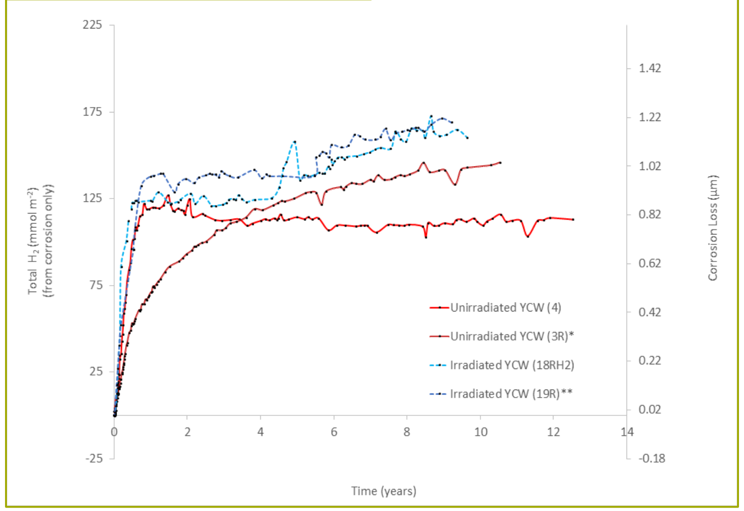
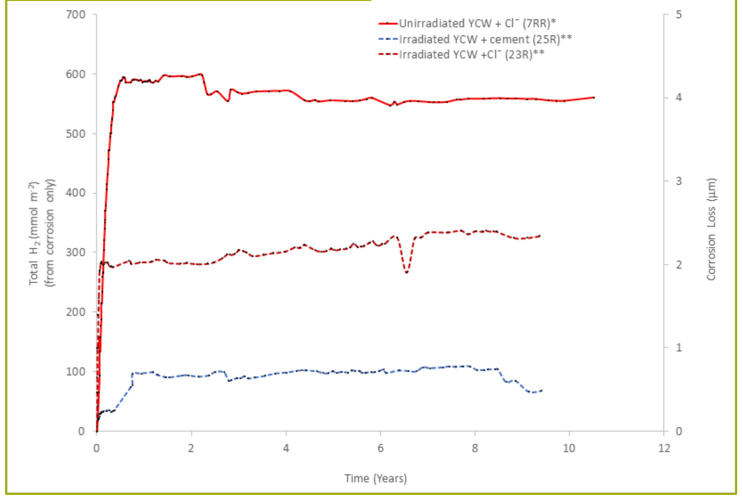
[$S_2O_3^{2-}$]: 100 mg/L
T = 25°C, 50°C, 80°C
γ = 25 Gy/h

Pickled, 25 °C



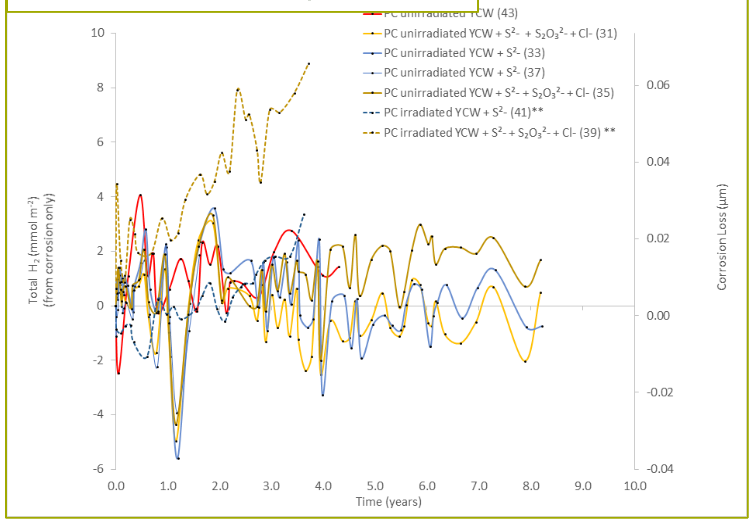
- Irradiated YCW corrosion rate past 5 years = **0.045 µm/year**
- Unirradiated YCW corrosion rate past 5 years = **0.025 µm/year**

Pickled, 80 °C



- For all unirradiated cells the total gas generation is immeasurably small
- Irradiated YCW +S^{-2} +$S_2O_3^{2-}$+Cl^- corrosion rate over all 4 years = **0.013 µm/year**
- Irradiated YCW +S^{-2} corrosion rate over all 4 years **< 0.01 µm/year**

Pre-corroded, 25 °C



- Irradiated YCW +Cl- corrosion rate past 5 years = **0.048 µm/year**
- Steady state corrosion rate is comparable to that measured at 25 °C
- Total gas generation is greater than at 25 °C and is due to initial corrosion rate

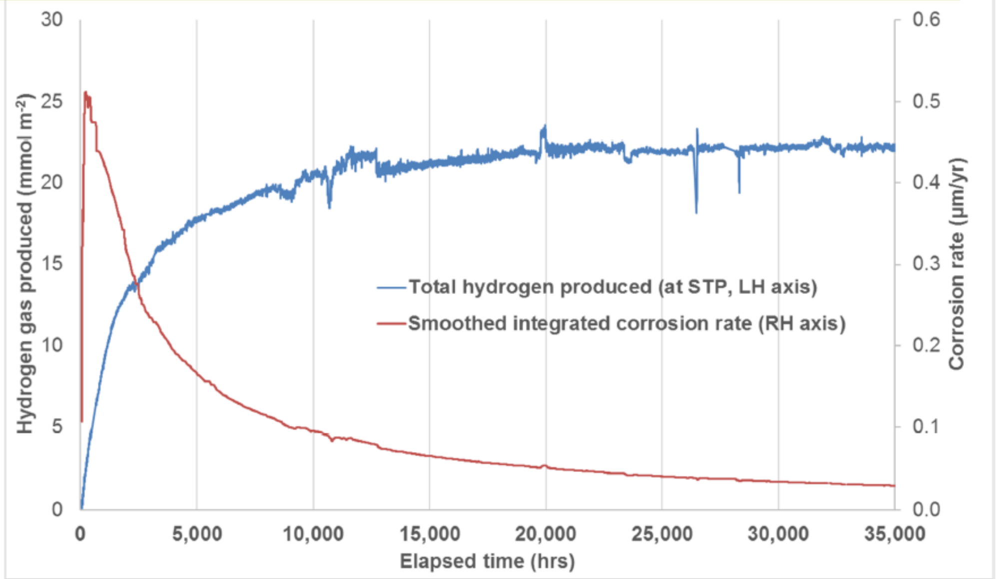
Uniform corrosion

Results: autoclaves with pressure transducer

Boundary conditions:
[Cl$^-$]: 100 mg/L
[S^{2-}]: 500 mg/L
[S$_2$O$_3$$^{2-}$]: 100 mg/L
T = 25°C, 50°C, 80°C
γ = 25 Gy/h

(Limit of detection: <1 nm/year)

