On the water chemistry of fusion power plants

Compatibility Between Coolants and Materials for Fusion Facilities and Advanced Fission reactors

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Ivo Moscato, G. Agnello, P. Chiovaro, A. Quartararo

On behalf of EUROfusion DEMO Central Team

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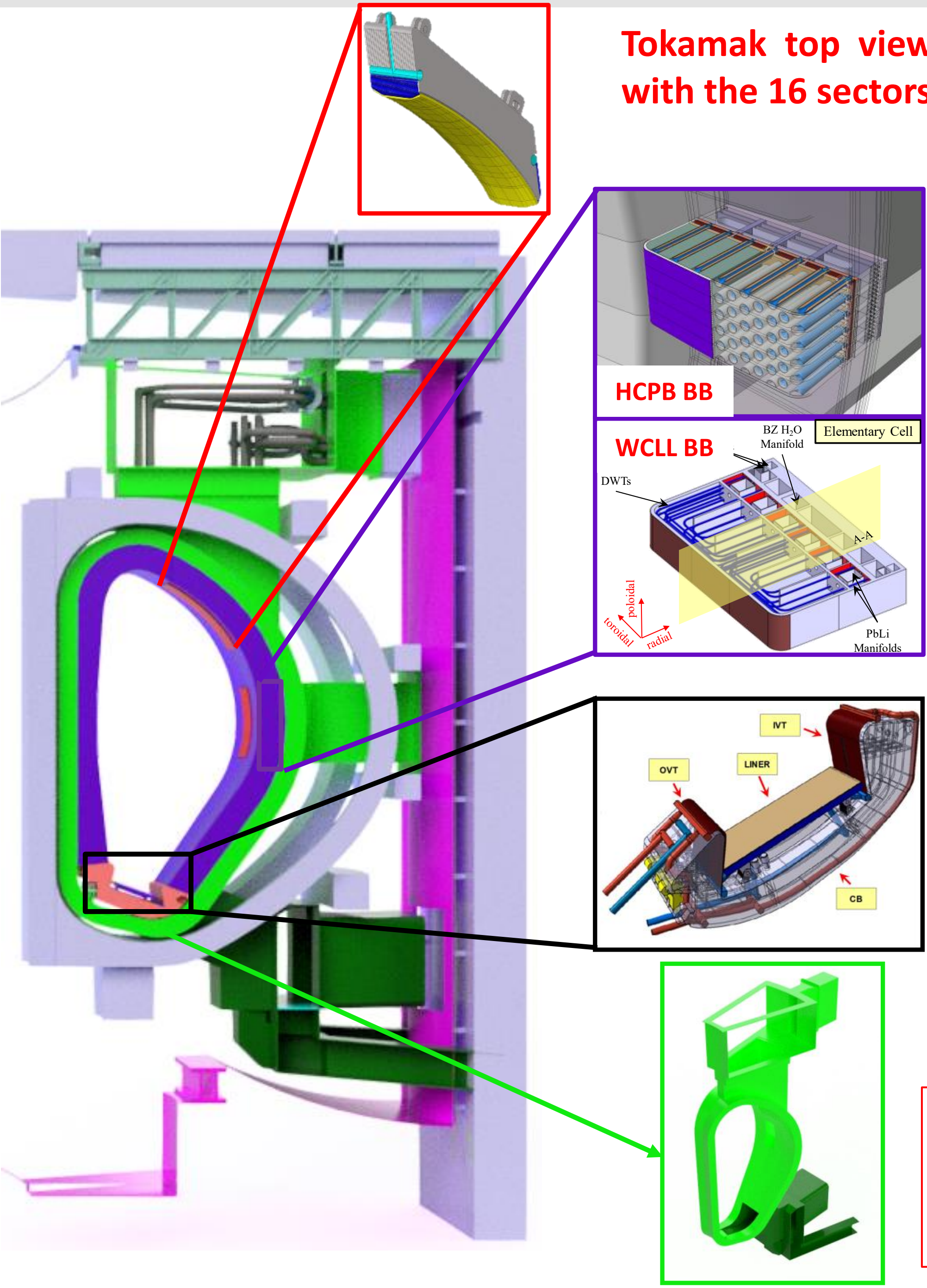
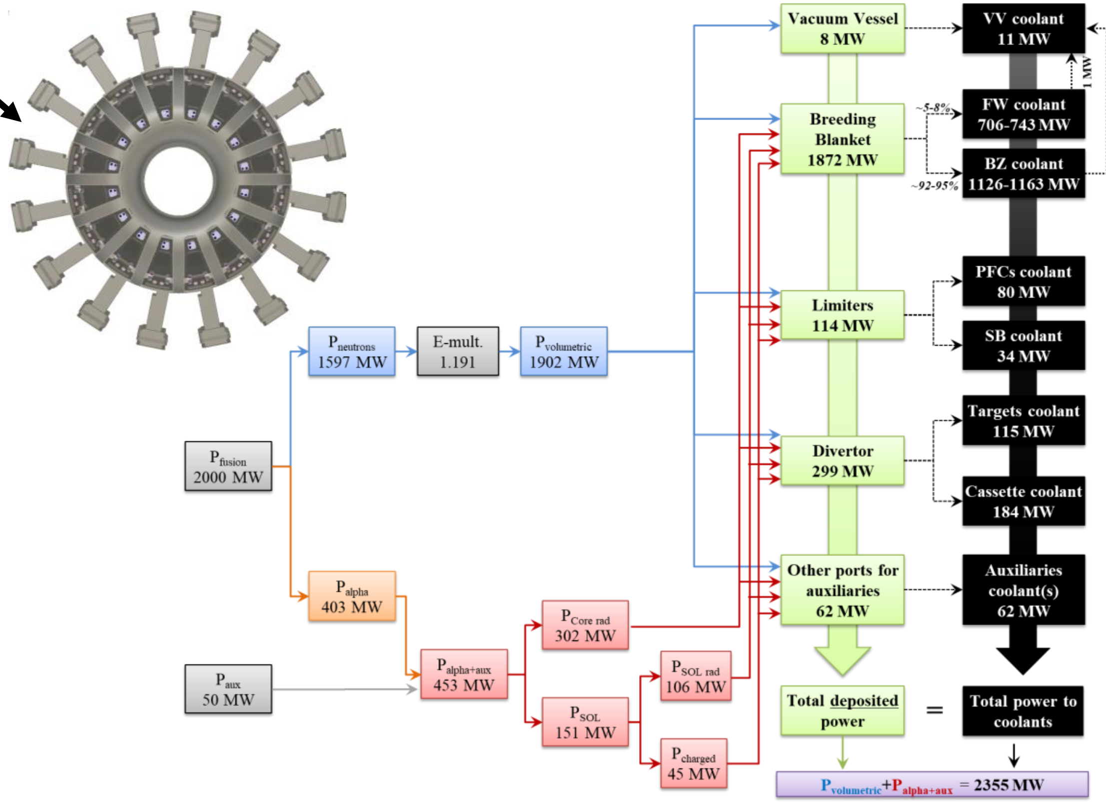
Main DEMO In-VV components

