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Materials Assessment for FLiBe Fusion Blankets

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September 2024

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Materials Science and Technology Division

MATERIALS ASSESSMENT FOR FLiBe FUSION BLANKETS

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September 2024

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1. INTRODUCTION

This evaluation was prepared at the request of DOE-FES and expands on an earlier evaluation prepared by Wilson, Wiffen and Keiser in 2015 (attached as Appendices A and B). Additional useful information for materials in fission molten salt reactor systems that use FLiBe can be found in a prior NRC report [Busby 2019]. The purpose of this report is to review the considerations that will determine the fusion blanket structural materials that will be suitable for use in a FLiBe breeder-coolant fusion power plant (FPP). *Identifying a fusion-relevant structural material that is sufficiently compatible with FLiBe is a key issue to be addressed.* The constraints and trade-offs made in structural materials selection include the usual power generation requirements such as mechanical properties, fabricability and durability, which assumes reasonable compatibility with the working fluid. For an FPP, additional constraints include neutron economy (breeding ratio), resistance to irradiation damage and low activation (i.e. waste disposal) characteristics.

2. FUSION BLANKET SELECTION

There has been increased recent attention on commercializing fusion energy as a potential source of greener and more sustainable power production [Beaufait 2023]. While the US fusion materials program has been focused on the dual coolant lead lithium (DCLL) [Malang 2011] blanket and magnetic confinement fusion (MCF) for the past 20 years, there is commercial interest in exploring other concepts including inertial confinement fusion. In MCF, the plasma is magnetically confined inside a tokamak or stellarator. One of the main purposes of the blanket is to extract heat from the reactor to both cool the first wall and produce power. The other main purpose is to breed tritium, which is not available in nature, but is needed for a sustained D-T fusion reaction. Tritium can be produced when neutrons from the plasma interact with Li, with ^{6}Li being the most favorable reaction:

$$^{6}\text{Li} + \text{n} \rightarrow {}^{4}\text{He} + \text{T}$$

Thus, the blanket breeding material must include ^{6}Li either as a liquid or solid. Candidate solid breeder materials include mainly lithium metal oxides, such as L_2TiO_3 [Shmayda 2022]. Many recent reactor designs feature higher power densities and neutron fluxes, which could potentially lead to failure modes in solid breeder materials and have led to a preference for liquid breeders [Forsberg 2017]. The liquid candidates typically combine the breeder (Li) with a neutron multiplier (Be or Pb); these candidates include Li, eutectic Pb-16at.%Li, and 2LiF-BeF_2 molten halide salt, commonly referred to as FLiBe. Another less investigated salt option is FLiNaBe (LiF-NaF-BeF_2) which has a lower melting point compared to FLiBe (305°C vs. 459°C) [Yamashita 2018, Shmayda 2022]. Also, the LiF-BeF_2 phase diagram suggests that the lowest melting temperature is near 0.48LiF-0.52BeF_2, ~365-375°C [Romberger 1972, Benes 2009, Romero-Serrano 2009]. Given the temperature limitation of reduced activation ferritic martensitic steels (RAFM) to 550°-600°C and the need to keep the salt ~50 or more degrees above its freezing point, a lower salt melting temperature is likely required to enable a concept based on these materials. One advantage of FLiBe over the other liquid candidates is its lower electrical conductivity, decreasing any potential operational complications arising from the interactions with the strong magnetic fields in the reactor [Forsberg 2017] such as the magneto-hydrodynamic (MHD) pressure drop; interference of a conducting fluid with the operation of magnetic sensors necessary to control tokamak plasmas is a primary reason for the selection of FLiBe [Kuang 2018]. However, the Lorentz forces developed in these fields can cause charge separation, which may affect the free energy and kinetics of the reactions between the FLiBe salt and the walls of the blanket [DeVan 1979]. With renewed interest in FLiBe blanket concepts, the purpose of this report is to explore the current state of materials-related understanding associated with using FLiBe, primarily focusing on compatibility issues. Compatibility of structural materials with Li and Pb-Li have been the subject of many studies over the past 50 years [Jun

2020]. Much less effort has been focused on FLiBe compatibility, especially with the end of research on molten salt fission reactors in the 1970's [Rosenthal 1970].

3. PURPOSE AND IMPORTANCE OF FLIBE FUSION BLANKETS

Recently, Commonwealth Fusion Systems (CFS) has focused on using FLiBe as the breeder/coolant in MCF reactor blankets. The FLiBe salt (typically LiF-BeF_2; 66 mol%, 34 mol%) also serves as the heat transfer fluid removing the generated heat from the structural materials and plasma-facing surface. Heat transfer is usually by radiation from the plasma core to the shell, followed by convection from the shell to the FLiBe salt [Beaufait 2023]. Heat generated by neutron interactions in the blanket and shield is also conducted to the coolant. The coolant circulates at near atmospheric pressure with an estimated peak operating temperature of 600-700°C [Forsberg 2017] and a minimum temperature well above the FLiBe melting temperature of 459°C. A salt-compatible, low-activation structural material operable in these conditions has not yet been identified.

FLiBe provides good radiation shielding [Beaufait 2023] and has some attractive thermal hydraulic properties, such as the largest volume-specific heat capacity and highest boiling point [Forsberg 2017], but also some unattractive ones, such as its high viscosity and low thermal conductivity [Wong 2005]. Compared to other fluoride salts, such as NaF-ZrF_4, LiF-NaF-ZrF_4 or LiF-ZrF_4, FLiBe exhibits one of the lowest melting points (459°C); however, the melting point can be lowered by increasing the BeF_2 fraction up to the eutectic point at 0.48LiF-0.52BeF_2, where it reaches 365°C [Benes 2009]. The latter salt was used in combination with ferritic steel in early salt blanket designs in a separately-cooled configuration, in which the salt breeder flowed slowly through steel tubes (the first wall and other structures were cooled by helium) [Moir 1985].

The viscosity of this lower melting point eutectic mixture is significantly higher than conventional FLiBe, a key challenge to be resolved for use in self-cooled designs (e.g. those explored in [Wong 2005] and proposed by CFS [Kuang 2019]). In order to function as a first wall coolant, high heat removal (> 0.25 MW/m^2) is required, which is improved by high flow velocities; these, combined with the high viscosity (Figure 1), lead to high pressure drops. Preliminary investigations conducted at ORNL [Gehrig 2024] indicate that the pressure drops may be unacceptably high for the eutectic mixture (52% BeF_2), exceeding 2 MPa (a figure of merit commonly applied to liquid metal MHD pressure drops) across the first wall. As the mixture composition is changed, a better design window begins to open around 48% BeF_2 (Figure 1). The flow velocities required to adequately cool RAFM are still high, and the feasibility of this high viscosity mixture considering the flows through the remainder of the blanket and balance of plant still need to be resolved.

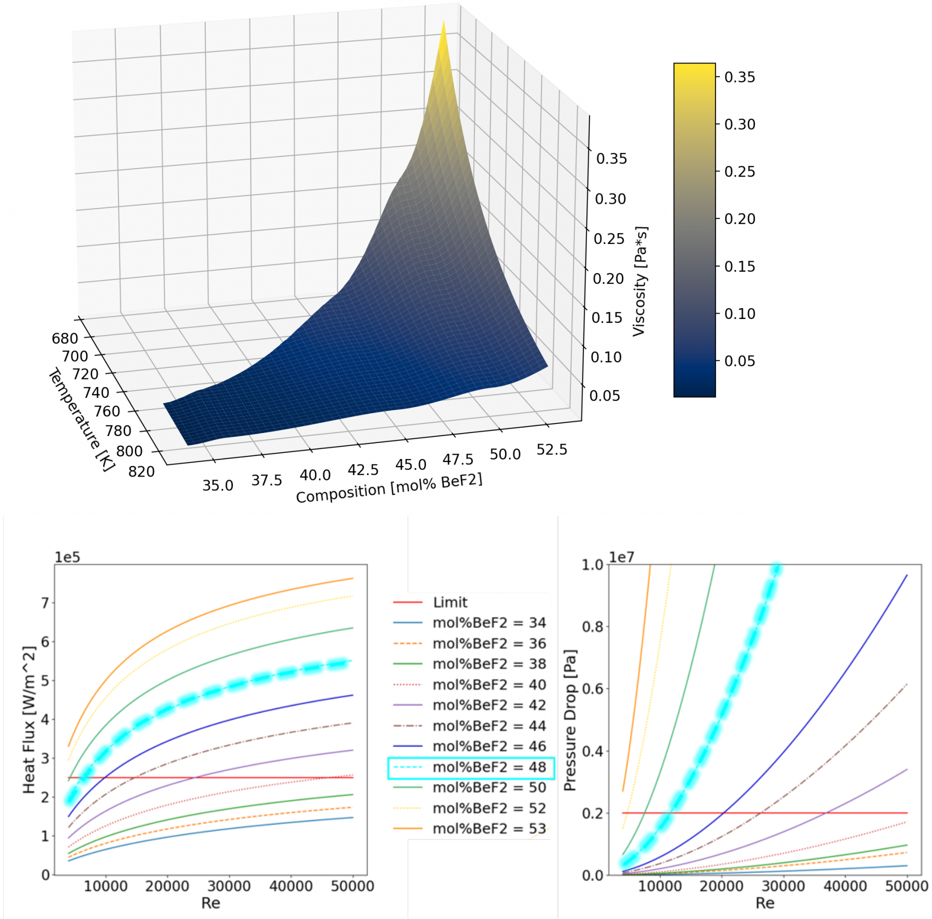

Figure 1. Viscosity (top), heat removal ability (center) and pressure drop (right) of LiF/BeF2 mixtures in 4x3 cm FW coolant channels [Gehrig 2024].