YCW + 500 mg/l S2-, pre-corroded, 25 °C

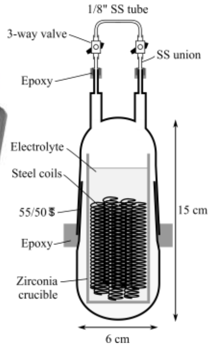


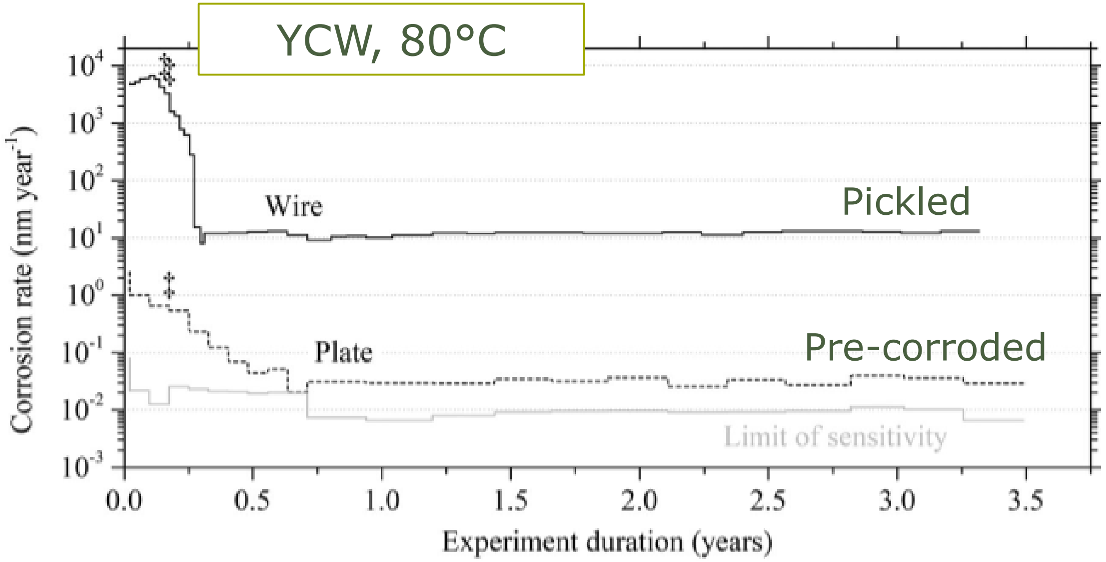
After approximately one year's exposure the corrosion rate had dropped to less than **0.03 µm/year** (still decreasing)

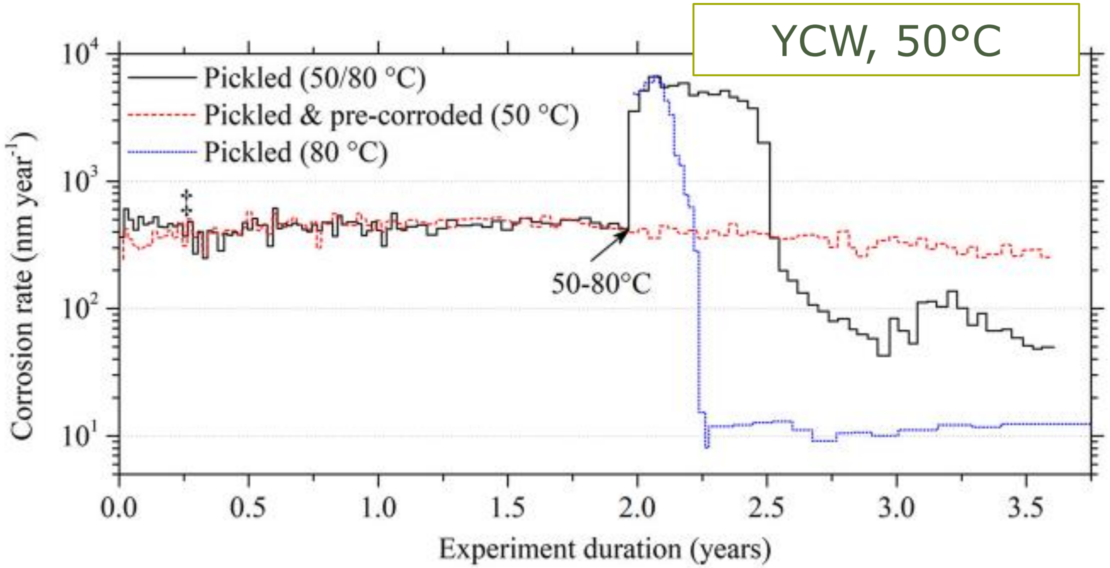
Currently transferring all glass cell experiments (operating >10 years) to autoclaves.

Uniform corrosion

Results – hydrogen sensor *(Detection limit: ~0.01 nm/y)*







- Effect of the steel composition/form
- **Wire** corrodes at **10 nm/year**
- **Plate** corrodes at **0.03 nm/year**

composition

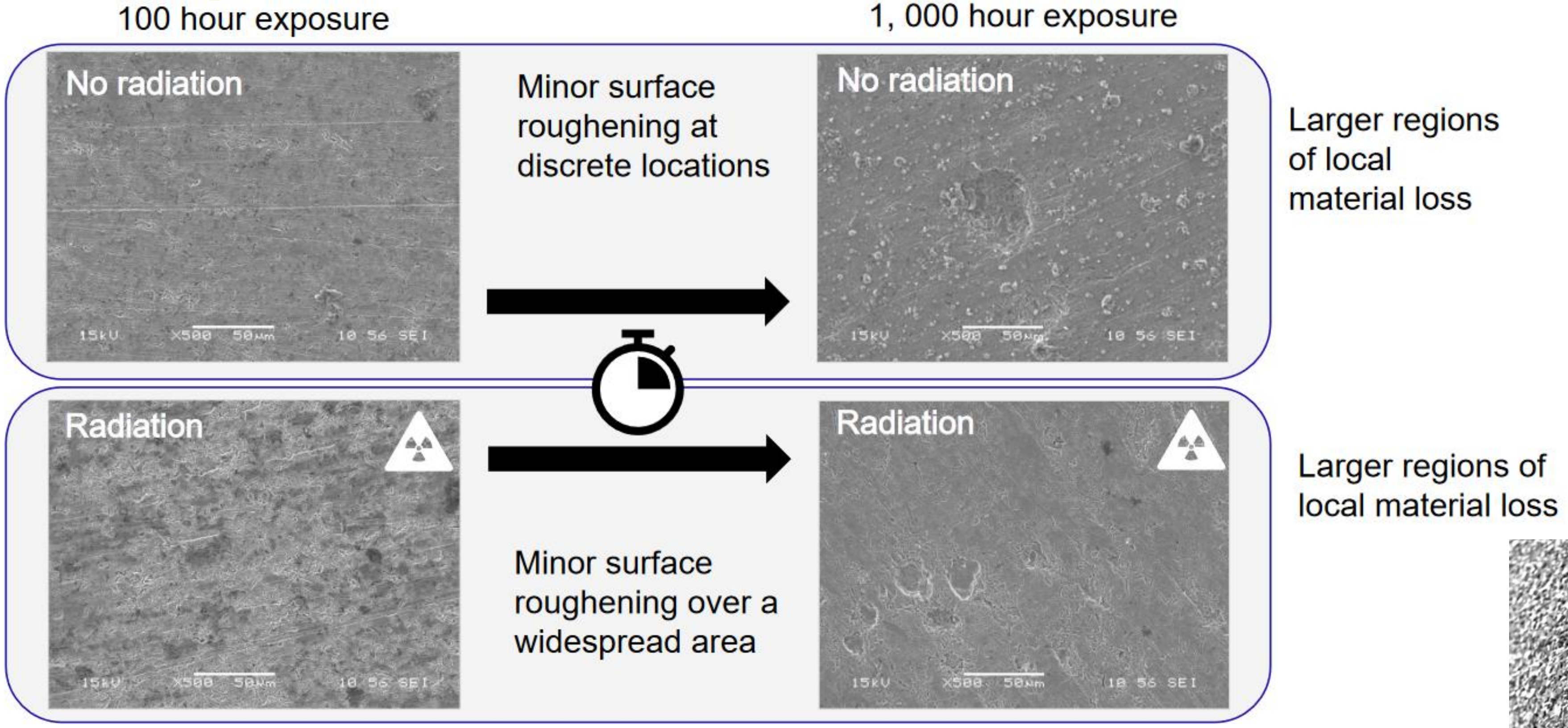
microstructure

form

- **Effect of temperature on passivation?**
- 50°C → unexpectedly high corrosion rate
- Exactly same conditions as a previous cell at 80 °C, corroding at 10 nm/yr.
- Temperature change to 80°C → lower LT corrosion rate

