

# Effect of magnetic field on the aqueous corrosion behaviour of Eurofer

R. Burrows<sup>1</sup>, A. Baron-Wiechec<sup>2\*</sup>, C. Harrington<sup>2</sup>, S. Moore<sup>3</sup>, D. Chaney<sup>3</sup>, R. Springell<sup>3</sup>, E. Surrey<sup>2</sup>

<sup>1</sup>Reactor Chemistry and Corrosion, National Nuclear Laboratory, UK

<sup>2</sup>UK Atomic Energy Authority, Culham Centre for Fusion Energy, Abingdon, OX14 3DB, UK

<sup>3</sup>University of Bristol, Interface Analysis Centre, UK

## Abstract

In defining the corrosion control requirements for DEMO, the impact of the mixed Eurofer/ AISI 316 steel system, the presence of significant amounts of tritium permeating from the breeder material, and the effects of magnetic field should additionally be considered throughout. A substantial amount of data related to corrosion resistance of structural materials is available for industrial applications in fission, but applies to different materials and neutronic conditions. Experimental work is being carried out under DEMO Breeding Blanket Project of the EUROfusion programme, which will further develop the understanding of irradiation effects. However, there is very limited information regarding magnetic field-assisted corrosion under conditions relevant for the fusion environment readily available in the literature. This work reviews current knowledge and progress in establishing the possible influence of the intense magnetic field on corrosion behaviour of the main structural material, Eurofer-97, in the breeding blanket. Preliminary corrosion experimental results of Eurofer-97 coupons, obtained by using a simple apparatus that allows exposure to a magnetic field intensity of 0.88 T and temperatures up to 80°C in water at atmospheric pressure, are presented.

Keywords: Eurofer, Corrosion, Magnetic field, DEMO, Breeding Blanket, WCLL

## 1. Introduction

The water coolant circuits of the DEMO fusion power plant will experience extreme conditions that will challenge the coolant-facing structural materials. Namely, high energy neutron irradiation to high cumulative doses, elevated temperature and pressure, the influence of tritium and intense magnetic fields [1]. The effect of a magnetic field on corrosion behaviour is an unusual and not very well understood variable, particularly important when material contains magnetic phases. Prior work has generally been at much lower field intensities than those expected for the breeding blanket coolant location, but does show clear effects on corrosion behaviour, with both inhibiting and enhancing effects reported, dependent on the effect on mass transport and corrosion product morphology.

This paper reports initial progress in establishing the possible influence of the intense magnetic field on corrosion behaviour of the main structural material in the breeding blanket, Eurofer-97, a reduced activation ferritic-martensitic (RAFM) steel. Three apparent mechanisms by which the high magnetic field could affect corrosion and related processes have been postulated.

*Modification of the adherent corrosion layer:* The Eurofer-97 corrosion product film is expected to comprise a high proportion of magnetite which has a high magnetic moment and so may be structurally affected by growth within the field, as sub-domains attempt to align to the magnetic field direction. This could credibly lead to increases or decreases in corrosion rate, as the film could foreseeably become denser and more protective, or porous and less passivating. Such observations have been made previously [2] although not

for materials comparable to Eurofer-97 or conditions relevant to DEMO coolant circuits.

*Interaction with corrosion product particulates:* It is foreseeable that the high magnetic field will interact with any precipitated or spalled corrosion product particulates with a tangible magnetic moment. The predominance and nature of such particulates is not known and is difficult to predict with accuracy. For instance, PWR primary circuits may accumulate significant inventories of nickel and iron based corrosion products as a result of release from the nickel based alloy steam generator tubes and subsequent mobilization, while VVERs which are stainless steel based circuits generally suffer much less from this problem. A generic assumption would be that a high magnetic field will tend to favour deposition of any corrosion product particulates on the surfaces of the coolant channels, as it will effectively increase mass transport rates of the particles to the wall where they may impinge and adhere. Assuming that this effect will be strongest at locations with the highest field would point to enhanced deposition in the breeding blanket, particularly at inboard locations. In addition, it is known that the morphology of precipitation products is also affected by the presence of magnetic fields [3].