Another challenge associated with molten salt blankets is the marginal tritium breeding ratio. This can be improved by the addition of a neutron multiplier, in particular beryllium [Konishi 2017], which can potentially increase the tritium breeding ratio (TBR) from 1.05 to more than 1.3, thereby increasing the overall efficiency and reducing the amount of generated nuclear waste [Shmayda 2022]. Molten salt blanket designs [Moir 1985, Wong 2005, Kuang 2018] invariably include it for this reason. Pure beryllium is typically included in the form of small pebbles [Scaffidi-Argentina 2000, Wong 2005]. In light of the high swelling and tritium retention in pure Be, other alternatives, such as BeO are considered. However, BeO may not be compatible with FLiBe or have adequate mechanical properties [Scaffidi-Argentina 2000]. More recently, beryllide intermetallic compounds [Mishima 2007] such as $Be_{12}Ti$ have been developed (primarily for use with solid breeder designs) that alleviate the swelling and tritium retention issues associated with pure beryllium; these potentially enable a move away from pebbles to larger solid forms. The possibility of combining beryllides with molten salts has the potential to significantly improve TBR [Humrickhouse 2023]. Though lower multiplier volume fractions (e.g. around 30 vol% Be [Cheng 2003]) have frequently been employed, the optimal ratio for tritium breeding is rather higher [Fischer 1988], as shown in Figure 2. Though the additional metal component of the beryllides does have an absorbing effect, optimal fractions are still ~75-80% multiplier. Investigations of a FLiBe blanket with immersed multipliers at this optimal fraction added to the FNSF design revealed TBRs ~1.3 without lithium enrichment, see Figure 2. Moreso than in liquid metal blankets, the breeding was concentrated in the front of the blanket, mostly within the first 45 cm.

While this model is somewhat idealized in that it lacks any internal structure between the first and back walls (i.e. an "immersion" blanket), the TBR is nevertheless sufficiently high (and can be increased further via ^{6}Li enrichment) that it gives a degree of confidence that there is sufficient margin to account for more detailed engineering design, design integration issues, and uncertainties in nuclear data. While the immersed beryllide could in principle also supply a necessary redox chemistry control function, it must also not give rise to significant multi-material interactions with other materials in the salt. The feasibility of the concept requires further design effort and experimental investigation of these compatibility issues.

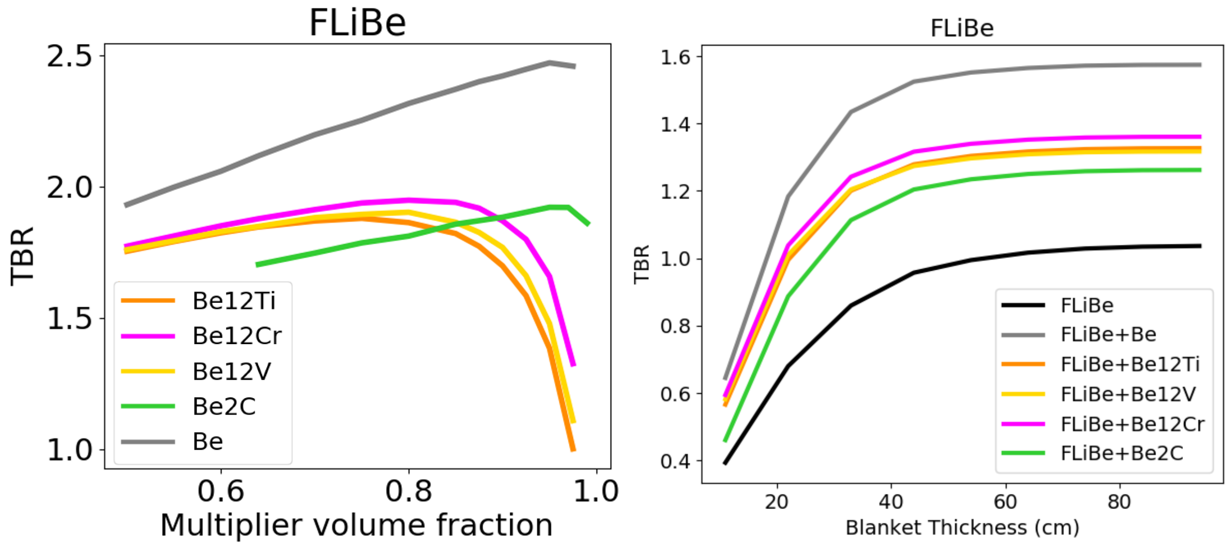

Figure 2. Optimal multiplier volume fraction in an ideal (1.5 m completely surrounding the plasma) blanket (left); TBR of an "immersed multiplier" (at optimum fraction) blanket in the FNSF (right), as a function of blanket thickness (inboard and outboard to 50 cm; outboard only beyond 50 cm). Natural lithium enrichment is used in all cases.

4. STRUCTURAL MATERIAL SELECTION FOR FLIBE FUSION BLANKETS

Despite its attractive characteristics, there are also challenges associated with using FLiBe salt as a fusion blanket coolant/breeder material, and they are mostly related to its compatibility with the material used for the blanket structure. Even though FLiBe can be considered non-reactant when pure, that is a misconception. Solid-liquid equilibrium is established when the chemical potential of all the constituents of the solid (e.g. alloying elements) in the salt is equivalent to their chemical potential in the solid. This equilibrium is altered by irradiation and by the presence of moisture or other impurities, which can create very corrosive conditions for materials that contact molten FLiBe [e.g. Raiman 2018]. Generally, the most common products produced by neutron irradiation of FLiBe are HF, O_2 and H_2O [Tanaka 2001, Terai 2001]. Neutron irradiation generates tritium (T) which may result in TF formation, which is chemically similar to HF [Terai 1998, Nagasaka 2009]. Moisture can react with the hygroscopic BeF_2 component of the salt generating HF, based on the following reaction:

$$BeF_2+H_2O \leftrightarrow BeO + 2HF$$

Similarly metallic impurities in the salt can lead to a reaction when a metal halide with a higher stability (MF_z) will still react with a more noble metal (N) [e.g. DeVan 1969]:

$$yMF_z + zN \leftrightarrow zNF_y + yM$$

Figure 3 shows the redox potential for various elements in fluoride salts. Thus, for example, if a stainless steel containing 16%Cr and 2%Mn were exposed to a salt containing NiF_2 as an impurity, one would expect more dissolution of Cr and Mn from the steel compared to a salt with no NiF_2 impurity.
To reduce the salt potential due to T or other impurities, a redox agent can be added to the salt. Be is a good redox agent for FLiBe because it has a strong tendency to form stable BeF_2, due to its very low chemical potential, defined as [Olander 2002, Petti 2006, Calderoni 2009, Keiser 2022]:

$$\mathrm{DG} = -\mathrm{RTln}(p_{F2})$$

The addition of Be can serve as a redox regulating agent [Wong 2005] that serves a dual purpose:

a) it captures the free fluorine in the system, which is a byproduct of FLiBe irradiation:

$$\mathrm{xM} + F_2 \rightarrow \mathrm{xM}F_{2/x}$$

b) it also helps reduce TF to T_2, the ratio TF/T_2 dictates the salt redox potential, which in turn, regulates the extent of corrosion [DeVan 1979, Ihli 2008, Cheng 2003]:

$$2\mathrm{TF} + \mathrm{Be} \rightarrow \mathrm{Be}F_2 + T_2$$

T_2 is then recovered and recycled back to the fusion reactor [Cheng 2003, Fukada 2012].

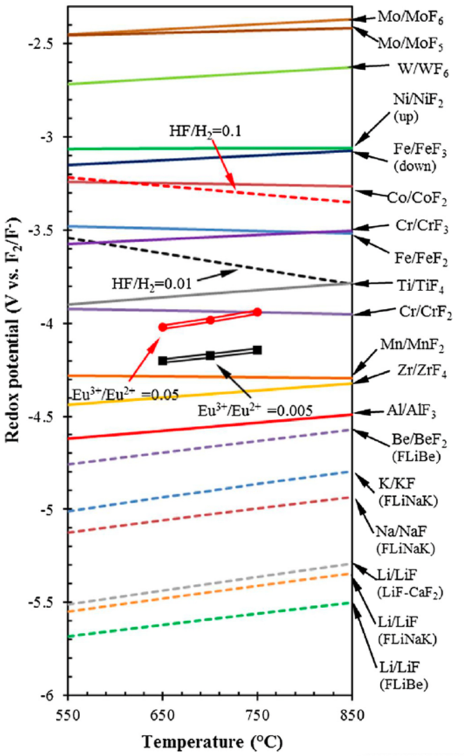

Figure 3. Calculated redox potentials of various elements as a function of temperature in fluoride salts from HSC Chemistry v.9.0. Solid lines are for metal oxidation at 1ppm concentration. The dotted lines are for oxidation of reductants. HF/H2 rations are for 1 atm total pressure. Eu data in FLiNaK (FLiNaK often is used as a surrogate for FLiBe). [Zhang 2018]

It is thus apparent that compatibility of structural materials in FLiBe is a complicated phenomenon. Potential candidate materials are addressed in the following sections where the limited compatibility data (shown in Figure 4) are addressed. Since the testing procedure and salt purity have a strong effect on the results [Raiman 2018], it is difficult to compare the various datasets available. The test variables include exposure time, salt purity, salt volume-specimen surface area ratio and capsule/crucible material [Pint 2023] that are not shown in Figure 4, which only captures the effect of temperature.