Several clients to feed



Tokamak top view with the 16 sectors



Current DEMO baseline foresees 16 tokamak sectors.

Several In-Vessel components encompassed by the VV.

- **Breeding Blanket**: 80 segments (48 outboard BB + 32 inboard BB)
- **Divertor**: 48 cassettes (3 per tokamak sector)
- **Limiters**: 20 discrete limiters are currently considered.
- **Vacuum Vessel**: 16 sectors
- **Other auxiliaries** (additional heating antennas, port plugs etc.)

Due to the different requirements of the clients, a single coolant circuit cannot be adopted. Several coolant systems to be developed (final number not defined yet).

How the DEMO Tokamak coolants system looks like?

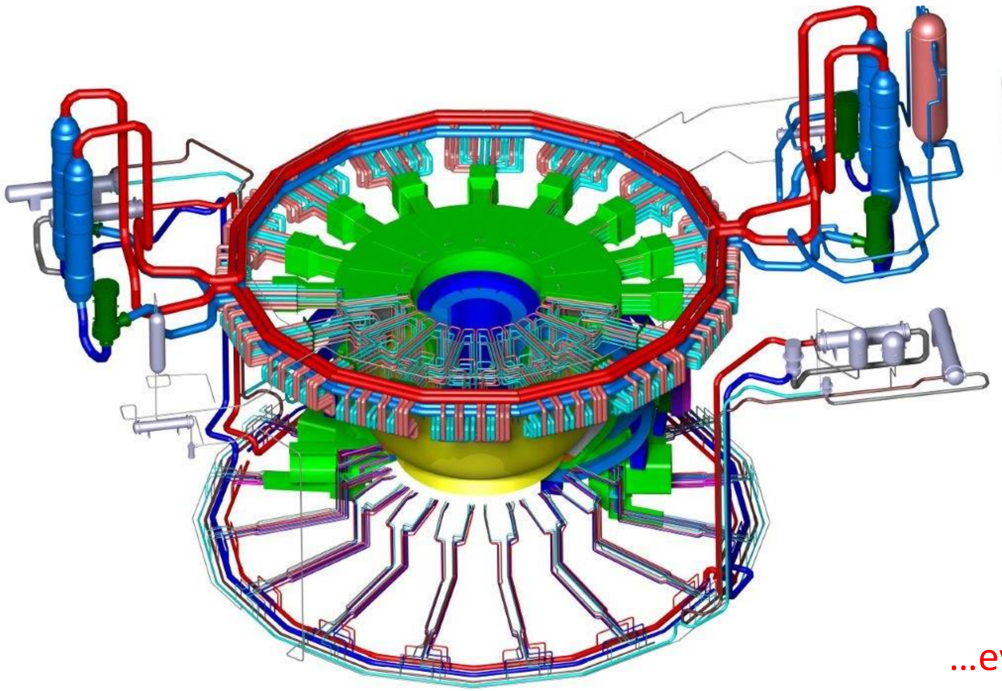
Comparison with Nuclear Power Plants

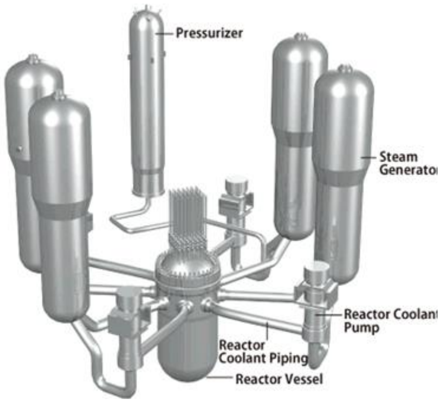
Quantity	Breeding blanket PHTS	Shielding Components PHTS	High Heat Flux PHTS
Nom. thermal-power [MW]	1900	230	240
Primary water volume [m^3]	630	140	280
Primary avg. temperature °C	312	195 (312)*	133
Primary pressure [MPa]	15.5	3.5 (15.5)*	5.0
Mass flow rate [kg/s]	9754	1718	9394

