

Chemistry and corrosion research and development for the water cooling circuits of European DEMO

C. Harrington^{a,*}, A. Baron-Wiechec^a, R. Burrows^b, R. Holmes^b, R. Clark^b, S. Walters^b, T.L. Martin^c, R. Springell^c, J. Öijerholm^d, R. Becker^d, P. Gillén^d, R. Torella^e, E. Lo Piccolo^e

^a UK Atomic Energy Authority, Culham Centre for Fusion Energy, Abingdon, Oxon, OX14 3DB, UK

^b National Nuclear Laboratory, 102B Stonehouse Park, Stonehouse, Gloucestershire, GL10 3UT, UK

^c School of Physics, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, UK

^d Studsvik Nuclear AB, SE-611 82, Nyköping, Sweden

^e RINA Consulting - CSM S.p.A, Via Di Castel Romano, 100 - 00128, Roma, Italy

ARTICLE INFO

Keywords:
Chemistry
Corrosion
DEMO
Blanket
Divertor
Eurofer-97

ABSTRACT

The European DEMO design will potentially use single-phase water cooling in various components that require protection against corrosion. Coolant conditions will be similar to those of fission plant but with additional considerations arising from materials choices (Eurofer-97, CuCrZr) and 14 MeV neutron irradiation. Presently, many aspects of the water chemistry and corrosion behaviour are not well defined, and several strands of work, reported here, are ongoing to address these challenges under the EUROfusion framework in collaboration with industrial partners to leverage knowledge and expertise from elsewhere in the nuclear industry.

Starting with the water-cooled lithium-lead blanket concept and considering the interaction of water with Eurofer-97, the foundation of this work has been the definition of a working water chemistry specification, supported by a review of relevant operating experience from light water fission reactors to understand the potential for technology transfer. Radiolysis modelling has been used to assess options for suppression of oxidising species under high energy neutron irradiation as these can be corrosive to components within the plant. High temperature water corrosion testing facilities have also been employed to expand the corrosion database and supplement existing experimental activities in the EUROfusion programme.

In-vessel cooling of the divertor will use CuCrZr tubes under lower-temperature, high flow velocity conditions, which will lead to different considerations compared to the blanket and the potential for flow-accelerated corrosion. Additionally, high, unidirectional, heat fluxes lead to a radial temperature profile and the possibility of sub-nucleate boiling. A separate test setup, currently under construction, to expand this corrosion database is described.

1. Introduction

The European Demonstration fusion reactor (DEMO) aims to pave the way to commercial fusion power plants by pursuing a pragmatic approach to technology choices [1]. The device will output hundreds of megawatts of net electricity with pulse lengths of several hours. To achieve large scale power generation of this order, efficient and reliable cooling is required of the in-vessel heat sources and single-phase water cooling is a leading technology option that fits with the pragmatic ethos of DEMO. However, challenges remain related to the novel material choices and extreme environment and mitigation of material corrosion issues and the control of water chemistry are such challenges [2]. These are broadly issues that have been faced in other industries, most

notably the fission community, where extensive experience is available for potential knowledge transfer. This paper presents an overview of a chemistry and corrosion programme, undertaken within the EUROfusion work programme, designed to leverage capability from industry partners to supplement on-going research and development within the fusion community.

2. Blanket and divertor design

The primary heat source within DEMO is the breeder blanket, of which the water-cooled lithium-lead (WCLL) concept is one design option. This component, shown in Fig. 1, consists of a set of box-like modules that line the wall of the vacuum vessel, through which molten

* Corresponding author.

E-mail address: Chris.Harrington@ukaea.uk (C. Harrington).

<https://doi.org/10.1016/j.fusengdes.2018.12.095>

Received 3 October 2018; Received in revised form 29 November 2018; Accepted 29 December 2018

Available online 10 January 2019

0920-3796/ Crown Copyright © 2019 Published by Elsevier B.V. All rights reserved.