4.1 RAFM STEELS

Candidate RAFM steels have attractive mechanical properties and irradiation resistance in fusion environments, including low irradiation-produced swelling [Wong 2004b]. The primary alloying element is Cr, which can range between 8 and 12% [Zinkle 2000]. The alloys are nominally Fe-Cr-W with specific alloy compositions shown in Table 1. RAFM steels are a leading structural material candidate for a variety of blanket types, including solid breeders, Pb-Li, Li and FLiBe. However, they are limited in temperature to ~550°C due to creep strength and with the relatively high melting point of FLiBe (459°C), that leaves a relatively small operating window. As mentioned previously, a higher BeF_2 content in the salt with a lower melting point (<400°C) might be attractive for RAFM steels.

Steels are generally considered compatible with FLiBe [Sagara 2006, Kondo 2009c] with several examples in Figure 4 (i.e. JLF-1 and F82H). There are several classes of advanced RAFM steel. For example, to achieve temperatures above 600°C, oxide dispersion strengthening might be considered [Klueh 2002, Maziasz 2002, Wong 2004a, 2004b, Ohnuma 2009, Was 2019] with a nano-scale dispersion of oxides rich in Y and Ti. In this case, the Cr content could be higher than the 8-11% found in RAFM steels. Fully ferritic steels with 12-18%Cr could potentially operate up to 800°C [Zinkle 2017] but α' embrittlement is a concern at 475°C [Grobner 1973] and at even lower temperatures with irradiation [Field 2015]. Additional alloying elements such as Zr and Ta might further improve mechanical properties [Rahmanifard 2016]. Blanket studies assumed that ODS steels could operate in FLiBe up to 700°C [Wong 2004b], perhaps by using a protective coating such as ~10µm W or Ta [Wong 2004a]. However, very little work has been done to confirm that these materials are actually compatible with FLiBe at these temperatures. It should be noted that both Zr and Ta produce significant decay heat after irradiation, that Zr will transmute to long-lived isotopes that may challenge low-level waste disposal criteria, and the tritium gettering properties of Ta likely make it unsuitable as a coating in contact with breeder materials.

The FLiBe corrosion mechanism has been characterized as a competition between fluoridation and oxidation [Muroga 2008, Terai 1998, 2001, Tanaka 2001]. However, this may be less relevant in highly purified FLiBe [Kelleher 2015] where the O content is low and oxidation should not occur. Unfortunately, halide salt impurity levels are rarely documented in detail [Sulejmanovic 2021] so it is not possible to specify what level of O is low enough to minimize corrosion. As will be discussed later, the focus in much of the molten salt literature is on Cr dissolution. However, both Fe and Cr (as well as Mn) in steels readily dissolve in FLiBe which is different from Ni-based alloys. Based on Figure 3, the Ni matrix is more inert than Fe in FLiBe.

Table 1. Composition of several RAFM steels [Kondo 2019, Pint 2024]

	Fe	Cr	W	C	Mn	V	Ta	Ti	Si	N
F82H	88.9	8.1	1.8	0.10	0.45	0.20	0.09	<0.002	0.08	0.010
JLF-1	Bal.	9.0	1.9	0.09	0.49	0.20				
Eurofer97	Bal.	9.0	1.1	0.11	0.40	0.15-0.25	0.06-0.09			
CNA	Bal.	8.7	1.3	0.12	0.50	0.05	0.06	0.12	0.16	0.002

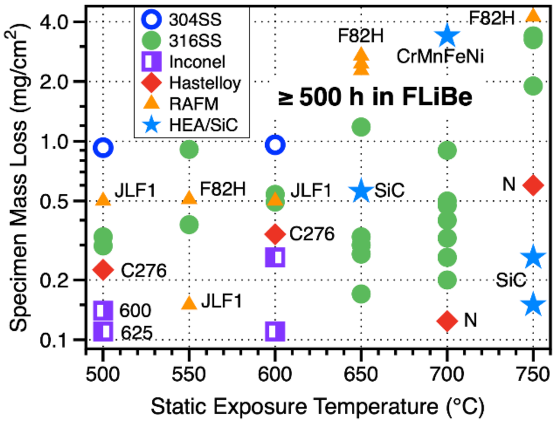

Figure 4. Literature mass loss data for static exposures to FLiBe for 500-3000 h [Tanaka 1998, 2001, Zheng 2015, 2016, 2018, Yang 2022, Pint 2024].

Micro-alloyed variants of RAFMs, termed "castable nanostructured alloys" (CNA) by ORNL, also are being developed for superior irradiation resistance and mechanical properties [Tan 2018, 2020] due to their higher density of ultrafine carbide or carbonitride precipitates. Their compatibility with purified eutectic FLiBe remains unknown.

4.2 AUSTENITIC STAINLESS STEELS

Although perhaps less relevant for fusion blanket applications because of the elevated Ni content, most of the recent literature data on FLiBe compatibility has focused on austenitic stainless steels for fission applications (i.e. molten salt reactor [Le Brun 2007, Serp 2014]), Figure 4. Type 316H has been a particular focus and may be relevant for fusion balance of plant applications. Similar to ferritic steels, both Fe and Cr (and Mn) dissolve in the salt, so mass losses for steels tend to be higher than for Ni-based alloys as Ni is less likely to form a fluoride compared to Fe and Cr fluorides, Figure 3. As noted above, testing in FLiBe is sometimes performed using different methods and salt purity so the results (including those in Figure 4) are quite variable [Raiman 2018]. Figure 5 shows an example of the metallic impurities dissolved in commercial purity FLiBe salt before and after 1,000 h exposures of 316H specimens in 316H capsules at 650°C. The as-received FLiBe salt had relatively low metallic impurities. As noted above, both Fe and Cr dissolved in the static capsule experiment. However, when the same experiment was performed with a Be addition to the salt, no Fe dissolved and the Cr dissolution was reduced [Pint 2021]. This illustrates the effectiveness of a redox additive in lowering the salt potential and reducing dissolution. Finally, using a thermal convection loop (TCL) made from 316H tubing, [e.g. Raiman 2022] the Cr and Mn contents in the FLiBe salt after 1000 h flowing in the TCL were higher (Figure 5) but the Fe content was actually lower after the exposure [Pint 2022]. This kind of information can be used to develop predictive models but needs data generated for fusion-relevant materials.

4.3 NI-BASED ALLOYS

Figure 3 suggests that Ni-based alloys may be more compatible with FLiBe because of the low stability of NiF_2. Efforts at ORNL to use molten salts like FLiBe for fission reactors resulted in the development of a new alloy, Alloy N, later known commercially as Hastelloy™ N (Ni-7Cr-16Mo) [McCoy 1970]. This alloy was successfully used for the Molten Salt Reactor Experiment [Haubenreich 1970, Rosenthal 1970] that

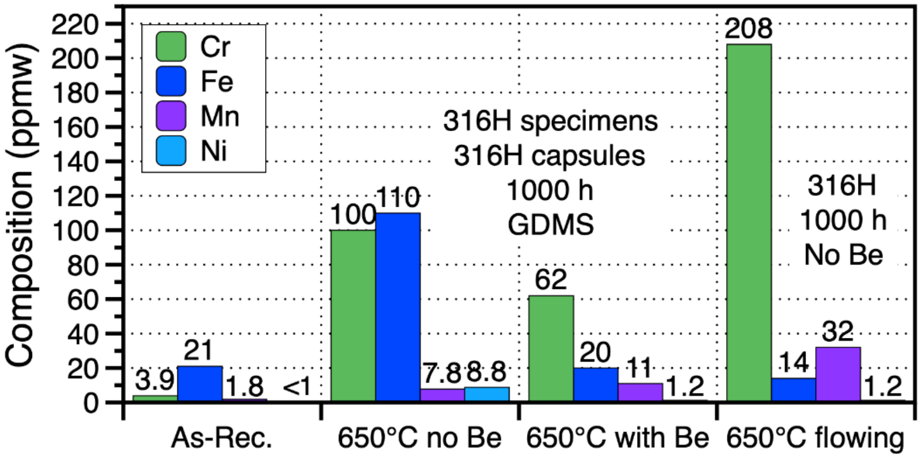

Figure 5. Impurities in FLiBe before and after static and flowing exposures in 316H tubing.

operated at ORNL in the late 1960's for >13,000 h at ~700°C. The relative performance of alloy N and other Ni-based alloys such as C276 (Ni-6.3Fe-15.7Cr-0.4Mn-15.8Mo-3.3W), 600 (Ni-7.0Fe-15.7Cr) and 625 (Ni-4.1Fe-21.9Cr-9.1Mo) also are shown in Figure 4, typically with the lowest mass losses at each temperature shown. Alloy N is a solid solution-strengthened alloys limited to ~700°C operation and current efforts are in progress to develop similar 7-8%Cr alloys with higher strength for MSR applications [Muralidharan 2017]. However, Ni alloys are generally ruled out for fusion applications especially because of long-term waste issues because Ni (and Mo in alloy N) are not "reduced activation" elements [Piet 1990, Zinkle 2000], also because of He generation and embrittlement [Rowcliffe 2009, Zinkle 2013], and furthermore will produce a very high amount of decay heat [Humrickhouse 2022].