Oxide film characterization

Exposure to YCW



100 hour exposure

1, 000 hour exposure

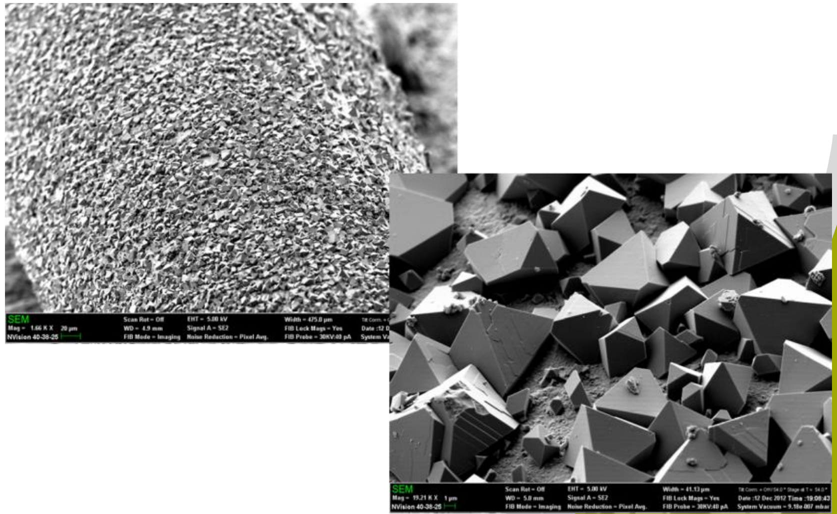
Minor surface roughening at discrete locations

Larger regions of local material loss

Minor surface roughening over a widespread area

Larger regions of local material loss

The outer surface of the film changed from mixed maghemite/ magnetite to pure magnetite from 100 to 1000 hours exposure

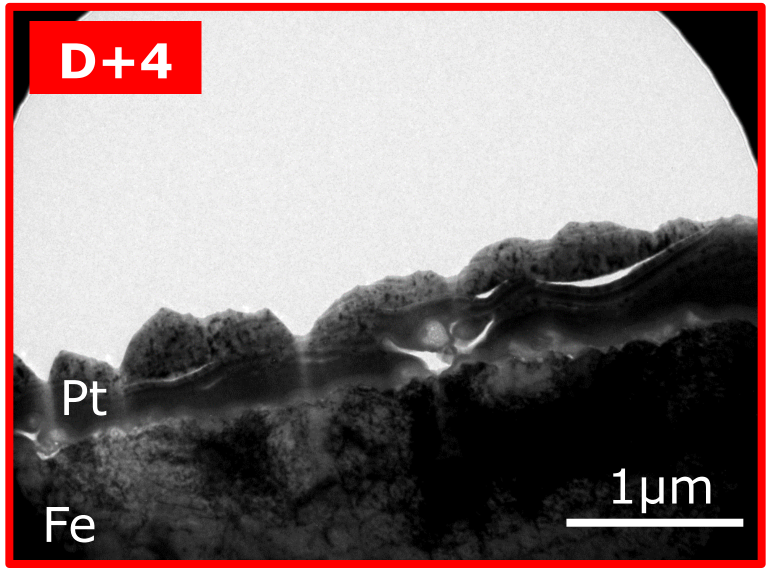


- In the long-term corrosion products predominantly composed of **magnetite**
- Thickness corrosion product layer ~ 2-3 µm (after ~ 5 years)

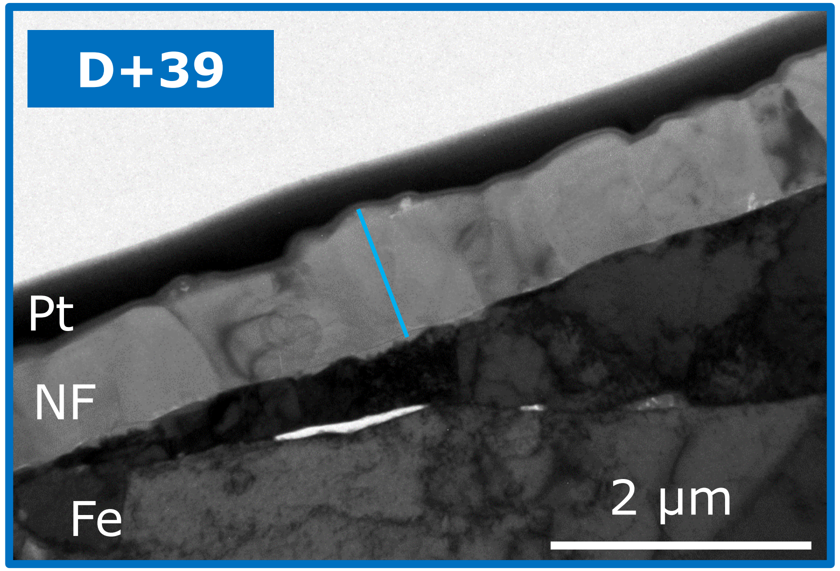
Oxide film characterization

Exposure to cementitious solutions

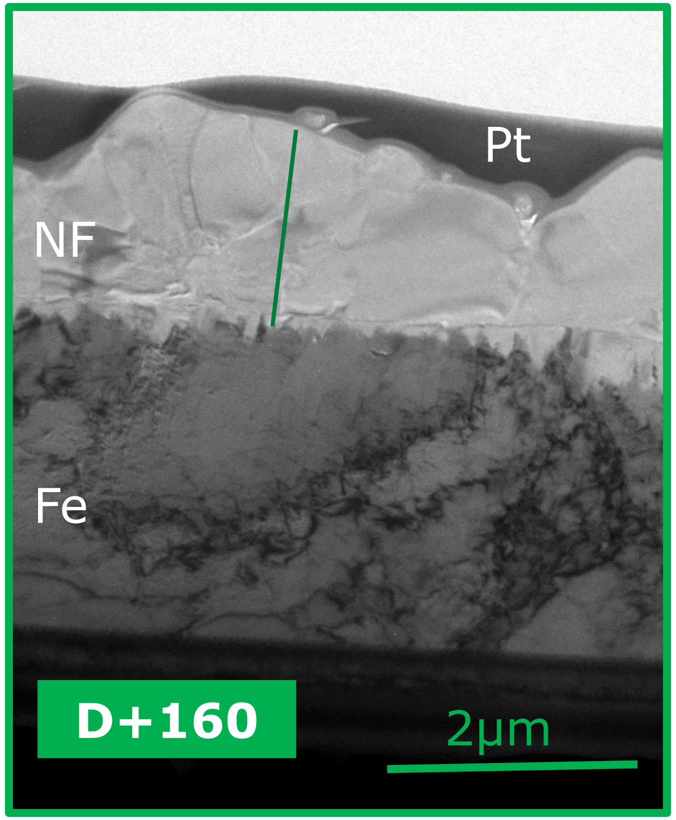
TEM measurements



D+4 : Layer too thin to be observed



D+39 : Outer layer = 1 µm
Inner layer = 0.1 µm
Border at the interface.



