Corrosion and SCC initiation of unirradiated and ion irradiated stainless steels in B-Li coordinated water chemistries

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B water chemistry

UPW vs 8000 ppm B

Influence of irradiation

ACPs & mitigating options

B water chemistry

Borated water chemistry in fusion & fission

Borated water as a neutronic shield (95% ^{10}B) in fusion vacuum vessel: 8000 ppm B in DTT, 13400 ppm B in KSTAR and JT60SA vs ≤ 2400 ppm B (19.8% ^{10}B) in PWRs.

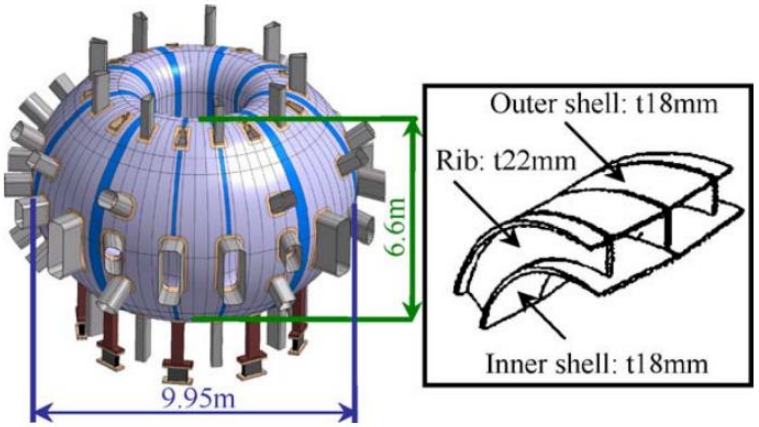
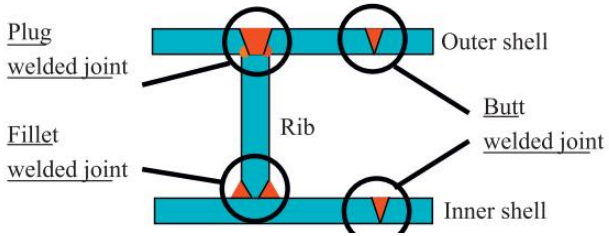
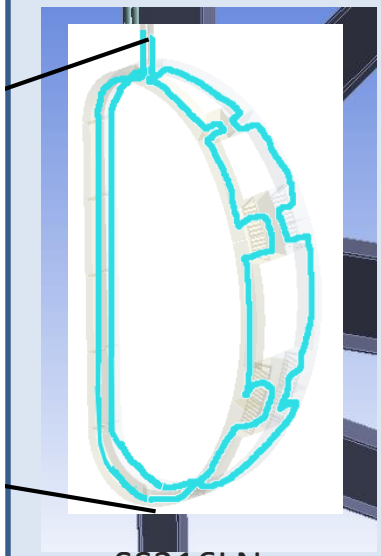


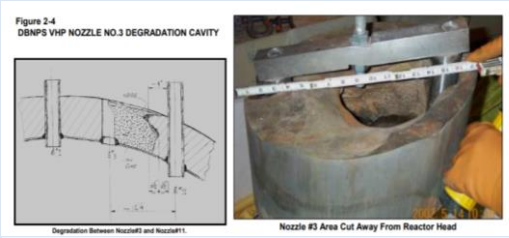
Fig. 1. VV of JT-60SA and its cross section.



Water & Borated water in DTT VV



Borated water (8000 ppm B, enriched with 95% of ^{10}B)



Borated water corrosion (60 years experience in PWRs/VVERs)

Eg: $B(OH)_3 + 2H_2O = B(OH)_4^- + H_3O^+$

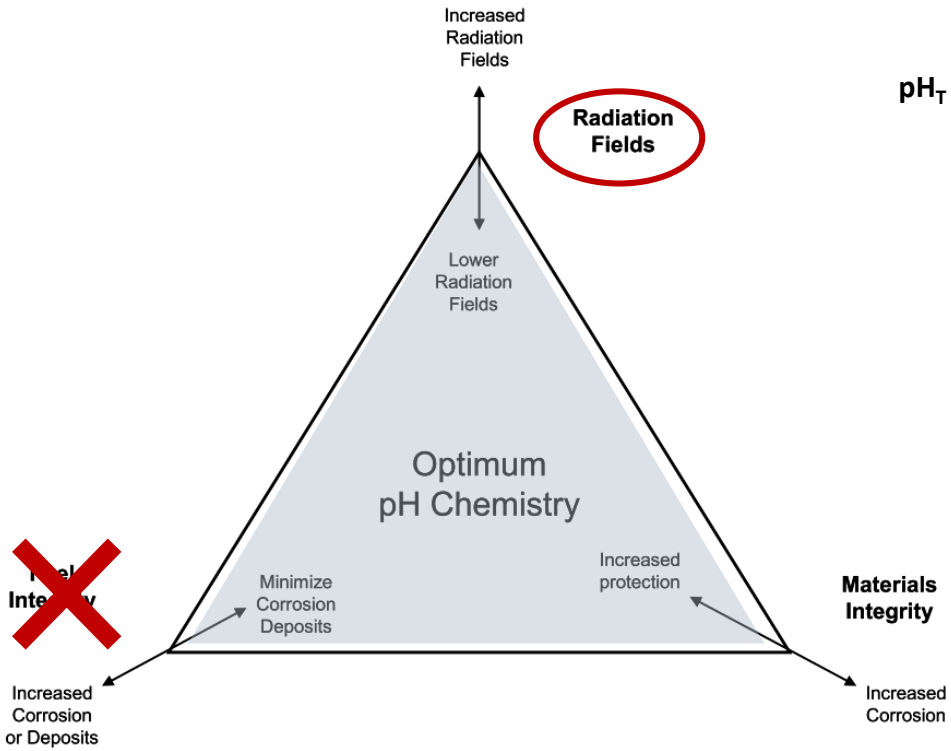
$H^+ + e^- = H$

$Fe = Fe^{2+} + 2e^-$ or $Fe^{3+} + 3e^-$

PWRs generally operate with natural boric acid; enriched boric acid (EBA) regime 40% in ^{10}B is being pursued to reduce amount of H_3BO_3 to be added and reduce amount of LiOH (99.95% enriched in ^7Li) to reach pH_T between 6.9 and 7.4 at 300 °C. French PWRs aim for a pH_T=7.2. DTT considers 8000 ppm B without addition of LiOH, which brings pH < 3.7 at 60 ℃.

S. Asano et al. "Fundamental welding R&D results for manufacturing vacuum vessel of JT-60SA", Fusion Engineering and Design, 2011

Water chemistry guidelines



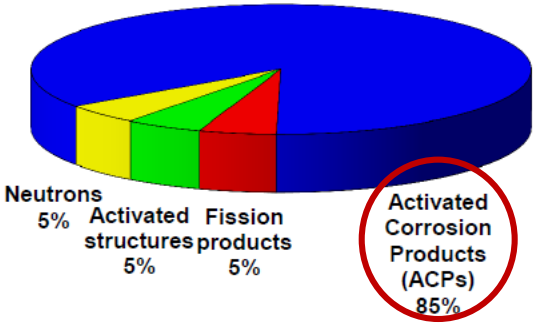
Pressurized Water Reactor Primary Water Chemistry Guidelines, EPRI

In fusion: no concern on fuel integrity; optimum water chemistry to minimize radiation fields and maximize materials integrity

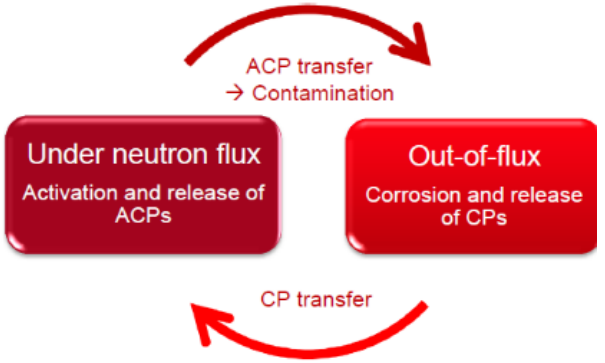
For example:

pH_T 7.4 ↑ 6.9 corrosion release rates ↓ fuel cladding corrosion ↑ Li

Collective dose for operation and maintenance of PWRs



Principle of contamination transfer in a nuclear cooling system

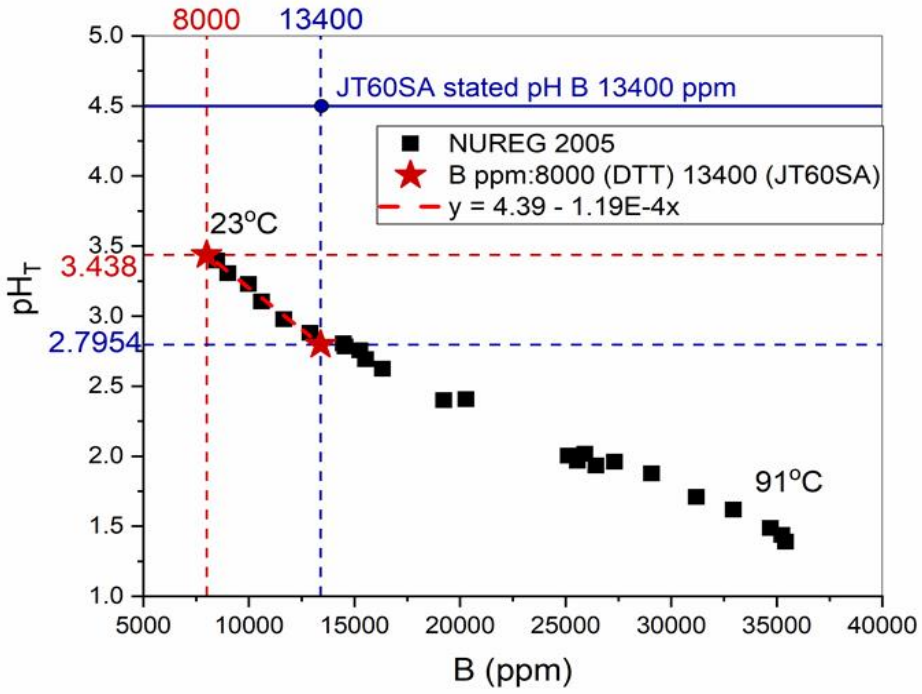


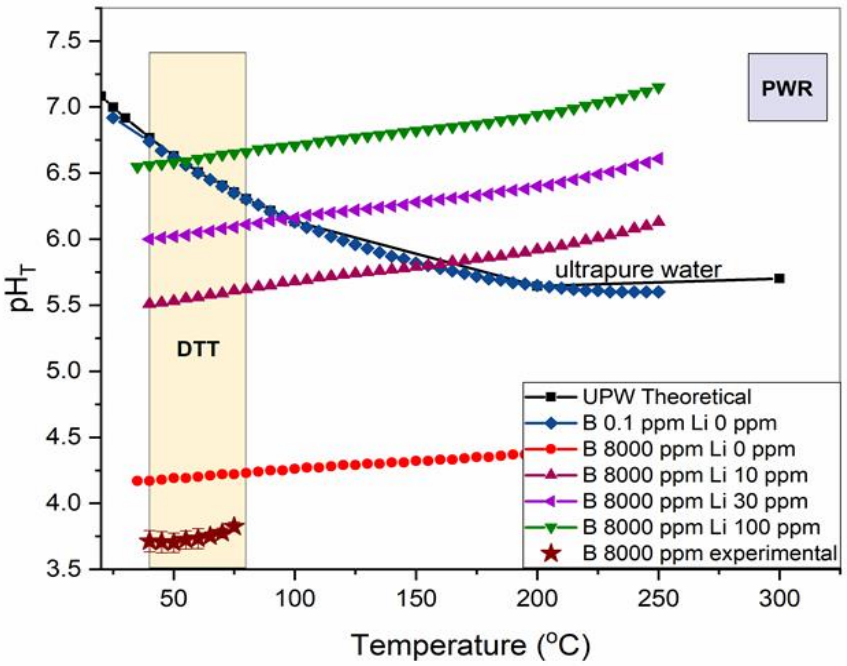
Courtesy F. Dacquait, N. Terranova

pH: LWR vs JT60-SA, DTT, KSTAR

High concentration of boric acid > 8000 ppm B, high enrichment (95% in the isotope ^{10}B) are required to shield superconducting coils in fusion.
Water chemistry in DTT is not yet optimized.