4.4 SILICON CARBIDE FIBER-REINFORCED SIC MATRIX COMPOSITES (SIC/SIC)

A SiC matrix with SiC fiber ceramic matrix composite (CMC) is considered an attractive option as a blanket structural material. Among the good characteristics of SiC CMCs are the low induced radioactivity, low decay heat and swelling, high irradiation creep resistance, and high temperature operation [Sawan 2003, Sawan 2013, Koyanagi 2018]. Sawan [2003] compared the service life of a SiC/SiC structure in a Be/FLiBe/SiC first wall blanket concept to a PbLi/SiC concept and considered factors including displacement damage, He gas generation and burnup rate that affect lifetime.

Figure 4 shows several results for high purity chemical vapor deposited (CVD) SiC exposed to FLiBe at 650°C and 750°C in static Mo capsules. More extensive results were reported by Koyanagi [2023], Figure 6. All of the specimens showed a mass loss. Figure 6a shows various monolithic SiC specimens including the CVD SiC result in Figure 4, high resistivity (Hi-R) and low resistivity (Lo-R) grades and a-SiC. These specimens are compared to graphite coated with pyrolytic C. The mass losses were much higher for CVI SiC/SiC specimens shown in Figure 6b, one with Hi-Nicalon Type S fibers and the other with Tyranno SA3 fibers [Koyanagi 2023]. Surprisingly, temperature had little effect on the mass loss of the CMCs. Particularly at 750°C, the results for CVD SiC show much lower mass loss than Fe- and Ni-based alloys. This makes SiC/SiC composites promising for FLiBe blanket structures, and worthy of further evaluation.

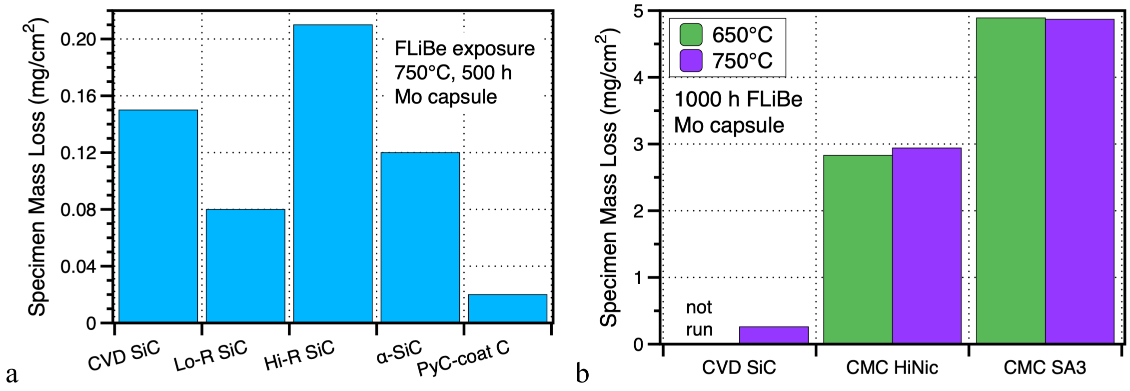

Figure 6. Specimen mass loss after exposure of ceramic specimens for (a) monolithic specimens exposed for 500h at 750°C and (b) CMC specimens exposed for 1000h at 650° and 750°C.

4.5 VANADIUM-BASED ALLOYS

Vanadium alloys with Cr, Ti and Si additions are attractive structural material candidates because of their low activation, radiation tolerance, high thermal conductivity and good compatibility with Li [Smith 1995]. Both the US and Japan produced 100-1000 kg heats of V-4Cr-4Ti that were evaluated in both countries, usually associated with a V/Li blanket concept.

A concern about using V alloys is the high O solubility which results in alloy embrittlement [DiStefano 2000, Pint 2005] and V_2O_5 melts at 670°C resulting in catastrophic oxidation at higher temperatures [Keller 1991]. For FLiBe compatibility, the presence of O_2 impurity in the salt or from the environment is a concern [Terai 1998, Nishimura 2001, Nagasaka 2009], and oxygen also will be produced continuously in the salt via fluorine transmutation. The reported formation of oxides on the surface of V-4Cr-4Ti after FLiBe exposure suggests that the salt was not sufficiently purified. A very recent exposure of V-4Cr-4Ti in static commercially purified FLiBe for 500 h at 650°C showed a mass gain of 0.03 mg/cm^2 [Pint 2023]. Post-exposure characterization of this specimen and the salt is still in progress, but, nominally, the small mass change suggests good compatibility, similar to what would be expected for other refractory metals.

A relevant issue is that, in general, FLiBe may not be a good match with vanadium alloys because of the effect on the tritium inventory. Since the solubility of tritium in V is high but is low in FLiBe, the pairing of these materials may not be tenable due to a high tritium inventory expected in the V alloy walls [Muroga 2014]. A robust tritium permeation barrier compatible with FLiBe would need to be developed.

4.6 OTHER MATERIALS

4.6.1 Refractory metals (excluding V)

In general, refractory metals have good compatibility with FLiBe. Many of the experiments shown in Figure 4 used a Mo capsule to contain the salt. However, Nb and Mo are ruled out for fusion use because of neutron activation/waste disposal concerns (low activation limits.) Also, Ta has short-term activation issues that makes it an unlikely candidate [Piet 1990, Zhang 2023]. Furthermore, Nb and Ta are prone to absorbing O from the atmosphere leading to embrittlement, similar to V alloys. Devan [1979] speculated that the required redox potentials needed to use Nb and V alloys in FLiBe were not attainable under fusion reactor conditions, but this has not been confirmed. Tungsten would appear to be the most likely refractory metal with applicability to fusion conditions and good FLiBe compatibility. It has been suggested as a potential coating material [Wong 2004a, Forsberg 2020]. However, it is unlikely that tungsten could ever be used as a structural material in a FPP.

4.6.2 Copper alloys

Copper alloys such as CuCrZr, CuNiBe and dispersion-strengthened copper are of interest for fusion applications, but not as structural materials. They are used primarily at low temperatures <300°C [Zinkle 2000], perhaps in plasma control systems and would not be in contract with FLiBe, which melts at 459°C.

4.6.3 High entropy or compositionally complex alloys

There has been considerable recent research on high entropy alloys (HEAs) and related materials. However, based on Figure 3, the salt will selectively attack the least noble element in the HEA. For example, for $Cr_{18}Mn_{27}Fe_{27.5}Ni_{27.5}$, a very high mass loss was observed in Figure 4 as Mn was selectively attacked at 700°C during 1000 h in static salt [Elbakshwan 2019]. Until a HEA with attractive creep, compatibility and activation properties is identified, they are unlikely candidates for near-term fusion systems.

5. ASSESSING MOLTEN SALT COMPATIBILITY

As indicated in Figure 4, the available data for materials exposed to FLiBe is not very extensive and most of the data are for stainless steels and Ni-based alloys that are not candidate fusion blanket materials. Interpreting the results is further complicated because there is no accepted standard for assessing molten salt compatibility or salt purity. As noted above, Figure 4 shows mass change data as a function of temperature, but other parameters including exposure time, capsule material, salt volume and purity will affect the mass change. Thus, the results reported in the literature are difficult to compare.

In general, molten salts can cause a range of corrosion-related problems including mass transfer and metal dissolution, which can degrade material performance and contaminate the salt. Additional corrosion concerns which may be significant in the high-magnetic field environment of a fusion reactor will include acceleration of corrosion due to the presence of a magnetic field [Cantor 1973]. Historically, compatibility testing of materials in molten salts can be classified into two general categories: static and dynamic or flowing experiments [Vreeland 1953]. In static tests, the molten salt is in contact with the test material and the exposure is conducted at a constant temperature for a specified time. These tests are frequently performed because they are relatively easy to conduct. However, while they can quantify dissolution and reaction product formation, they cannot be used to study mass transfer, which is a major concern with working fluids. In a temperature gradient, dissolved material from the hot side can precipitate out of the liquid as it cools and the solubility decreases. Thus, in order to study mass transfer, flowing tests are needed which allow the salt to flow in a temperature gradient, usually with a constant flow rate for a fixed time period. Aside from one recent Type 316H SS TCL experiment with FLiBe [Pint 2022], most of the flowing FLiBe data are >45 years old and most focused on Ni-alloys or austenitic stainless steels that are less relevant to fusion reactors. Additional relevant insights may also be obtained by studying corrosion effects in flowing experiments in the presence of fusion-relevant magnetic fields. A brief overview of the various experimental methods is provided below:

5.1 STATIC MOLTEN SALT TESTS

After the thermodynamics have been assessed, as in Figure 3, static compatibility testing is used to provide baseline compatibility results and exclude materials that perform poorly. Typically, static corrosion tests are performed in an inert environment such as gloveboxes or in welded capsules or sealed containers. Each method has its advantages and disadvantages. The glovebox test is usually the quickest and simplest test as it only requires a crucible, test specimens, salt and a furnace inside a glovebox. This type of experiment also enables *in situ* electrochemical salt monitoring. However, impurities in the cover gas (e.g. argon) may be gettered by the salt and increase impurities during the duration of the exposure.