*Magnetohydrodynamic (MHD) effects:* The presence of both a high magnetic field and current flows (from corrosion processes) can lead to induced magnetohydrodynamic fluid flow. These are complex phenomena but have been studied through simulation and experiment for various systems [4, 5], including the LiPb system within DEMO [6]. The water coolant circuit differs significantly in that it has a much higher flow rate and a considerably lower conductivity, which would tend to suggest that MHD effects would be lower order. Consider also, however, that the occluded solution

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\*Corresponding author: [aleksandra.baron-wiechec@ukaea.uk](mailto:aleksandra.baron-wiechec@ukaea.uk)

within pits or under corrosion scabs could have a much higher ionic concentration and hence local conductivity. In addition to this, though possibly of lower importance, the use of any alkalisng agent would increase the bulk conductivity. The possible enhancement of mass transport rates within an occluded cell (see Fig. 1), where streaming potentials or currents might otherwise be relatively low (diffusion controlled) could be more significant. This mechanism has been observed during artificial pit experiments by Tang & Davenport [7]. Again, the impact is difficult to judge since increased mass transport could enhance corrosion product transport away from an active site and so increase rates, but conversely could also remove the aggressive species and thereby result in pit re-passivation.

The following sections of this paper give a summary of the DEMO plant and operating conditions (Section 2), followed by an overview of the relevant literature on corrosion behaviour of materials exposed to high magnetic fields (Section 3). The results from some initial tests involving the exposure of Eurofer-97 to water at elevated temperature in a magnetic field are described in Section 4 to provide an improved level of information specific to this material and a starting point for subsequent, more detailed investigations.

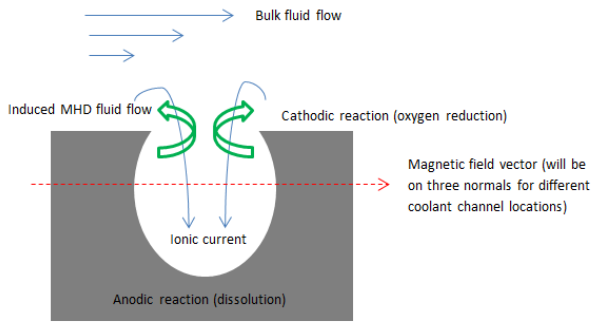


Fig. 1: Representation of possible MHD effect on pitting or crevice corrosion within a high magnetic field.

## 2. Plant description

The EU DEMO baseline design defines a reactor of  $\sim 2$  GW thermal power output with a net electric output of  $\sim 500$  MW delivered to the grid in pulses of  $\sim 2$  hours separated by dwell periods of  $\sim 0.5$  hours. The breeding blanket provides the functions of breeding tritium, removing nuclear heat from the plasma, and shielding of the vacuum vessel and other components from the direct neutron flux. The water-cooled lithium-lead (WCLL) blanket design [8, 9] is a set of modular boxes that form the inner wall of the tokamak, through which LiPb flows slowly to generate tritium. A set of coolant pipes manufactured from Eurofer-97 carry water in a radial-toroidal direction to extract the heat deposited (Fig. 2). The First Wall is the front face of each module, cooled independently and consisting of a Eurofer-97 steel plate with water cooling channels. Module dimensions are 1.0 m and 1.4 m in width and 0.55 m and 0.9 m in radial thickness (inboard and outboard respectively).

The WCLL concept utilises a primary coolant of pressurised water with nominal conditions of 15.5 MPa

pressure, a reactor inlet temperature of  $295^\circ\text{C}$ , and an outlet temperature of  $328^\circ\text{C}$ . During the dwell period, the primary coolant continues to flow at, or close to, its nominal flow rate, and the average coolant temperature remains the same; that is, the inlet temperature will increase while the outlet temperature decreases to maintain an average temperature of  $311.5^\circ\text{C}$ . The flow velocity of the coolant inside the blanket coolant channels is  $2\text{--}3\text{ m s}^{-1}$ , in the feeding pipes inside the vacuum vessel that provide flow to each module the velocity is around  $7\text{ m s}^{-1}$ , and elsewhere outside of the vacuum the velocity is higher at around  $18\text{ m s}^{-1}$ . The total residence time of the coolant in-vessel where the highest fields are present is of the order of 5-10 seconds.