Optimised water pH_T



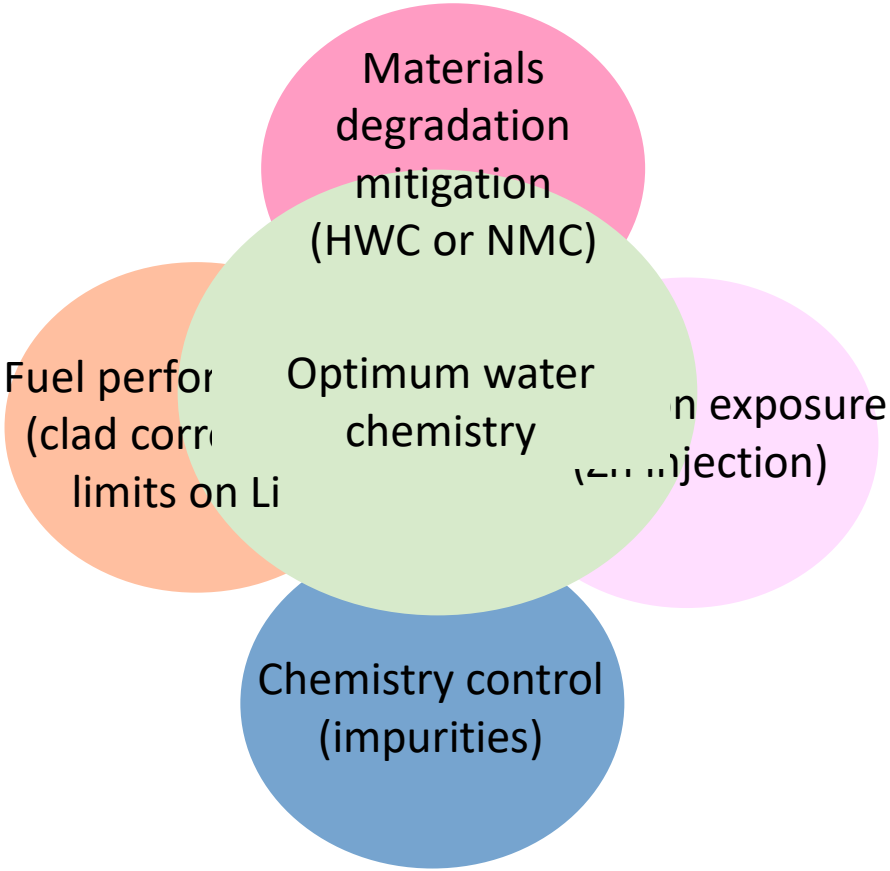


- Discrepancy between pH stated in JT60SA (pH=4.5) PID vs experimental data (pH=2.8)
- DTT borated water 8000 ppm B shows a pH = 3.6 at 60 °C

Tailoring water chemistry

LWRs:

- Addition of additives (LiOH, KOH)
- Oxygen scavengers
- Hydrogen
- Control of contaminants
- Noble metal chemical addition (NMCA) in BWRs
- Zn injection to reduce ^{60}Co incorporation



ITER:

is considering water chemistry control

Effect of irradiation: SCC/IASCC

weld, HAZ, manufacture, installation, surface treatments

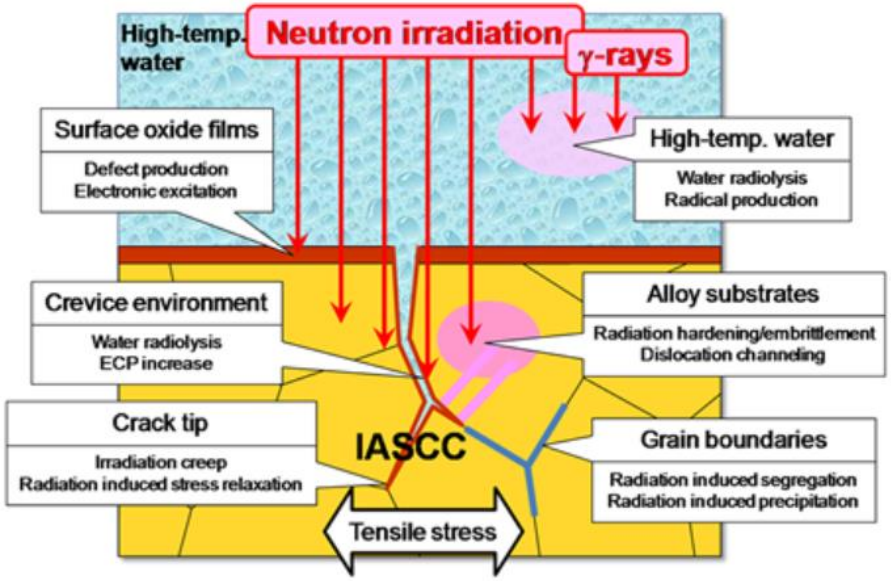
Stress & strain

Material

Chemical elements, radiation-induced segregation or depletion, defects

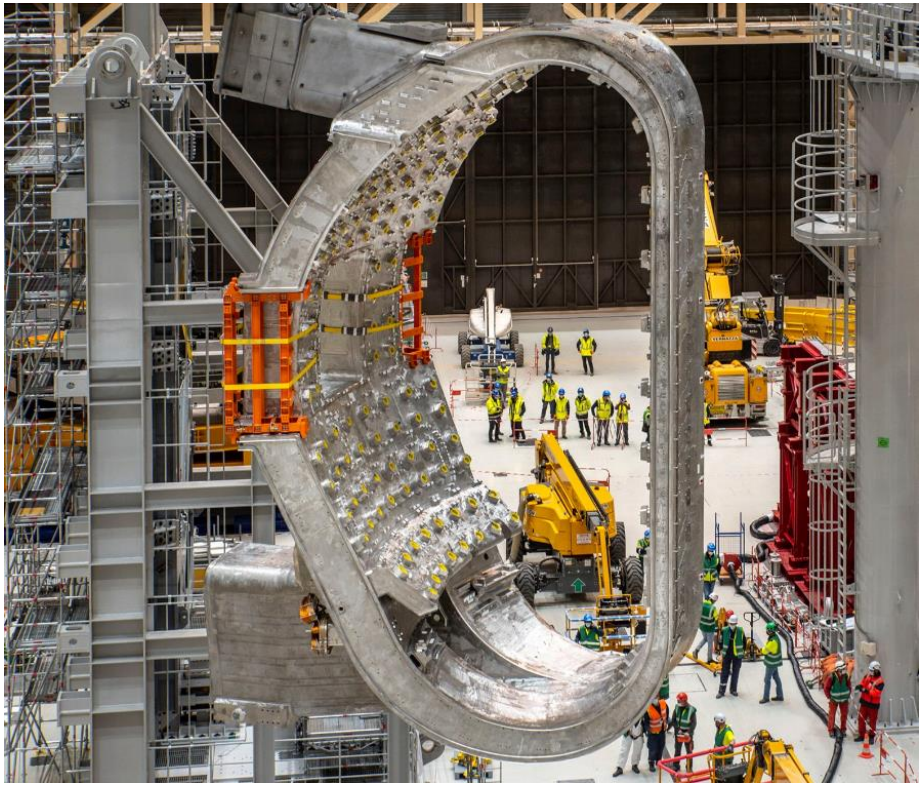
Environment

Radiation induced damage, radiolysis, hydrogen effects, contaminants



https://www.jsm.or.jp/ejam/Vol.2.No.4/NT/31/article.html

RPV (fission) vs VV (fusion)



The RPV has been built by France by Framatome. Courtesy EDF.

In fission power plants IASCC in stainless steels is generally considered above 3 dpa (temperatures >260 °C), hence in ITER and future DEMO design stainless steels have been chosen for structural part of the VV considering a damage below 2.75 dpa.(*)

* C. Bachmann et al., Containment structures and port configurations, Fusion Engineering and Design, 2022

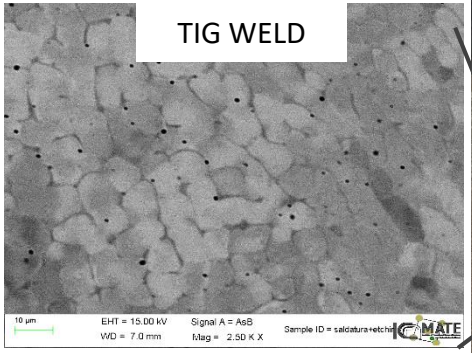
https://www.nucnet.org/news/first-reactor-pressure-vessel-complete-and-ready-for-delivery-12-5-2022

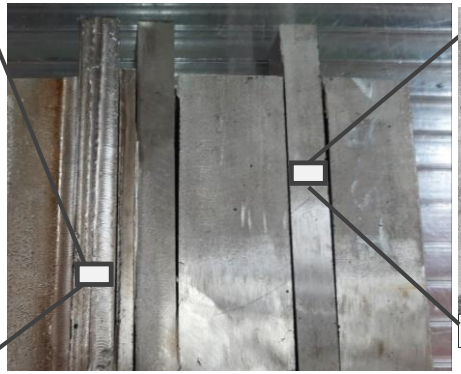
https://www.facebook.com/ITEROrganization/photos/pb.23363014706.-2207520000../10159295636269707/?type=3&eid=ARB4NAX9UciLGiK1Z-07wKnnqVDHdWGkjAmPkZ9rvuFeuo23DjXz5JIjwoGFeryz1mGBW4QJCmmjMr91&locale=nl_NL&paipv=0&eav=AfZ_C2D9S3TkagDxYfjPmibTM_Qyp5g-ro1ZpREld6r6BnoxKuHKyzgW1L4Ha7tNir0&_rdr