**Values for high temperature option;*

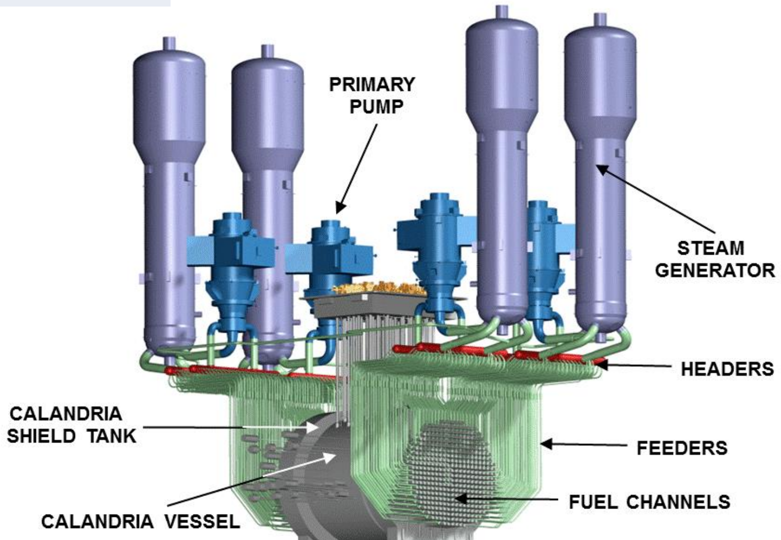
4-loop PWR of 3 GW_{th} has about 350 m^3

CANDU-6 has about 150 m^3 heavy water inventory





...even if you try hard to imagine it, it's hard for a tokamak to look like a pot...



...it doesn't look like the Calandria neither, **but** CANDU's layout is optimized since decades to have:

- Separate cooling circuits
- Feeders, headers
- main equipment on the two opposite side of the building.

Corrosion and its control in fusion environment

Main materials used in DEMO PHTSs

In-vessel components
- **EUROFER-97** → breeding blanket, shielding components
- **Copper based alloy** – High heat flux components
- **SS 316L(N)-IG** → High heat flux components and vacuum vessel

Ex-vessel components
- **Low alloy steels** → base materials for pressure vessels (cladded)
- **Austenitic SS 304/316 (or variants)** → piping and vessels cladding
- **Nickel based alloy** → steam generator tubes and vessels cladding

EU-DEMO circuits	**Breeding blanket**			**Shielding components**			**High heat flux components**		
	Alloy	Area* [m²]	[%]	Alloy	Area* [m²]	[%]	Alloy	Area* [m²]	[%]
In-flux									
- ***tubes/channels***	Eurofer97	10288	**54**	Eurofer97	1572	**42**	CuCrZr	303	**6**
- ***manifolds***	Eurofer97	9445		Eurofer97	28		316L(N)-IG/ Eurofer97**	310	**6**
- ***others***	-	-		Eurofer97	1566		TBD	49 (ST)	**1**
Steam generator/ heat exchanger tubing	I-690/ I-800	11715	**32**	I-690/ I-800	2800	**37**	I-690/ I-800	1050	**21**
Primary coolant pipework	304 SS	5090	**14**	304 SS	1625	**21**	304 SS	3250	**66**
Total		**36538**			**7591**			**4962**	

**All surfaces are approximate values*
***Less likely option*

Nuclear Power Plants	**CANDU-6 (2.1 GW_{th})**			**W-3 Loop (2.7 GW_{th})**		
	Alloy	Area* [m²]	[%]	Alloy	Area* [m²]	[%]
In-flux						
- ***Fuel***	Zircaloy-4	3500	**24**	Zircaloy	5530	**24**
- ***Pressure tubes***	Zr-Nb	800		-	-	-
- ***Others***	403 SS	800	**4**	SS I-718	1185 514	**5** **2**
Steam generator/ heat exchanger tubing	I-800	10750	**59**	I-690/ I-800	13600	**59**
Primary coolant pipework	Carbon Steel*	2300	**13**	Stainless steels	2372	**10**
Total		**18150**			**23201**	

**about 10% of feeder area is 2-1/4 Cr-1 Mo steel*

Corrosion and its control in fusion environment

Several forms of corrosion–Chemical conditions for materials' protection

Macro-localized corrosion

- General or uniform corrosion
- Galvanic corrosion
- De-alloying corrosion
- Velocity phenomena->erosion-corrosion, cavitation, impingement, fretting and FAC
- Crevice corrosion

Micro-localized corrosion

- Crevice corrosion
- Pitting corrosion
- Intergranular corrosion
- Corrosion fatigue
- Stress corrosion cracking

Two main objectives for the water chemistry control:

- protect the pressure boundary materials' integrity
- control of dose rates by minimising production and transport of corrosion products

EUROFER-97 → Low O_2, Alkaline pH, low ionic impurities

Copper based alloy – Very limited O_2, neutral or alkaline pH, high water purity

Stainless steels/nickel alloys → Limited O_2, alkaline pH, Low Cl^-

Choice of the alkalizing agent

Is tritium a problem or an asset?

