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# INSIGHTS INTO PROSPECTIVE FUSION REACTOR COOLING SYSTEMS FROM FISSION REACTOR COOLING CIRCUITS

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*The next generations of nuclear fusion reactors, including ITER and DEMO, will consider several different cooling systems for heat dissipation, power generation and tritium breeding. This includes the water-cooled lithium-lead blanket (WCLL) design, which bears significant similarities to the water-cooled circuit in a pressurised water fission reactor. Preparatory work has begun to analyse how the water chemistry regimes used in light water reactors (LWRs) might be adapted to a fusion cooling system. Mitigation procedures from LWRs such as hydrogen water chemistry, zinc and noble metal addition may prove useful in controlling the rate of corrosion in a WCLL circuit, a system which is also subject to aggressive radiolysis products of water and high flow velocities. In addition, a fusion cooling system must cope with several unique challenges, including higher neutron energies and fluxes, thermal excursions from plasma instability and strong magnetic fields up to 10T.*

## 1 INTRODUCTION

The European demonstration fusion power plant (DEMO) is currently in the design phase and is considering two design options for the breeder blanket (BB). One option is the water-cooled lithium-lead (WCLL) arrangement, where the energy emitted from the fusion plasma is converted into heat by a molten lithium-lead system. In order to maintain a thermal equilibrium, water is used to remove heat from the BB and is subsequently used to generate electricity.

The conditions within the irradiated water coolant circuit comprised in WCLL can be compared to the reactor coolant system of a fission pressurised water

reactor (PWR), which provided the design basis for this part of the plant. There are key differences which have been identified in previous reports,<sup>1,2</sup> notably the fast neutron spectrum, the presence of intense magnetic fields and high levels of tritium and the use of an advanced material, namely the reduced activation ferritic-martensitic (RAFM) steel Eurofer -97.

Eurofer-97 is one of several RAFM steels under development for use in fusion applications – others include F82-H and JLF-1 from Japan, CLAM from China and 9Cr-2WVTa from the USA. These steels are designed to maintain structural strength at high temperatures with high irradiation resistance,<sup>3</sup> but without the use of elements typically present in structural steels like Ni and Co that form long-lived radioisotopes when transmuted by neutron irradiation. RAFM steels replace these elements with alloying elements that have relatively short lifetimes after they become activated.<sup>4</sup> Typically this means replacing Mo, Nb and Ni in favour of elements such as W, V and Ta. As a result, most RAFM steels contain 8-9 wt.% Cr, 1-2 wt.% W, 0.4-0.5 wt.% Mn and 0.1-0.25 wt.% each of Ta, V and C.

As the European candidate RAFM steel, Eurofer-97 is expected to be used for the DEMO breeding blankets and will be used in the European test blanket modules of ITER<sup>5</sup>. After normalization at 980 °C for 27 minutes and tempering at 760 °C for 90 minutes it displays a ferritic-martensitic structure with  $M_{23}C_6$  carbides at the prior austenite grain boundaries and lath boundaries, as well as smaller MX precipitates within subgrains.<sup>6</sup> The alloy has also been produced using an oxide-dispersed (ODS) version, where nanoparticles of yttrium oxide are dispersed within the Eurofer-97 matrix, giving higher

strength at high temperatures and creating sinks for vacancies and transmuted He.

In this work we will explore preliminary studies on Eurofer-97, where we investigate the effects of typical fission water chemistries on early stage corrosion, as well as the impact of short-term thermal heat treatments on corrosion susceptibility. We will also discuss how strong magnetic fields can influence the formation of corrosion products in certain orientations.<sup>7</sup> As fusion power moves towards larger-scale, power-generating reactors, the insights from fission reactor chemistry become increasingly valuable.

## II LWR WATER CHEMISTRY

The water chemistry regime within light water reactors has evolved substantially with time and operating experience, and still varies between plant design, operator and country. Despite these differences, a number of practices are becoming applied more uniformly across the 298 PWRs and 73 BWRs operating worldwide.<sup>8</sup> Water chemistry guidelines have been established by industry organisations corresponding to each of the major LWR fleets, in response to several corrosion-related issues that developed over decades of LWR reactor operation. These guidelines can be grouped into three broad categories of reactor design – boiling water reactors (BWR),<sup>9,10</sup> water-water energetic reactors (VVER)<sup>11</sup> and pressurized water reactors (PWR).<sup>12-15</sup> Each guideline document aims to give best practice to maintain a water chemistry that minimizes out-of-core radiation fields, activity in chemical and radioactive wastes and planned discharges to the environment, whilst ensuring the integrity of the pressure vessel, fuel cladding and interfaces with any secondary or auxiliary cooling circuits. There is also a need to control unwanted impurities within the coolant that might lead to neutron activation (e.g. transition metal ions) or enhanced corrosion (e.g. halide anions).

These guidelines typically recommend the addition or removal of particular species to maintain performance – such as ensuring ultra-high purity water in the BWR guidelines for Japanese plant,<sup>10</sup> and the addition of dissolved hydrogen to maintain reducing conditions. Often there are competing needs for these additives within a coolant circuit – for instance the majority of an LWR primary coolant circuit should be kept in a reducing environment to prevent breakaway oxidation and stress-corrosion cracking, whilst some locations of the BWR reactor coolant system may require oxidizing conditions to mitigate concerns such as flow-accelerated corrosion (FAC). It is likely that similar tradeoffs will be required in a fusion cooling circuit, but the higher radiation fields mean that further analysis of the appropriate dissolved hydrogen levels are required.

