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Active Redox Control of Molten Salts For Fusion Blankets

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1 Technical Overview

1. Problem Statement

Commonwealth Fusion Systems (CFS) is working to risk-retire aspects of technologies related to Fusion Energy System (FES) blanket technology. CFS is actively investigating the molten salt LiF-BeF_2 (FLiBe), a novel blanket material, for fusion energy machines.

The role of the blanket in a fusion tokamak is to capture neutrons produced by fusion reactions in the plasma and carry thermal energy to a heat exchanger. It is also to breed tritium, which is then separated and used as fuel. The large temperature range over which FLiBe remains a liquid enables high-efficiency heat transfer and single-phase fluid cooling inside the device. FLiBe has been used extensively in molten salt nuclear applications because of its low neutron activation.

One drawback to the use of FLiBe is that significant degradation to structural materials can occur via impurity driven corrosion, a process that is exacerbated at the high temperatures expected in tokamak internal components like the vacuum vessel. The use of FLiBe for commercial fusion applications will require the application of corrosion mitigation strategies, including monitoring impurities and salt chemistry, controlling impurity levels, and ensuring that salt-facing structural materials are protected.

The approach taken here is to monitor corrosion caused by FLiBe in real time, and to enable local control of corrosion rates by adjusting impurity concentrations in molten FLiBe.

Redox control has previously been demonstrated for controlling corrosion in FLiBe salts used in molten-salt nuclear applications. Control over the salt redox state is typically achieved by contacting the salt and structural materials with metallic beryllium (Be) [1, 2]. In FES, there is an added challenge due to free fluoride ions that are generated through transmutation reactions. These ions can subsequently combine with tritium (T) bred from the blanket material to form TF, which is highly corrosive to a variety of structural materials [1].

Active redox control using Be with real-time sensor output was intended to be demonstrated in this work. The success or failure of the active corrosion mitigation system is judged by the corrosion potentials of an exposed Hastelloy C-276 and inert tungsten (W) electrodes, which can be directly observed using electrochemical techniques such as open circuit potential monitoring. The overall effectiveness of those additions in preventing weight loss and maintaining the microstructural integrity of the alloy were evaluated.

2. Work Scope

We have achieved success on the major goals set forth in the proposal. This work used electrochemical reference and inert electrodes in FLiBe to detect the presence of corrosion products. Active, real-time redox control was achieved through the introduction of Be metal directly into FLiBe. The addition of Be lowers the redox potential of the salt to values where structural metals are thermodynamically prevented from oxidizing.

The electroanalytical techniques used in this project are widely employed to identify corrosion products at medium and low concentrations. These techniques can also quantify the amounts of corrosion products if performed with the correct methodology.

During the course of the project, existing redox control and analytical methods previously utilized by SRNL were evaluated for their applicability to real-time active corrosion control of CFS' FLiBe blanket system. Specifically:

1) Inductively coupled plasma mass spectrometry (ICP-MS) and inductively-coupled plasma optical emission spectroscopy (ICP-OES) were performed with SRNL-sourced research grade FLiBe (<10 ppm total impurities, according to the manufacturer) to determine composition and trace impurity levels.
2) LECO analysis was conducted to quantify oxygen and hydrogen concentrations in SRNL-sourced research grade and fusion machine grade (<100 ppm total impurities) FLiBe.
3) SRNL built an inert atmosphere corrosion cell for operation at ~600 °C. The cell was constructed from Ni-based superalloys with a pyrolytic boron nitride crucible insert.
4) Corrosion rates of Hastelloy C-276 coupons were determined from immersion experiments to gravimetrically determine generalized corrosion.
5) SRNL tested and verified the operation of molten salt reference electrodes that incorporated the redox couple Ni/NiF_2 to establish a reference point and allow for quantifiable voltametric methods.
6) Electrode arrays and reference electrodes were located close to the Hastelloy sample. The electrodes were constructed as long rods that could be raised and lowered to perform potential monitoring after operations when samples are lowered.
7) Beryllium metal was introduced to the FLiBe as a redox control additive, and the potential of the system was measured over time.

This project, defined by the above tasks, set a baseline for corrosion rates and the effectiveness of added Be for redox control.

