**fission and fusion WATER cooling circuits: chemistry, corrosion mitigation and materials**

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The need to satisfy the world’s ever-increasing demand for a low carbon, secure and affordable electricity and energy source is one of the greatest challenges of this century[1]. Nuclear fusion technology is aiming to join the family of non-greenhouse gas emitting electricity sources, currently consisting of renewables and nuclear fission power plants. For the realization of the first commercial fusion reactor, multiple challenges are yet to be solved, but the technological transfer from 60+ years operational experience of fission power plants, including materials research, cooling circuit optimisation and corrosion mitigation strategies, can be key to ensure the success of fusion reactors. This is especially the case as fusion reactors are expected to use similar coolants and structural materials as the current light water reactors fleet (LWRs).

The challenges faced by materials in nuclear power plant cooling circuits are very unique. Materials need to maintain their mechanical properties intact for 40+ years (and even 60+ or 80+ years for current fission power plants) while operating at temperature, around 300°C for the current LWR fleet, up to 530°C for the UK’s Advanced Gas cooled Reactors (AGRs) and up to 1000°C for future designs of Very High Temperature Reactors (VHTR), under neutron irradiation (up to 100 dpa) and in a corrosive environment. In the past, nuclear fission plants have exploited various coolants for research purposes or for commercial purposes (energy and electricity production): gases, liquid metals and molten salts, although water is by far the most common in current designs. The Generation IV roadmap for advanced reactors anticipates the use of liquid metals (lead & lead/bismuth eutectic or sodium), gases (helium), water and molten salts (mainly fluorides) as coolants [2]. Potential fusion reactor coolants are quite similar, with water, gases (helium) and liquid metals (lithium, lead/lithium) [3] under consideration. Notably, two types of innovative fission reactors are already in operation in the world: the high temperature gas (helium) cooled reactor-pebble bed module (HTR-PM) in China and the sodium fast reactors Beloyarsk Nuclear Power Station (BN-600 and BN-800) in Russia.

Although learning from advanced fission reactors will have a lot of helpful overlap with fusion, some challenges remain unique to the nuclear fusion community, such as the 14 MeV fusion relevant neutron load and spectrum and its interaction with materials, which will need to be addressed in an International Fusion Materials Irradiation Facility (IFMIF)[4]. Materials development for fusion has progressed so far through testing in nuclear fission reactors. At the same time, technological progress typically developed by the nuclear fusion community, like manufacturing of low activation materials to minimise long lasting radioactive waste, can also benefit the fission community. In the roadmap to the realisation of electricity from fusion thanks to ITER and finally DEMO power plant[3] operation, several experimental machines are being constructed to address some of the key unsolved technological challenges. These machines are the Italian Divertor Tokamak Test Facility (DTT)[5], Korea Superconducting Tokamak Advanced Research (KSTAR) and Japan Torus-60 Super Advanced (JT60SA)[6]. For the successful realization of these experimental machines, a synergy from fission experience has already started and will be described in this report.

### Water chemistry, corrosion and stress corrosion cracking (SCC) in LWRs and fusion machines

Water chemistry [7][8][9] and the mechanistic understanding of corrosion issues[10][11] in LWRs is being extensively investigated by the fission community. Within the water-cooled reactors family, Pressurized Water Reactors (PWRs) and Voda Voda Energo Reactor (VVERs) have a controlled water chemistry regime that mainly uses boric acid and a base (LiOH or KOH) for maintaining an optimum pH. The main aim of LWRs water chemistry is to ensure: materials integrity, fuel cladding integrity and minimize out-of-core radiation fields brought upon by the redeposition of activated corrosion products[12][13]. The addition of boric acid (H3BO3) to the water serves as a reactivity control agent since 10B isotope has a high absorption cross section for thermal neutrons. Natural boric acid contains approximately 19.8%10B[11], the remaining ~80% consists of 11B, which has a lower thermal neutron absorption cross section. PWRs operate with naturally boric acid[14], though recently some plants have been converted to use enriched boric acid (up to 40% in 10B), to reduce the amount of boric acid and LiOH (99.95% enriched in 7Li) to be inserted in the cooling circuit to operate between pHT=6.9 and 7.4 [7]. Other additives are injected to minimise water radiolysis and to maintain a reducing atmosphere. Reducing conditions and a very pure water (free from contaminants) have proven to be beneficial to counteract corrosion problems such as pitting, crevice corrosion and SCC in PWRs. Boiling water reactors (BWRs) also use pure water free from pH-control additives (conductivity<0.1 µS/cm at 25 °C [15]).