### II.A Zinc and NobleChem™

Both PWRs and BWRs have increasingly injected depleted zinc into the coolant water (typically 5-30 ppb) for a number of reasons: mitigation of primary water stress corrosion cracking (SCC) initiation in nickel-based alloys and steels, corrosion product generation, reduced crud deposition on fuel surfaces and dose rate reduction.<sup>16</sup> Neutron activation of the naturally occurring <sup>64</sup>Zn isotope produces the radioisotope <sup>65</sup>Zn, and so Zinc depleted in <sup>64</sup>Zn is usually used to reduce radiation fields and low level wastes.<sup>17</sup> Zinc injection has been shown to benefit the corrosion performance of austenitic stainless steels,<sup>18</sup> but relatively little is known of zinc injection's effect on martensitic steels and Eurofer-97 in particular.

The practice of adding platinum nanoparticles to reactor coolant water to efficiently mitigate SCC in steel components<sup>19</sup> has evolved from the first time it was used in the 1990s such that BWR plants are moving towards an injection regime of 'little and often' or even continuous doping, and away from the traditional large-scale platinum dosing that occurs at relatively long time intervals.<sup>20</sup> Moving towards a continuous injection of platinum at low concentrations will lead to better dispersion of nanoparticles across the system surfaces (including within any new cracks), as well as producing nanoparticles that have enhanced catalytic properties. A homogenous distribution of very small platinum nanoparticles is understood to be required to ensure that intergranular stress corrosion cracking (IGSCC) mitigation remains effective.<sup>21,22</sup>

Even low loadings (<0.1 µg/cm<sup>2</sup>) with small particles can be sufficient (in opposite to higher loadings with few large particles). A series of trials at the US Nine Mile Point plant that commenced in October 2018 will test a new passive platinum injection regime<sup>23</sup> introducing a dilute platinum solution into the system without the use of pumps. Ultrasonic inspection of cracks will be conducted to assess the impact on crack growth rates, and results will be reported by EPRI. The outcome of this trial will be a useful guide to inform the noble metal chemical addition strategy for the DEMO WCLL system, should this mitigation measure be applied.

Recent research on the catalytic and deposition behaviour of platinum nanoparticles<sup>24</sup> suggested that the size of the nanoparticles has a large impact on their catalytic activity, and that the size of the nanoparticles produced can be controlled by varying the dilution of the platinum solution. The impact of flow velocity on nanoparticle deposition indicates that higher platinum loadings can be achieved in turbulent flow regimes when compared with laminar flow regimes. Regarding transport of the nanoparticles, diffusion was identified as the key

factor, with smaller particles exhibiting faster rates of diffusion. In BWR plant, smaller platinum nanoparticles appear to be more desirable on the whole. Injection of Pt into a WCLL circuit will depend on the effect of the higher flux in a fusion reactor on radiolysis constituents and the relative effectivity of dissolved hydrogen concentrations.

## II.B Alternatives to Li as an alkalising agent

In response to the worldwide shortage of Li-7 supply that occurred in 2015<sup>25</sup>, alternative alkalising agents are being investigated for use in Western-design PWRs. Given its expected technical and operating cost benefits, KOH is the primary candidate to replace Li-7, particularly due to the extensive experience of using KOH as a pH control agent in Soviet Union-design VVER reactors.

Despite the expected benefits of using KOH, there are a number of technical uncertainties that must be resolved before Western-design PWRs could adopt KOH as a pH control agent. These include the following issues:<sup>26-27</sup>

- Nickel-based alloys are not present in VVER reactors, so their compatibility with KOH is not well understood;
- The potential for the formation of local corrosive environments due to enriched KOH concentrations requires further investigation;
- The combined effect of irradiation and various KOH concentrations on stainless steels is not well understood;
- Given the higher volumes of KOH required to achieve the optimal pH (compared with LiOH), the impact this could have on existing coolant dosing, purification and waste processing systems requires further investigation;
- The production and effects of activated potassium (K-42) in the coolant system is not well understood;
- Li-7 will already be in the PWR coolant system through the B-10 ( $n, \alpha$ ) Li-7 reaction, resulting in a more complex pH control system (i.e. two alkalising agents must be monitored and controlled in parallel), therefore better Li/K models are required for pH control;
- The existing KOH and potassium borate thermodynamic databases must be expanded to include higher temperature data.

As a result of the issues identified, a number of materials qualification programmes<sup>26</sup> are planned to investigate the impact of KOH on the behaviour of fuel cladding, stainless steels and nickel-based alloys. The general approach is to conduct accelerated testing to measure the difference in material cracking behaviour in

LiOH versus KOH systems, with autoclave experiments to be carried out at various operating conditions (start-up, shutdown and midcycle operating regimes). With the strong push to move away from LiOH and towards KOH in PWR plant, this raises questions as to the suitability of LiOH as an alkalising agent in the DEMO WCLL. Outputs from the KOH qualification programmes for PWRs will provide valuable data towards determining the most suitable alkalising agent for use in the DEMO WCLL. Consideration should be given to exploring the possibility and suitability of including Eurofer-97 in the KOH qualification programmes that are planned by the nuclear fission community; while continuing the Eurofer-97 testing already being carried out under the EUROfusion programme.

## III NEW CHALLENGES IN FUSION COOLANT SYSTEMS

### III.A Magnetic Fields

The water cooling system in a WCLL system has many similarities to a PWR reactor, but there are several parameters that differ significantly due to the fusion reactor environment. One key factor that has received attention only recently is the extremely high magnetic field, which in DEMO may reach anywhere from 4 T to 10 T during peak operation. As most metal systems intended for fusion reactors will contain some magnetically susceptible materials, it is expected that this will lead to an effect on their corrosion behavior.