3. Results

Purified, research-grade FLiBe was procured from AlphaTech Research Corp and stored in an inert Ar glovebox prior to use/testing. The composition of the salt, as determined by ICP performed by both the manufacturer and SRNL, is shown in Table 1. The concentrations of oxygen and hydrogen in both research- and fusion machine-grade FLiBe, as obtained from LECO analysis, were also analyzed; the results are displayed in Table 2. The results in Table 2. appear to be similar in range to those shown recently in literature [3].

Table 1. FLiBe compositions obtained from ICP Analysis.

Research-Grade FLiBe											
Source of Data: ICP Method	**LiF (mol %)**	**BeF$_2$ (mol %)**	**Na (ppm)**	**Al (ppm)**	**Cr (ppm)**	**Cu (ppm)**	**Fe (ppm)**	**Mn (ppm)**	**Ni (ppm)**	**Pb (ppm)**	**U (ppm)**
Alpha Tech Analysis 1: ICP-MS	68.5	31.5	29	4.86	<1	4.92	<1	<1	<1	<1	<1
Alpha Tech Analysis 2: ICP-MS	67.4	32.6	62	5.69	<1	<1	<1	<1	<1	<1	<1
Alpha Tech Analysis 3: ICP-MS	68.7	31.3	69	5.97	<1	<1	<1	<1	<1	<1	<1
Alpha Tech Analysis 4: ICP-MS	68.4	31.6	76	7.63	<1	2.45	<1	<1	<1	<1	<1
Alpha Tech Average: ICP-MS	68.3	31.8	59	6.0	<1	2.3	<1	<1	<1	<1	<1
SRNL: ICP-MS with 5X Dilution	66.7	33.3	NA[1]	<10							
SRNL: ICP-MS with 2X Dilution	66.4	33.6	NA[1]	<10							
SRNL: ICP-OES with 2X Dilution[2]	64.5	35.1	<1	<10							

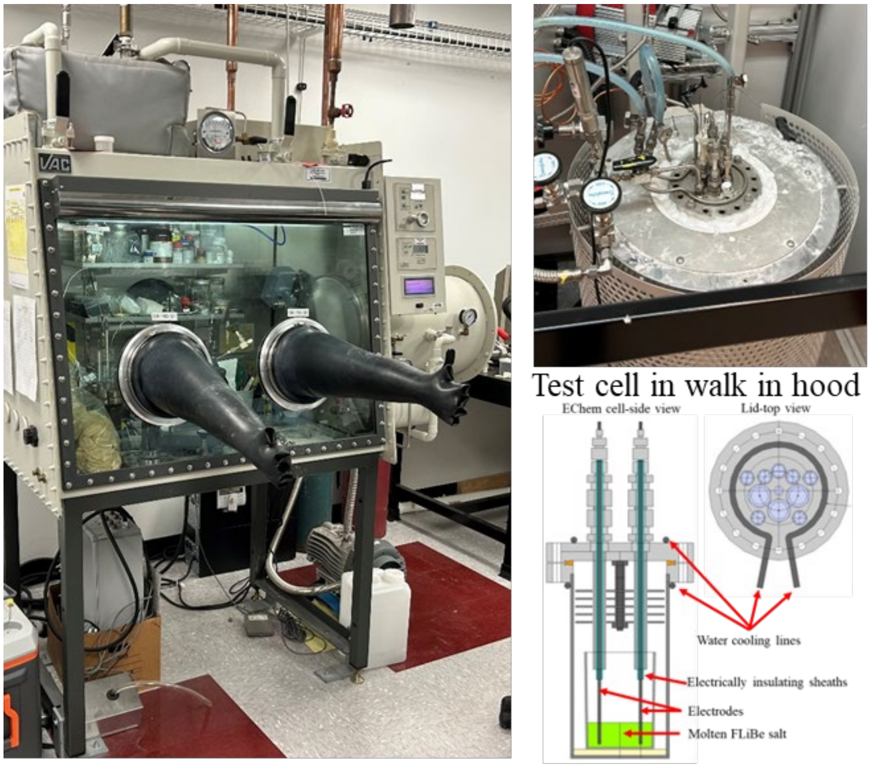
[1] Not analyzed using ICP-MS

[2] Analysis showed Si present at concentrations of ~5 ppm, or 0.4 mol%

Table 2. Concentrations of O and H in FLiBe from LECO Analysis.