D+160 : Outer layer =1,3 µm
Inner layer = 0,2 µm
Border at the interface
(nanometric)

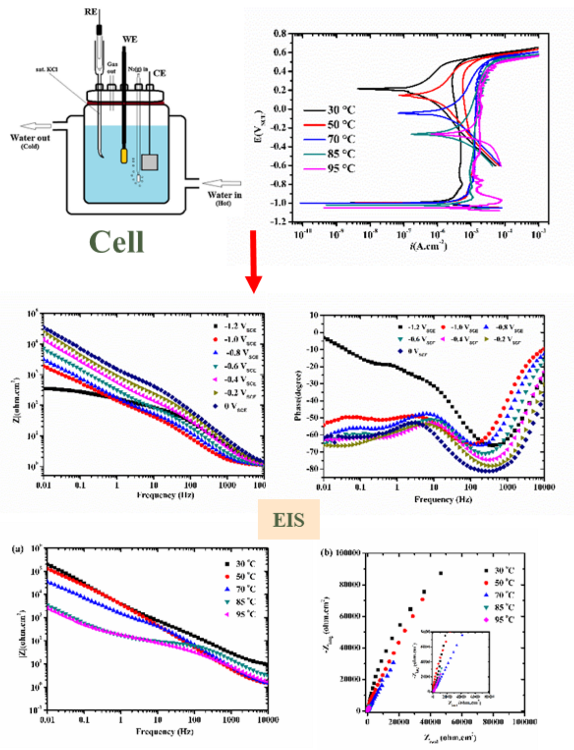
- Bi-layer structure
- More complex composition than the corrosion products in YCW: outer and inner layer are composed of calcium, silicon, iron and oxygen (and traces of aluminum).

Pitting corrosion

Experimental details

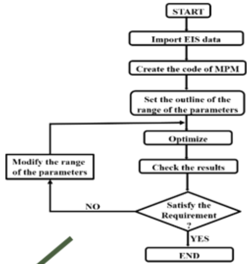
- **Experiments**

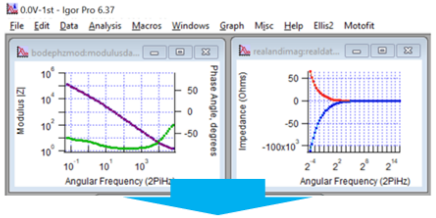
EIS data:



Optimization process

Igor Pro Software



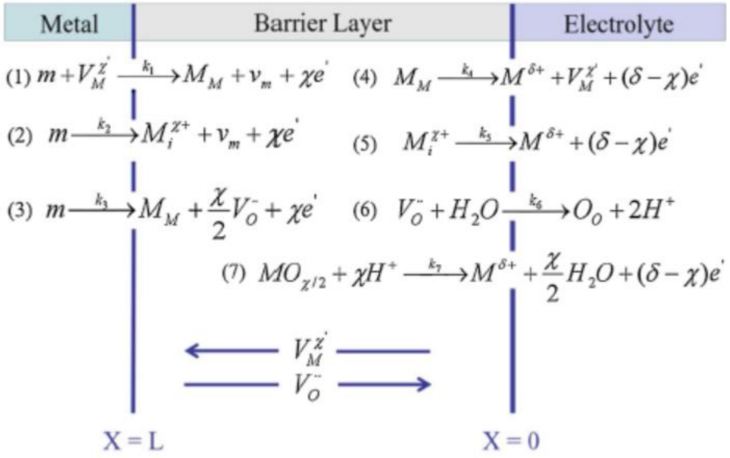


Parameter values after optimization of the mixed potential model on the experimental impedance data for carbon steel in the SCPS with 0.1 M NaCl at 30 °C (pH = 13.3, 30 °C) at different applied potentials.

Potential	−1.2 V_{SCE}	−1.0 V_{SCE}	−0.8 V_{SCE}	−0.6 V_{SCE}	−0.4 V_{SCE}	−0.2 V_{SCE}	0 V_{SCE}
α	0.25	0.26	0.25	0.25	0.24	0.26	0.25
$k_2^{00}(mol\ cm^{-2}\ s^{-1})$	7.56×10^{-7}	7.46×10^{-7}	6.36×10^{-7}	4.36×10^{-7}	7.42×10^{-7}	9.64×10^{-7}	7.36×10^{-7}
$k_3^{00}(mol\ cm^{-2}\ s^{-1})$	2.72×10^{-7}	2.52×10^{-7}	2.78×10^{-7}	2.66×10^{-7}	4.32×10^{-7}	5.05×10^{-7}	3.52×10^{-7}
$k_7^{00}(mol\ cm^{-2}\ s^{-1})$	7.12×10^{-7}	7.12×10^{-7}	5.56×10^{-7}	7.12×10^{-7}	6.69×10^{-7}	6.13×10^{-7}	6.12×10^{-7}
$k_2(mol\ cm^{-2}\ s^{-1})$	1.68×10^{-13}	1.82×10^{-13}	1.74×10^{-13}	1.65×10^{-13}	1.59×10^{-13}	1.60×10^{-13}	1.75×10^{-13}
$k_3(mol\ cm^{-2}\ s^{-1})$	1.58×10^{-13}	1.59×10^{-13}	1.24×10^{-13}	1.59×10^{-13}	1.49×10^{-13}	1.37×10^{-13}	1.37×10^{-13}
$k_7(mol\ cm^{-2}\ s^{-1})$	7.12×10^{-7}	7.12×10^{-7}	5.56×10^{-7}	7.12×10^{-7}	6.69×10^{-7}	6.13×10^{-7}	6.12×10^{-7}
$\varepsilon\ (V.cm^{-1})$	3×10^6	3×10^6	3×10^6	3×10^6	3×10^6	3×10^6	3×10^6
σ	69283	70000	65983	76560	70000	75632	75981
$C_i^0(cm^{-3})$	1.01×10^{20}	4.81×10^{20}	5.47×10^{20}	6.53×10^{20}	4.58×10^{20}	3.96×10^{20}	3.41×10^{20}
C_O^0????(cm^{-3})	1.86×10^{19}	4.16×10^{19}	4.74×10^{19}	7.73×10^{19}	1.40×10^{20}	1.31×10^{20}	1.48×10^{19}
$D_i\ (cm^2 s^{-1})$	5.22×10^{-18}	5.80×10^{-1}[illegible]	4.[illegible] $\times 10^{-18}$	9.90×10^{-18}	5.00×10^{-18}	5.16×10^{-18}	5.49×10^{-18}
L_{ss}(nm)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
$\hat{i}_0(A/cm^2)$	1.78×10^{-7}	1.58×10^{-7}	1.8 × 10[illegible]	1.34×10^{-7}	1.62×10^{-7}	1.80×10^{-7}	1.49×10^{-7}
$i_0(A/cm^2)$	8.10×10^{-8}	7.19×10^{-8}	8.19×10^{-8}	6.10×10^{-8}	7.38×10^{-8}	8.21×10^{-8}	5.21×10^{-8}
$i_{HER}(A/cm^2)$	-6.84×10^{-7}	1.02×10^{-9}	1.07×10^{-7}	1.80×10^{-7}	3.73×10^{-7}	6.77×10^{-7}	7.46×10^{-7}
$i_{HER,a}(A/cm^2)$	3.95×10^{-8}	7.11×10^{-8}	1.41×10^{-7}	1.84×10^{-7}	3.74×10^{-7}	6.77×10^{-7}	7.46×10^{-7}
$i_{HER,c}(A/cm^2)$	-7.31×10^{-7}	-7.00×10^{-8}	-3.53×10^{-8}	-3.45×10^{-9}	-1.33×10^{-9}	-3.91×10^{-10}	-9.94×10^{-11}
$i_{ss}(A/cm^2)$	9.47×10^{-8}	9.86×10^{-8}	8.64×10^{-8}	9.39×10^{-8}	8.92×10^{-8}	8.61×10^{-8}	9.01×10^{-8}