Welded or sealed capsule tests are somewhat more complicated than the glovebox tests because of the need to seal the capsules by either welding or other gas-tight sealing methods. The welded capsule experiments used at ORNL are shown in Figure 7. The advantage of welded capsules, which include inner and outer capsules, is that there is a very low chance of impurity ingress during the test.

Figure 7. (a) schematic of ORNL welded capsule experiment using parts shown in (b) including graphite spacer to prevent interaction between the inner Mo capsule and outer SS capsule; (c) capsules in a box furnace for exposure.

Crucible tests without welding (e.g. conducted in a bolted shut vessel placed into a furnace) are sometimes done outside the glovebox but with an argon cover gas which has a similar contamination risk as a glovebox. If the seal fails on a crucible test, the salt might become contaminated.

Pre- and post-exposure characterization after static exposures includes (1) mass change, (2) metallographic sectioning of the specimens to determine the depth of attack, (3) salt chemistry changes and (4) electrochemical assessments of the salt. Mass change alone can be misleading. Microstructure characterization provides a better assessment of any attack observed. Salt chemistry measurements determine which elements are dissolving and may identify reactions due to the choice of container. Electrochemistry is useful in understanding the reactions observed. All of these strategies carry over to flowing experiments.

An important parameter that is introduced in capsule experiments is the ratio of the volume of the salt in the capsule to the surface area of the sample. Pint et al. [2021] have suggested that this ratio should ideally be larger than 10 (cm^3/cm^2) to avoid rapidly increasing the concentration of any dissolving element in the salt. The ratio is greatly affected if the crucible/capsule is the same material as the specimen, which significantly increases the surface area for the same volume of salt [Doniger 2020, Pint 2023]. When the container is the same as the specimen, both surfaces are dissolving into the salt.

Finally, a key piece of information from static testing is post-test characterization of the salt using inductively coupled plasma optical emission spectroscopy (ICP-OES). Figure 8a shows measured levels of Cr and Fe in the salt for F82H and 316H specimens from some of the recent experiments [Pint 2024] shown in Figure 4. A methodology to predict compatibility of steels is being developed based on the hypothesis that dissolution of a given element in the salt will be proportional to its activity in the structural alloys [Pillai 2021, 2023]. Figure 8b shows some of the baseline dissolution data being collected using the same batch of FLiBe used in Figure 8a. Instead of exposing alloys, unalloyed Cr specimens were exposed in Mo capsules and unalloyed Fe specimens were exposed in steel capsules to avoid a Mo-Fe interaction [Pint 2022]. The values measured in the dissolution tests were similar to those measured when FLiBe salt was exposed in a 316H capsule, Figure 8b.

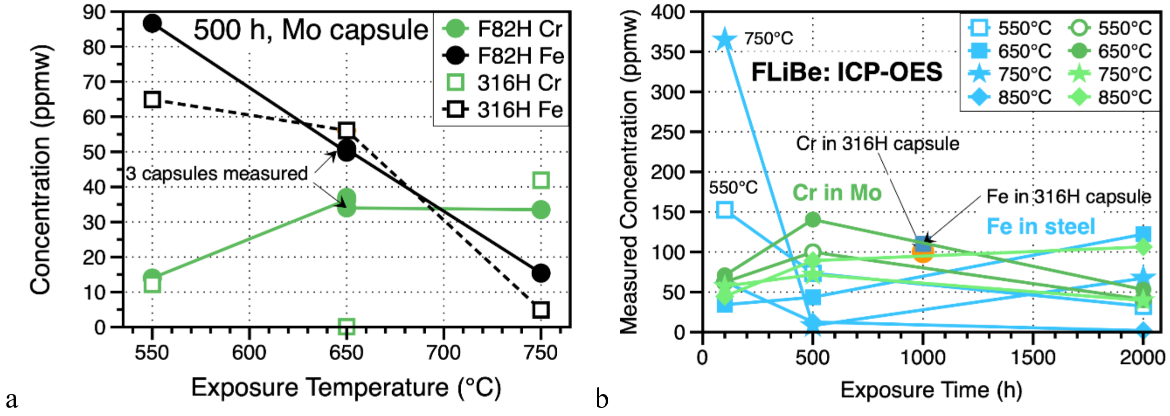

Figure 8. Salt Cr and Fe contents measured in commercial FLiBe salt (a) as a function of temperature after 500 h exposures of F82H and 316H and (b) as a function of time for unalloyed Cr and Fe specimens. The repeat F82H measurements in (a) showed excellent reproducibility.

5.2 FLOWING MOLTEN SALT TESTS

To better represent the flowing salt conditions in a blanket, dynamic tests in flowing salts are typically conducted in systems that include a temperature gradient. These tests have included simple rocking (‘seesaw’) or spinning tests [Vreeland 1953]. To avoid the use of pumps and valves but to achieve more uniform flow and produce more quantifiable results, thermal convection loops (TCLs) [Koger 1973, 1974, Keiser 1979, Raiman 2022, Pint 2022, Kelleher 2022] have been used since the 1950’s at ORNL [Vreeland 1953]. To achieve more prototypic conditions, a pumped or forced convection loop (FCL) is the natural progression in testing after TCL experiments. Many different methodologies were explored at ORNL during the 1950’s Aircraft Reactor Experiment (ARE) program and the 1960’s Molten Salt Reactor Experiment (MSRE). However, TCLs became the predominant test methodology by the end of the MSRE program. For example, seesaw tests are mentioned by Richardson [1952] but Adamson [1961] only mentions TCL testing. A stirring or spinning test may be the most basic dynamic test that is still occasionally used [Kondo 2010]. Vreeland [1953] mentioned a spinning test for increasing the salt velocity. However, no data were included in that report. Higher velocities were achieved in a ‘whirligig’ test developed at NACA in Cleveland (predecessor of NASA Glenn Research Center) with velocities up to 7.6 m/s [Desmon 1951, Vreeland 1953]. It was concluded that the high velocity resulted in a nearly isothermal test even when a temperature gradient was applied [Jordan 1955]. While a stirring test allows the salt to move, there is no temperature gradient to drive mass transfer, which is the primary objective of flowing experiments.

Rocker tests are a type of dynamic molten salt materials compatibility experiments that utilizes the mechanical rocking of a furnace by about 20 degrees in order to move the liquid salt from one end of a tube or capsule to the other. One of the tube ends can be placed outside of the furnace to provide a temperature gradient between the two ends.

A thermosiphon is a natural convection dynamic test consisting of a crucible with heating on one end and flow channels for the hot salt to move up and then back down for further heating [Tavakoli Mehrabadi 2016, 2017, Ignatiev 2006, 2008, 2013].

A TCL uses a temperature gradient between two parallel metallic sections to provide the driving force for natural salt circulation, Figure 9. The hot side is referred to as the hot leg (HL), and the cold side is called the cold leg (CL), with the temperature gradient typically in the range of 100C between the two legs [Vreeland 1953, Raiman 2022]. TCL setups have varied in size from microloops (less than kg salt quantities) [Kelleher 2022] to larger installations from a few to several hundred kilograms [Raiman 2022, Crowley 1963]. Depending on the size of the loop, the material being examined can either be the tubing itself for a "micro-loop" [Kelleher 2022] or individual samples arranged in various locations along the HL and CL sections for loops on the order of 1 m tall and 2-3cm tube diameter [Keiser 1977b, Pint 2019, 2022a, 2022b, Raiman 2022]. For the latter case, it was recommended that the examined samples be made of the same or similar alloy as the tubing to avoid galvanic corrosion between the two, which has been observed in the past between Alloy 600 tubing and 304 stainless steel (SS) samples [Koger 1970]. Longer duration experiments are typically suggested for a more accurate corrosion performance assessment. During a TCL experiment, the upper limit of the total duration depends on factors such as loss of power or blockage of flow, particularly in the CL section of the loop due to deposit accumulation [Koger 1973, Kelleher 2022].

The general corrosion behavior observed during a TCL experiment is affected by parameters, such as salt purity, time, peak temperature and the volume/surface area ratio [Manly 1957, Raiman 2022, Sridharan 2013] or even the surface condition of the specimens [Susskind 1960]. The temperature gradient between the HL and CL creates conditions similar to a galvanic corrosion mechanism, where the HL exhibits dissolution and the CL exhibits deposition [Wang 2018].

In order to generate more prototypical conditions with controlled velocity and temperature gradient, a pumped or forced convection loop (FCL) is needed [Crowley 1963, Huntley 1973]. An example FCL at ORNL is shown in Figure 10 which uses FLiNaK salt. A second FCL was built to study chloride salts [Robb 2019, 2020, 2022]. Historically, FCL corrosion testing was focused on Ni-based materials such as Inconel™ 600 (Alloy 600) and Hastelloy™ N for the MSRE [Crowley 1963, Huntley 1973]. Flow velocity was shown to have a limited impact on corrosion, so FCL and TCL experiments yield similar results with less infrastructure investment with a TCL experiment [Manly 1957, Britsch 2019].