The required amount of hydrogen added depends on the corrosion potential. In PWRs, 15-50 cm3 (STP) H2/kg H2O are usually inserted in the coolant to suppress the formation of oxidising species induced by water radiolysis. A study from Christensen [16] has showed that a much lower value of H2, around 5 cm3/kg H2O, would be sufficient to suppress water radiolysis. Hydrazine is also currently added in the primary circuit of PWRs as an oxygen scavenger[7], while in VVERs both ammonia or hydrazine are injected [8]. Ammonia and hydrazine radiolytically decompose into hydrogen during reactor operation. Reducing conditions enhance primary circuit materials integrity by limiting SCC of stainless steel, fuel clad corrosion and corrosion products. To further minimise out-of-core radiation fields due to corrosion, zinc injections or noble metal coating and on-line noble metal chemical addition (NCMA)[11] have been tested in nuclear fission power plant primary circuits. Similar water chemistry options are now being considered for the European DEMO water cooling loop [17][18] by choosing a slightly alkaline pHT = 7.1 – 7.4 through the addition of LiOH or KOH.

During power plants operation some issues related to boric acid corrosion at high concentrations[19][20] were reported, especially on the ferritic steel used for the reactor pressure vessel. These information are useful to the nuclear fusion community since many experimental fusion reactors, notably DTT, KSTAR and JT60SA, exploit the use of boric acid at high concentrations in the vacuum vessel (VV) cooling loop. In DTT VV the requirement is to obtain neutron shielding of the superconducting coils with the use of borated water ensuring neutrons heating below 1 mW/cm3 [21]. 8000 ppm in B enriched to 95% in 10B (4.58 wt% H3BO3) is needed in DTT VV, this is well above the current experience of boric acid addition in PWRs. The temperature and pressure in the DTT are much lower than the ones found in PWRs, however, pH of borated water increases with increasing temperature. The operation at low temperature for the DTT VV means that water pH is quite acidic, pH60C=3.6[18],[20]. The experience from PWRs can help tailor the water chemistry for DTT VV by choosing an appropriate level of LiOH or KOH addition. Still, more research is needed given the much higher concentration of the boric acid and the alternation between borated water and hot nitrogen gas at 200°C in the DTT VV for baking purposes which may induce crystallisation of boric acid in crevices and enhance the risk for localised corrosion in stainless steels. Furthermore the presence of strong magnetic fields may have an effect on corrosion mechanism and deposition[22]. Additional corrosion mitigation strategies that are established in nuclear fission power plants and that could be transferred to nuclear fusion reactors start-up phases are the pre-operational hot performance tests[23]. These procedures verify that the cooling circuits are operating well prior to load the nuclear fuel. Tailored water chemistry regime during hot performance/functional tests of PWRs were used to improve the passivation procedure of stainless steels in order to reduce the formation of corrosion products. This has been conducted in the UK Sizewell B PWR, for example, by tailoring boric acid and hydrogen[24].

### ACPs codes for radioprotection

Another synergy between nuclear fission experience and nuclear fusion development can be found in the development of activated corrosion product (ACPs) codes. In PWRs it is found that the largest fraction of occupational dose is induced by the presence of ACPs in the primary cooling circuit due to the presence of 60Co and 58Co produced from 58Ni(n,p) reaction. Similarly, in ITER (International Thermonuclear Experimental Reactor or “The Way” in Latin), up to 80% of occupational dose related to water cooling circuit operation is related to ACPs. Codes such as PACTOLE[25] developed by the fission community, CEA, to predict corrosion behaviour and activation in PWRs cooling circuits have been adapted to ITER heat transfer systems by adding different water coolant chemistry options, operating temperature and materials (Cu alloys). This new code was called PACTITER[26]. PACTITER v2.1 was optimised with dedicated experiments that enabled to measure copper corrosion and stainless steels releases at temperature (50-200°C) and velocities relevant to ITER primary cooling circuits[27] to become PACTITER v3.3[27]. PACTITER v3.3 does not allow the addition of boric acid though, since borated water is not envisaged to be used in ITER.