For example: Optimization parameters

Extrapolation of the long-term behavior by means of the MPM



(1) $m + V_M^{\chi'} \xrightarrow{k_1} M_M + v_m + \chi e'$

(2) $m \xrightarrow{k_2} M_i^{\chi+} + v_m + \chi e'$

(3) $m \xrightarrow{k_3} M_M + \frac{\chi}{2} V_O^{\cdot\cdot} + \chi e'$

(4) $M_M \xrightarrow{k_4} M^{\delta+} + V_M^{\chi'} + (\delta - \chi)e'$

(5) $M_i^{\chi+} \xrightarrow{k_5} M^{\delta+} + (\delta - \chi)e'$

(6) $V_O^{\cdot\cdot} + H_2O \xrightarrow{k_6} O_O + 2H^+$

(7) $MO_{\chi/2} + \chi H^+ \xrightarrow{k_7} M^{\delta+} + \frac{\chi}{2} H_2O + (\delta - \chi)e'$

$\xleftarrow{\quad} V_M^{\chi'}$

$V_O^{\cdot\cdot} \xrightarrow{\quad}$

Butler-Volmer Equation

Hydrogen electrode reaction:

$$H_2 + 2OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2H_2O + 2e^- \longrightarrow i_{HER} = \frac{e^{2.303\eta/b_a} - e^{-2.303\eta/b_c}}{\frac{1}{i_0} + \frac{e^{2.303\eta/b_a}}{i_{l,f}} - \frac{e^{-2.303\eta/b_c}}{i_{l,r}}}$$

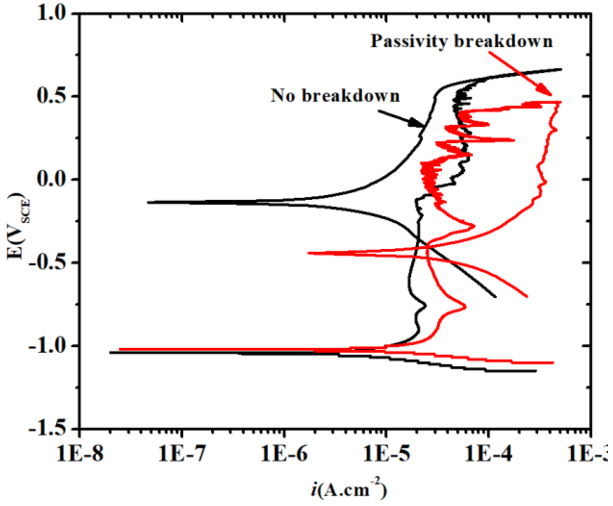
Cathodic impedance:

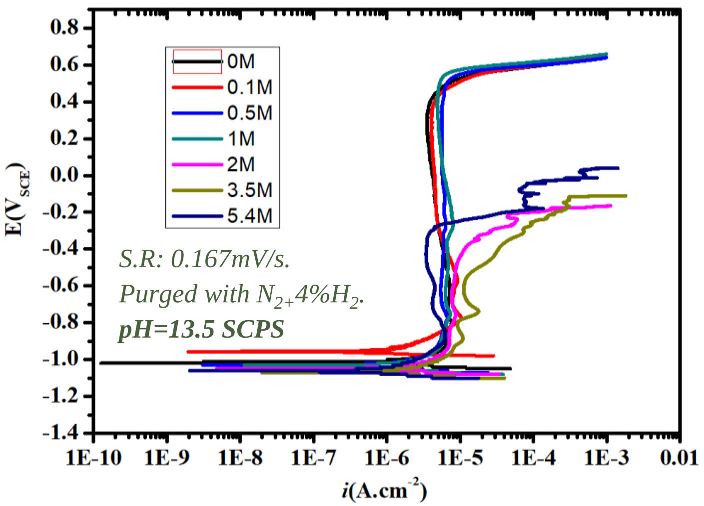
$$Y_{HER} = \frac{di_{HER}}{dE} = \frac{DN' - ND'}{D^2}$$

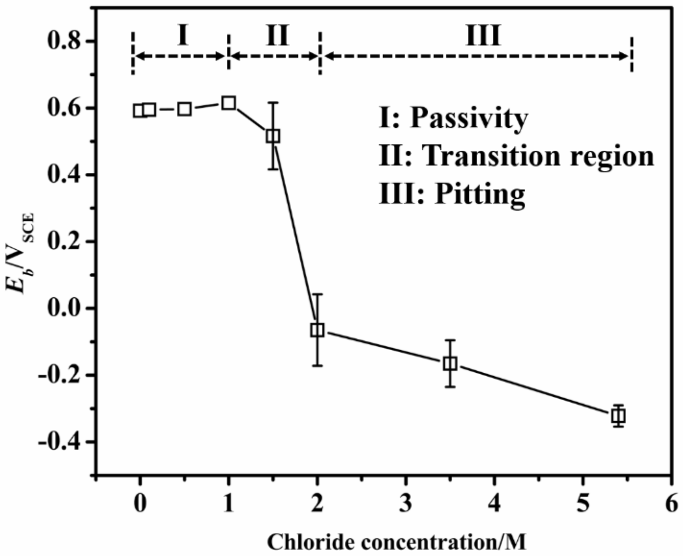
Focus on chloride pitting
No other aggressive species are taken into account