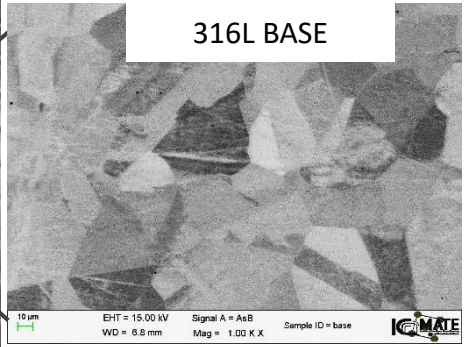
UPW vs 8000 ppm B

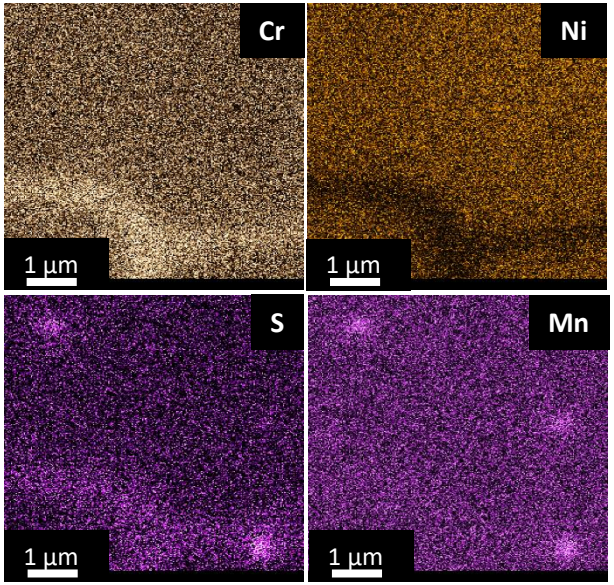
ITER VV welds and 316LN-IG , 316L base

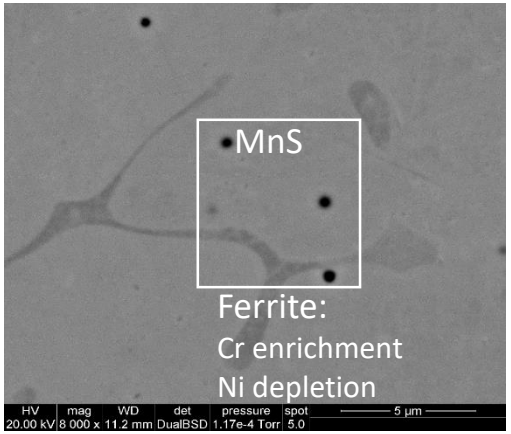
Samples from Mangiarotti SpA:
- 316L base metal
- 316L weld (TIG & SMAW)
- 316LN-ITER GRADE



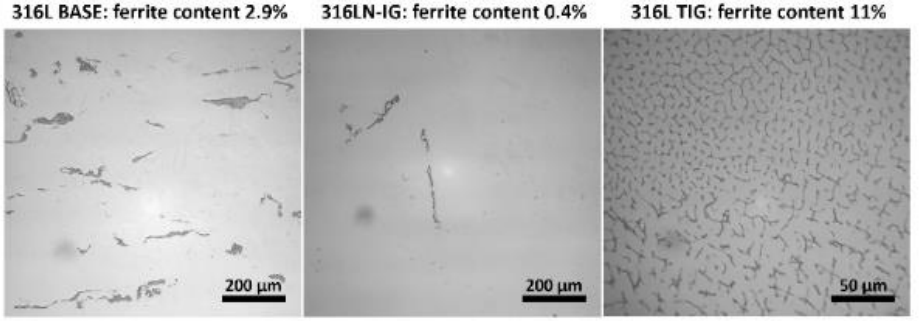






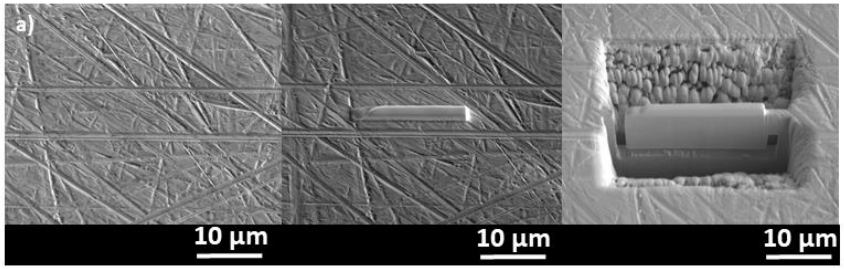


TIG weld: MnS inclusions
Austenite : 20 % Cr % 10 % Ni
Ferrite : 25% Cr & 5% Ni

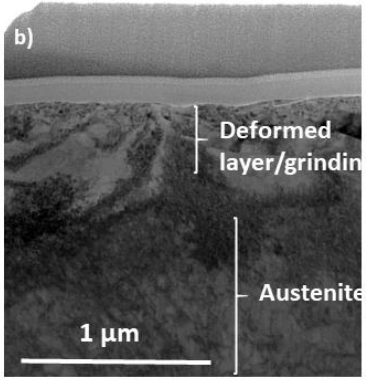


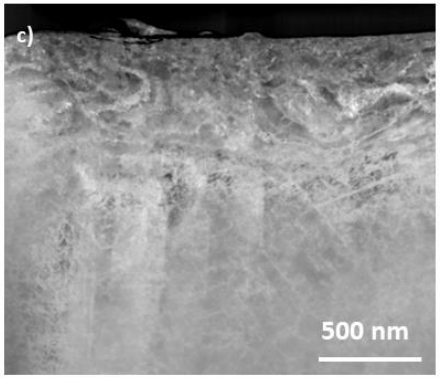
C. Gasparrini et al., IEEE Transactions on Plasma Science, 2022

General corrosion: samples preparation



Metal release were performed using 12 mm × 10 mm × 1 mm samples ground with 1200 grit SiC paper surface finish to align with previous experiments on 316L steels by Atapour et al. [21].

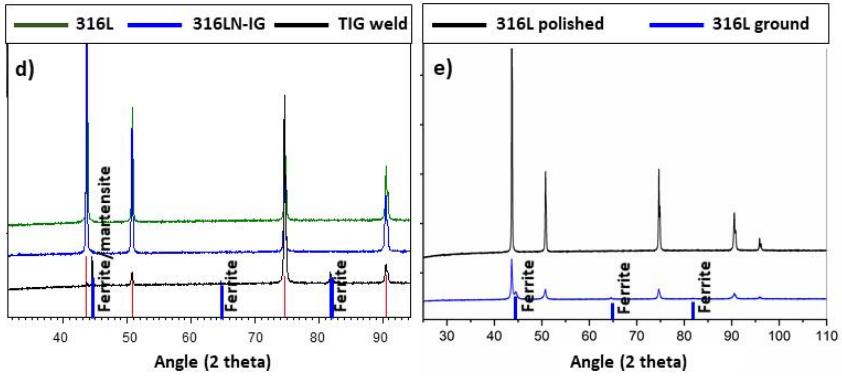


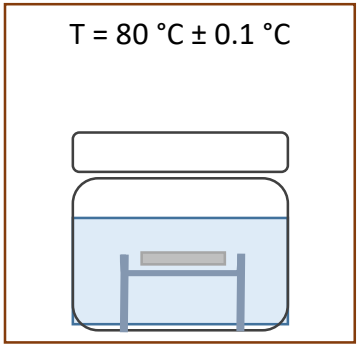


Passivated oxide layer (3 months)

Deformed layer/grinding effect (martensite peaks detected)

Austenite

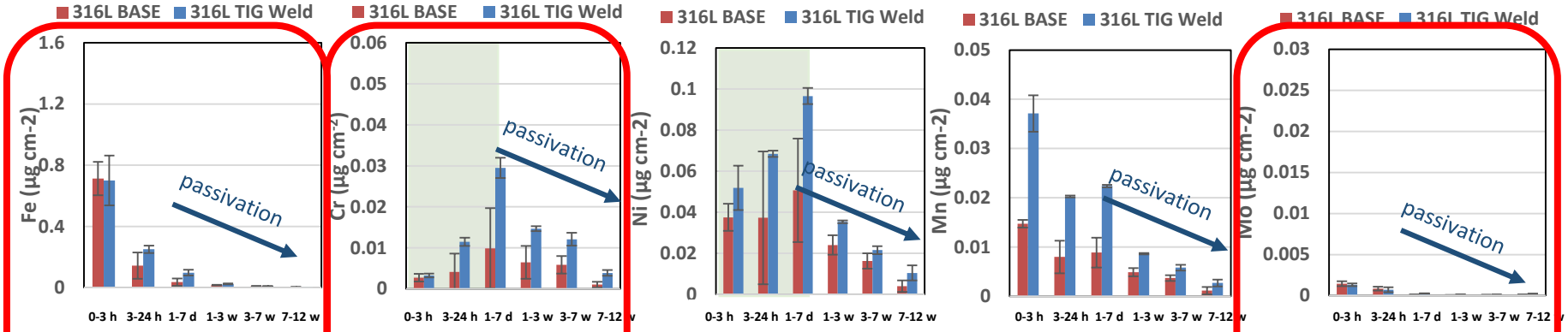




Water: 30 mL
Sample dimensions:
10 x 12 x 1 mm^3
Experiments based on
ASTM C1220-17, M. Atapour et al.
Electrochimica Acta, vol. 354, Sep. 2020