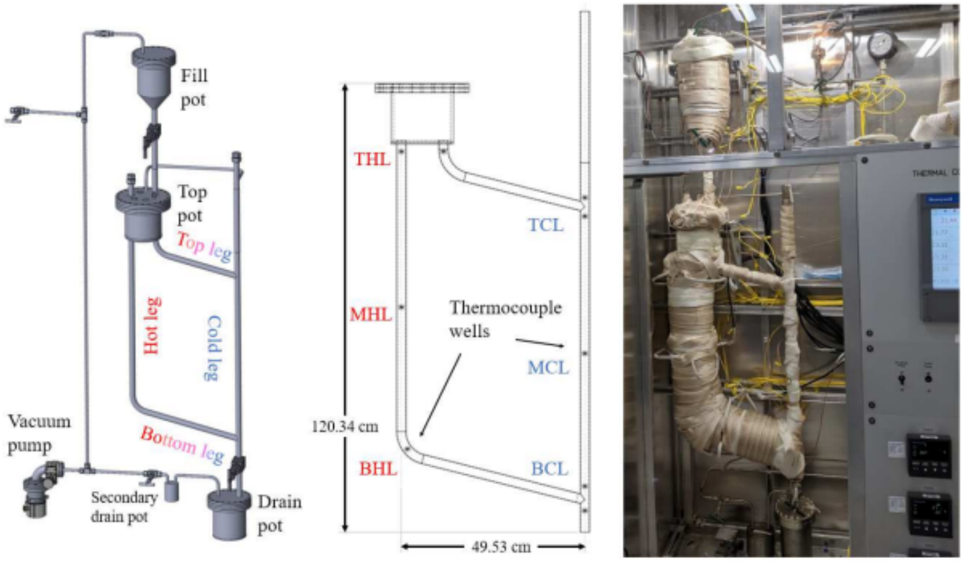

Figure 9. The current ORNL thermal convection loop (TCL) design including a 3D rendering, 2D drawing and image during operation including the heaters and insulation. In the 2D drawing, thermowells are shown at the top (T), middle (M) and bottom (B) of the hot leg (HL) and cold leg (CL).

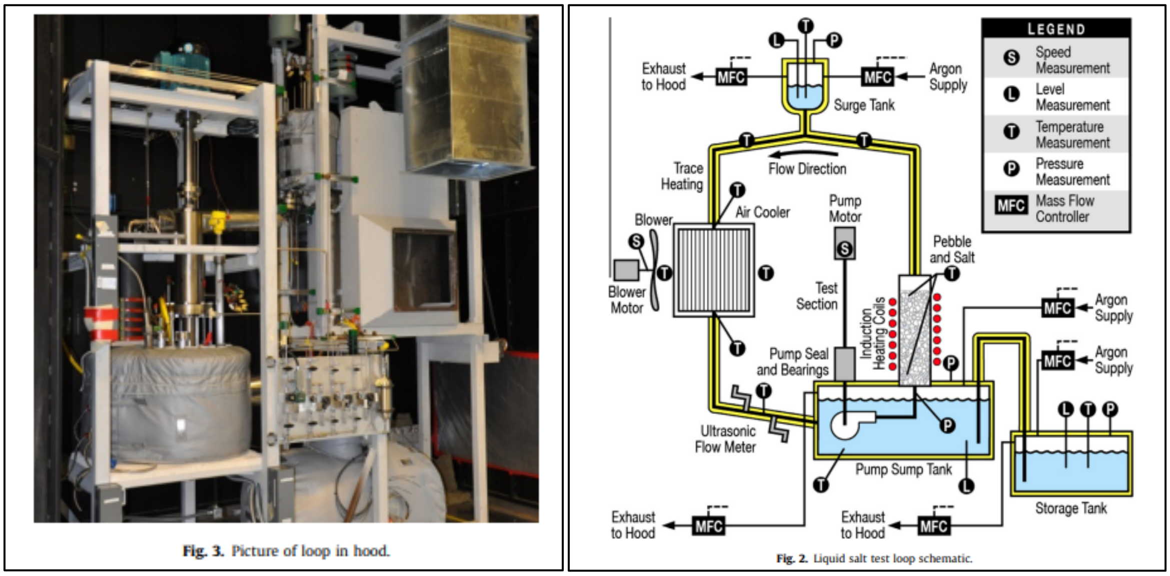

Fig. 3. Picture of loop in hood.

Fig. 2. Liquid salt test loop schematic.

Figure 10. FLiNaK forced convection loop (FCL) at ORNL [Yoder 2010, 2014].

6. CONCLUSIONS

One of the key materials issues for a FLiBe-based fusion blanket concept is the compatibility of the structural and functional materials with FLiBe. However, little compatibility data exists for fusion-relevant materials in FLiBe. The limited data available are mainly static data conducted under a variety of conditions making it difficult to draw conclusions. In general, the evaluation of fusion-relevant data for materials in FLiBe has not progressed to flowing testing or studying the effect of magnetic fields or irradiation on corrosion. Historically, a low-Cr Ni-based alloy (alloy N) was used for the Molten Salt Reactor Experiment (MSRE), which used fuel salts based on FLiBe at ~700°C. Current molten salt fission reactors are focused on austenitic stainless steels as structural materials with a few completed static and flowing experiments that have shown good compatibility of Type 316H stainless steel with purified FLiBe at 550°-650°C and selective dissolution of Cr and Fe. A few static experiments with RAFM steels in FLiBe have shown small mass losses. However, a primary concern is that RAFM steels may be limited to 550°-600°C due to their creep properties. For traditional 2LiF-BeF$_2$ salt, the 459°C melting temperature leaves a very narrow operating window. Thus, the compatibility and physical properties of lower melting point salts (e.g. LiF-BeF$_2$ at ~400°C) need to be explored for use with RAFM steels, and their neutronic and thermal hydraulic performance needs to be more thoroughly assessed. At 750°C, SiC-SiC composites specimens have shown small mass changes in static FLiBe and appear to have good compatibility but flowing testing is needed to confirm this assessment. Vanadium-based alloys may have acceptable compatibility but are not likely a good match for FLiBe because of tritium inventory issues that would require an effective tritium permeation barrier.

7. FUTURE RESEARCH DIRECTIONS AND KNOWLEDGE GAPS

A broad-based screening of fusion relevant structural materials in FLiBe (and perhaps FLiNaBe) with and without redox control (Be) is needed to understand their relative behavior in a purified FLiBe salt at blanket-relevant temperatures. Since the 2LiF-BeF$_2$ salt melts at 459°C, these studies must be conducted at 550°C and higher. For RAFM steels, lower melting point salts need to be evaluated to allow for a wider operating window.

A number of authors have pointed out that tritium generation from lithium, a main function of FLiBe in the blanket, will alter FLiBe compatibility. Continuous oxygen and nitrogen production via fluorine transmutation is also likely to affect compatibility. Thus, an improved understanding about mitigating any effect of tritium using redox control or other means is needed.

Application of coatings as barriers against corrosion in the fusion blanket environment could enhance the compatibility between structural material and coolant [Zinkle 2017]. This is a relatively unexplored solution but difficult to implement in practice based on the historic experience with coating durability for long-term service in power generation applications. For a V/FLiBe concept, a tritium permeation barrier concept also would have to be developed.

Once FLiBe-compatible materials are identified (along with relevant salt compositions), flowing experiments will be needed to better understand compatibility in a temperature gradient where mass transfer can occur. Also, dissimilar material interactions must be assessed similar to the tests of SiC and FeCrAl in flowing Pb-Li, where a strong reaction was observed at a peak temperature of 700°C [Pint 2021, Romedenne 2023].

After the baseline material performance has been established in flowing FLiBe, the effect of magnetic fields on structural material compatibility must be investigated in a forced convection loop.

For the FLiBe blanket concept to advance, compatible materials identified based on FLiBe performance in the absence of neutron irradiation will eventually need to be assessed/demonstrated in a radiation environment. In the MSRE, alloy N was unexpectedly embrittled by the fission product Te, a new concern that was not fully resolved before the end of the program [McCoy 1978].

Finally, the questions that will arise for the multi-material heat transfer circuits likely to be required in a FPP have not been addressed. An engineered power generating system will include pumps, valves, piping transitions, heat exchangers, etc., unlikely to consist of a single material composition. The compatibility issues that arise are beyond the detail provided in current conceptual designs. A multi-material system will introduce new compatibility concerns that will need to be evaluated.

8. RECOMMENDATIONS

This review has revealed that the database of fusion-relevant materials exposed to FLiBe in an FPP blanket is very small (see Figure 4). This lack of relevant data must be addressed first through static tests and then via flowing tests, i.e. thermal convection loops, in order to identify appropriate structural materials and combinations of structural and functional materials for FLiBe-based fusion blankets. Other issues that require attention involve developing a better fundamental understanding of salt purity effects that would support the development of predictive compatibility models. Currently, the lack of data prevents effective modeling of material corrosion compatibility except for thermodynamic calculations (e.g. Figure 3) that provide useful information but do not predict reaction rates.

1. Industry communication: A starting point for this research topic should be industry engagement to gage interest, understand design concepts and unanswered concerns, establish data needs and identify research priorities. A workshop is suggested to discuss the potential experimental

program where key issues are discussed and go/no-go criteria are established for the various concepts.