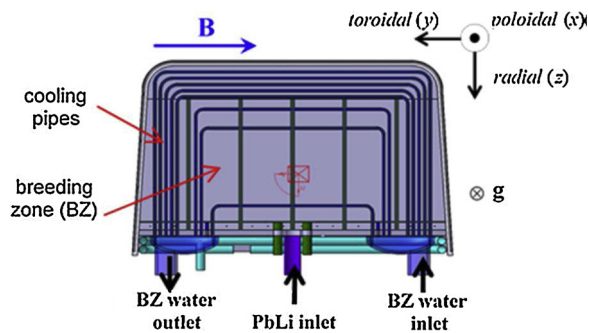


Fig. 1. Radial-toroidal cross-section of a WCLL blanket module (adapted from [3]).

lithium lead (LiPb) flows. The LiPb absorbs the energy emitted by the plasma in the form of neutrons, generating heat removed by cooling tubes carrying pressurized water coolant through the LiPb volume. The structural material of the tubes and module is Eurofer-97, a reduced activation ferritic-martensitic (RAFM) steel. Nominal conditions of the WCLL coolant are intentionally similar to those of traditional pressurized water reactors with an inlet temperature of 295 °C, an outlet temperature of 328 °C, and a pressure of 15.5 MPa [3].

The divertor is a second significant heat source in DEMO that experiences extremely high heat fluxes from the plasma exhaust and therefore has highly demanding cooling requirements. For the main plasma facing units (PFUs) of the divertor, experiencing the most direct heat loading, several design solutions are under consideration. Most assume a tungsten monoblock, receiving the heat flux on its top surface, with a CuCrZr tube carrying pressurized water through the block [4]; one example is shown in Fig. 2. Due to the challenging cooling requirements, this water must have a high velocity (12–16 m/s) and a nominal inlet temperature of 130 °C, outlet temperature of 137 °C, and a pressure of 4.0 MPa.

2.1. Chemistry and corrosion challenges

The challenge for both the divertor and breeder blanket work packages is to define suitable water chemistry guidelines that ensure a sufficient operational lifetime for the components in question. This requires an understanding of corrosion mechanisms affecting the coolant-facing materials and the chemistry control options available. For fission plant, the chemistry and corrosion understanding is underpinned by many years of development, testing, and operational experience. This comprehensive level of knowledge is not currently present for fusion. In leveraging knowledge from fission, specific experience in the means of controlling pH, maintaining reducing conditions, and improvements to corrosion resistance are directly applicable, while techniques to predict the generation of radiolysis products or perform materials testing are also of high value.

At the same time, specific aspects of the fusion environment pose

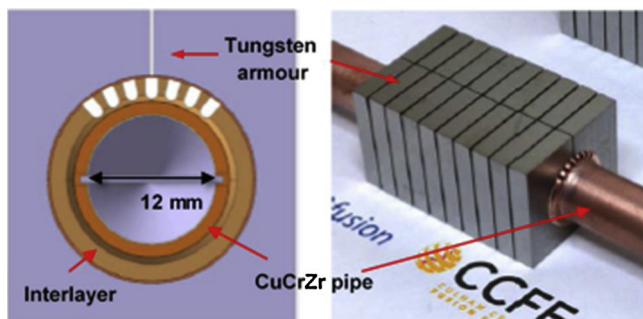


Fig. 2. Divertor monoblock cross-section and mock-up.

additional and unique challenges, most notably, the irradiation of coolant by 14 MeV neutrons, the presence of high strength magnetic fields, elevated levels of tritium in the coolant, and the operational duty of the reactor itself, such as the pulse-dwell cycle and maintenance regime [5].

3. WCLL studies

3.1. Development of chemistry guidelines

As a first step towards a chemistry specification to address the challenges of the WCLL breeder blanket, RINA Consulting CSM (RC-CSM) proposed different water chemistries with the aim of minimizing corrosion and suppressing radiolysis phenomena. Water chemistries proposed were based upon ultrapure water with addition of lithium hydroxide and hydrogen, or ammonia and hydrogen. This is driven by a rationale to reduce corrosion through a neutral or moderated alkaline buffered water solution, which promotes a protective passive film on the steels, while hydrogen addition is an efficient means of suppressing the concentration of corrosive oxidizing species resulting from radiolysis.