LiOH, KOH or NaOH are common alkalizing agent used to increase water pH

NaOH: ruled out due to higher risk of caustic SCC

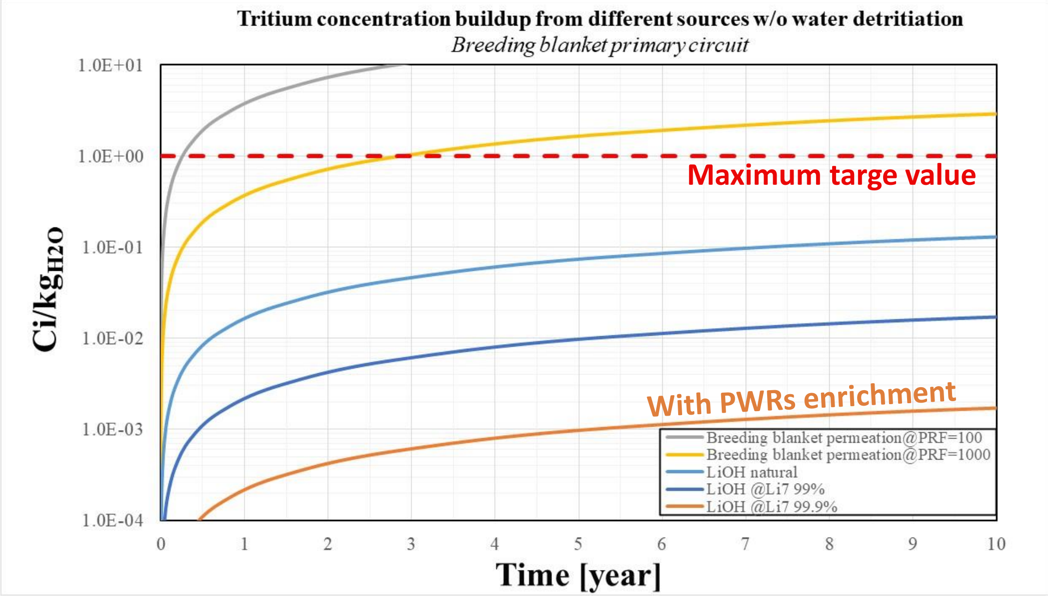
- *$^{23}Na(n,\gamma)\,^{24}Na \rightarrow T_{1/2} \approx 15$ h; 1.37 + 2.7 MeV gammas*

KOH: WWER experience, EPRI studies

- *$^{39}K(n,\gamma)\,^{40}K \rightarrow T_{1/2} \approx 1.25 \cdot 10^9$ y; 1.46 MeV gamma*
- *$^{41}K(n,\gamma)\,^{42}K \rightarrow T_{1/2} \approx 12.3$ h; 1.5 MeV gamma*

LiOH: Western PWRs experience

- *$^{6}Li(n,He)^{3}H$ and $^{7}Li(n,n\alpha)\,^{3}H \rightarrow T_{1/2} \approx 12.7$ y;*



Main data in a nutshell:

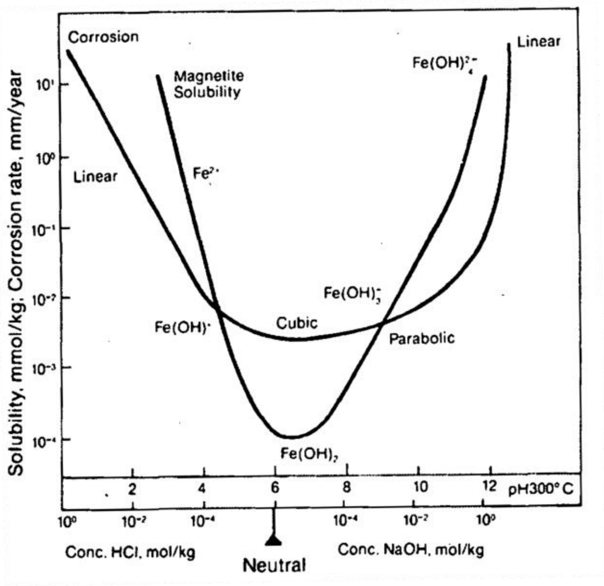
- > 320 g/day of tritium being produced in breeding blanket.
- With coatings reducing by a factor 100 the tritium permeation, migration into coolant can be as high as 450 mg/day → **water detritiation system needed**
- Production from natural LiOH in coolant would be max. 2 mg/day → **negligible**
- Tons of depleted ^{7}Li available from ^{6}Li enrichment, thus completely different supply chain respect to western PWRs → **Cost effective solution**

LiOH is currently judged as the most elegant solution for fusion power plants

Corrosion and its control in fusion environment

pH level for circuits equipped with Eurofer97

Corrosions in steels show a broad minimum in slightly alkaline conditions. Fe_3O_4 solubility mirrors the minimum.