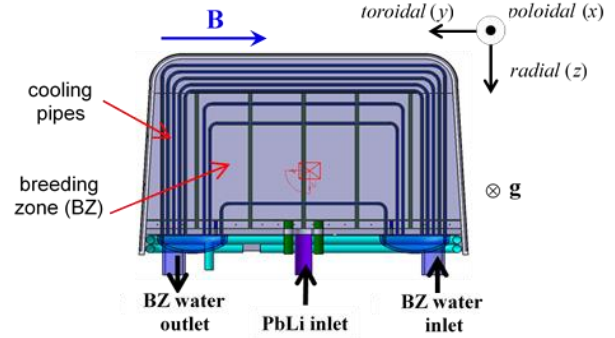


Fig. 2: Radial-toroidal cross-section of an individual WCLL blanket module (adapted from [8]).

The magnetic field seen by the coolant channels varies with position. The toroidal magnetic field varies with a  $1/r$  dependence and the blanket modules have a radial thickness of around 1 m, leading to fields from 9.9 T to 8.6 T across the inboard blanket and from 4.2 T to 3.7 T across the outboard blanket, both in a radial direction.

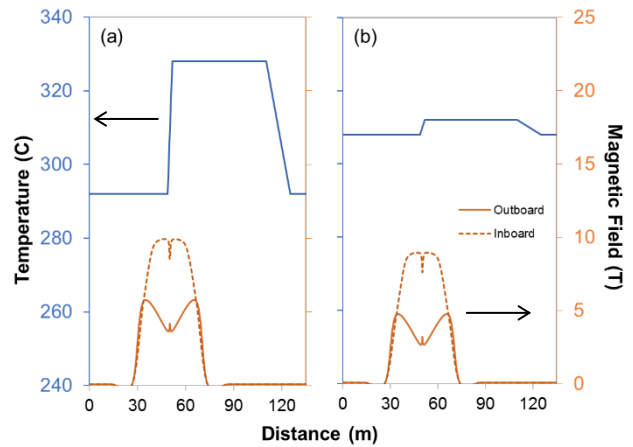


Fig.3: Indicative magnetic field and temperature with distance around the WCLL coolant loop for a notional circulating coolant volume in (a) pulse and (b) dwell conditions.

Additional contributions to the magnetic field arise from the ferromagnetic structural material itself and due to the poloidal field generated by the poloidal field coils and the plasma. These add around 0.5 T to the total field. During the dwell period, the toroidal field coils will

remain energised, leaving the total field largely unchanged relative to that during the pulse, although the poloidal field component will not be present.

Figure 3 shows illustratively the temperature and field experienced by a notional coolant volume as it flows around the coolant circuit and equatorial midplane blanket modules during pulse and dwell. Coolant enters the vessel via the upper port and, after an initial increase, the magnetic field increases or decreases depending on whether it flows to the inboard or outboard side.

### 3. Literature review corrosion of metallic alloys under influence of magnetic field.

Investigations into the effect of magnetic fields on corrosion have been carried out on a number of different metals and alloys, within different conditions. These are summarised briefly below, although none have yet addressed the impact on aqueous corrosion of Eurofer-97 or comparable steel in high temperature water.

Ručinskien *et al.* [10] studied the effect of a magnetic field on the corrosion of AISI 303 stainless steel in a  $\text{FeCl}_3$  solution with the field direction perpendicular to the surface of the metal. It was found that the magnetic field inhibited corrosion, as evident from an increase in repassivation potential, decrease in mass loss, and reduction in pit number. Voltammetric measurements performed on both Pt and stainless steel electrodes revealed that the cathodic reaction was accelerated by the presence of a magnetic field. This magnetoinhibition was explained as a result of a passive layer formed whilst within the magnetic field with a passivation capacity higher than that formed in the absence of the field.