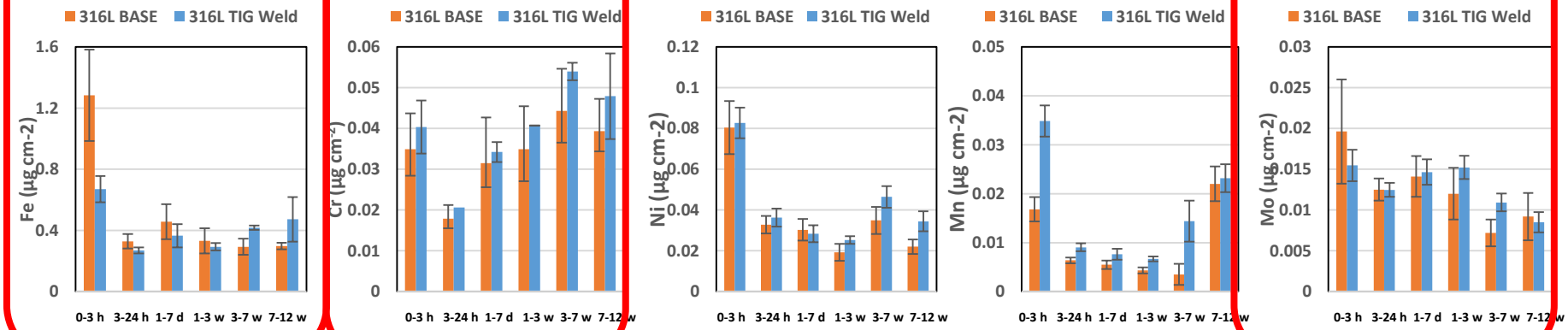
Metal releases from 316L in 8000 ppm B

Ultrapure water at 80 °C, pH_T = 6.3



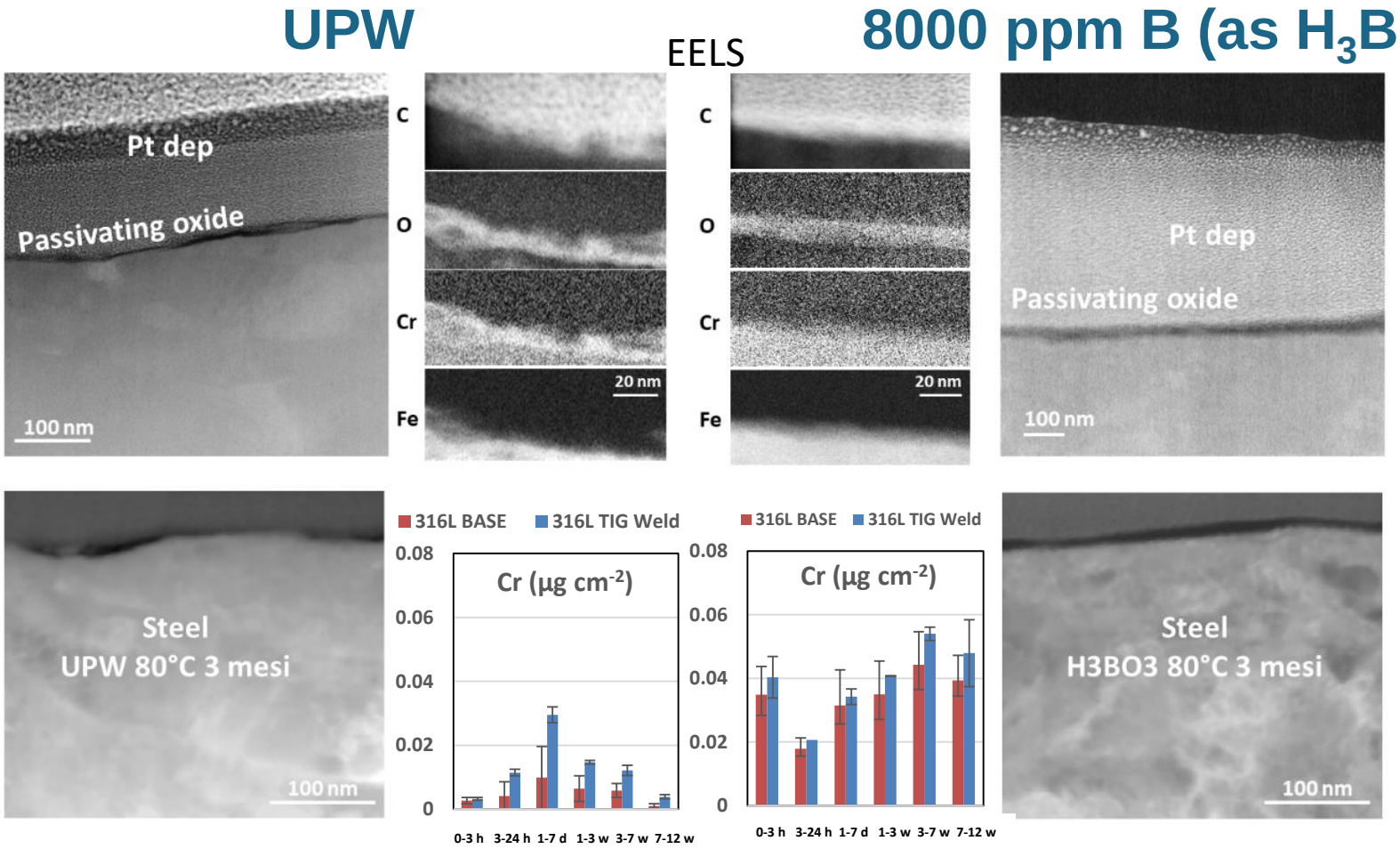
h: hour d: days w: weeks

Borated water (8000 ppm B) at 80 °C, pH_T = 3.6



Unpublished, under review

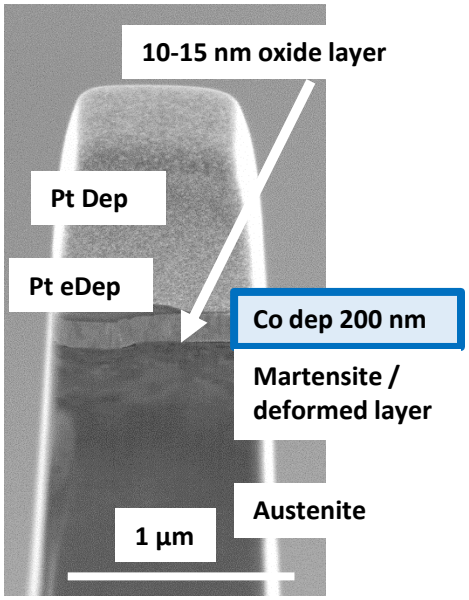
STEM-EELS characterisation of passive layer

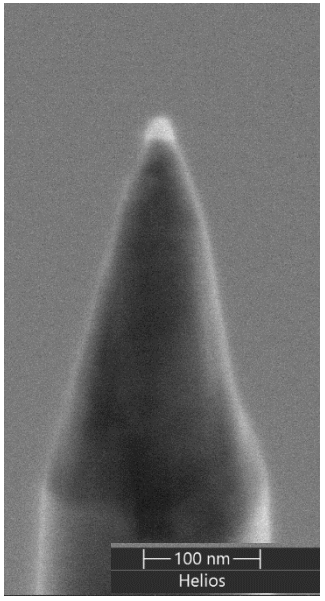


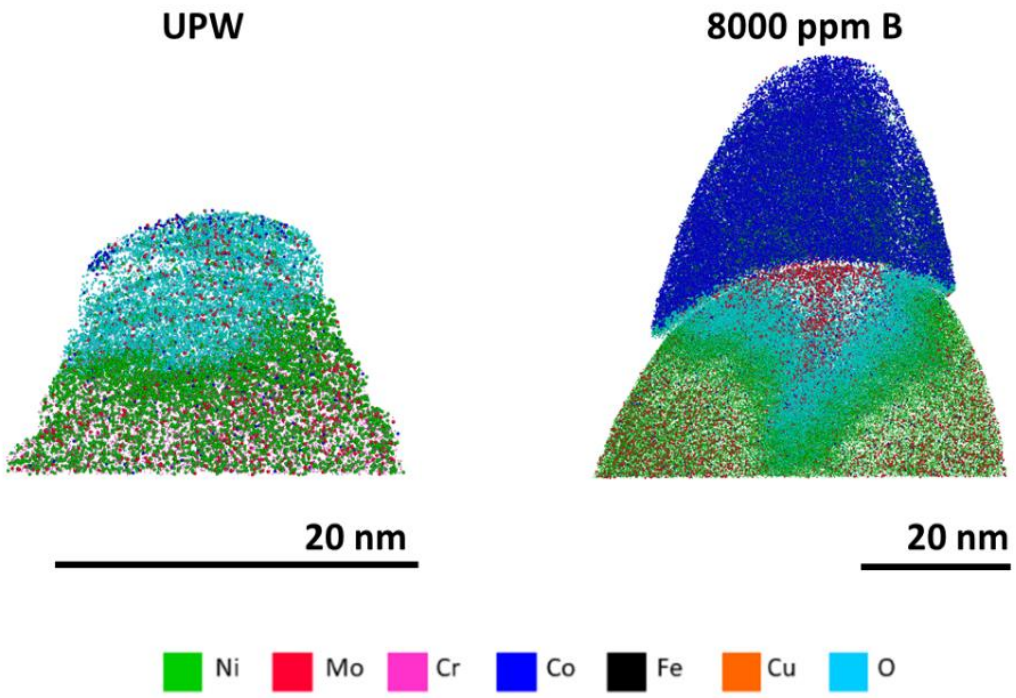
Oxide passive layer formed on SS316L steel samples exposed to UPW and 8000 ppm B water at 80°C for 12 weeks was characterized with TEM and EELS: thickness <20 nm and Cr and O were detected.

Unpublished, under review

APT preparation

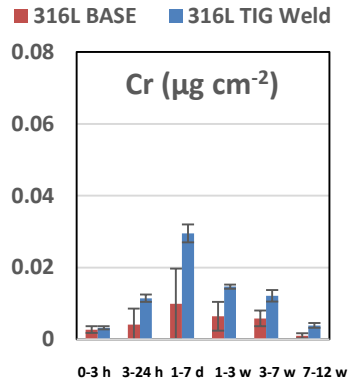


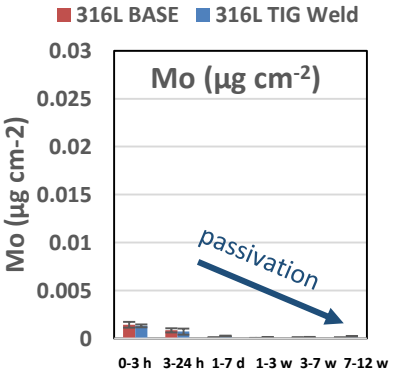




APT reconstruction for two tips representatives of samples analysed for 2 aqueous environments, in blue is shown the protective Co cap deposited on top prior to APT preparation (Co cap less thick in UPW sample APT tip, but it is still possible to delineate the oxide top surface)