Pitting corrosion

Effect of chloride





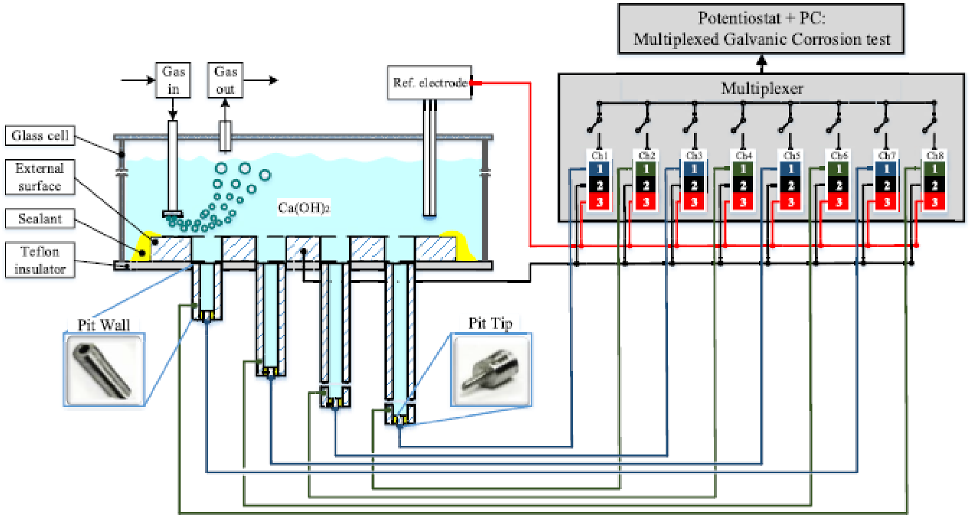


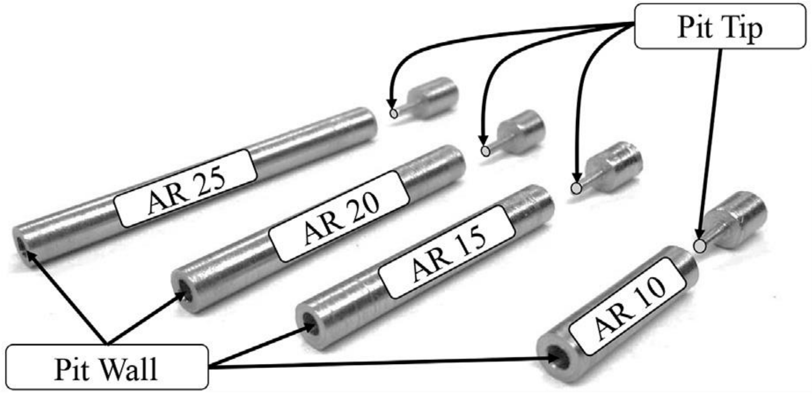
- **The breakdown potential (E_b) decreases with increasing chloride concentration.**
- **Cl^- <1M**, no passivity breakdown occurs on carbon steel in SCPS.
- **Cl^- >2M**, pitting corrosion occurs. The E_b decreases with increasing chloride concentration.
- When the Cl- of SCPS is 1.5M, passivity breakdown occurs at random, indicating that **1.5M is the Cl^- concentration for the transition of carbon steel from passivity to passivity breakdown in simplified concrete pore solution.**

Pitting corrosion

Artificial pit experiment

- **Experimental confirmation that, even if pits nucleate in the oxic period, they cannot maintain differential aeration during the anoxic period → no further pit activation**
- **The pit cavity becomes polarity inverted,**
  → hydrogen evolution occurs within the cavity
  →(metal oxidation) occurs on the external surface
- **The solution within the cavity is expected to become more alkaline** than the external environment and
- **Cations (e.g., Na⁺) are preferentially transported into the pit and chloride ejected from the pit**.



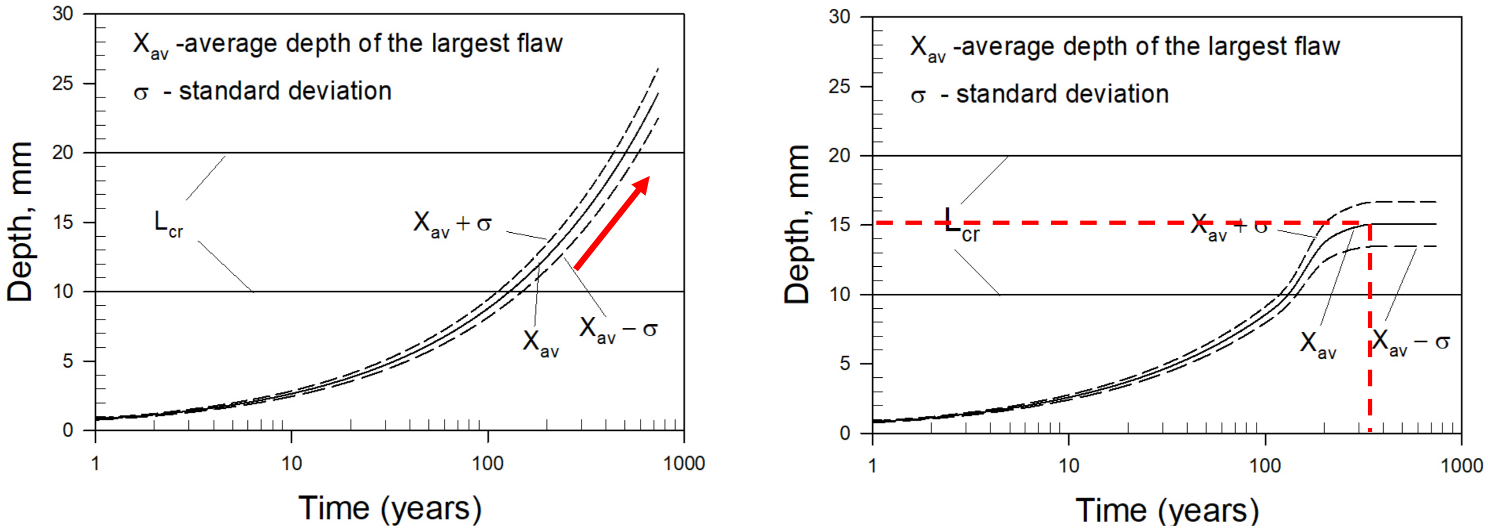


Long-Term modelling approach

- **Deterministic Monte Carlo Simulation**: keep track of each stable pit that nucleates, propagates, and repassivates on the metal surface.
  - →Simulation of the following processes
    - →**Pit nucleation rate**
    - →**Pit propagation rate**
    - →**Probability of pit repassivation**

Assumption:
Pit nucleation occurs immediately after metal exposure, during the high temperature, oxic period.

Average depth of the deepest pit as a function of time



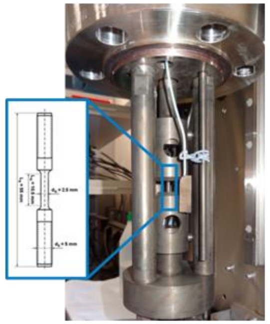
No repassivation considered

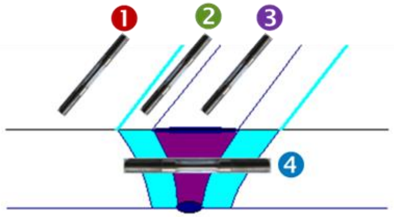
Repassivation considered

Pitting represents no threat to the integrity of the overpack
(if corrosion allowance = 15 mm)

Stress corrosion cracking (welds)

- SSRT tests were conducted on base and welded samples:
  - Base and welded samples (SAW, MIG/MAG, RPEB)
  - Anoxic conditions
  - T = 140°C
  - Open circuit potential/applied potential
  - YCW (pH 13.5)
    (in the presence or absence of agressive species)





- SSRT tests at OCP and at applied potential:
  - **OCP**: **no increased SCC susceptibility**, typical stress-strain behaviour of a ductile material.
  - **Applied potential**: so far, the potential **does not seem to have a significant effect on the SCC susceptibility** and the stress-strain behaviour of carbon steel in high pH solutions.