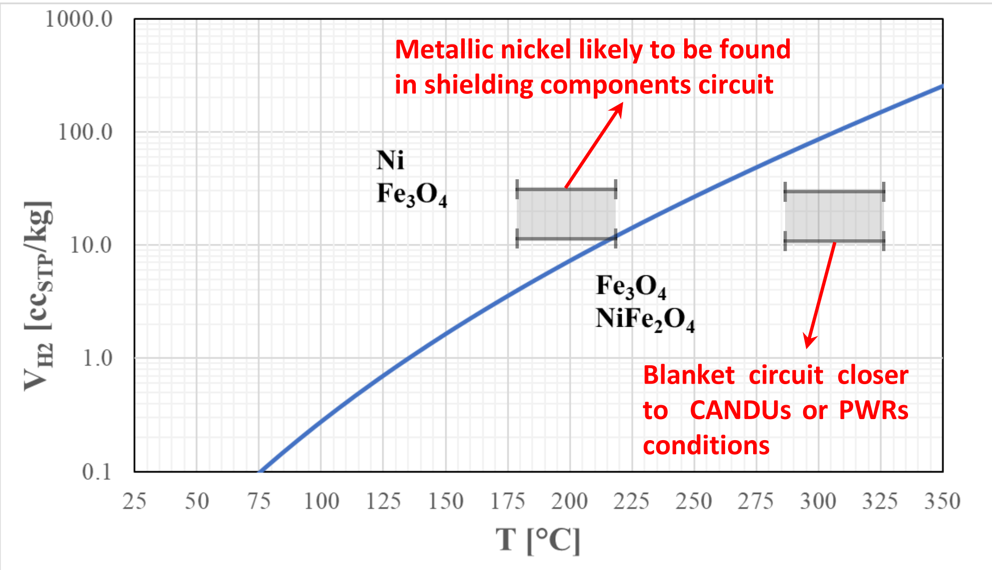
After G.M.W. Mann (1977).

Slightly alkaline condition, with pH_{25} between 10 to 12 would be beneficial to limit general corrosion

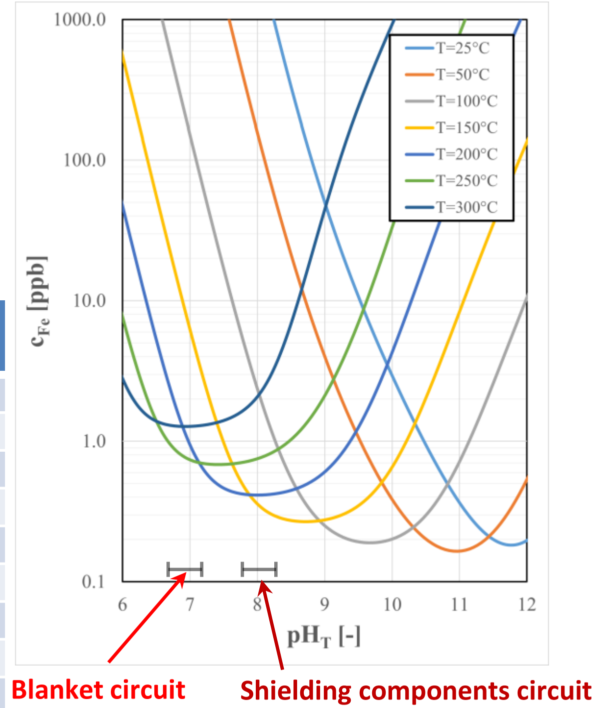
→ In practice, pH_{25} kept below 11 to minimize the possibility of generating caustic environments

Corrosion of Eurofer97 higher than SS and Inconel.

→Magnetite anticipated to be dominant as Fe/Ni> 2



T [°C]	pH_T min solubility	pH_{25} min solubility	Li ppm
25	11.81	11.81	63.78
50	10.97	11.69	47.14
100	9.71	11.44	25.75
150	8.69	11.07	10.39
180	8.32	10.94	7.68
200	7.94	10.69	4.20
250	7.43	10.30	1.69
300	6.95	9.65	0.37
310	6.79	9.40	0.20