To assist in the water chemistry definition, the UK's National Nuclear Laboratory (NNL) has been engaged to provide industrial support, drawing upon expertise in reactor chemistry and corrosion studies. Competing and contrasting requirements for light water reactor (LWR) fission plant have firstly been reviewed alongside the operating conditions of DEMO [6]. The most common LWR designs are the Boiling Water Reactor (BWR), the Pressurized Water Reactor (PWR), and the Water-Water Energetic Reactor (VVER). The VVER and PWR have similar operating conditions that match closely with DEMO (285 °C/325 °C inlet/outlet temperature, 15.5 MPa pressure), while the two phase BWR system has slightly different conditions (275 °C/285 °C inlet/outlet temperature, 7.5 MPa pressure); however, all have relevance to DEMO.

The drivers for development of chemistry guidelines for these reactors include: maintaining the primary coolant boundary and fuel-cladding integrity; minimizing external radiation fields and wastes; and maintaining core reactivity [2]. For DEMO, the first of these requirements can be replaced with equivalent statements on maintaining the integrity of the coolant boundary and the structural material of in-vessel components, and minimizing external radiation fields and wastes. However, there is reduced need to consider the impact of water chemistry on nuclear reactivity.

The requirements review highlighted the use of boric acid in PWRs to suppress reactivity, particularly early in the fuel cycle, requiring the addition of an alkalinizing agent, such as lithium or potassium hydroxide, to restore the optimum pH. In a two-phase system, boric acid does not carry over to the steam phase and hence BWRs do not use boric acid addition, instead relying on ultra-high purity water. For DEMO, with no boric acid, both approaches may be relevant, but the use of alkalinizing agents is considered likely for maintaining the ideal pH.

Maintaining reducing conditions in the water helps to mitigate corrosion by suppressing the concentrations of oxidizing species. LWRs achieve this through addition of hydrogen, ammonia, or hydrazine. Hydrogen dosing is considered most relevant to DEMO due to a desire to avoid tritiated ammonia products and has therefore been selected as the preferred approach. Underpinning of the required concentration of hydrogen addition is obtained through radiolysis modelling. The FAC-SIMILE code has been used at NNL for modelling PWR coolant loops for many years and a similar model has been adapted to simulate the DEMO coolant circuits [6]. As a result of this modelling, there is confidence that a concentration of hydrogen between 10 and 50 cc/kg will be sufficient to suppress radiolysis.

Other recent LWR developments include the addition of noble metal nanoparticles to catalyse the combination of hydrogen and oxidising species on coolant circuit surfaces. Noble metal chemical addition

Table 1
WCLL working water chemistry.

Parameter	Value
pH _T (at 311 °C)	7.2 to 8.0
Li (as LiOH)	0–2 mg/kg
Dissolved hydrogen	10 to 50 cc/kg
Dissolved oxygen	< 10 µg/kg
Anion impurities (Cl, F, SO ₄)	< 10 µg/kg
Cation impurities (Mg, Na, Si)	< 50 µg/kg
Noble metal addition or zinc injection	To be determined

(NMCA) and On-line NobleChem™ (OLNC) are two proprietary methods to achieve this that would be relevant to WCLL. Similarly, zinc injection has gained acceptance for LWRs, as it reduces corrosion product generation by changing the composition of oxide films, and this may be relevant to DEMO.

The review of requirements has led to the working water chemistry specification in Table 1, to be refined with future underpinning. This is applicable to nominal operating conditions only as different operating modes, such as cold shut-down, will lead to different parameters.

3.2. Corrosion prediction & testing

Despite some studies on the corrosion performance of Eurofer-97 and similar RAFM steels in high temperature water [7], there remain significant gaps in the corrosion database that prevent a precise water chemistry being defined at present. Plans are pursued to utilize the LVR-15 reactor at CV-Rez to expose Eurofer samples to relevant coolant conditions in tandem with an applied neutron dose [3]. However, experiments such as this can be complex and costly to set up and therefore additional investigations are required.