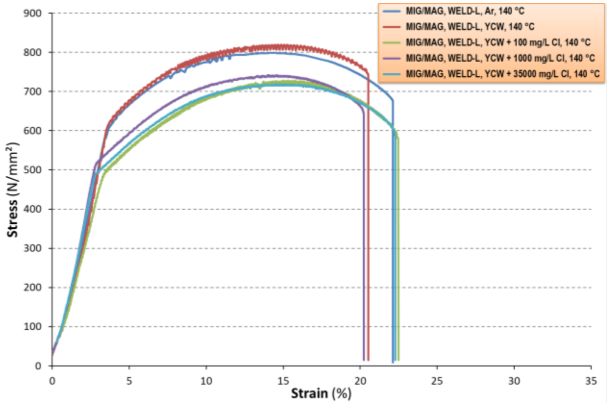
Stress corrosion cracking (welds)

Typical results

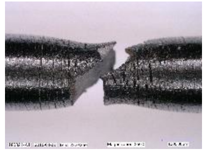
MIG/MAG welding

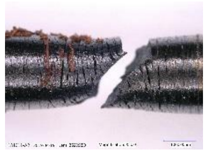
WELD-L

Longitudinal



Condition	YS (MPa)	UTS (MPa)	EaF (%)	TTF		RA	
				(hours)	TTFR	(%)	RAR
Ar	567.0	798.0	22.1	124.7		47.3	
YCW	605.0	816.0	20.5	116.0	0.93	37.8	0.80
YCW + 100 mg/L Cl^-	492.0	725.9	22.5	124.9	1.01	43.4	0.92
YCW + 1000 mg/L Cl^-	522.2	740.3	20.2	112.5	0.90	32.3	0.68
YCW + 35000 mg/L Cl^-	491.7	717.7	22.0	122.2	0.98	33.9	0.72

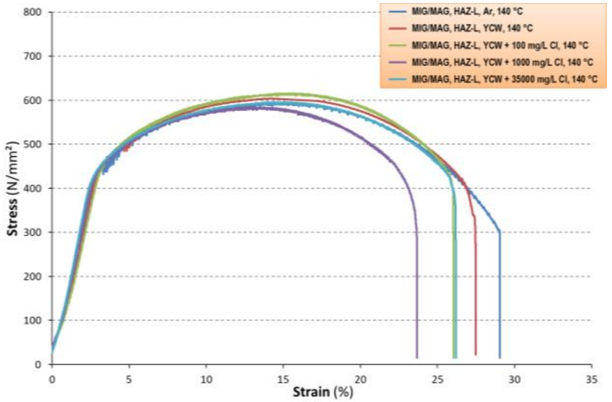

100 mg/L Cl$^-$


1,000 mg/L Cl$^-$

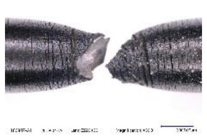

35,000 mg/L Cl$^-$

HAZ-L

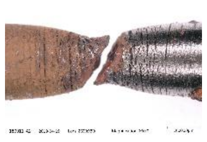
Heat-affected zone - Longitudinal



Condition	YS (MPa)	UTS (MPa)	EaF (%)	TTF		RA	
				(hours)	TTFR	(%)	RAR
Ar	403.0	592.0	29.1	163.4		82.6	
YCW	424.0	603.0	27.5	154.6	0.95	67.3	0.81
YCW + 100 mg/L Cl^-	437.0	614.5	26.5	147.4	0.90	60.6	0.73
YCW + 1000 mg/L Cl^-	406.3	582.5	23.7	131.4	0.80	59.7	0.72
YCW + 35000 mg/L Cl^-	404.1	594.5	26.2	145.5	0.89	60.6	0.73

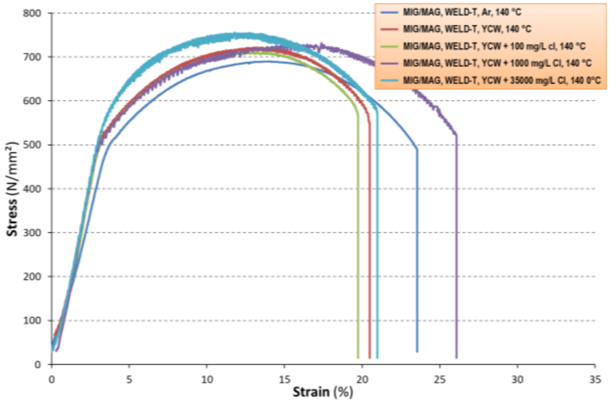

100 mg/L Cl$^-$


1,000 mg/L Cl$^-$

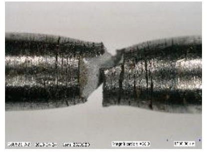

35,000 mg/L Cl$^-$

WELD-T

Transversal



Condition	YS (MPa)	UTS (MPa)	EaF (%)	TTF		RA	
				(hours)	TTFR	(%)	RAR
Ar	503.0	690.0	23.5	133.8		64.1	
YCW	507.0	719.3	21.0	116.6	0.87	48.6	0.76
YCW + 100 mg/L Cl^-	490.3	709.8	19.7	109.6	0.82	46.0	0.72
YCW + 1000 mg/L Cl^-	487.8	725.9	25.8	143.2	1.07	61.5	0.96
YCW + 35000 mg/L Cl^-	529.1	749.6	21.0	116.6	0.87	51.9	0.81

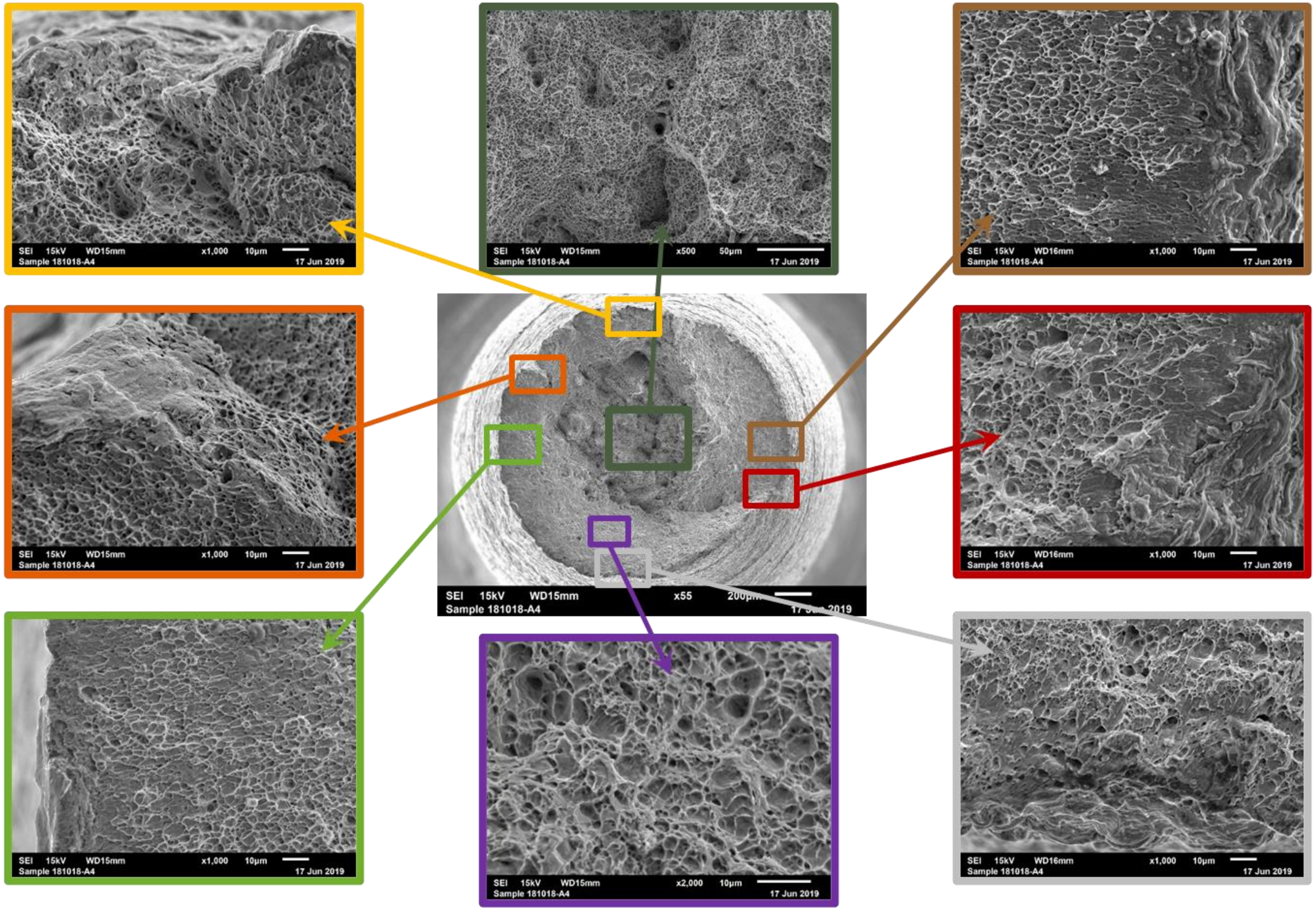

100 mg/L Cl$^-$


1,000 mg/L Cl$^-$


35,000 mg/L Cl$^-$

Stress corrosion cracking (welds)