2. RAFM steel compatibility: Figure 4 shows initial static data for F82H and JLF-1. Aside from repeating some of these experiments for other advanced RAFM steels, including CNA and ODS steels, the suggested next step is to design, build and operate a flowing TCL experiment to better understand RAFM steel compatibility in FLiBe. A primary concern is identifying the tubing material. Initial discussions with Dr. Nozawa at QST in Japan identified that F82H tubing may be available for TCL construction. If this is not the case (or the size is not appropriate, a non-RAFM 9%Cr steel could be substituted (e.g. Grade 92) for the tubing material and RAFM specimens exposed in the hot and cold legs of a Gr92 loop. Initial results could be compared to results for austenitic stainless steels (e.g. type 316H) exposed in a similar manner to determine the degree of dissolution and mass transfer at 650°C for 1000 h. To address safety concerns and provide a baseline, the tubing material will need to be tested in static salt for 1000 h at 650°C prior to TCL operation. Assuming tubing and purified salt are available, preliminary experiments and the RAFM steel TCL could be conducted for approximately $500,000.
3. SiC: Figures 4 and 6 show initial promising static exposure data for high purity monolithic SiC and SiC/SiC composites. Similar to the point above, a flowing test involving SiC would require a TCL made from SiC or a material that is relatively inert to FLiBe, which has been difficult to identify [Pint 2023]. If SiC is exposed to FLiBe in a steel TCL, a dissimilar material reaction between SiC and Fe and Cr dissolved in the FLiBe may occur, similar to what was observed for PbLi [Pint 2021]. Recommended action is a scoping study or additional analysis to develop a path forward for a tubing material for a SiC flowing TCL test and to identify industry interest in SiC for a FLiBe blanket.
4. Vanadium alloys: The recent 650°C result was conducted [Pint 2024] in order to address earlier results that suggested poor FLiBe compatibility. Those results could be related to the O level in the FLiBe since V alloys have a high O solubility [Pint 2005] and may readily react with O in the FLiBe. Similar to SiC, this is a promising static FLiBe result but the pathway to a flowing FLiBe test is uncertain regarding the TCL tubing material that would be appropriate to use with V alloy specimens. Vanadium alloy tubing is not readily available. The V-4Cr-4Ti/Li TCL experiment [Pint 2009] used specially ordered V-4Cr-4Ti tubing and the TCL experiment was conducted in a vacuum chamber (to protect the V-4Cr-4Ti from oxidation). Unfortunately, that chamber is no longer available. The recommendation is to first conduct a screening test to evaluate the interaction between V-4Cr-4Ti and steel (RAFM and SS) capsules to determine if that is a possibility. However, Fe and Mn dissolution from the steel may diffuse into V alloy specimens, which would make this a poor option. The second recommendation, similar to the SiC recommendation, is an additional study to develop a path forward for tubing materials for a V alloy flowing FLiBe TCL test and determine details of industry interest in V alloys for FLiBe blankets. A third issue that needs further analysis is quantifying the need for a tritium permeation barrier that is compatible with both V alloys and FLiBe.
5. Alternative salt compositions: Salts with a lower melting point (eutectic at 378°C vs. 459°C for $2LiF\text{-}BeF_2$) are likely required to match the operating window for conventional RAFM steels. However, an initial static compatibility assessment is needed with all of the candidate fusion-relevant materials and a comparison to similar results in the standard FLiBe salt. Depending on the outcome, this assessment could proceed to TCL testing, particularly for RAFM steel, as noted above. The implications of the significant viscosity increase that results from the increased BeF_2 content in such mixtures need to be comprehensively assessed to ensure feasibility, including impacts on flows through the FW, blanket, and balance of plant, power cycle design, and pumping power assessments.
6. Multipliers: Adding neutron multipliers improves the marginal TBR of FLiBe and is likely important to providing adequate design margin for fuel cycle closure. The most attractive configurations from a neutronics standpoint are immersed Be or beryllide multipliers, which may

also provide necessary chemistry control mechanism, but the compatibility of these materials, including any potential multi-material interactions in the presence of both salt and steel (or other structural materials), needs to be assessed.

7. Salt purity: Defining the needed FLiBe composition to achieve good compatibility is fundamental for all materials. Recent work [Pillai 2021, 2022] has identified a methodology for predicting salt compatibility using Fe and Cr dissolution rates using unalloyed Cr and Fe specimens in static salt, Figure 8b. The baseline data in Figure 8b requires verification. Examination of Figures 8a and 8b indicates a strong temperature effect for Fe dissolution from the static steel specimen test that was not observed for Fe-based alloy specimens exposed to the same batch of FLiBe. Additional similar experiments are needed with Be additions and intentional impurity additions: e.g., Li_2O, Li_3N or NiF_2, to understand how redox and impurity additions affect the dissolution of Cr and Fe. These experiments are relatively inexpensive and important understanding could be achieved for developing salt purity standards and predictive models for an initial investment of ~$100,000.
8. Salt-hydrogen interactions: A final fundamental experiment will address a concern in the literature about H/T generation affecting FLiBe compatibility. A proposed initial experiment is to load H into, for example, a RAFM steel specimen and then expose the H-containing specimen to static FLiBe to see if H would diffuse from the alloy into the salt and affect the reaction rate with FLiBe. An initial set of experiments could be conducted for approximately $50,000.

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APPENDIX A. FLIBE FOR FUSION REACTORS – CONCEPTUAL DESIGN CONSIDERATIONS BASED LARGELY ON ORNL EXPERIENCE

APPENDIX A. FLiBe FOR FUSION REACTORS – CONCEPTUAL DESIGN CONSIDERATIONS BASED LARGELY ON ORNL EXPERIENCE

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Background and Scope

Molten fluoride salts are excellent coolant and heat transfer media. The technology for their use with salt-cooled fission reactors, mainly as FLiBe, was developed at ORNL in the Molten Salt Reactor (MSR) program of the 1950s and 1960s. This work, continuing at a lower level until the present, has produced a large body of data and experience on the use of these salts. This includes properties of the salts, techniques for purification and handling, chemical processing technology, understanding of the corrosion and compatibility with solid structural materials, and the behavior in irradiation environments. Much of this data is of potential importance in designing and evaluating fusion reactor concepts that use FLiBe as the tritium breeding and/or heat transfer fluids.

This paper provides a brief look at consideration of using FLiBe in several conceptual fusion reactor designs that drew on ORNL experience. Following the main report is an appendix (labeled Appendix B) outlining the ORNL experience with FLiBe.

Why FLiBe?

Molten fluoride salts, especially the $2LiF–BeF_2$ salt called FLiBe, has been suggested as the primary tritium breeding and blanket loop coolant for fusion systems because of inherent advantages that include high temperature stability and low electrical conductivity. A US-Japan collaborative study has enumerated the key feasibility issues associated with the use of FLiBe as (1) corrosion of structural material by the molten salt, (2) tritium behavior and control in the molten salt blanket system, and (3) safe handling practices and releases from FLiBe during an accidental spill [1]. These issues have been treated at least at a preliminary level in a few fusion reactor design studies.

Fusion Reactor Conceptual Designs Using Molten Salts

At least two groups have developed limited conceptual designs that use the FLiBe molten salt for tritium breeding in the reactor blanket. The HYLIFE-II [2] design team, led by Ralph Moir at LLNL, has developed a concept that uses a molten salt blanket on an inertially confined fusion power plant. This design uses an array of FLiBe jets to protect the reaction chamber wall, with tritium bred in this thick liquid wall. An expected advantage of this system is the ability to use conventional power plant structural and piping materials due to the chamber protection of the wall by the flowing molten salt. Versions of this design have also been discussed as hybrid reactors, using added fissile material in the blanket to enhance energy production. The second main design approach using FLiBe is the Force Free Helical Reactor, FFHR (Ref -3), led by the NIFS lab in Japan. This design uses a heliotron-type magnetically confined plasma surrounded by a self-cooled FLiBe tritium breeding blanket. Versions are considered using ferritic steel structures, limited in temperature by the creep properties of the alloy, or the vanadium alloy V-4Cr-4Ti, allowing higher temperature operation. Challenges identified with the FFHR concept include low tritium breeding ratio (requiring lithium enriched in ^6Li and extra beryllium in the blanket), careful chemical control of the system (to manage F and HF concentrations and corrosion), and tritium recovery from the blanket.

The APEX/ARIES study teams in the US have considered FLiBe in a comparison of breeding/cooling fluids, but found problems due to required high temperatures, tritium breeding ratios, and a suitable structural material for the temperatures needed. The AFS/FLiBe FW/blanket concept (Ref -4) uses an advanced nano-composite ferritic steel (ODS type) structure to contain the FLiBe breeder and coolant. There have also been some neutronics calculations of ARIES reactor concepts modified by the use of FLiBe coolant to replace Li or PbLi. The goal was to evaluate the tritium breeding ratio (TBR) and to otherwise improve on the concepts; some non-US concepts even added weapons grade plutonium to the molten salt to increase power density, a concept quite unlikely to find international acceptance!

Structural and Piping Materials

Selection of the structural material for molten salt containment will be limited by strength, corrosion resistance and response to the high flux neutron irradiation environment. The MSRE fission reactor experiment successfully used the Ni-based Alloy N (Hastelloy™ N) to contain the molten FLiBe at desired high operating temperatures. However, this alloy is not attractive for use in a fusion power system due to both the rapid loss of structural properties in the high neutron flux of a fusion system, and because of the production of long-lived radioactive products in the alloy. This has led to the consideration of using various steels, V, or other alloys. Ferritic steels will be limited by creep strength to about 550ºC, which is too close to the FLiBe melting temperature for an acceptable heat transfer circuit. ODS steels may allow higher temperatures, but remain in development. A V alloy with added Cr and Ti has been suggested but is not supported by an industrial production or experience base nor is the needed design data available. Corrosion considerations are discussed in Appendix B. None of the candidate alloys have been pursued to the point of showing a clearly acceptable or superior choice.