A number of works have investigated the corrosion of iron and low carbon steel under magnetic fields. Bikul'chuyus *et al.* [2] investigated the corrosion of low-carbon steel in tap water in a permanent 0.05 T field using gravimetric and electrochemical methods over period of 2 hours in circulating water at up to 70 °C. It was found that the presence of a magnetic field decreased the rate of corrosion by 14% on average, regardless of temperature. This was attributed to the presence of the field favouring the formation of an adherent corrosion product film rather than transport away from the surface. Lu *et al.* [11] investigated the anodic polarisation behaviour of iron within 0.5 M sulfuric acid solutions with and without a 0.4 T DC magnetic field. It was found that the presence of an applied magnetic field accelerates the cathodic diffusion process and has little effect on the anodic polarisation. Cathodic limiting current densities were observed to increase when a magnetic field was applied. Further work in 2005 [12] used similar conditions to investigate the effects of a 0.4 T horizontal magnetic field on the electrode processes of iron within sulfuric acid solutions with dichromate. It was found that polarisation resistance significantly decreased (thus decreasing corrosion resistance) in the presence of a magnetic field. Nasher & Shalash [13] measured the magnetic field effect on the activation-controlled dissolution and hydrogen reduction

reactions occurring on iron in solutions of up to 5% NaCl. Results revealed an increase in the rate of corrosion for samples placed in the magnetic field.

Sueptitz *et al.* [14] found that the current density of iron in sulphuric acid could be increased or decreased by altering the configuration of the magnetic field to the electrode, due to its effect (via Lorentz force and magnetic field gradient force action) on surface pH during anodic dissolution. Additional work [15] investigating the influence of high gradient magnetic fields on the anodic dissolution of iron in sulfuric acid resulted in observation of a localisation of the material loss within all potential regions of anodic dissolution of iron, with the exception of the passive region. The anodic current density was also affected by the presence of the magnetic field, again attributed to Lorentz force and field gradient effects.

In 2010, Li *et al.* [16] investigated the effect of a magnetic field on pitting corrosion in pure magnesium by stochastic approaches, and identified an increase in the pitting corrosion susceptibility as a result of the magnetic field. It was observed that the field altered the pit initiation mechanism, from the parallel birth and death stochastic model to the parallel birth stochastic model. The mechanism for pit growth was unchanged by the magnetic field, however there was a change in the growth rate: stable pits were more likely to grow with higher growth rate and develop into larger pits.

The influence of a magnetic field (0.2 T or 0.08 T) on the electrochemical reactions occurring on a copper electrode in 0.5 M HCl by EIS, EN and potentiodynamic polarisation curve measurements was explored by Garcia-Ochoa *et al.* [17]. Lorentz forces were minimised by aligning the symmetry axis of the magnetic field with the ion flow. It was found that the presence of a magnetic field affected cathodic reactions considerably, with an increase in corrosion rate in the presence of oxygen in acid media, or a decrease in the absence of oxygen. The corrosion potential was shifted towards anodic values in the presence of oxygen, or a cathodic shift in the absence of oxygen. Furthermore, it was found that the hydrogen ion reduction reaction was retarded by the magnetic field, as such, corrosion current was also lowered. Changes to the morphology of the electrodeposits were also observed as a result of the presence of the field. The corrosion of Ag and Cu within nitric acid solutions was found to be partially suppressed by a magnetic field of up to 5 T [18]. The effect was considered to be the result of the removal of the catalyst from the electrode and electrode surface passivation, due to Lorentz force.