Magnetic fields have been shown to increase corrosion in the coolant surface in a PbLi system,<sup>28</sup> whilst other studies have demonstrated changed corrosion behaviour in pure iron,<sup>29</sup> AISI 303 stainless steel,<sup>30</sup> and thin film metals.<sup>31</sup> Typically corrosion rates increase when in a parallel field due to increased pit formation and local stirring, whilst in a perpendicular field the corrosion rates decrease.

Recent work has explored the effect of a 0.88 T magnetic field on the corrosion of Eurofer-97 reduced activation ferritic-martensitic steel in a series of salt solutions at different temperatures.<sup>1,7</sup> These preliminary studies have demonstrated that this relationship between magnetic field orientation and corrosion behavior exists for Eurofer-97, with an increased thickness of magnetite in the parallel field and a variation in Cr segregation behavior and oxide thickness. When designing the layout of coolant pipes in a fusion reactor, the alignment of the pipe surfaces to the magnetic field will need to be considered to control corrosion product build-up.

### III.B Plasma Excursions

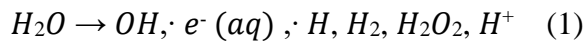
During production of Eurofer-97 and other RAFM steels, the tempering step is an important part of acquiring the desired microstructure for optimal mechanical performance. Microstructural stability has been demonstrated for test heat treatments between 400 °C and 600°C up to 10,000 hours,<sup>32</sup> although M<sub>23</sub>C<sub>6</sub> and MX precipitates both increase in size during ageing above 500 °C, and changes in Cr and Fe concentrations have been observed at grain boundaries.<sup>33</sup>

However, over longer time scale heat treatments and for shorter exposures above 650 °C, more substantial microstructural evolution might be expected. Recent work at the University of Bristol has shown that even a few hours exposure above 650 °C can result in substantial microstructural reorganization<sup>1</sup> including carbide dissolution and reprecipitation, and this is highly likely to result in a change in the corrosion resistance of the metal.

Plasma excursions due to vertical displacement events (VDEs) and Edge Localised Modes (ELMs) have been estimated to release energies of 50-100 MJ/m<sup>2</sup> for VDEs and between 6 and 12.6M J/m<sup>2</sup> ELMs to the first wall of ITER and/or DEMO, but are estimated to typically last durations of just 0.3-1 s for VDEs and 0.6 ms for ELMs.<sup>34-36</sup> As a result, whilst some thermal transients of Eurofer-97 components might be expected, the impact of repeated intense, short duration heating events needs to be studied further to understand the influence on microstructure, creep and corrosion behavior. Work simulating the magnitude of such thermal transients on the cooling circuits and structural materials behind the front wall in the event of plasma excursions is ongoing.

### III.C Higher Radiation Fields

As the coolant water in WCLL will be exposed to ionising radiation, it will undergo radiolytic decomposition to yield a range of chemically reactive species:

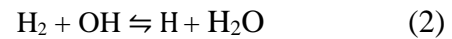


The reaction rates of these primary radiolysis products with each other is extremely high and they will also quickly react with other solute species or vessel surfaces. When the radiation field is constant, a steady state is reached with stable concentrations of each decomposition product. Steady-state concentrations of oxidising species like H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> can dramatically affect the corrosion of structural materials. Understanding their concentrations helps to better determine the level of hydrogen addition needed to obtain reducing conditions.

Development of a suitable model for DEMO has been undertaken based on LWR radiolysis models to

investigate water radiolysis yields under 14 MeV neutron irradiation. As the WCLL flow channel is a complicated system to model, the modelling exercise began with a simplified approach, which has been incrementally made more sophisticated. The initial radiolysis model incorporated reaction schemes and rate constants published by Boyd, Carver and Dixon<sup>37</sup> which have been validated by comparison with experimental data.<sup>38</sup> Recent developments to this model have incorporated the well-established data set of Elliot and Bartels<sup>39</sup> which gives radiolytic yields and reaction rate constants up to 350 °C. In addition, the model uses yields (G-values) appropriate to the high-energy neutron radiation field and a more realistic (though still highly simplified) representation of the system geometry and operating parameters.

The existing models for LWR radiation fields developed by Elliot and Bartels<sup>39</sup> comprise 21 reactions describing the interaction of the primary radiolysis products, as well as 10 reversible protonation/deprotonation reactions. Recent revisions have re-evaluated the activation energy for the equation:



These more recent studies<sup>40,41</sup> found that the kinetics of the reverse (H + H<sub>2</sub>O) reaction is higher than in the original Elliott and Bartels model. Similarly, it is necessary to take into account the interaction of hydrogen peroxide with oxidised metal surfaces within the circuit compared to the Teflon-coated tubes in the original model. These rates are key to the sensitivity of the model in calculating steady state H<sub>2</sub> and O<sub>2</sub> concentrations in a model WCLL circuit where the radiation fields are higher than in the LWR circuit. Further development of this model will lead to a better understanding of the parameters expected within the WCLL coolant.

## IV CORROSION STUDIED ON EUROFER-97 IN LWR CONDITIONS

### IV.A Oxidation of Eurofer-97 in LWR conditions

Whilst there has been considerable work on the mechanical properties and irradiation resistance of Eurofer-97, relatively little has so far been done to understand its corrosion behavior in LWR coolant scenarios. Here we present some preliminary work to characterize the early-stage oxidation behavior of Eurofer-97 after it has undergone short-term thermal treatment.