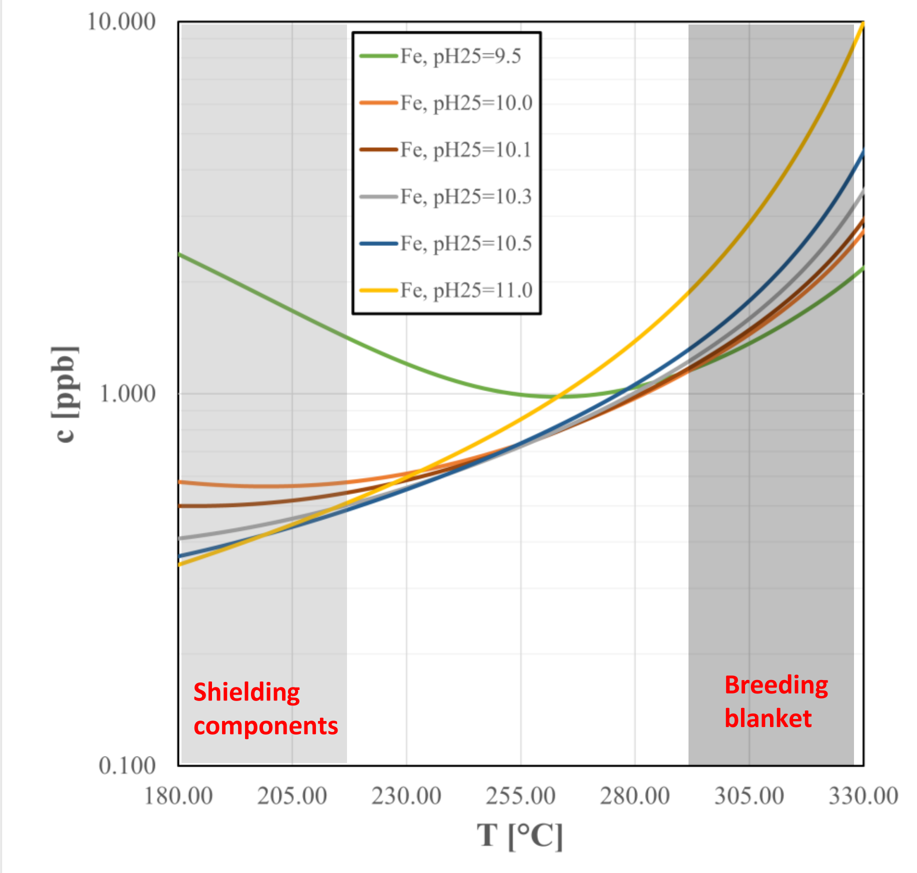
Corrosion and its control in fusion environment

pH level for circuits equipped with Eurofer97.

Positive solubility gradients within in-flux areas are expected to minimize precipitation in the small channels and tubes → less radioactivation, but also cleaner heat transfer surfaces (heat transfer, pressure drops.

- For breeding blanket circuit (T_{ave}≈310°C) is recommended the following operating band: **9.5< pH_{25} <10.5** (0.26 ppm< Li < 2.7 ppm)
- For shielding components (T_{ave}≈195°C), slight shift of the minimum pH_{25} is suggested to minimize deposition onto in-flux surfaces avoiding → **10.1 < pH_{25} <10.5** (1.1 ppm< Li < 2.7 ppm)

Assessments on maximum lithium concentration to be made → 2.7 ppm are currently assumed.



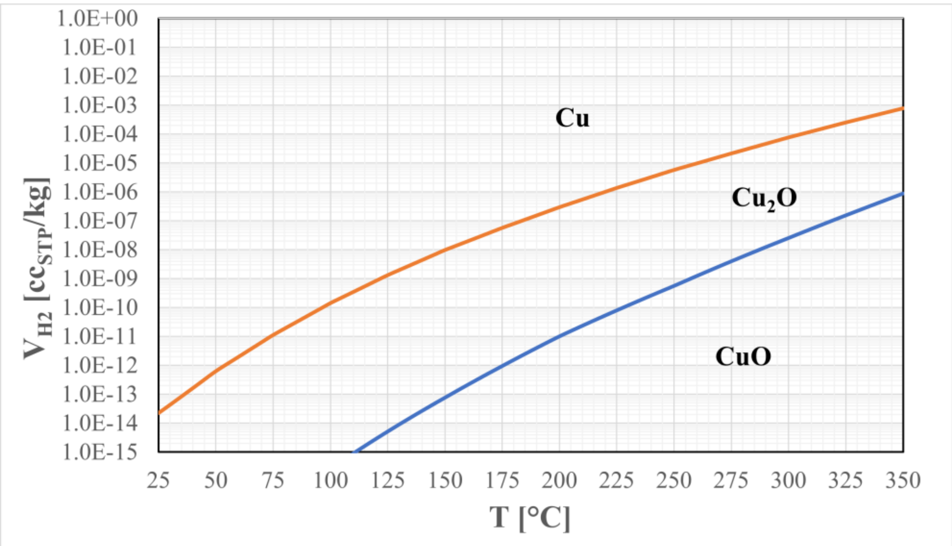
Simplistically:

$$\frac{dW_{in-flux}}{dt} = -R - k_{dis/pre}[C_w(T) - C_b(T)] - k_{er}W_{in-flux} + k_{dep}C_{ins}$$

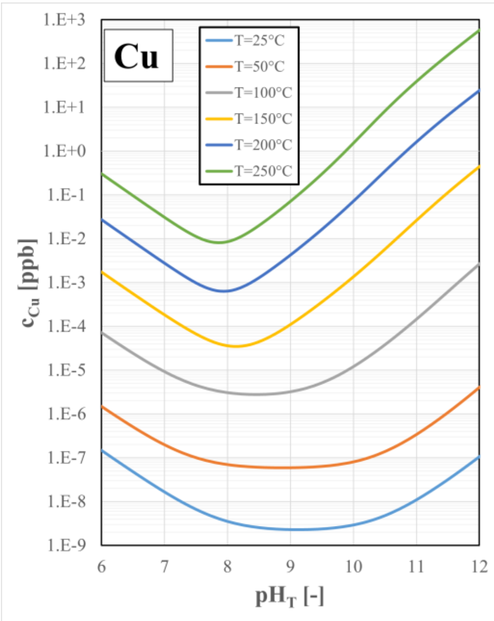
For positive solubility gradient, scale tends to dissolve from hotter wall to cooler water and no precipitation occurs

pH level for circuits equipped with CuCrZr

- Reducing conditions are said to be needed to protect Cu from corrosion – if reducing conditions are guaranteed, thermodynamics shows that only metallic copper will be stable
- Consistent with results from Montford and Rummery (1975), who found mainly Cu in metallic form in the crud on Monel 400 (31%wt Cu, 66%wt Ni) tubes operated between 250 and 295 °C and pH_{25} 9.5-10.5.
- EPRI reports on BWRs and fossil plants suggest to maintain pH_{25} around 9 in stations equipped with copper alloys – however means for pH control for boilers could be of limited relevance for closed loops working in subcooling conditions such a EU-DEMO high heat flux components.