A mechanistic investigation into magnetic fields effects was undertaken using artificial pits by Tang & Davenport [7]. This simulated pitting corrosion using one-dimensional artificial pits and two-dimensional pits in metal thin films. It was found that, for ferromagnetic materials (iron, cobalt, nickel), pitting dissolution was affected significantly by the presence of a magnetic field. Upon the application of a parallel magnetic field, pitting dissolution increased. This was the result of local

stirring within the artificial pits produced as a result of the Lorentz force and the high field gradient force causing an increase in the diffusion-limited current. In comparison, the application of a perpendicular magnetic field resulted in a reduction in pitting dissolution. This was caused by paramagnetic corrosion products being drawn towards the surface of the metal by the field gradient force, forming a protective layer.

Pondichery *et al.* [19] investigated the effects of a 0.75 T external magnetic field on a range of materials, both non-magnetic and ferromagnetic, within 3.5% NaCl solution. By comparison of the electrochemical behaviour by both potentiodynamic polarisation and corrosion potential vs. time tests, it was found that the magnetic field has a notable effect on both the corrosion rate and the corrosion potential. An increase in corrosion rate and a cathodic shift of corrosion potential was observed for ferromagnetic materials (416 stainless steel, 1018 carbon steel), whereas for non-magnetic materials (304 stainless steel, Ti alloy, pure Zn) no such effect was measured.

Of all the studies outlined, those with most relevance to Eurofer-97 are likely to be those on AISI 416 martensitic steel [19]. The observation that corrosion rates were enhanced for this material is in common with many of the other studies, although this appears to be determined by other application dependent factors, such as geometry and transport processes. Overall these findings point to the likelihood of a magnetic field effect on the corrosion of Eurofer-97 and therefore underline the value of further work.

Studies have been performed into magneto-hydrodynamic (MHD) effects on corrosion of Eurofer-97 [20] and other materials [21] in flowing LiPb, although these are considered to have limited relevance to behaviour in water coolant.

## 4. Corrosion Tests on Eurofer-97 within a Magnetic Field

### 4.1 Methodology

A simple apparatus was employed to expose coupons of Eurofer-97 to a high magnetic field at temperatures up to 80 °C at atmospheric pressure. Samples were held within a glass tube in thermostatically controlled water within the annulus of a Halbach array of NdFeB magnets (see Fig 4). The array was rated as having an annulus field intensity of 0.88 T, which was confirmed with a magnetic field meter and found to be constant within the annulus. The corrosion coupons were held either within the annulus or well outside it (zero field) with nylon monofilament. In order to avoid heating and possible demagnetisation of the magnet, a cooling jacket comprised of PTFE tubing was placed between the glass tube (outer diameter 27 mm) and the array (inner diameter 30 mm). A perfusor syringe was used to maintain a constant solution level and the solution was deoxygenated by a continuous low flow rate sparge of nitrogen. The top of the tube was filled with stainless steel wool and uppermost ceramic fibre lagging to reduce the ingress of oxygen into the system. Samples of

Eurofer-97 were cut into coupons of approximately 5 x 5 x 1 mm, ground to SiC P1200, degreased in isopropanol, washed in demineralised water and dried prior to aqueous exposure. Test solutions were composed of high purity demineralised water with additions of NaCl and citric acid (Analytical grade, Fisher Scientific).



Fig. 4: Apparatus employed for initial trials on Eurofer-97 corrosion within a magnetic field.

The post-exposure samples were analysed by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) using a TESCAN Mira3 XMH FE-SEM microscope equipped with an X-Max 80 EDS detector from Oxford Instruments. The electron beam was operated at 10-30 kV. X-ray diffraction (XRD) spectra were recorded with an X'pert Pro MPD with a Cu source. All spectra were normalised to the Fe(400) reflection and phase identification performed by comparison with standard literature.

### 4.2 Results and Discussion

Exposure tests on Eurofer-97 in demineralised water were found to produce only very slow film formation at temperatures between 60 and 80 °C, whereas the addition of 100 mg kg<sup>-1</sup> Cl with the adjusted of pH to 3.5 with citric acid enhanced the corrosion rate. A mild but visible darkening of the sample surface occurred, with a change in hue, indicative of the formation of a corrosion film. Nonetheless, the changes in mass recorded for samples corroded over periods of up to 140 hours at 60 °C were too small to allow any gravimetric distinction between those within and without the magnetic field. Visual inspection showed some differences in the hue of the corrosion film and in some cases an evident greater darkening of the samples within the field, although other replicates showed less distinct contrast.