APT chemical composition analysis on passive layer





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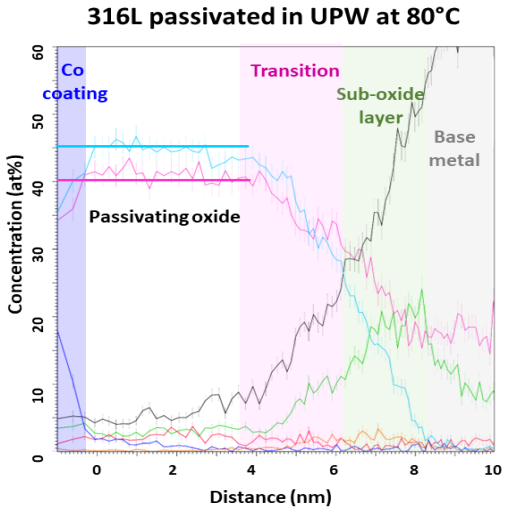
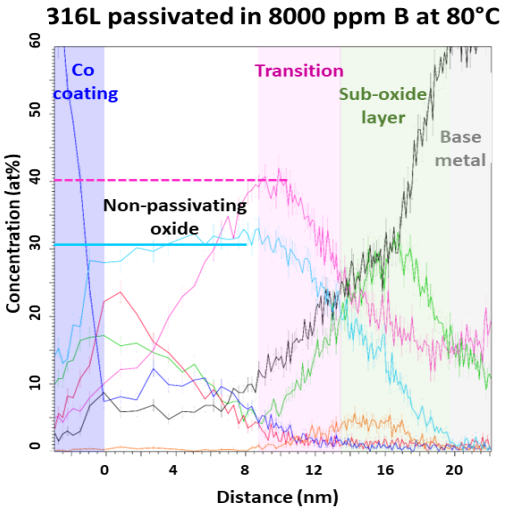
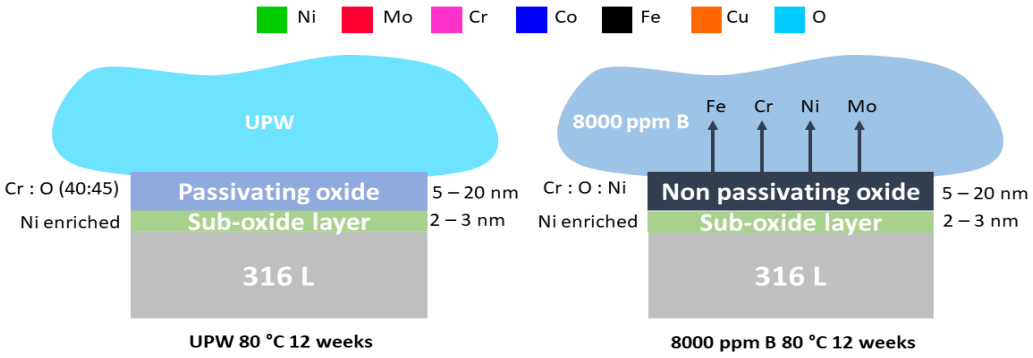
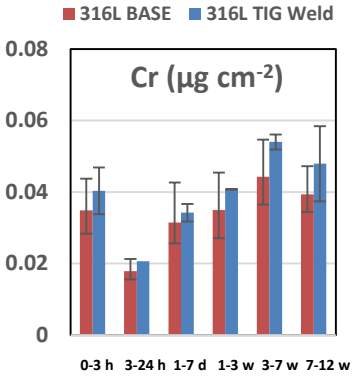
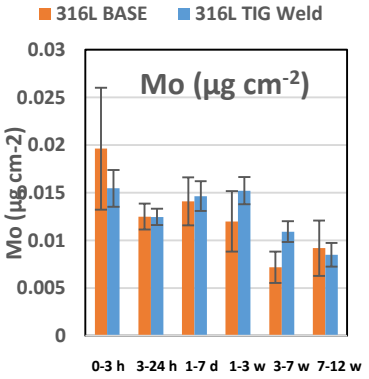






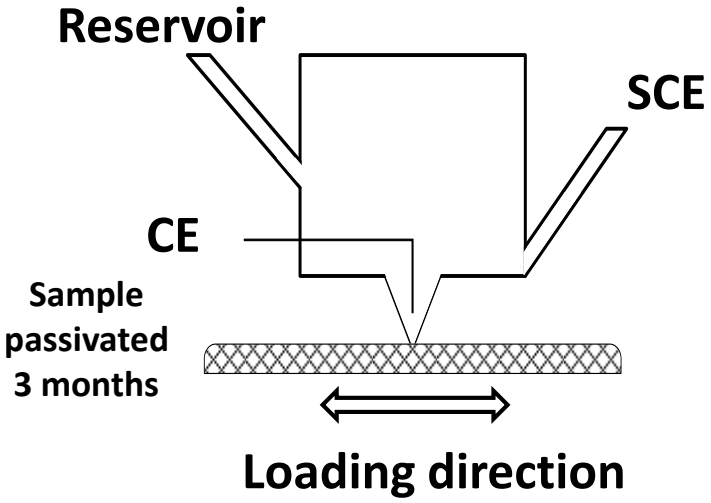


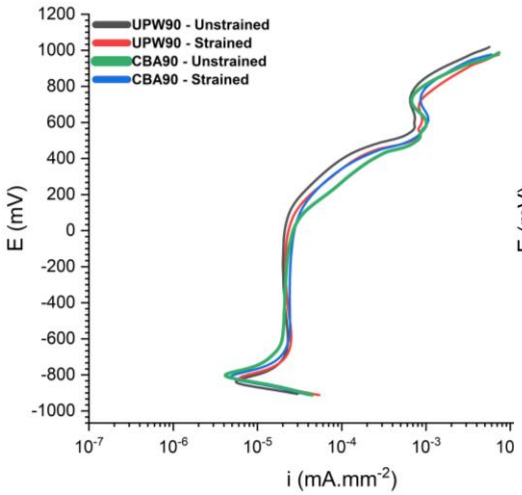


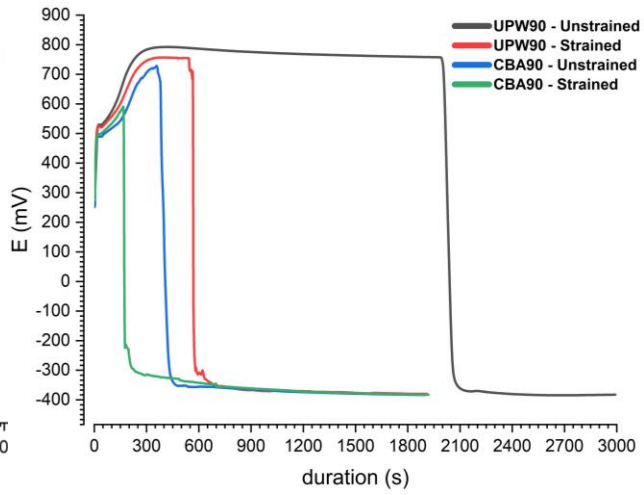
Oxide layer chemical composition was different in UPW compared to 8000 ppm B, thickness remained in the same range (<20 nm). UPW oxide layer was characterised by a flat profile of fixed concentration of Cr and O (40 : 45) acting as a protective diffusion barrier (very low metal releases quantified by ICP-MS). The oxide formed in 8000 ppm was characterised by a non-homogeneous chemical composition: Cr was not constant, Ni and Mo were enriched at the interface oxide/water: this is consistent with the higher releases measured in 8000 ppm B water inferring that metal transfer develops through the non-protective oxide layer.

SCC initiation testing

Microcapillary electrochemical polarization methods, 3.5% NaCl distilled deionized water for a comparative study







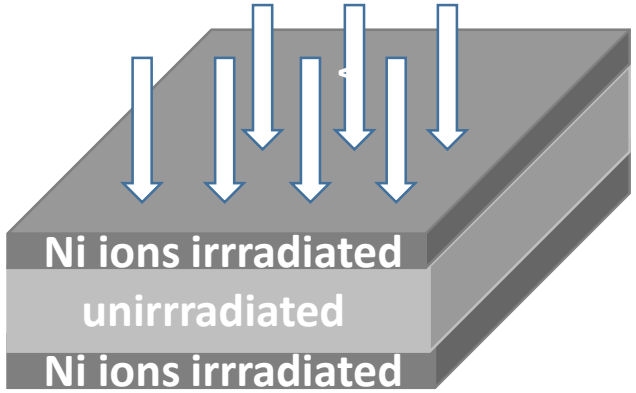
Potentiodynamic polarization curves : better performance of passivated samples in UPW than 8000 ppm B passivated samples in passive layer breakdown zone. Galvanostatic polarization results confirms better performance of the passive layer in unstrained condition for UPW samples compared to 8000 ppm B samples.

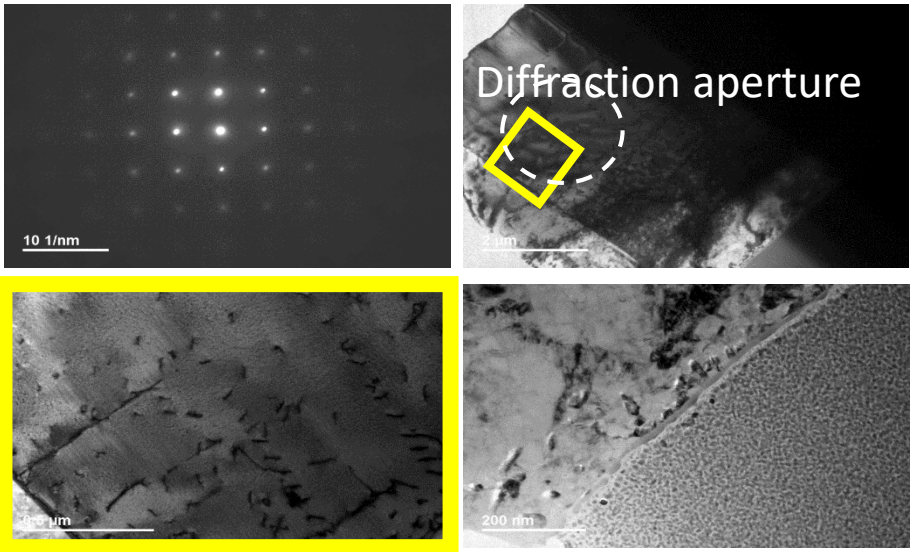
Influence of irradiation

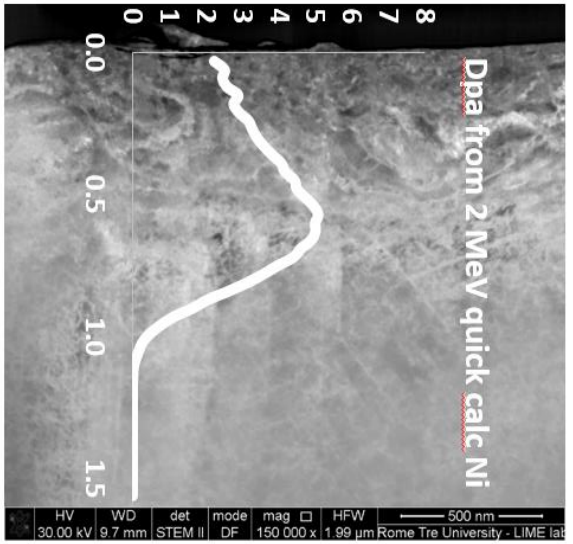
Ni ions irradiation

System: ANTARES Accelerator
Ions: Nickel, 2 MV
Fluence: 3e^{15} ions/cm^2 for each side.
Area irradiated: 1 cm^2