Specimens of Eurofer-97 were cut into 48 6x4x2 mm<sup>3</sup> samples using a Struers accutom and washed in acetone, methanol, isopropanol and distilled water. Samples were inserted into 12 quartz vials and then

heated to 1600 °C to close them. They were subsequently degassed before closure at 680 °C to degas the samples before being placed into the tube furnace for thermal ageing. The specimens were then aged in a furnace for 168 hours at temperatures of 550 °C, 650 °C, 750 °C and 850 °C. After thermal ageing the quartz vials were removed from the tube furnace and quenched in water before grinding to a P1200 finish using SiC grit paper.

experienced a thermal heat treatment of (a) 550 °C (b) 750 °C (c) 850 °C for 168 hours.

After ageing, the heat treated Eurofer-97 specimens were mounted and exposed to hot water conditions in a static autoclave for 336 hours at 290 °C. Two exposures were carried out on separate samples – one with deionized water and the second in a solution of 1 ppm of zinc acetylacetonate provided in a dihydrate powder form (Sigma Aldrich).

Figure 1 shows the oxide surfaces of three polished Eurofer-97 specimens, previously having had heat treatments for 168 hours at 550 °C, 750 °C and 850 °C respectively. Using a Helios Nanolab focused ion beam, the oxide films were cross-sectioned, and their average film thickness measured.

The specimen heated at 550 °C has oxidized less, with only sporadic coverage of oxide crystals and the polish lines still visible, and a ~320 nm thick oxide layer. In the 750 °C heat treatment, a uniform homogenous magnetite layer has formed with a grain diameter of 0.5-1 µm and the oxide layer has grown to ~355 nm. In the 850 °C heat treatment, some oxide crystals are still visible but there are substantial deposits above the oxide which EDX shows are carbon-rich and may be linked to the dissolution of large carbides formed during this high temperature ageing step. In addition, after the 850 °C heat treatment substantially more corrosion layer has formed, with a thickness of ~460 nm.

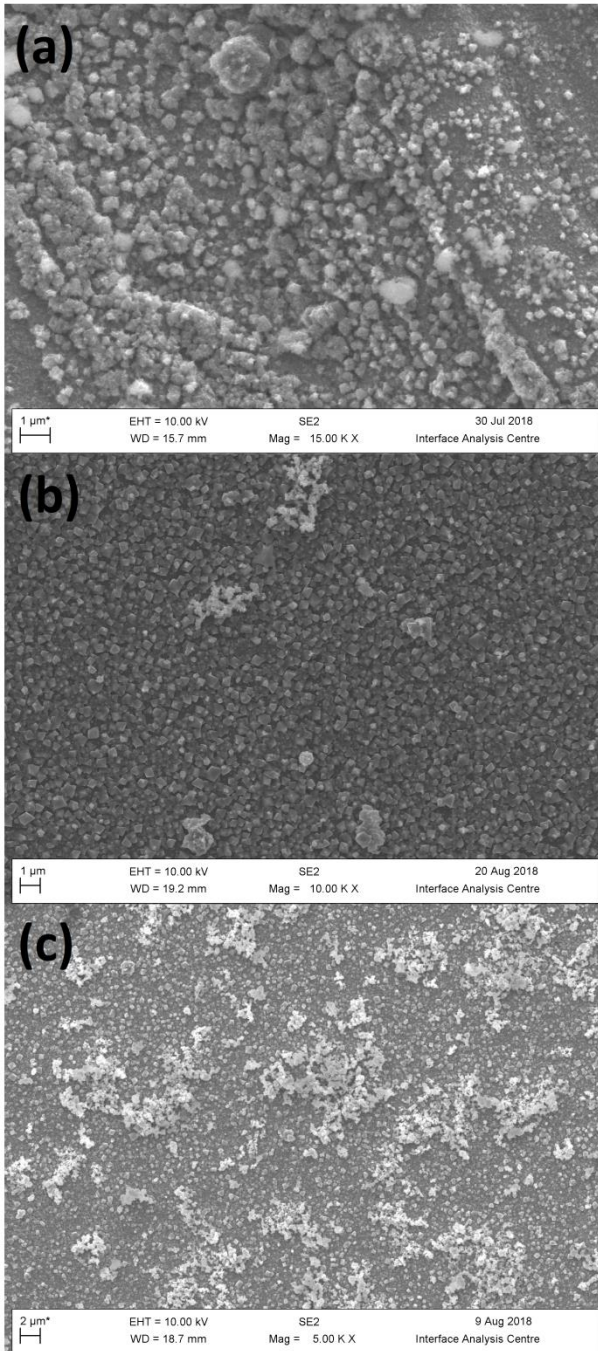


Figure 1: Oxide surfaces of Eurofer-97 samples exposed to 290 °C water for 336 hours. Each substrate previously

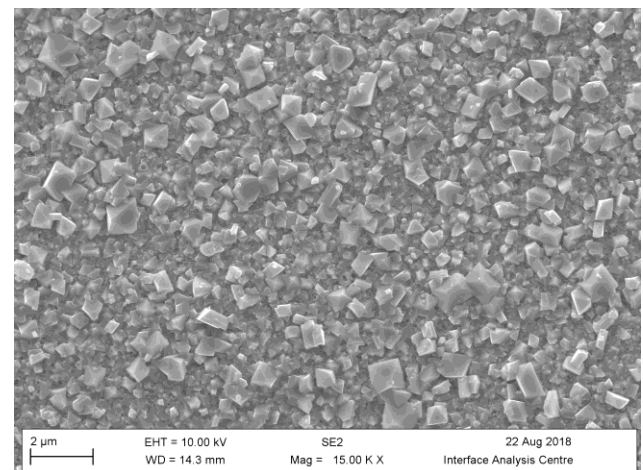


Figure 2: Typical morphology of a Eurofer-97 sample exposed to a 168 hour 750°C heat treatment after 336 hours at 290°C in the presence of 1ppm Zinc acetylacetonate.