The PACTITER code was chosen by RC-CSM to predict the corrosion of DEMO-relevant materials. Results obtained for Eurofer-97 and AISI 316 L were validated by corrosion test exposures in a rotary autoclave. Coupons were exposed for 1000 h at 300 °C, 15.5 MPa, and a flow velocity of 2 m/s. Ultrapure water was used, with an oxygen concentration below 10 ppb, and buffers of 2 ppm of Li as LiOH and, as alternative, 500 ppm of ammonia.

Corrosion rates obtained were in the range of 2–8 µm/y, in good agreement with outputs from the PACTITER code. The results can be considered a preliminary assessment regarding *general corrosion* of Eurofer-97 steel piping in steady state plant conditions and suggest that this may not be the critical concern for the structural integrity of the cooling system. Deeper investigation will be necessary to evaluate the effect of different water chemistry parameters, temperature, pressure, magnetic field effects, and fluid-dynamics. Further investigation will also be necessary to understand the effect of transient conditions and the response of dissimilar microstructures (i.e. base material, weld joint, and heat affected zones). Evaluation of susceptibility to localized corrosion such as stress corrosion cracking, historically problematic for the LWR fleet, remains to be studied in more depth and could present the limiting corrosion failure mode.

Supplementary testing is therefore being investigated at NNL and the University of Bristol. One such setup involves development of a micro-channel assembly using a Eurofer-97 electrode positioned under a thin gasket within a transoptic body suitable for electrochemistry and microscopy [6]. A recirculating flow loop and the narrow flow channel enables high flow velocities, allowing investigation of flow-accelerated corrosion (FAC) with in-situ electrochemical testing.

Development of micromechanical corrosion tests are also of significant value. A method has been investigated in which a focused ion beam is used to create a pre-stressed cantilever at a microscale, which can be exposed to hot water and the susceptibility to stress corrosion cracking observed [6]. Initial tests using unirradiated 304 stainless steel are considered to show promise, although some optimization of the

cantilever dimensions and stressing is necessary. Development of new techniques such as these will be of value to fusion due to the inherent difficulty in obtaining large amounts of irradiated material and will also be of benefit to current and advanced fission as a means of reducing cost and testing times by working with smaller activated inventories. Hence, there is great value in developing these techniques jointly between the two communities.

4. Divertor studies

Understanding corrosion of the divertor cooling tube presents some overlapping challenges with the WCLL in terms of radiolysis effects and chemistry control, and magnetic field effects. However, there may also be differences in mitigation techniques to control, for instance, oxidizing species, as their recombination with dissolved hydrogen will be slower at the lower temperatures and affected in unknown ways by the CuCrZr surface, requiring further consideration.

Differences surrounding the fundamental corrosion mechanisms of concern relate to the CuCrZr material and the high water velocity through the tube. Additionally, although the bulk water temperature is intended to be around 130 °C, the high heat flux and uniaxial heat flow will lead to a temperature gradient around the circumference of the tube and a hot spot at the point closest to the tungsten armor surface. The temperature at this point may reach up to 350 °C [4], leading to the potential for sub-nucleate boiling. Combined with the high flow velocity, there is potential for significant flow-accelerated corrosion.

Previous studies undertaken for ITER, in which a similar divertor design is envisaged, found a concerning high corrosion rate for CuCrZr samples exposed to high velocity jet impingement, particularly at high temperature and under oxidizing conditions [8]. For DEMO, therefore, work has been started to investigate the potential for FAC by simulating as closely as possible the operational conditions inside a test section of CuCrZr tubing. This work has been commenced with Studsvik-Nuclear AB as the industry partner, a nuclear services company based in Sweden with specific experience in corrosion testing.

The test rig, shown in Fig. 3, is currently being set up and is an adaptation of the Studsvik High Velocity Flow Loop (SHFL). The loop features a heater and cooler to control the system temperature and two pumps: a low flow pump to generate the system pressure and a recirculation pump to generate the high velocity flows required. The loop allows for dosing of the water with various dissolved gases and chemical species. The test section consists of CuCrZr tubing held within a stainless steel jacket to maintain the pressure boundary.