316LN-IG were exposed to a 3 dpa damage on the passive layer (threshold for IASCC : 3 dpa and temperatures >260 °C)







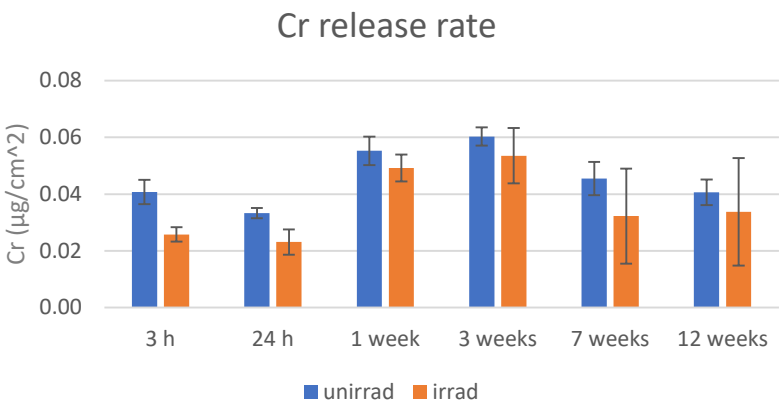
Passive oxide layer

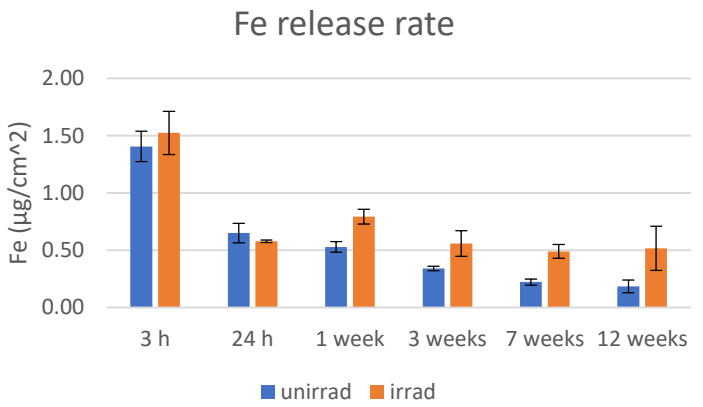
Deformed layer/grinding (martensite)

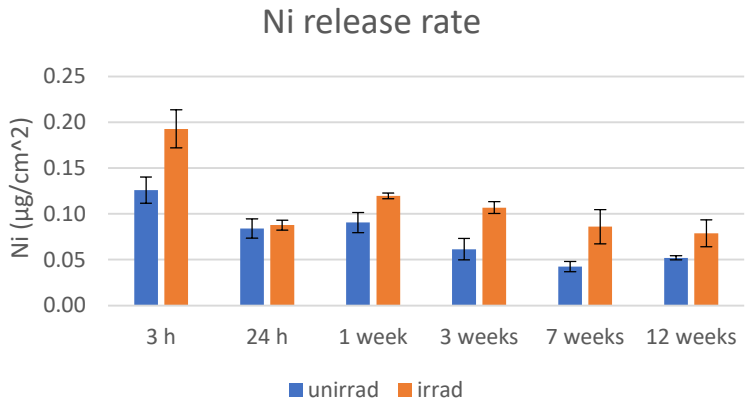
Austenite

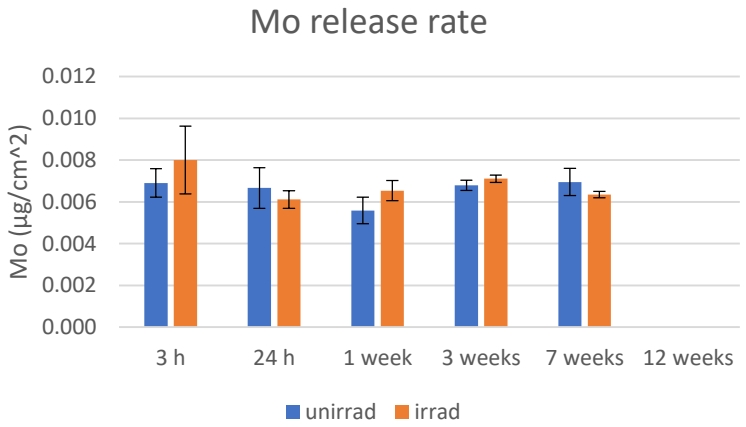
General corrosion and localised corrosion initiation were tested using non-conventional small scale technique to test general corrosion and SCC initiation of ion irradiated specimens. Tests were performed on unirradiated and Ni ion irradiated 316LN-IG samples.

Metal release: unirradiated vs ion irradiated 8000 ppm B



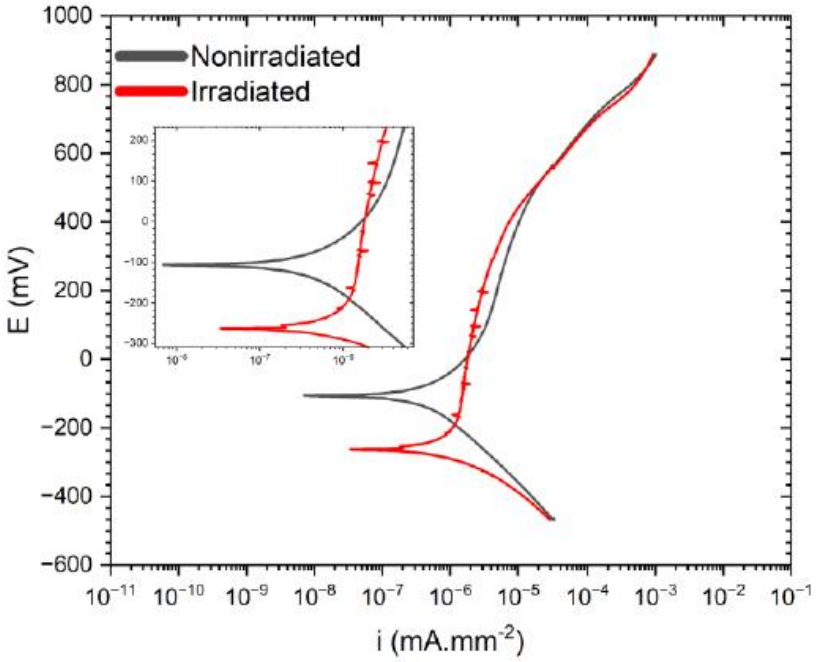


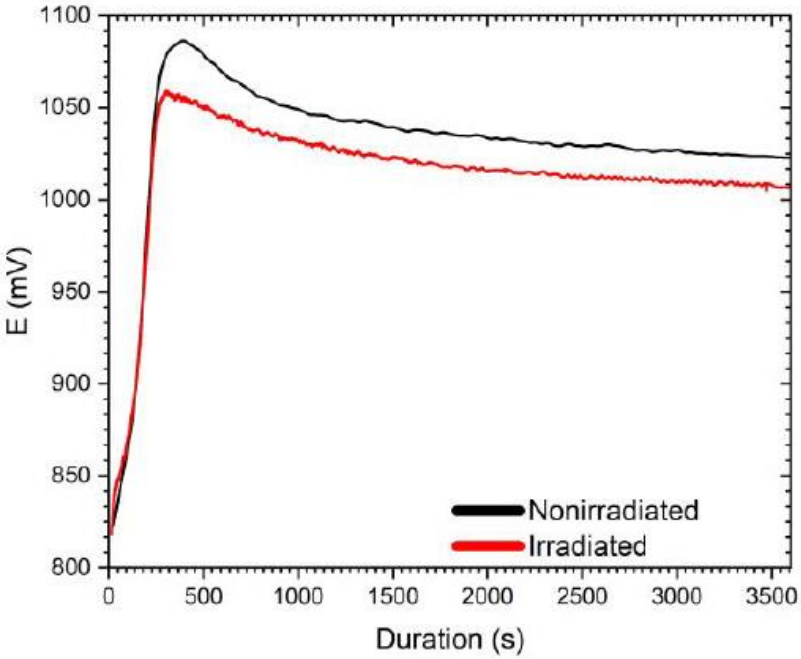




Fe and Ni releases were larger from Ni ion irradiated samples than unirradiated. Higher releases of Ni during first sampling (after the first 3 hours of exposure) were detected (may be related to Ni ions implanted, in first 50 nm approx. 1-3 ppm are expected from SRIM/TRIM simulations). Higher releases of Fe from ion irradiated samples were measured after 7 days exposure and onwards compared to unirradiated ones. Higher releases could be related to a less efficient passive layer grown on ion irradiated samples compared to unirradiated ones. Cr releases did not show significant difference.

Localized Corrosion Initiation Analysis





Ni ion irradiated samples showed a lower localized corrosion resistance compared to unirradiated samples. Potentiodynamic and galvanostatic measurements revealed higher perturbations in the ion irradiated samples, indicating lower integrity of the ion irradiated samples. Galvanostatic experiments showed a lower potential, suggesting reduced resistance of the passive layer due to the effect of ion irradiation.