Research-Grade FLiBe		
Sample	**Oxygen (ppm)**	**Hydrogen (ppm)**
A1	76	0[1]
A2	39	0[1]
A3	37	3.7
Average	51	N/A
Standard Deviation	22	N/A
Fusion Machine-Grade FLiBe		
Sample	**Oxygen (ppm)**	**Hydrogen (ppm)**
B1	369	40.2
B2	348	16.3
B3	339	23.2
Average	352	27
Standard Deviation	15	12

[1] Values slightly negative and interpreted as 0



Beryllium Glovebox

EChem cell side view

Figure 1. Schematic of the immersion test setup.

Because FLiBe has potential safety concerns related to the possible formation of various beryllium and fluoride compounds, significant effort was exerted to ensure safe testing operations. As seen in Figure 1 (left), a portion of a glovebox was dedicated to beryllium work. Here, the FLiBe salt was placed in airtight electrochemical cells for transport from the glovebox to a walk-in fume hood (top right of Figure 1). In the fume hood, a flow of argon cover gas that exited through a mineral oil bubbler was established. The electrochemical cell itself allowed for telescoping various electrodes down and up, into and out of the molten FLiBe, respectively.

The cell operated at ~600 °C, usually ± 5 °C, with the furnace set above that temperature and its offset depending on the cell in use. Temperatures were recorded for three different cell designs using type-K thermocouples with Ni sheaths. In the second and third sets of experiments, thermocouples were immersed in the reference electrode (RE) salt solutions of proprietary reference electrodes, which where themselves immersed in the primary crucible containing FLiBe salt. The temperature readings were logged using a National Instruments USB-TC01 temperature logger.

Static corrosion tests were conducted at 600 °C for 100 h with Hastelloy C-276 coupons immersed in molten research-grade FLiBe salt contained in a pyrolytic boron nitride (PBN) crucible. Photographs captured before and after removal of the test coupons from the PBN crucible are shown in Figure 2(a) and 2(b), respectively. As evident in the figure, the coupons were fully immersed in the FLiBe salt for the duration of the corrosion test. Characteristics of the immersion test coupons are provided in Table 3. Based on the post-test weights of the samples, the average corrosion rate of Hastelloy C-276 in FLiBe under the current conditions is 6.2 µm/yr.

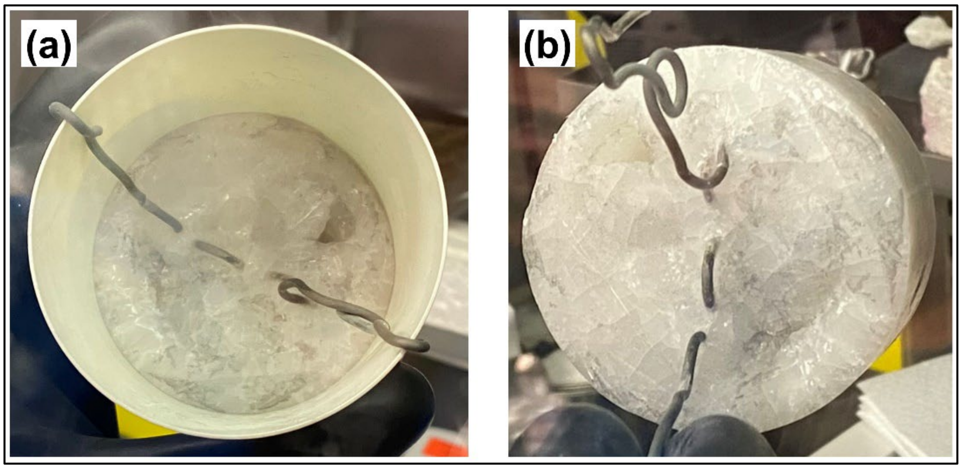


Figure 2. Post-test photographs taken (a) before and (b) after removal of the Hastelloy coupons from the PBN crucible.

Table 3. Immersion test coupon characteristics before and after immersion.

Sample ID	Initial Weight (g)	Total Area (cm^2)	Final Weight	Corrosion Rate ($mg/cm^2/day$)	Corrosion Rate (µm/y)
Hastelloy-1	8.5060	8.94	8.5052	0.021	8.8
Hastelloy-2	8.4416	8.95	8.4397	0.051	20.9
Hastelloy-3	8.4118	8.91	8.4128	-0.027	-11.1

At the conclusion of the static testing, four series of electrochemical tests were undertaken. Electrode configurations for test series three and four are shown in the left and right of Figure 3, respectively. In test series three, three different containers were evaluated to form stable reference points for the electrochemical measurements; sintered boron nitride utilizing a 1 mol% NiF_2 solution was ultimately found to be successful. In test series four, the solution was spiked with $FeCl_2$ as an oxidant to react with the Hastelloy C-276 electrode prior to immersion of the Be electrode, thereby forming a corrosive salt containing Fe^{2+} and Cr^{2+} contaminants. The Be electrode contacting the salt was expected to eventually fix the redox state of the salt, remove contaminants from the salt, and minimize any further corrosion of the Hastelloy C-276.