An SEM image of the surface of a reference sample prepared by grinding alone without aqueous exposure is shown in Figure 5a. The surface of a sample exposed to demineralised water at 80 °C with no magnetic field for 100 hours is shown in Figure 5b and shows no sign of corrosion attack. A slight increase in oxygen is

indicative of the formation of a thin protective oxide layer. Secondary electron images of sample surfaces exposed to  $100 \text{ mg kg}^{-1}$  Cl at pH 3.5 for 100 hours at  $60^\circ\text{C}$ , with 0.9 T field and no field are shown in Figures 5c and 5d respectively. Both samples are characterised by a thicker oxide layer than that produced in demineralised water. The chemical compositions analysed by EDX

indicate presence of various forms of iron hydroxide and possibly hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The XRD analyses indicated the likely presence of highly textured magnetite alongside other unidentified phases. Additional analyses are required to confirm the dominant corrosion products, but the presence of magnetite is expected due to the deoxygenated exposure conditions.

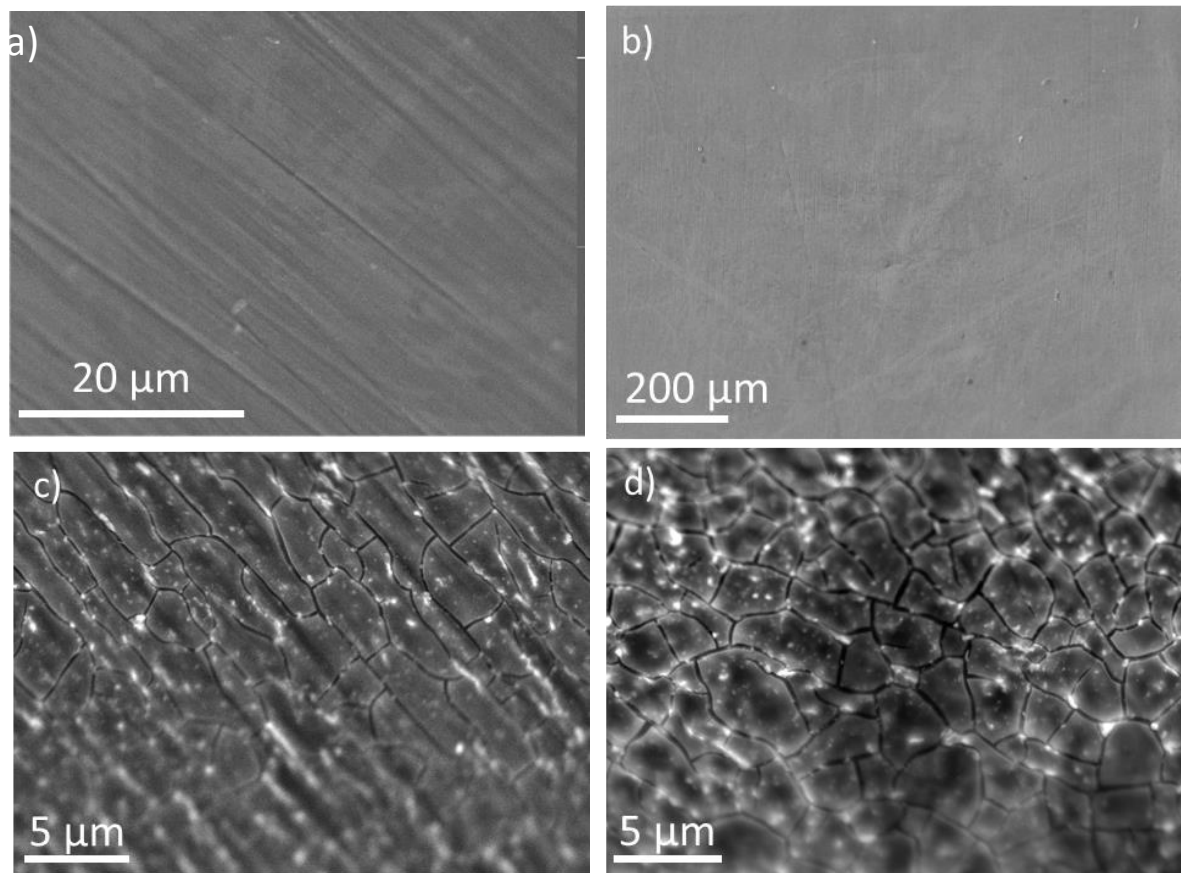


Fig. 5: (a) Reference sample, (b) sample exposed to demineralised water at  $80^\circ\text{C}$  without magnetic field, (c) sample exposed to Cl at  $60^\circ\text{C}$  in presence of 0.9 T magnetic field, (d) sample exposed to Cl at  $60^\circ\text{C}$  without magnetic field.

EDX point analysis of the surface shows enrichment of the corrosion product layer in W up to 1.55 wg.% (control: 1.09 wg.%), Cr up to 12.10 wg.% (control: 8.82 wg.%), and Ni up to 0.09 wg.% (control: 0.015 wg.%). Higher enrichment is observed in sample exposed in the magnetic field. The cracked pattern observed on the oxide layer is attributed to dehydration after removal from the electrolyte. Interestingly the crack pattern of the oxide layer in Figure 5d looks uniform, without any particular orientation. On the contrary, the crack pattern on the sample formed within the magnetic field (Figure 5c) tends to form parallel lines, as if the layer formed compact elongated islands along one direction and less compact zones in between. It might be speculated that the magnetic field affected the oxide film formation due to the presence of ferrimagnetic magnetite. However, no definitive evidence can be presented based on the current analysis.

## 5. Summary

A comparison between the expected conditions in the DEMO breeding blanket WCLL water coolant circuit,