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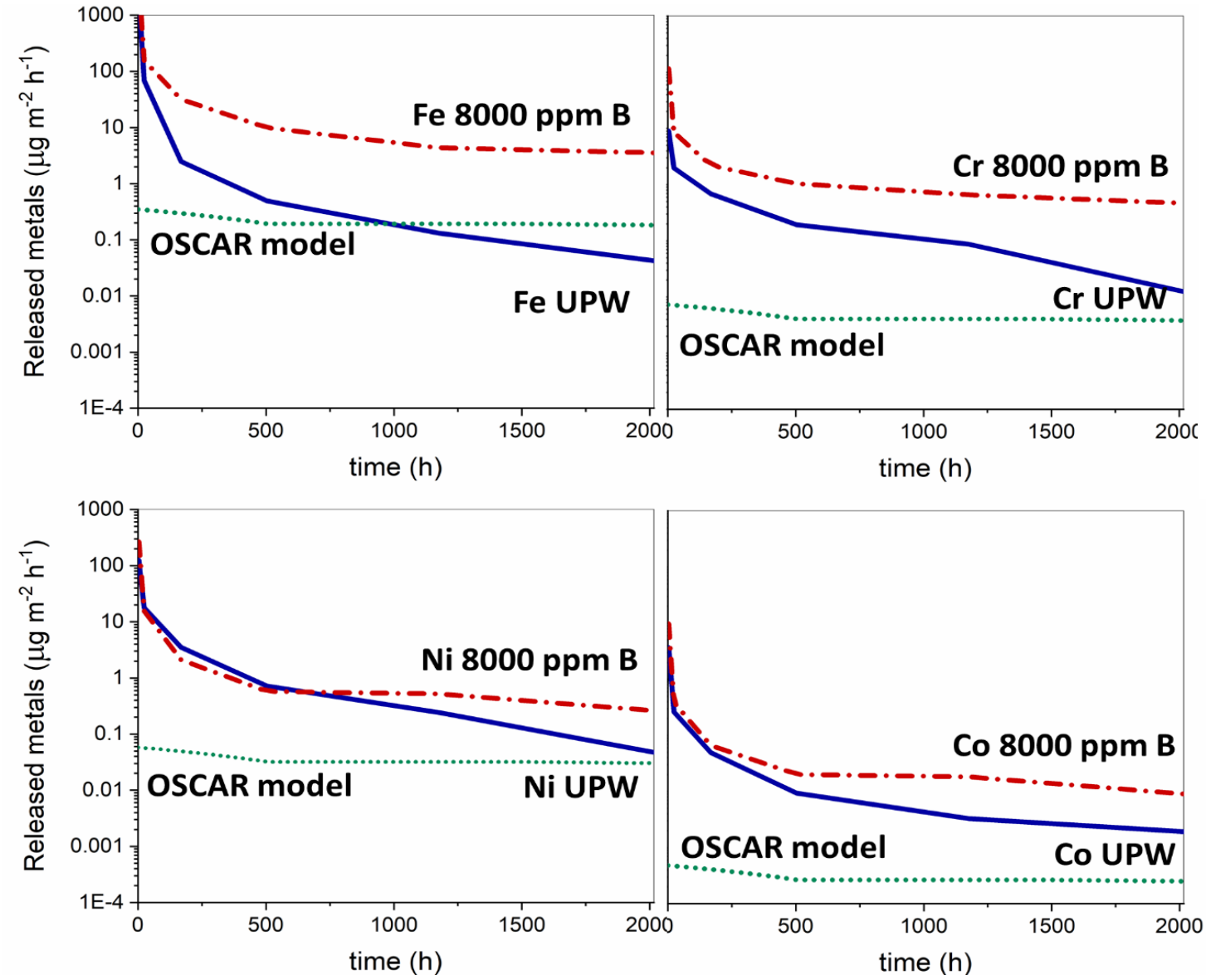
ACPs & mitigating options

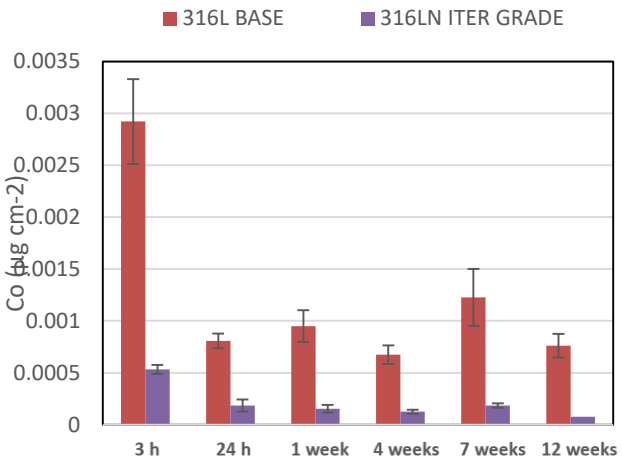
ACPs calculations: experimental vs code prediction

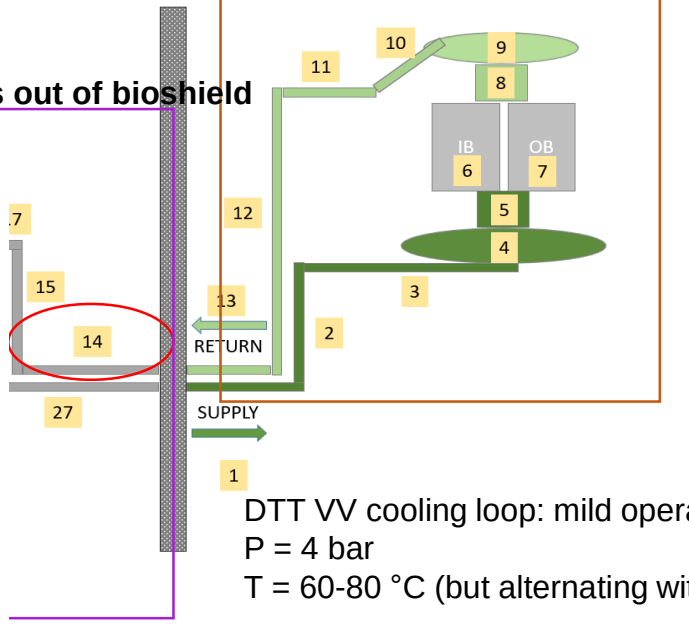


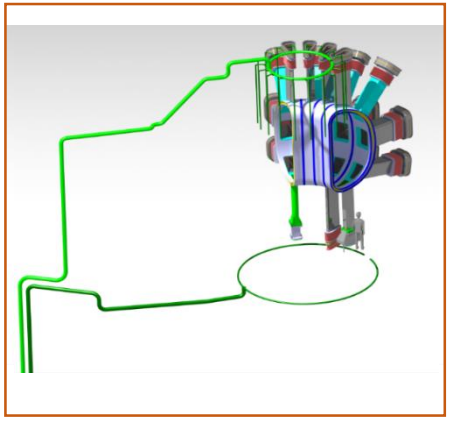
Irradiation: ACPs formation and deposit out of bioshield

DTT VV case study

ACP in deposits out of bioshield

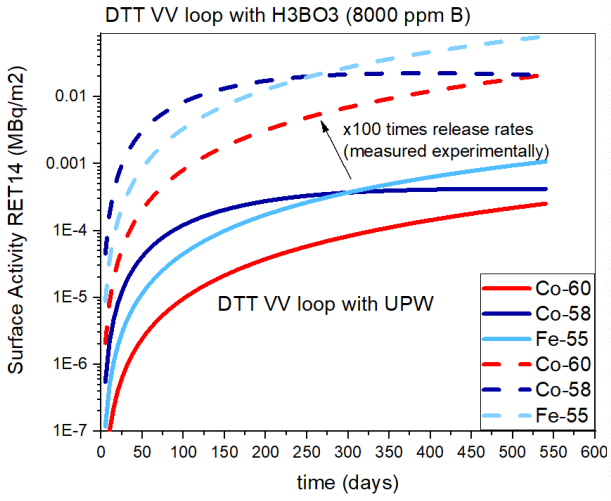


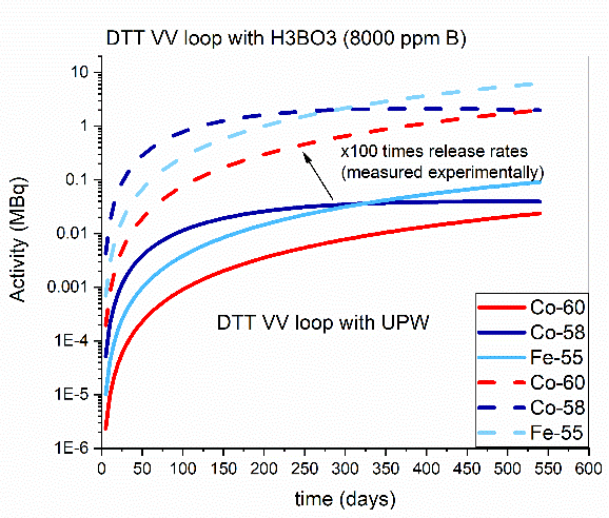




DTT VV cooling loop: mild operating conditions compared to PWRs
P = 4 bar
T = 60-80 °C (but alternating with hot gas 250 ° C)

Concentration of boric acid is high: 8000 ppm B





Only ACP in deposits are plotted

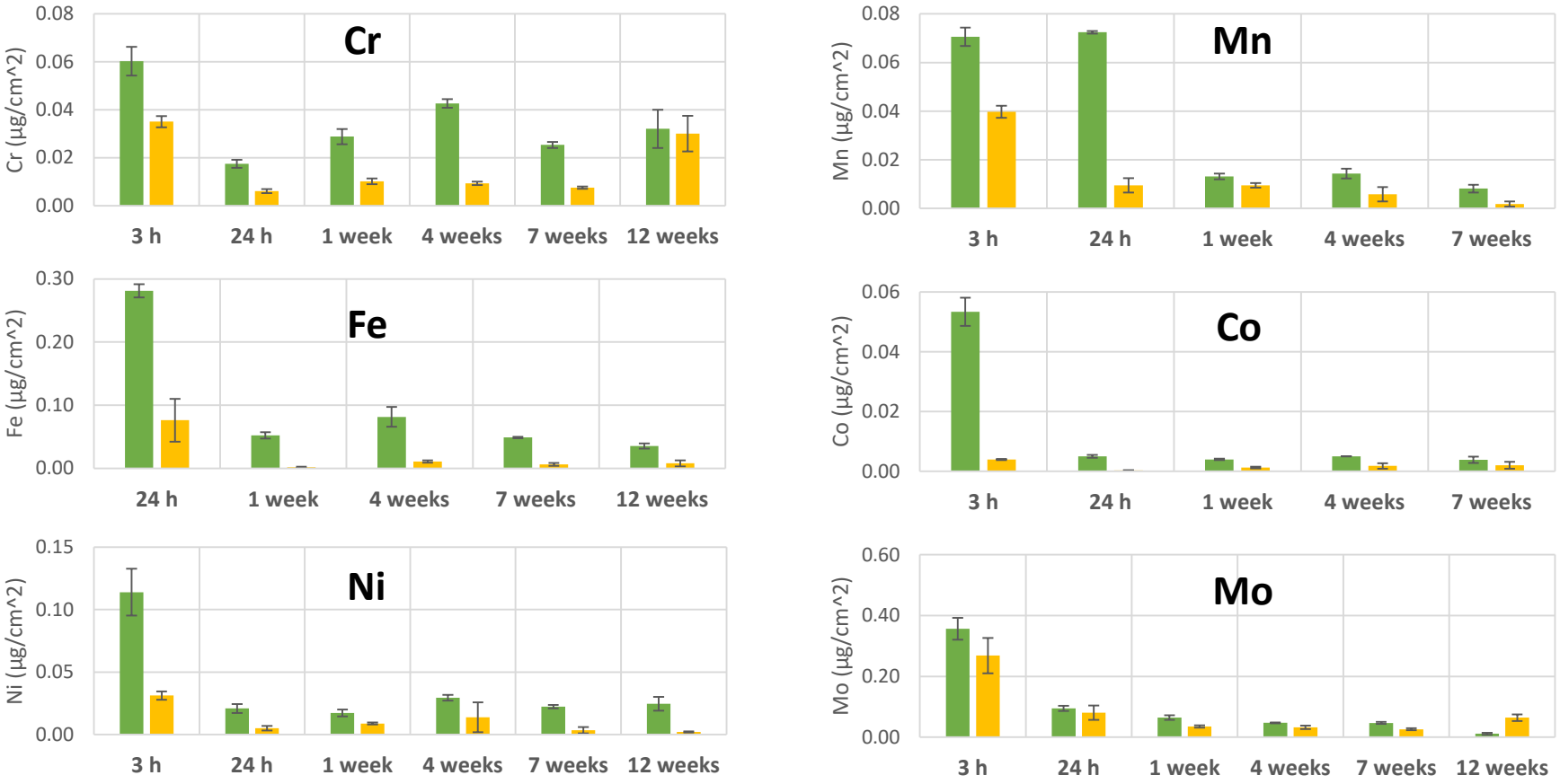
Water chemistry influence on corrosion rate: effect of boric acid on ACP deposition. Metal release rates measured on unirradiated samples (UPW and 8000 ppm B) were used,
OSCAR Fusion (v1.3) cannot simulate water chemistry with large B additions (it was tailored to ITER needs): these simulations run with 1 ppm O_2 and 0 ppm H_2, no 8000 ppm B

C. Gasparrini et al., under review

Mitigation options: LiOH addition

316L 8000 ppm B 5.7 Li pH_{60C} = 4.7

316L 8000 ppm B 57 Li pH_{60C} = 5.6



Metal releases decreased when 316L was exposed to B-Li water chemistry.
Fe, Cr, Co, Mn, Ni releases from 316L in 8000 ppm B in 57 ppm Li were the lowest. The decrease in release for Ni was approximately 1 tenth when comparing results obtained in 5.7 ppm Li compared to 57 ppm Li. Mo releases did not seem affected.