In comparison, a sample of the Eurofer-97 material exposed to the same 336 hour 290 °C corrosion experiment but with 1 ppm of zinc acetylacetonate added to the deionized water shown in Figure 2 displayed a

much more consistent and regular oxide surface with clear octagonal magnetite species present. In the Zinc exposed sample, the grain diameter appears to be larger at 1-2 $\mu$ m with more distinct octahedral facets.

#### IV.B Online NobleChem™ application to Eurofer-97

In addition to the static autoclave experiments, a series of online NobleChem™ applications were applied to the Eurofer-97 specimens described previously at the high-temperature water flow loop based in the Paul Scherrer Institut (see Ref. 17 for details). Specimens were exposed to high purity water (conductivity at inlet of 0.055  $\mu$ S/cm) at 280 °C for 285 hours, with 80 ppb of dissolved hydrogen and 300 ppb of dissolved oxygen at the inlet. 200  $\mu$ g of Pt (as  $\text{Na}_2\text{Pt}(\text{OH})_6$ ) was injected at a rate of 20  $\mu$ g per hour during the experiment.

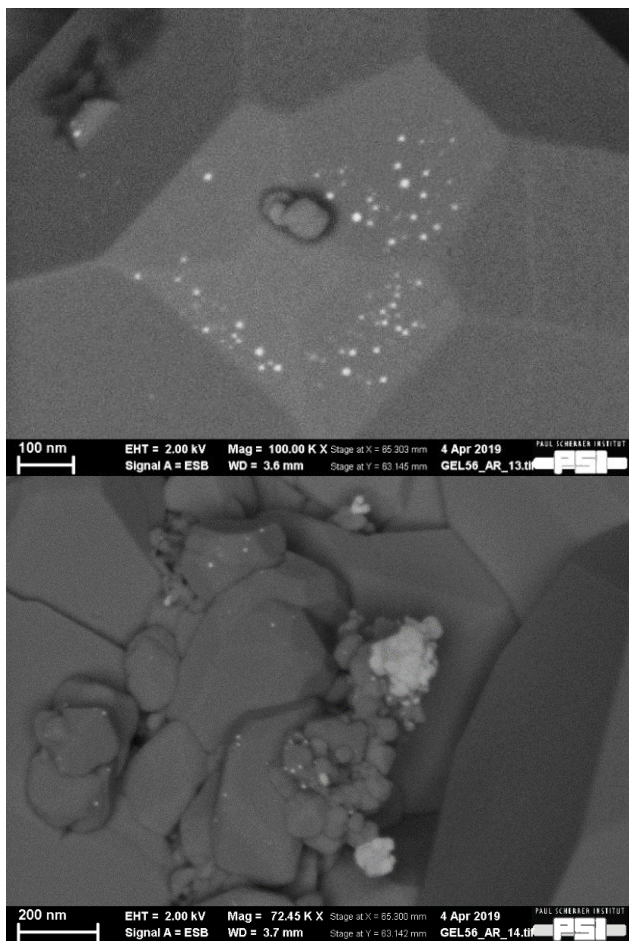


Figure 3: Examples of platinum nanoparticle deposition on unaged Eurofer-97 in a flow loop held at 280 °C for 285 hours, with 80 ppb of hydrogen and 300 ppb of oxygen.

Figure 3 shows examples of Pt nanoparticle deposition on an unaged Eurofer-97 specimen during flow loop exposure. The SEM backscatter detector is used, where the platinum nanoparticles show clearly as bright contrast. The nanoparticles show a sporadic coverage with more platinum nanoparticles located on certain facets of the oxide. The mean platinum particle size is 11 nm, which is comparable to what was found on 304L stainless steel coupons also exposed to the NobleChem™ application during this experiment.

These preliminary studies are a beginning to understanding the interaction between Eurofer-97 and representative LWR water chemistry together with the effect of short-term heat treatments. More comprehensive studies are required to assess the effectiveness of hydrogen water chemistry, zinc and NobleChem™ on the corrosion behavior of fusion materials such as Eurofer-97, particular when taking into account the influence of the higher radiation fields and magnetic fields in a fusion environment. These preliminary studies are important preparation for the development of a fusion-focused flow loop for understanding the differences between a fusion and fission cooling loop.

#### V APPLYING FISSION BEST PRACTICE WATER CHEMISTRY TO FUSION

It is necessary to consider the developments and operating experience in LWR coolant circuits to provide the technical underpinning for WCLL water chemistry and in particular how this translates into the conceptual water chemistry guidelines for a future fusion coolant circuit. One key development in this consideration, which has been mentioned in the preceding sections is the likely adoption of nickel-based alloys (NBAs) into the primary heat transfer system (PHTS) out of vessel heat exchangers. This is a significant change from previous considerations of the WCLL water chemistry specification. Overall, this will tend to converge the water chemistry requirements with PWR primary chemistry, although key differences still exist, such as the absence of soluble neutron poison (boron) and constraints on alkali concentration arising from Zircaloy surfaces. Additionally, the clear corrosion mitigation, dose reduction and low  $\text{H}_2$  utilisation benefits that BWRs experience through online NobleChem™ application warrants further exploration for use in WCLL; possibly resulting in a WCLL chemistry regime that is a hybrid of current best practice in BWR and PWR coolant systems.