To understand the influence of an acidic water chemistry (8000 ppm B borated water) in the DTT VV, PACTITER v2.1 was used. PACTITER v2.1, however, overestimated pHT of 8000 ppm B: pH40C,PACTITERv2.1=4.2 while pH60C,experimental=3.65[18], implying that solution aggressiveness is underestimated. Results obtained using this code showed that the addition of LiOH had a beneficial effect in terms of decreasing alloying elements solubility but worsened both releases and deposits compared to the case where no LiOH was added in borated water[18], which is counterintuitive. Experiments performed on stainless steel coupons submerged in either UPW or borated water (8000 ppm B) showed an increase in metal releases in borated water. Further experiments are necessary on borated water with LiOH additions to confirm the need of adding a base to neutralise the pH for the DTT VV cooling circuit. From PACTITER v2.1 the addition of 30 ppm Li as LiOH in 8000 ppm B showed a pH60C,PACTITER v2.1=6.05, which is close to the natural pH of ultrapure water, pH60C, UPW =6.5[28]. To obtain DTT relevant information, a novel ACP code developed for PWRs is now being used. The new code, developed by CEA, called OSCAR[29] benefits from an improved water chemistry module based on the PHREEQC. It is also able to handle different water chemistry regimes: reducing/oxidising, acid and alkaline and low temperature operations which are DTT relevant. The fusion relevant version of the code is called OSCAR-Fusion. OSCAR-Fusion v1.3 is being used to simulate ACPs formation and transfer in the DTT VV cooling circuit considering different water chemistries, research and development is still needed though since boric acid addition is not currently possible beyond 100 ppm B.

### Steels development for Generation IV reactors and fusion reactors

The development of ferritic/martensitic 9%Cr irradiation tolerant steels is another synergy between nuclear fission and fusion research and development. EUROFER97 [30]is being developed as the reduced activation ferritic martensitic (RAFM) steel for the DEMO divertor cassette body and breeder blanket. Corrosion of EUROFER97 under tailored water chemistries is currently being investigated to understand the reliability of this material in the long term[18]. EUROFER97is expected to experience a neutron damage of 4.38dpa/year [31] at temperatures that will need to be above 180°C to counteract embrittlement due to neutron irradiation and helium embrittlement [32]. Stainless steels have the drawback of swelling during operation under high dpa, while ferritic steels undergo neutron irradiation embrittlement, hence they are not considered for high dpa applications in fusion reactors. The development of EUROFER97 for nuclear fusion machines ITER and DEMO can be compared to the development of P91 and T91 steels proposed for Gen IV[2][33] reactors. P91 and T91 steels are candidate materials for the pressure vessel within the reactor core of VHTR which are expected to withstand an operating temperatures of ~600 °C along with a neutron damage of 0.01 dpa/year[34] and are being considered for applications in DEMO. VHTR is expected to operate for 60 years, the pressure vessel will see a total neutron damage of 0.6 dpa in its entire operating lifetime. EUROFER97 performance in fusion reactors up to neutron damage levels of 0.6-6dpa and at temperatures of 20-600°C is needed. There is a wide variety of studies investigating the hardness increases in EUROFER 97 using ions as an analogue for neutron damage. Nevertheless, it is still necessary to quantify the extent of reduction in ductility. The shallow penetration depth of ion irradiation prevents macro-scale tensile testing but it is possible to extract tensile properties via micro-tensile testing. In fact, micro-tensile testing has been successfully applied to ODS steel (MA957) and SA508 grade 3 steel where bulk tensile properties on a micro-scale were reproduced and helium embrittlement could be measured[35][36]. A deeper knowledge can definitely be gained if micro-tensile testing is applied to helium ion irradiated EUROFER 97 which hasn’t been done to date.

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