and the relatively limited available literature on the effect of high magnetic fields on corrosion of steels suggests that some effect can be expected on the performance of the Eurofer-97 coolant-facing structural material, due to it being ferromagnetic and the primary corrosion product formed under deoxygenated conditions (magnetite) being ferrimagnetic.

Initial scoping corrosion tests on Eurofer-97 coupons under elevated, but nonetheless relatively low temperature and magnetic field (compared to the DEMO operating conditions), have indicated qualitative differences in corrosion film morphology as a result of the magnetic field. More aggressive chemical conditions were used to increase the extent of corrosion which would not be representative of bulk circuit conditions although could be notionally related to enhanced impurity concentrations in occluded regions such as crevices. These tests are too limited to provide indications as to the likely extent of any deleterious effect on the service performance, however, in the literature, high magnetic fields were generally found to

increase corrosion rates for ferromagnetic materials

Changes in corrosion layer behaviour within the irradiated coolant circuit could have an associated impact on uptake and release of activated species which could affect the radiation fields in out of flux circuit locations due to redeposition. The high magnetic field could also have an effect on any circulating corrosion product particulate which is likely to be held up and could have a higher likelihood of deposition on surfaces, with the possibility of “crud-bursts” when the magnetic field is removed at the end of an operational phase.

Should a significant enhancement of corrosion rates associated with high magnetic field be identified, then clarification of the mechanism by which this occurs may allow mitigations to be identified. One of the main mitigations which can be proposed if ongoing work in this area suggests a possible corrosion performance issue is the use of an extended “hot functional test” during the DEMO commissioning phase. This would aim to develop the Eurofer-97 corrosion film fully before the first plasma is produced and in the absence of a magnetic field. The potential for modification of the existing corrosion product when the field is applied would need to be considered, but this approach, alongside other measures, has been effective in ensuring passivation and low corrosion product release in commercial LWR plant.

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