The target values for pH and hydrogen concentration in particular should be identified by more detailed speciation modelling of the relevant corrosion products

expected to arise from Eurofer-97, AISI 316L(N) and the steam generator NBA. In order to allow comparisons with industry standards, a convention for calculation of high temperature pH ( $pH_T$ ) for WCLL should be considered, in particular the definition of the reference temperature, whether this is the average temperature or a nominal value of 300 °C. The optimal pH values for solubility control should then be reconciled against the best available information on corrosion control. This will necessarily require updating against the developing underpinning of Eurofer-97 corrosion as well as the WCLL and PHTS designs.

The critical hydrogen concentration for suppressing radiolysis is known to be much lower than the concentrations typically applied in PWR coolant. High levels of hydrogen can increase SCC initiation and as the WCLL will be new plant, there is the opportunity to optimize at a lower hydrogen concentration to avoid initiation, compared with existing PWR plant where there may be pre-existing cracks. The impact of hydrogen concentration on Eurofer requires clarification and reconciliation against the known NBA behavior.

Similarly, the use of Pt injection in a PWR-like WCLL circuit is still a matter of discussion and subject to the levels of hydrogen injection in this higher flux regime. Pt-deposition acts as a catalyst to use the available hydrogen more efficiently. Online NobleChem™ could offer a greater efficiency at the same hydrogen level if radiolysis suppression is complicated by mass transport or local sub-nucleate boiling, or it could allow a lower level of hydrogen dosing which is worthy of consideration for a new irradiated coolant plant circuit with an advanced material and limited operating experience in the expected circuit conditions.

The adoption of NBAs would also place a firmer emphasis on the potential use of zinc injection into the coolant circuit as this is well known to reduce radiation fields arising from activation of corrosion products, as well as being beneficial to corrosion. The question of whether zinc may improve the corrosion performance of Eurofer-97, may be supplanted by a simpler question of establishing that it is not detrimental to it. On the basis of the currently available information and noting some of the uncertainties outlined above, outline water chemistry guidelines for the DEMO WCLL water coolant are proposed in Table 1.

TABLE I: Proposed WCLL Water Chemistry parameters

Parameter	Target	Notes
$pH_T^*$	Target pH value to be defined. Expected to	Requires optimisation for all coolant facing circuit surfaces, Eurofer-97,

	lie in pH range 7.2 - 7.8 based on potential adoption of NBAs in PHTS heat exchangers.	austenitic steels, NBAs, to reduce solubility gradient (vs T) and corrosion rates/initiation times * reference T is assumed as circuit $T_{AVE}$ subject to definition of a convention for this plant.
[LiOH], [KOH], [NH <sub>3</sub> ]	As required to achieve target $pH_T$ .	Advantages for use of KOH should be considered in terms of current international development for adoption in PWR chemistry
Dissolved oxygen	<10ppb	As low as possible (though some part of the coolant circuit may require higher [O <sub>2</sub> ] to address FAC.
Dissolved hydrogen	Target value to be defined Expected to be in range 1-20 cc (STP) kg <sup>-1</sup>	Requires optimisation to reduce solubility gradients and corrosion initiation/propagation. Consider effect of possible ammonia dosing on dissolved hydrogen.
Conductivity (at 25 °C) -Make-up water	<0.1 $\mu S cm^{-1}$	NB: pure water is 0.055 $\mu S cm^{-1}$
Conductivity (at 25 °C) -Coolant	According to alkali concentration.	
Impurity anions (Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , F <sup>-</sup> )	As low as possible Each less than 25 ppb, combined less than 50 ppb.	
Zn injection	Priority for further development Effect/impact on Eurofer-97 currently lacks technical underpinning.	Significant reduction in NBA corrosion product release and uptake. Likely benefit to NBA, austenitic steel and Eurofer-97 corrosion performance.
Noble metal	Possible	Potential benefit to



addition	secondary mitigation.	corrosion Performance.
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## VI. CONCLUSIONS

The water chemistry regimes for various light water reactor designs have been developed over decades to establish a set of guidelines to control the corrosion behavior (both general and localized) of coolant systems specific to each reactor design. A water-cooled breeder blanket module in a fusion reactor will need to consider the levels of dissolved oxygen, hydrogen, zinc and NobleChem™ and the control of pH<sub>T</sub> and conductivity currently determined for fission reactors, but also will experience additional challenges such as higher neutron energies and fluxes, thermal excursions from plasma instabilities and high magnetic fields.

In this paper we have discussed a number of the state of the art in light water reactor water chemistry guidelines, and how developments like alternative alkalizing agents should be adopted early by the fusion community to achieve best practice from the start of operation. We also present some preliminary studies on corrosion of the reduced activation ferritic-martensitic steel Eurofer-97 proposed for ITER and DEMO in hot water conditions that were designed to simulate existing PWR and BWR corrosion mitigation techniques. Further development of such approaches is required to refine and optimize water chemistry guidelines for future fusion plants with water cooled circuits.