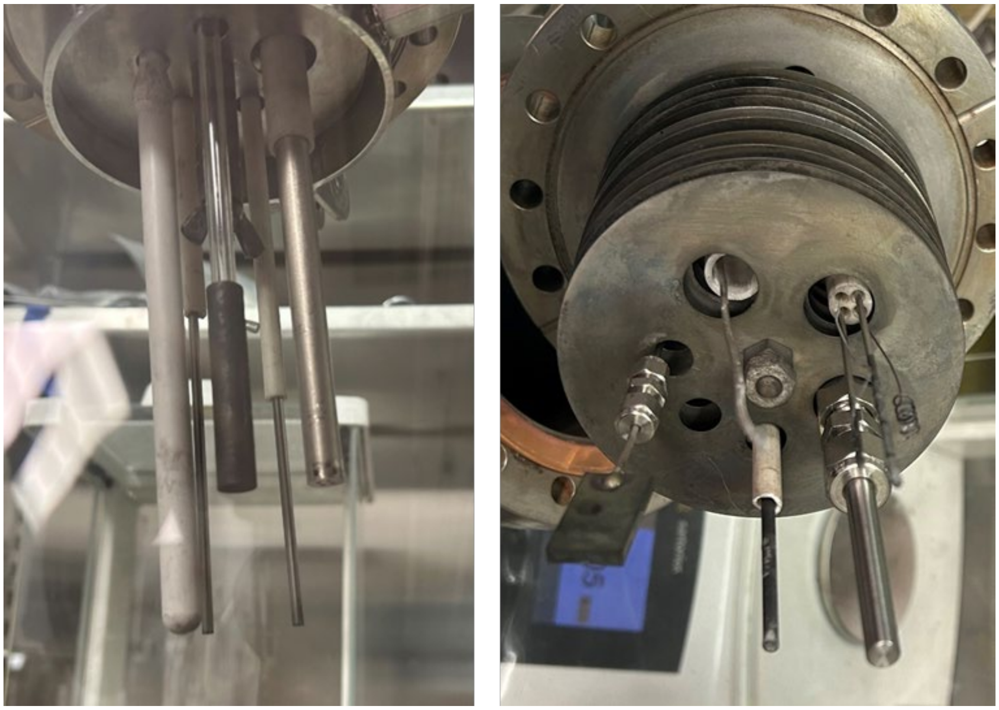


Figure 3. Electrodes from test series 3 (left) and 4 (right) as seen from the bottom of the thermal baffles.

Figure 4 shows results from an electrochemical technique called square wave voltammetry, an especially sensitive electroanalytical method. Starting from the top for the upper set of curves and the bottom for the lower set of curves, each successive curve in the individual sets is about 2 hours later in time then working towards 0 current. Just prior to beginning measurements, a Be electrode contacted the salt, and this contact started to remove the contaminants.