- Thermodynamic data is still under development as regard other oxides that can form.
- **pH** range is tentatively set to **$9.0 < pH_{25} < 10.0$**



Radiolysis of water

Can we keep sufficient reducing environment?

Simplistically, ionizing radiation decomposes water to form the species H^+ , OH^-, H, OH, H_2, O_2, H_2O_2, e^-_{aq} and HO_2^-.
The stable products are H_2, H_2O_2 and O_2.

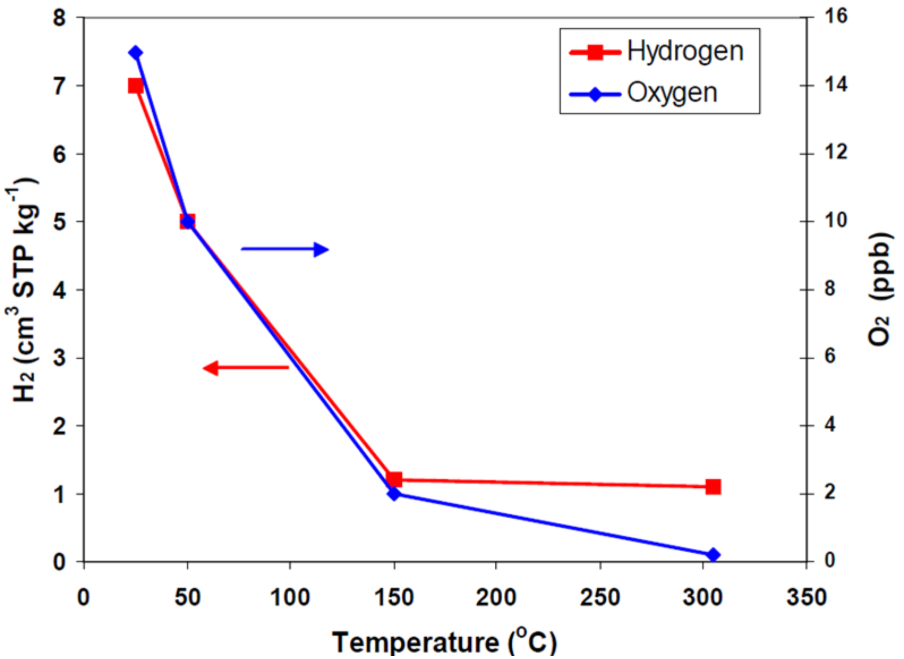
Reactions are reversible and <u>hydrogen addition</u> can suppress the H_2O_2 and O_2 formation

Recombination increases with temperature
→PWRs conditions are beneficial!

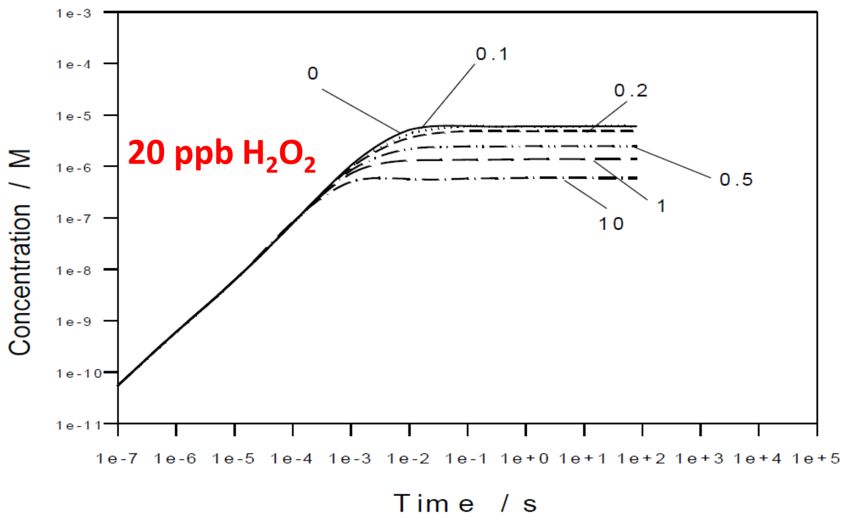
Oxidizing conditions could be difficult to suppress in cold circuits
→in high heat flux components electrochemical corrosion potential could remain high.

Hydrogen is still recommended to decrease the oxidant formation.

Preliminary selected range 10-25 cc (STP)/kg



Takiguchi, H., et al., In-Pile Loop Experiment and Model Calculations for Radiolysis of PWR Primary Coolant, Water Chemistry of Nuclear Reactor Systems 8, 2001.