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## REFERENCES

1. T. L. MARTIN, R. BURROWS, W. S. WALTERS, A. BARON-WIECHEC, C. HARRINGTON, A. BHARJ, A. SCORROR, T. SPARKS, S. HOWELL, A. SIBERRY, A.D. WARREN, R. HOLMES, R. CLARK and R. S. SPRINGELL, "Progress in
2. R. HOLMES, R. BURROWS, S. DICKINSON, W.S. WALTERS, L. PLATTS, R. CLARK, C. HARRINGTON, A. BARON-WIECHEC, E. SURREY, T. MARTIN, A. SIBERRY and R.S. SPRINGELL, "Chemistry and corrosion in the irradiated cooling circuits of a prototype fusion power station," in *The 21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, USA, (2018).
3. P. FERNANDEZ, A. LANCHI, J. LAPENA, M. SERRANO and M. HERNANDEZ-MAYORAL, "Reduced activation ferritic/martensitic steel Eurofer 97 as possible structural material for fusion devices. Metallurgical characterization on as-received condition and after simulated services conditions," IAEA International Nuclear Information System, (2004)
4. A. KOHYAMA, A. HISHINUMA, D. GELLES, R. KLUEH, W. DIETZ and K. EHRlich, "Low-activation ferritic and martensitic steels for fusion application," *Journal of Nuclear Materials*, **233-237**, pp. 138-147, (1996)
5. R. LINDAU, A. MÖSLANG, M. RIETH, M. KLIMIANKOU, E. MATERNA-MORRIS, A. ALAMO, A.-A. TAVASSOLI, C. CAYRON, A. -M. LANCA, P. FERNANDEZ, N. BALUC, R. SCHÄUBLIN, E. DIEGELE, G. FILACCHIONI, J. RENSMAN, B. SCHAAF, E. LUCON and W. DIETZ, "Present development status of EUROFER and ODS-EUROFER for application in blanket concepts," *Fusion Engineering and Design*, **75-79**, pp. 989-996, (2005)
6. P. FERNANDEZ, A. LANCHI, J. LAPENA, M. SERRANO and M. HERNANDEZ-MAYORAL, "Metallurgical properties of reduced activation martensitic steel Eurofer'97 in the as-received condition and after thermal ageing," *Journal of Nuclear Materials*, **301-311**, pp. 495-499, (2002)
7. R. BURROWS, A. BARON-WIECHEC, C. HARRINGTON, S. MOORE, D. CHANEY, T.L. MARTIN, J. LIKONEN, R. SPRINGELL and E. SURREY, "The possible effect of high magnetic fields on the aqueous corrosion behaviour of Eurofer", *Fusion Engineering and Design*, **136**, pp. 1000-1006 (2018)
8. INTERNATIONAL ATOMIC ENERGY AGENCY, Nuclear Power Reactors in the World, Reference Data Series No. 2, IAEA, Vienna (2018).
9. S. E. GARCIA, N. R. LYNCH, J. F. GIANELLI, M. L. JARVIS and A. J. JARVIS, "Recent Advances in

- BWR Water Chemistry,” in *International Conference on Water Chemistry of Nuclear Reactor Systems*, Sapporo, Japan, (2014).
10. H. HIRANO, N. USUI, H. KITAJIMA, H. KAWAMURA, Y. FUKABORI, J. SUZUKI, N. KAWAI, T. YAMAGUCHI, S. UEMURA, S. ONODERA, K. HISAMUNE, Y. UEYAMA and H. URATA, “BWR Water Chemistry Guidelines in Japan,” in *International Conference on Water Chemistry of Nuclear Reactor Systems*, Sapporo, Japan, (2014).
  11. V. A. YURMANOV, N. B. POVALISHIN and A. V. ARKHIPENKO, “Development of WWER Primary Water Chemistry Guidelines,” in *International Conference on Water Chemistry of Nuclear Reactor Systems*, Berlin, Germany, (2008).
  12. I. D. CURIERES, “The Evolution of Chemistry in PWR Nuclear Power Plants: Overview and Safety Perspectives,” in *International Conference on Water Chemistry of Nuclear Reactor Systems*, Sapporo, Japan, (2014).
  13. H. JAQUIER, “Chemistry Evaluation in French EDF Nuclear Power Plants,” in *International Conference on Water Chemistry of Nuclear Reactor Systems*, Sapporo, Japan, (2014).
  14. H. KAWAMURA, Y. SHODA, Y. TSUZUKI, H. HIRANO, Y. WATANABE, K. TAKEDA, T. TERACHI, N. ISHIHARA, A. TAKAHASHI, K. HISAMUNE, Y. NAKANO and T. NISHIMURA, “Primary Water Chemistry Guidelines for Japanese PWR Plants,” in *International Conference on Water Chemistry of Nuclear Reactor Systems*, Sapporo, Japan, (2014).
  15. J. MCEL RATH and K. FRUZZETTI, “EPRI Primary Water Chemistry Guidelines Revision,” in *International Conference on Water Chemistry of Nuclear Reactor Systems*, Sapporo, Japan, (2014).
  16. T. OHASHI, T. ITO, H. HOSOKAWA, M. NAGASE and M. AIZAWA, “Investigation of cobalt buildup behaviour and suppression by zinc injection on stainless steel under HWC conditions using simultaneous continuous measurements of corrosion and cobalt buildup,” *Journal of Nuclear Science and Technology*, **52**, 4, pp. 588-595, (2015).
  17. HITACHI-GE NUCLEAR ENERGY LTD, “UK ABWR Generic Design Assessment: Preliminary Safety Report on Reactor Chemistry,” GA91-9901-0041-00001, XE-GD-0152, Revision B.
  18. X. LIU, X. WU and E. H. HAN, “Effect of Zn injection on established surface oxide films on 316L stainless steel in borated and lithiated high temperature water,” *Corrosion Science*, **65**, pp. 136, (2012).
  19. P.V. GRUNDLER and S. RITTER, “Noble Metal Chemical Addition to BWRs for Stress Corrosion Cracking Mitigation: Theoretical Insights and Applications”, *PowerPlant Chemistry*, **16**(2), pp. 76-93 (2014).
  20. D. M. WELLS, P. L. FRATTINI, K. FRUZZETTI, S. GARCIA, J. MCEL RATH and M. MURA, “The Future of Nuclear Power Plant Chemistry,” in *21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, USA (2018).
  21. S. GARCIA, R. PATHANIA, L. LOOMIS and J. GIANNELLI, “Advancements in BWR IGSCC Mitigation Guidance with Noble Metal Chemistry,” in *21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, USA (2018).
  22. S. RITTER, P.V. GRUNDLER, S. ROWTHU and H.P. SEIFERT, “Assessment of the SCC mitigation capabilities of the noble metal chemical application technology in a Simulated BWR environment”, submitted to *Environmental Degradation*, Boston USA (2019)
  23. A. ODELL, C. CUSTER, M. MURA and J. GIANNELLI, “Next Generation of Noble Metal Application in Boiling Water Reactors,” in *21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, USA (2018).
  24. P. GRUNDLER, S. ROWTHU and S. RITTER, “Influence of Fluid Flow on Platinum Nanoparticles Transport and Deposition under Simulated Boiling Water Reactor Conditions,” in *21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, USA (2018)
  25. L. OLIVER, B. HELMERSSON, R. DEVITO and J. IYER, “Westinghouse VVER Fuel Experience and Fuel Qualification Need for Introducing KOH in Pressurized Water Reactors,” in *21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, USA (2018).
  26. P. CHOU, “Potassium Hydroxide for PWR Primary Coolant pH Control: Materials Qualification Testing,” in *21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, USA (2018).
  27. J. FANDRICH and E. DUDKA, “Investigations of an Alternative Alkalinization Strategy for Primary Coolant Conditioning of Pressurized Light Water Reactors,” in *21st International Conference on Water Chemistry in Nuclear Reactor Systems*, San Francisco, (2018).
  28. E. PLATACIS, A. ZIKS, A. POZNJAK, F. MUKTEPAVELA, A. SHISKO, S. SARADA, P. CHAKRABORTY, K. SANJAY, M. VRUSHANK, R. FOTEDAR and E. RAJENDRA, “Investigation of the Li-Pb flow corrosion attack on the surface of P91 steel in the presence of magnetic field,” *Magneto hydrodynamics*, **48**, 2, pp. 343-350, (2012).
  29. Z. LU, D. HUANG and W. YANG, “Probing into the effects of a magnetic field on the electrode processes of iron in sulphuric acid solutions with dichromate