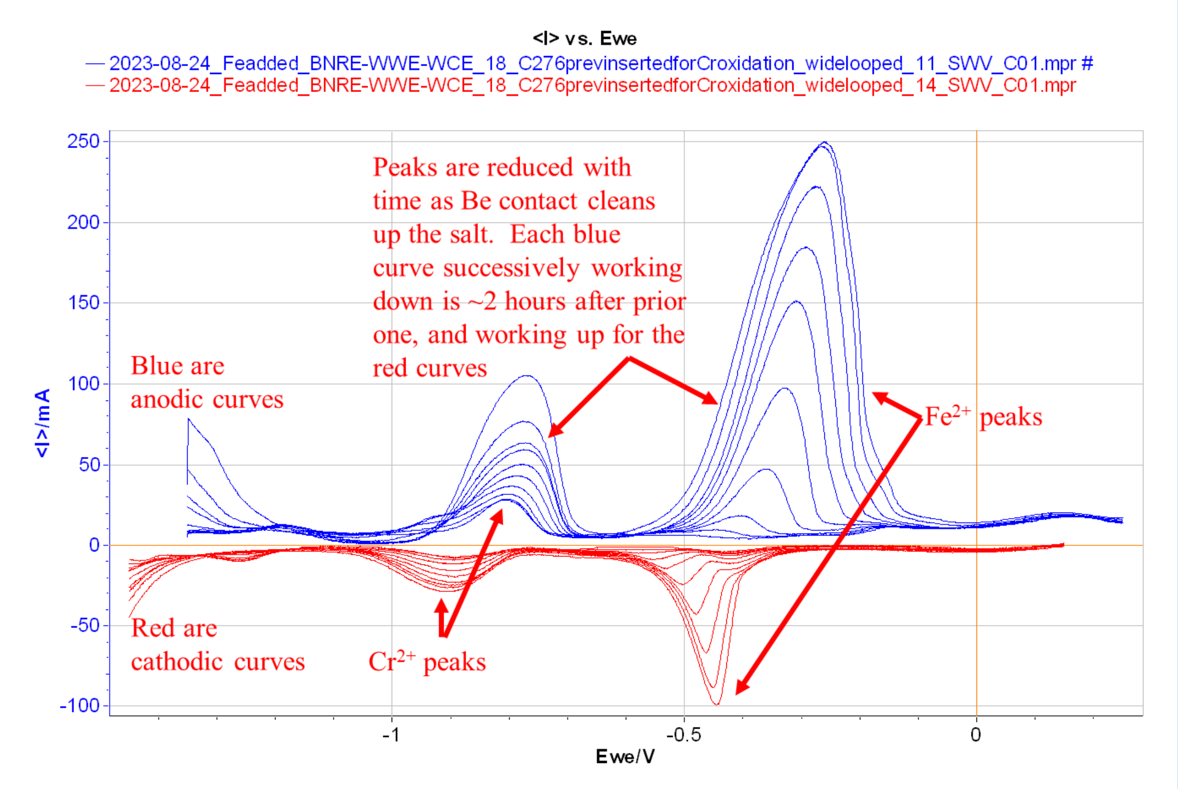


Figure 4. Electrodes from test series 3 (left) and 4 (right), as seen from the bottom of the thermal baffles.

The peak values for the contaminants are proportional to their concentrations. Upon taking the values for the anodic peaks from the square wave voltammetry results and plotting them with time, (Figure 5), we see a strong correlation with both Fe and Cr contaminant removal from the salt. Full removal of contaminants from the salt was projected to occur after 24.1 h.

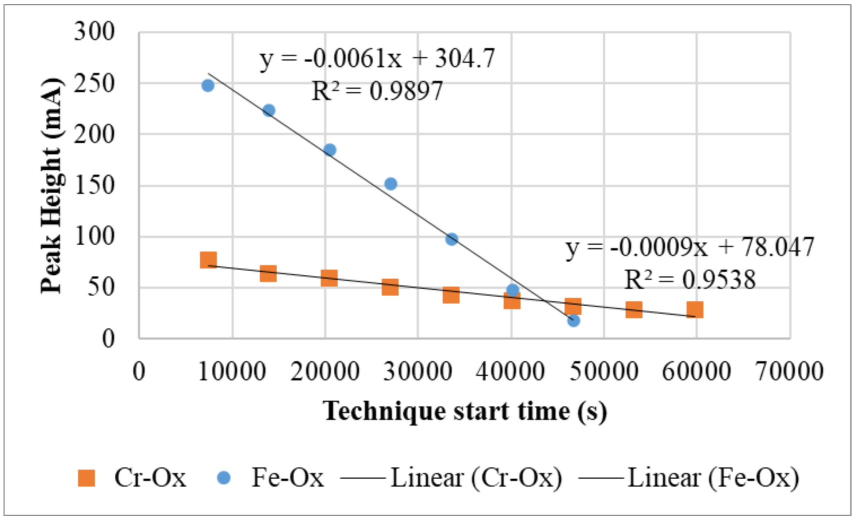


Figure 5. Peak height as a function of SWV measurement start for anodic peaks.

Figure 6 shows the electrochemical potential of the Hastelloy C-276 exposed to FLiBe during the same set of experiments when the Be contacting the salt starts to reduce its corrosive potential. When the electrodes are inserted, an initial jump in corrosion potential is observed as the salt is mixed. This is followed by a steady decrease over time as beryllium contact reduces the corrosivity of the salt.