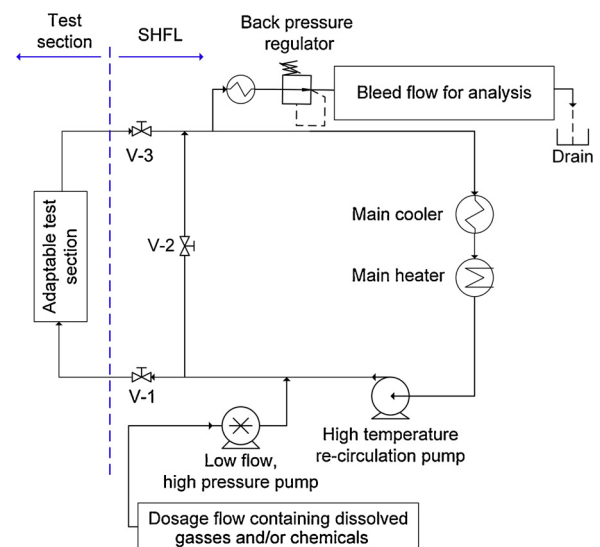


Fig. 3. Studsvik High Velocity Flow Loop.

Table 2
First divertor test exposure parameters.

Parameter	Value
Water temperature	150 °C
Water pressure	4.0 MPa
Flow velocity	10 m/s
Conductivity	< 0.1 $\mu\text{S}/\text{cm}$
Hydrogen peroxide	≥ 1 ppm
Dissolved hydrogen	0 ppm
Added impurities	0 ppm
Exposure duration	30 d (720 h)

The initial system parameters for the first test exposure are given in Table 2. Initially, the circulating water will be at the nominal bulk coolant temperature and no surface heat flux will be applied. Higher bulk coolant temperatures (simulating the up to 350 °C peak temperature) can then be investigated, before methods of applying the heat flux will be investigated to replicate possible nucleate boiling. Other future considerations include the impact of swirl tubes and potential corrosion mitigating coatings. Initial results from the first exposure of 30 days are expected by the end of 2018.

5. Conclusions

The water coolant circuits for the breeder blanket and divertor of DEMO present challenges for defining suitable chemistry guidelines for the operating plant. While there is likely to be overlap between chemistry control and corrosion mitigation strategies for the two components, differences in materials selection and corrosion mechanisms, which are not fully understood in either case, raise unique questions requiring further investigation. Several strands of work involving industry support are on-going in order to address these challenges. This

is of value not only in performing traditional corrosion testing, but also in leveraging knowledge transfer from the wider nuclear industry in areas such as chemistry control and modelling. Joint development issues, such as the development of micro-scale corrosion tests and other novel techniques, will be of value to both the fusion and fission communities.

Acknowledgments

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053 and from the RCUK [grant number EP/P012450/1]. Studsvik-Nuclear AB acknowledges support from the Swedish Research Council No 2017-00643. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

References

- [1] EUROfusion, European Research Roadmap to the Realisation of Fusion Energy, (2018).
- [2] R. Burrows, C. Harrington, A. Baron-Wiechec, A. Warren, Brighton, UK International Conference on Chemistry of Nuclear Reactor Systems (NPC2016)2016, International Conference on Chemistry of Nuclear Reactor Systems (NPC2016) (2016) 3–7 October.
- [3] L.V. Boccaccini, et al., Fusion Eng. Des. 109B (2016) 1199.
- [4] J.H. You, et al., Fusion Eng. Des. 16 (2018) 1–11.
- [5] A. Baron-Wiechec, et al., IAEA Workshop on Challenges for Coolants in Fast Neutron Spectrum Systems, Vienna, Austria, July (2017), pp. 5–7.
- [6] R. Holmes, et al., USA International Conference on Chemistry of Nuclear Reactor Systems (NPC2018), San Francisco 2018, International Conference on Chemistry of Nuclear Reactor Systems (NPC2018), San Francisco (2018) 9–14 September.
- [7] S. Van Dyck, R.-W. Bosch, Fusion Eng. Des 973 (2005) 75–79.
- [8] C. Orbitz, J. Öjjerholm, S. Wikman, E. Bratu, Nucl. Mat. Energy 9 (2016) 261–266.