- based on the fundamental electrochemistry kinetics,” *Corrosion Science*, **1471-1492**, 6, pp. 47, (2005).
30. A. RUCINSKIEN, G. BIKULCIUS, L. GUDAVICIUT and E. JUZELIUNAS, “Magnetic field effect on stainless steel corrosion in FeCl<sub>3</sub> solution,” *Electrochemistry Communications*, vol. 4, no. 1, pp. 86-91, 2002.
31. Y. C. TANG and A. J. DAVENPORT, “Magnetic field effects on the corrosion of artificial pit electrodes and pits in thin films,” *Journal of the Electrochemical Society*, **154**, 7, pp. C362-C370, (2007).
32. P. FERNANDEZ, M. GARCIA-MAZARIO, A. LANCHA and J. LAPENA, “Grain boundary microchemistry and metallurgical characterization of Eurofer'97 after similar service conditions,” *Journal of Nuclear Materials*, **329-333**, Part A, pp. 273-277, (2004)
33. T. ALLEN, L. TAN, J. GAN, G. GUPTA, G. WAS, E. KENIK, S. SHUTTHANANDAN and S. THEVUTHASAN, “Microstructural development in advanced ferritic-martensitic steel HCM12A,” *Journal of Nuclear Materials*, **351**, 1-3, pp. 174-186, (2006).
34. TH. LOEWENHOFF, T. HIRAI, S. KEUSEMANN, J. LINKE, G. PINTSUK and A. SCHMIDT, “Experimental simulation of Edge Localised Modes using focused electron beams – features of a circular load pattern”, *Journal of Nuclear Materials*, **415**, 1, pp. S51-S54 (2011)
35. A. LOARTE et al. “Transient heat loads in current fusion experiments, extrapolation to ITER and consequences for its operation”, *Physica Scripta*, **2007**, T128 (2007)
36. F. MAVIGLIA et al. “Effect of engineering constraints on charged particle wall heat loads in DEMO”, *Fusion Engineering and Design*, **124**, pp. 385-390 (2017)
37. A. W. BOYD, M. B. CARVER and R. S. DIXON, “Computed and experimental product concentrations in the radiolysis of water,” *Radiation Physics and Chemistry*, vol. 15, pp. 177-185, 1980.
38. H. A. SCHWARZ, “A determination of some rate constants for the radical processes in the radiation chemistry of water,” *J. Phys. Chem.*, **66**, pp. 255-262, (1962)
39. A. J. ELLIOT and D. M. BARTELS, “The Reaction Set, Rate Constants and G-Values for the Simulation of the Radiolysis of Light Water over the Range 20° to 350°C Based on Information Available in 2008,” AECL Report 153-127160-450-001, (2009)
40. Y. MUROYA, S. YAMASHITA, P. LERTNAISAT, S. SANGUANMITH, J. MEESUNGNOEN, J.-P. JAY-GERIN and Y. KATSUMURA, “Rate constant for the  $H^{\cdot} + H_2O \rightarrow \cdot OH + H_2$  reaction at elevated temperatures measured by pulse radiolysis,” *Phys. Chem. Chem. Phys.*, **19**, pp. 30834-30841, (2017).
41. D. SWIATLA-WOJCIK and G. V. BUXTON, “Reply to comment on the possible role of the reaction  $H + H_2O = H_2 + OH$  in the radiolysis of water at high temperatures,” *Radiation Physics and Chemistry*, **79**, pp. 52-56, (2010)