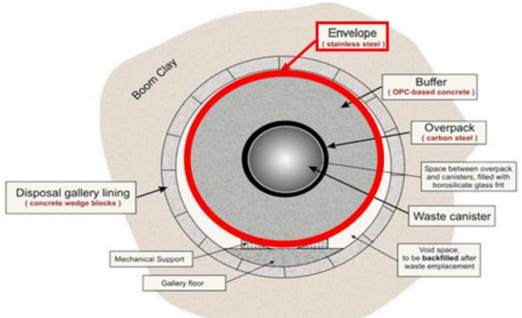
Typical results



SAW welding
longitudinal
1,000 mg/L

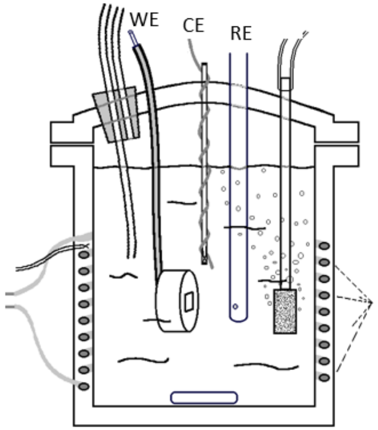
Envelope

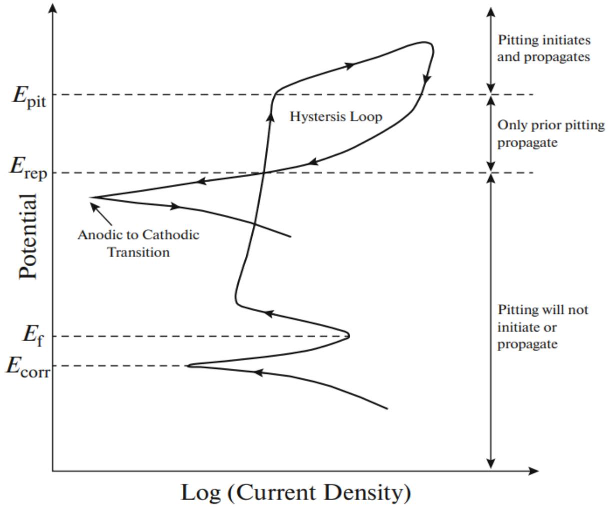
Selection of candidate materials



- List of candidate materials was studied (pitting and uniform corrosion behaviour

	Common denomination	UNS	Cr	Ni	Mo	C	N	Cu	Other	PREN
Austenitic →	316L	S31603	16-18	10-14	2-3	0.03	0.1	-	-	23
Nickel-based →	Alloy 825	N08825	19.5-23.5	38-46	2.5-3.5	0.05	-	1.5-3.5	Ti: 0.6-1.2	28
Nickel-based →	904L	N08904	19-23	23-28	4-5	0.02	-	1-2	-	32
Super Austenitic →	254 SMO	S31254	19.5-20.5	17.5-18.5	6-6.5	0.02	0.18-0.22	0.5-1	-	42
Nickel-based →	Al-6XN	N08367	20-22	23.5-25.5	6-7	0.03	0.18-0.25	0.75	-	43
Nickel-based →	Alloy 31	N08031	26-28	30-32	6-7	0.02	0.15-0.25	1-1.4	-	48
Lean Duplex →	LDX2304	S32304	21.5-24.5	3-5.5	0.05-0.6	0.03	0.05-0.2	-	-	22
Duplex →	DX2205	S31803	21-23	4.5-6.5	2.5-3.5	0.03	0.08-0.2	-	-	31
Super Duplex →	SDX2507	S32750	24-26	6-8	3-5	0.03	0.24-0.32	0.5	-	38
Super Duplex →	SDX100	S32760	24-26	6-8	3-4	0.03	0.2-0.3	0.5-1	W:0.5-1	37
Nickel-based + Mo →	C-276	N10276	15.5-16.5	Ca. 57	15-17	0.01	-	-	W:3.5-4.5 Fe: 4-7	-
Nickel-based + Mo →	C-4	N06455	16	Ca. 65	16	0.01	-	-	Fe:2	-
Nickel-based + Mo →	C-22	N06022	20-22.5	Ca. 56	12.5-14.5	0.01	-	-	W: 2.5-3.5 Fe: 2-6	-
Nickel-based + Mo →	C-2000	N06200	22-24	Ca. 67	15-17	0.01	-	1.3-1.9	Fe:3	-
Zirconium →	Zr702	R60702	-	-	-	-	-	-	Hf: 2 Zr: Bal.	-





- **Super austenitic 254 SMO = best candidate for pitting corrosion**
- **Corrosion rate of stainless steel in cement (CEM I): very low, not measurable. (< 0.01 nm/year)**

Conclusions and open questions

Conclusions and open questions

- **Uniform corrosion:**
  - v_{CORR}, volumetric method: 10 - 48 nm/year
  - v_{CORR}, pressure transducer = 20 – 30 nm/year
  - v_{CORR}, hydrogen sensor = 0.03 - 10 nm/year

Initial surface finish?

C-steel composition?

Microstructure

Pre-existing oxides?

- **Pitting corrosion**:
  - Pits (due to chloride) cannot propagate under the expected conditions in the supercontainer
  - Pits cannot reactivate during the anoxic period

Effect of S-species?

- **Stress corrosion cracking**
  - Currently no indication of increased susceptibiity

Effect of potential?

H-embrittlement possible?

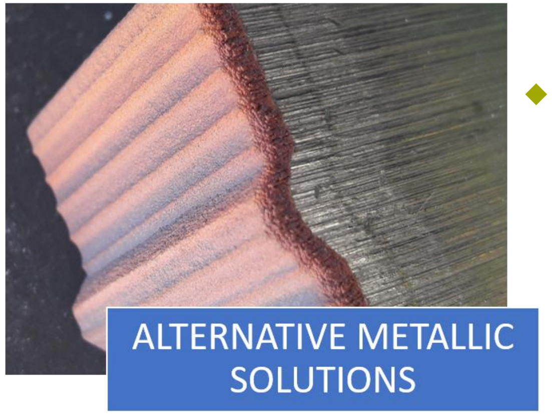
Alternative solutions?

- ONDRAF/NIRAS currently keeps a technological eye on alternative canister material solutions


NON METALLIC SOLUTIONS

- *Ceramic Materials and Coatings*
  - Bulk materials: SiO_2/Al_2O_3 & SiC-Cr
  - Coatings: TiO_2 & CrN

eurad
European Joint Programme on Radioactive Waste Management


ALTERNATIVE METALLIC SOLUTIONS

- *Metallic materials and coatings*
  - Bulk materials: Cu alloys
  - Coatings: Cu, Ti, Cr, Cu/Al_2O_3