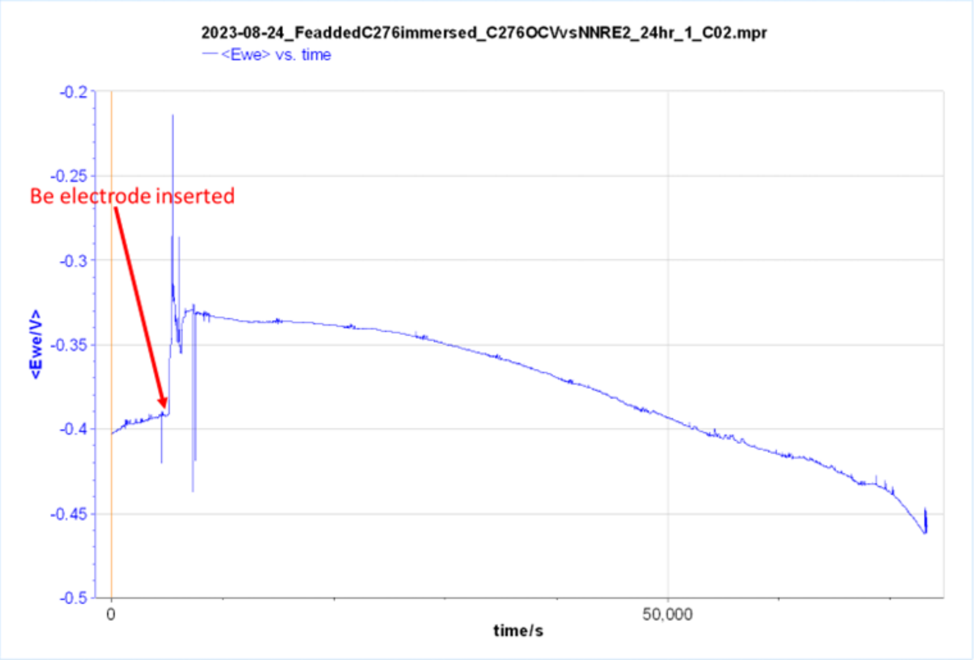


Figure 6. OCP results on the Hastelloy C-276 showing cathodic in potential with time as the impurities are depleted.

2 Impact

1. Use of Project Results

The ARC blanket is in the early stages of the design process, and significant R&D work still lies ahead. Particularly in the area of salt chemistry, there are important scientific and engineering questions that have not been fully addressed. This INFUSE project takes a meaningful step towards answering these questions and provides a springboard for CFS to continue this work both internally and with collaborators.

Over the course of this INFUSE project, third-party analysis of the initial and ongoing impurity levels in FLiBe salt from a commercial vendor was performed using state-of-the-art techniques. This includes metallic impurity analysis with ICP-MS and ICP-OES as well as LECO inert gas fusion analysis. These analyses provide a first step towards a fully repeatable and well-established set of processes for salt aliquot analysis.

This INFUSE project also considered electrochemical techniques for measuring both salt potential and salt impurity levels. Many impurities will eventually need to be quantitatively measured, but the techniques investigated in this project will be extended to consider other impurities of interest.

On the salt potential question, this project has provided an initial comparison of multiple types of reference electrodes. CFS will continue working towards an even higher performing iteration, but the INFUSE data is a strong starting point. This project also has further collaborative interest from other universities and salt companies that may lead to more joint investigations in the future.

2. Fusion Energy Impact

FLiBe is one of the dominant potential blanket materials that can breed tritium needed to fuel the deuterium-tritium nuclear fusion fuel cycle. It is inevitable that the salt will become corrosive during fusion operation, as tritium breeding will generate hydrofluoric acid which is highly corrosive to structural alloy materials. Beryllium contact has been demonstrated in this work to remove impurities whose corrosive nature are analogous to hydrogen fluoride corrosive effects. This work demonstrates a corrosion mitigation method in FLiBe salt, further de-risking its use as a fusion energy system blanket material.

3. Intellectual Property, Publications and Conferences

No IP was generated via this project. One presentation has been given so far which included some of this work by Luke Olson at the Fall 2023 Beryllium Health and Safety Committee Meeting. Two journal papers are expected to be published from this work and an in-depth technical report is in progress.

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