D.D. Macdonald, Corros. Mater. Degrad., (2022).

Activation of corrosion products

Preliminary approach to assess the activity levels in circuits (1/2)

- Large quantity of metals is released to the coolants due to the combination of huge wetted surfaces and relatively high corrosion rates of in-vessel material:
  - Eurofer97 is estimated to corrode at an average rate over 5 years up to 5.7 mg/dm^2mo
  - CuCrZr corrosion rate averaged over 2 years up to 130 mg/dm^2mo
- **Purification half-life up to 60 min** is recommended to effectively remove corrosion products and ensure high water purity → in case of breeding blanket circuit this implies a letdown flow around 1% of the loop mass flow rate (in PWRs generally 0.1%) → high temperature filtration needed?

Long-term CRUD specific activity [kBq g_{crud}^{-1}]	EU-DEMO			NPP
	Breeding Blanket PHTS	Shielding components PHTS	High Heat Flux components PHTS	AP600
^{58}Co	$5.08 \cdot 10^4$	$2.32 \cdot 10^4$	$4.25 \cdot 10^6$	$4.44 \cdot 10^5$
^{60}Co	$7.00 \cdot 10^4$	$1.39 \cdot 10^5$	$1.38 \cdot 10^6$	$2.22 \cdot 10^5$
^{59}Fe	$7.39 \cdot 10^4$	$3.70 \cdot 10^5$	$3.82 \cdot 10^6$	$1.85 \cdot 10^4$
^{54}Mn	$1.45 \cdot 10^6$	$7.26 \cdot 10^5$	$5.63 \cdot 10^4$	$5.18 \cdot 10^4$

It is expected that residual activities on surfaces will be comparable with fission power plants if not higher in some case

Activation of corrosion products

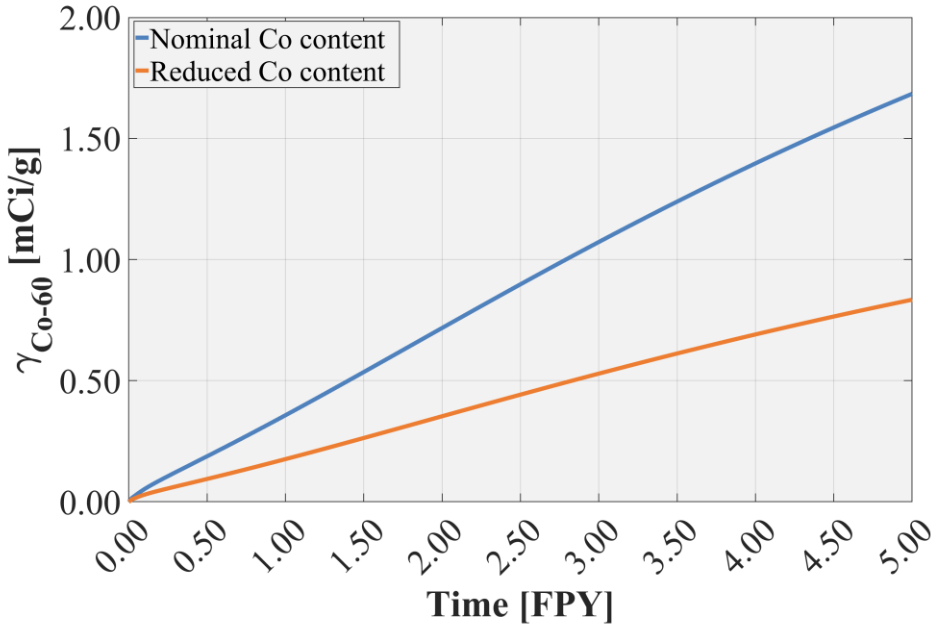
Preliminary approach to assess the activity levels in circuits

- The current specs for max. cobalt content in the main in-vessel materials are comparable with materials used in out-of-flux regions:
  - For CuCrZr, this could be acceptable because ^{60}Co generated from Cu itself via $^{63}Cu(n,\alpha)^{60}Co$ is generally dominant
  - Cobalt in Eurofer97 has a strong impact on the final ^{60}Co content in the circuits equipped with this reduced activation steel → nearly linear proportionality
  - Halving cobalt content in other ex-vessel material estimated to weight about 5%. → minor impact.

	Max. Cobalt [ppm]
Eurofer97	<100
CuCrZr	<500
SS 304	<500
SS 316L	<500
I-690	≤350 ≤150*
I-800	≤1000 ≤100*

**tubing material*

- For comparison, Zirconium alloys for fuel cladding have Co content as low as 20 ppm and release rates almost negligible.



Summary

- Corrosion issues and control must be carefully addressed since the early stage of the fusion power plant design
- Efforts should me made to reduce wetted surfaces and water inventories of the circuits, focusing chiefly on the in-vessel components
- LiOH is an alkalizing agent considered fully compatible with fusion power plant environment
- Tailored chemistry is possible for the different circuits and differentiation between copper-base circuits and Eurofer97 loops ease the control
- Radiolysis of water at low temperature must be carefully addressed
- Huge amount of corrosion product to be filtered to maintain water purity
- Further reduction of cobalt impurities in Eurofer97 should be pursued
- The presence of stainless steel in the in-vessel regions of HHFC increases ^{58}Co

Thank you for your attention