Conclusions

- DTT water chemistry at 80 °C was assessed using small scale techniques

- Fe – Cr – Ni – Mn – Mo and Co releases from 316L were much higher in 8000 ppm B solutions compared to UPW. After 12 weeks, Fe and Mo releases were ~100 times higher in 8000 ppm B than UPW. Cr releases were approximately 30 times larger in 8000 ppm B.

- APT revealed the formation of a protective oxide formed in UPW (Cr : O - 40 : 45). Oxide in 8000 ppm did not have a stable chemical composition: Cr released inmwater, Ni and Mo were enriched at the sub oxide interface. 8000 ppm B oxide was more prone to SCC initiation

- Metal releases showed enhanced Fe and Ni release from 3 dpa Ni ions iradiated 316LN-IG exposed to 8000 ppm B. Mo and Cr releases did not seem affected. Ion irradiated samples were more prone to localised corrosion initiation compared to unirradiated samples

- Effect of irradiation was estimated preliminarily using an ACP code (OSCAR-Fusion v1.3); where experimental release rates were used as input highlighting the importance of these data for ACPs calculations (100 times release rates ~ 100 times deposits at same water chemistry)

- Mitigating option: adding LiOH was proven to benefit general releases, 57 ppm Li in 8000 ppm B performed better than 5.7 ppm Li.

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Thanks for listening! Any question?

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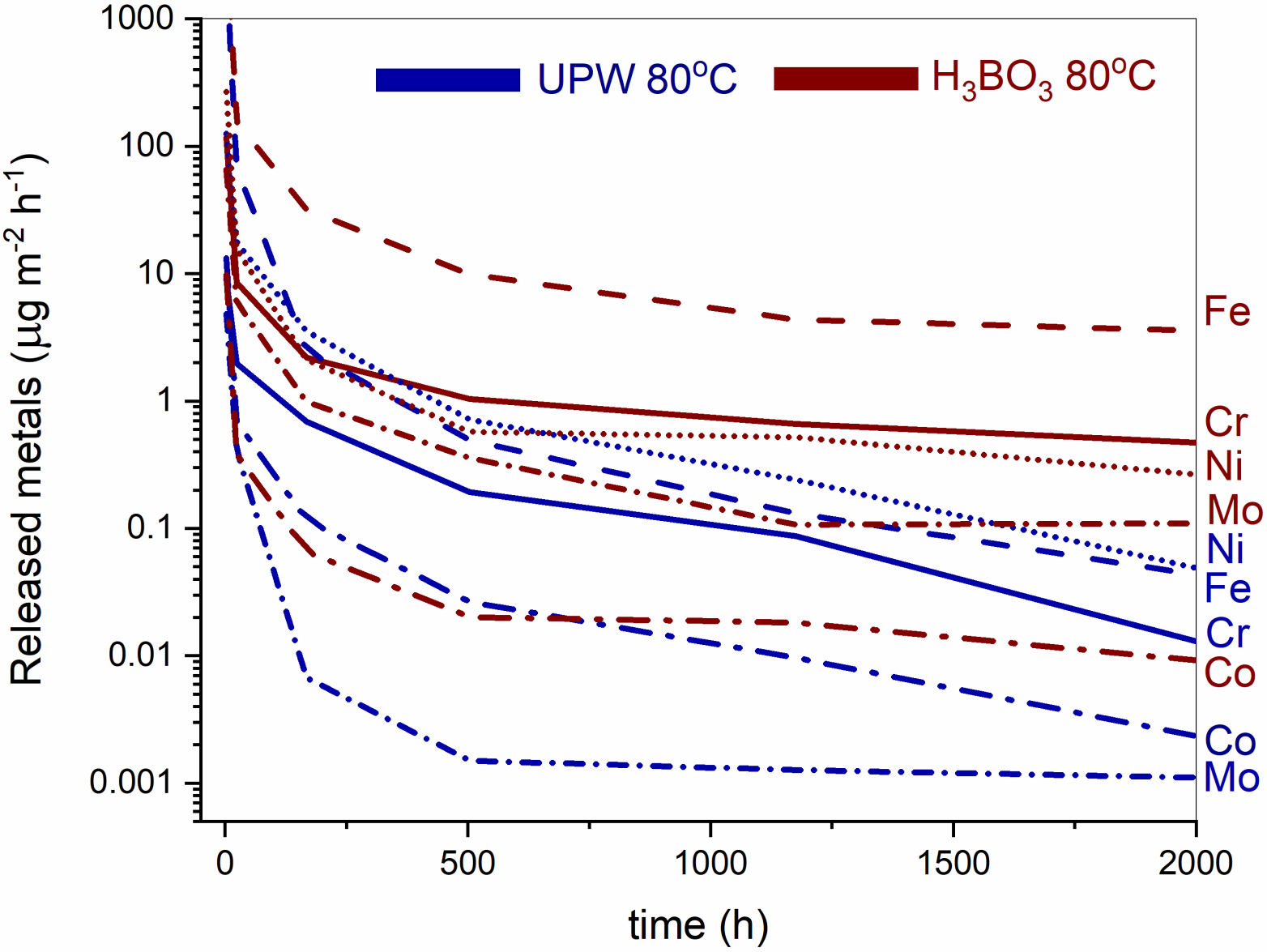
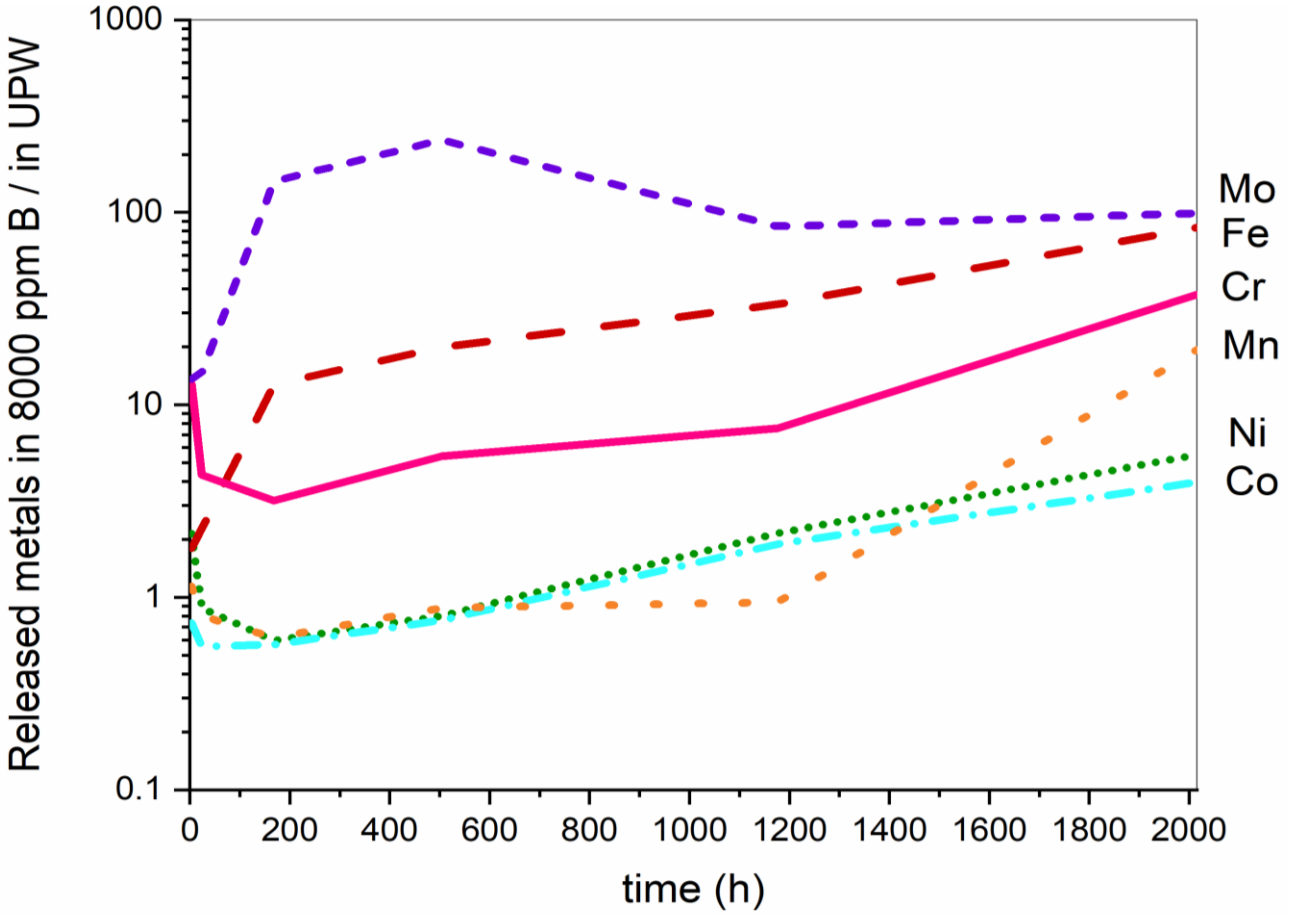

UPW 80°C
H3BO3 80°C
Released metals (µg m-2 h-1)
1000
100
10
1
0.1
0.01
0.001
0
500
1000
1500
2000
time (h)
Fe
Cr
Ni
Mo
Ni
Fe
Cr
Co
Co
Mo


Released metals in 8000 ppm B / in UPW
1000
100
10
1
0.1
0
200
400
600
800
1000
1200
1400
1600
1800
2000
time (h)
Mo
Fe
Cr
Mn
Ni
Co