Tritium Behavior and Control

The molten salt that will be used as the breeder/coolant fluid is unlikely to be the pure $2LiF\text{-}BeF_2$ eutectic composition. Although any concentrations of impurities should be small and controllable, of far greater importance is tritium product of the lithium breeding reactions, any material added to the solution for neutron multiplication (Be or other elements added to raise TBR), and any material required for REDOX control. The REDOX control (REDuction-OXidation reactions controlling T-TF balance) is needed to avoid corrosion of the containment structures by TF and for the tritium inventory and recovery processing. The result will be a complex chemical engineering system as a component of the fusion power plant. See Appendix B for more detail.

Tritium management in a FLiBe fusion blanket is certainly not a trivial exercise. Tritium solubility in the salt is very low, but solubility of TF is much higher. Tritium vapor pressure above the salt must be controlled to assure confinement. Permeation of the gas phase tritium through and inventory held by solubility in structural metals are major concerns. Selection of a V alloy structure could lead to unacceptably large tritium inventory under some operating scenarios (Ref -5). (However, there may be alternative methods of tritium system management.)

ORNL experience dealing with tritium in molten salts in the MSR program is reviewed in Appendix B. Quantities dealt with in that project were orders of magnitude lower than in a D-T fusion system, concern was with capture and sequestration of the tritium, so that experience has little application to the tritium containment and recovery needed in a fusion reactor.

Heat Transfer and Power Cycle

The FLiBe blanket that converts neutron energy to heat will do so either by direct circulation or with an embedded cooling circuit that transports heat energy to a power conversion system. Even if a separate cooling system is used, the FLiBe will have to be circulated for tritium management. Muroga et al (Ref. 5) and Sze and Wang (Ref. 6) have considered issues of the heat transfer and conclude that a system that will work can be designed. The main difficulty is that the salt has high viscosity at temperatures near the melting point, 459ºC, resulting in large pumping power requirements. This would especially be a problem with a ferritic steel structure, limited by creep strength to a maximum temperature of ~550 ºC and thus too narrow an operating temperature window for an effective heat transfer system. A vanadium alloy structure was offered as an alternative, allowing a maximum temperature optimistically estimated to be 700 ºC (Ref. 5).

Safety Concerns

An initial assessment of safety issues associated with use of FLiBe molten salt in fusion reactors was published in 1999 [7]. The conclusion was that "Qualitatively, the molten salt hazards appear to be manageable, since similar hazards have been, or are currently being, managed in other industries." Three areas that could present safety challenges are: (1) the thermal energy in the fluid, at high temperatures but low pressure, (2) radioactivity of the fluid, in particular from any contained impurities, and (3) the chemical toxicity of F and especially Be. All of these are challenges that can be handled by the system design.

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APPENDIX B – ORNL EXPERIENCE WITH FLIBE IN FISSION AND COMMENTS ON USE IN FUSION

APPENDIX B – ORNL EXPERIENCE WITH FLiBe IN FISSION AND COMMENTS ON USE IN FUSION

Introduction

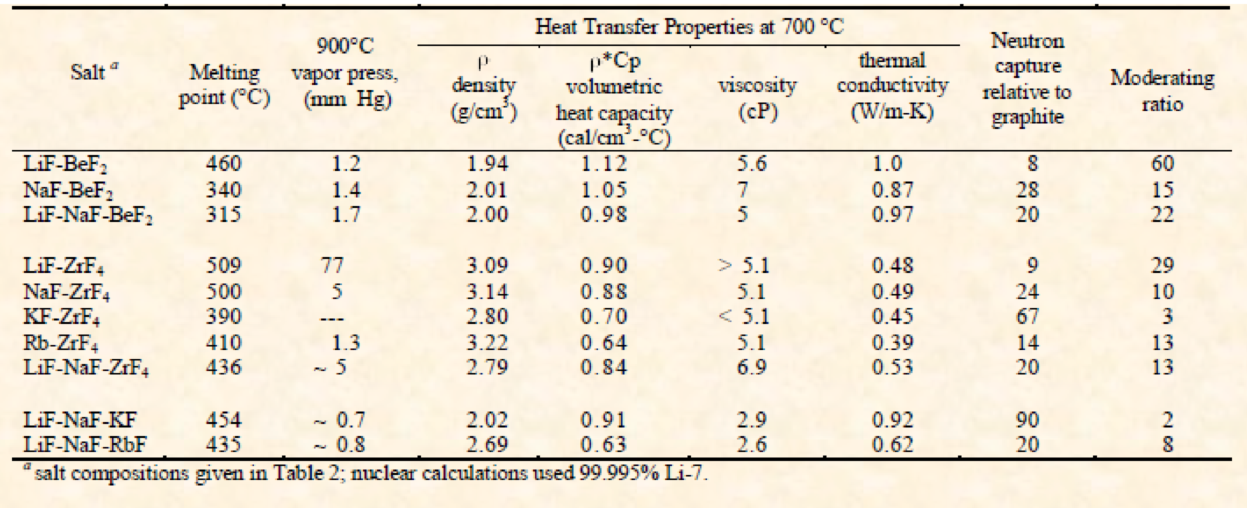
After several years of research and development (R&D) activities on molten salt reactor systems, the Aircraft Reactor Experiment began operation in 1954 at Oak Ridge National Laboratory (ORNL) to demonstrate the feasibility of operating a molten-salt fueled reactor at high temperature; fuel entered the core at 649°C and exited at 816°C when the reactor power level was 2.5 MW. A second demonstration, the Aircraft Reactor Test, was under development for several years before it was discontinued upon termination of the Aircraft Nuclear Propulsion Program in 1957-58. Subsequently, the Molten Salt Reactor Experiment (MSRE) at ORNL demonstrated that the desirable features of the molten salt concept could be incorporated into a safe and reliable civilian power reactor.[i] The 7.4 MW(t) MSRE, which operated from 549 to 649°C went critical in 1965 and was shut down in 1969 after a successful operating history of more than 13,000 full power hours. The success of the MSRE led to additional R&D in support of a molten salt breeder concept. Overall, extensive studies were conducted in salt chemistry, including phase behavior, purity requirements, radiation stability, materials for salt-containing structures (including physical and mechanical properties), corrosion, irradiation effects, etc. The majority of these studies were in support of applications up to 704°C.

Salt Purity and Materials of Containment

Salt composition and purity are intimately related to wetting characteristics and corrosion of materials of containment. The main impurities that must be removed to prevent severe corrosion of the container metal are moisture and oxides, so major efforts were directed at salt purification and analysis. Purification was achieved via a low temperature bake-out for removal of adsorbed water, HF/H_2 sparging for removal of oxides, H_2 sparging for removal of excess HF, and filtering for removal of residual solids.[ii] The fuel salt for the MSRE was LiF-BeF_2-ZrF_4-UF_4 (65-29-5-1 mol %), and the secondary coolant was molten 2LiF-BeF_2 (67-33 mol %; melting point of 460°C) (FLiBe) salt mixture. Various properties of 2LiF-BeF_2 including heat transfer properties at 700°C, vapor pressure at 900°C, and viscosity at 600, 700 and 800°C, have been complied and summarized by Williams (presented in **Error! Reference source not found.**, Figure 11. Viscosity of salts containing BeF2. (Williamsiii, [iv])

and Figure 12. Vapor pressure of salts containing BeF2. (Williamsiii, iv)).[iii, iv] During operation, fluorination (bubbling gaseous fluorine through the salt) was employed to remove uranium from the salt.

Table 2. Some physical properties of fluoride salts (Williams3, 4)



Salt [a]	Melting point (°C)	900°C vapor press, (mm Hg)	Heat Transfer Properties at 700 °C: ρ density (g/cm^3)	ρ*Cp volumetric heat capacity (cal/cm^3-°C)	viscosity (cP)	thermal conductivity (W/m-K)	Neutron capture relative to graphite	Moderating ratio
LiF-BeF$_2$	460	1.2	1.94	1.12	5.6	1.0	8	60
NaF-BeF$_2$	340	1.4	2.01	1.05	7	0.87	28	15
LiF-NaF-BeF$_2$	315	1.7	2.00	0.98	5	0.97	20	22
LiF-ZrF$_4$	509	77	3.09	0.90	> 5.1	0.48	9	29
NaF-ZrF$_4$	500	5	3.14	0.88	5.1	0.49	24	10
KF-ZrF$_4$	390	---	2.80	0.70	< 5.1	0.45	67	3
Rb-ZrF$_4$	410	1.3	3.22	0.64	5.1	0.39	14	13
LiF-NaF-ZrF$_4$	436	~ 5	2.79	0.84	6.9	0.53	20	13
LiF-NaF-KF	454	~ 0.7	2.02	0.91	2.9	0.92	90	2
LiF-NaF-RbF	435	~ 0.8	2.69	0.63	2.6	0.62	20	8

[a] salt compositions given in Table 2; nuclear calculations used 99.995% Li-7.

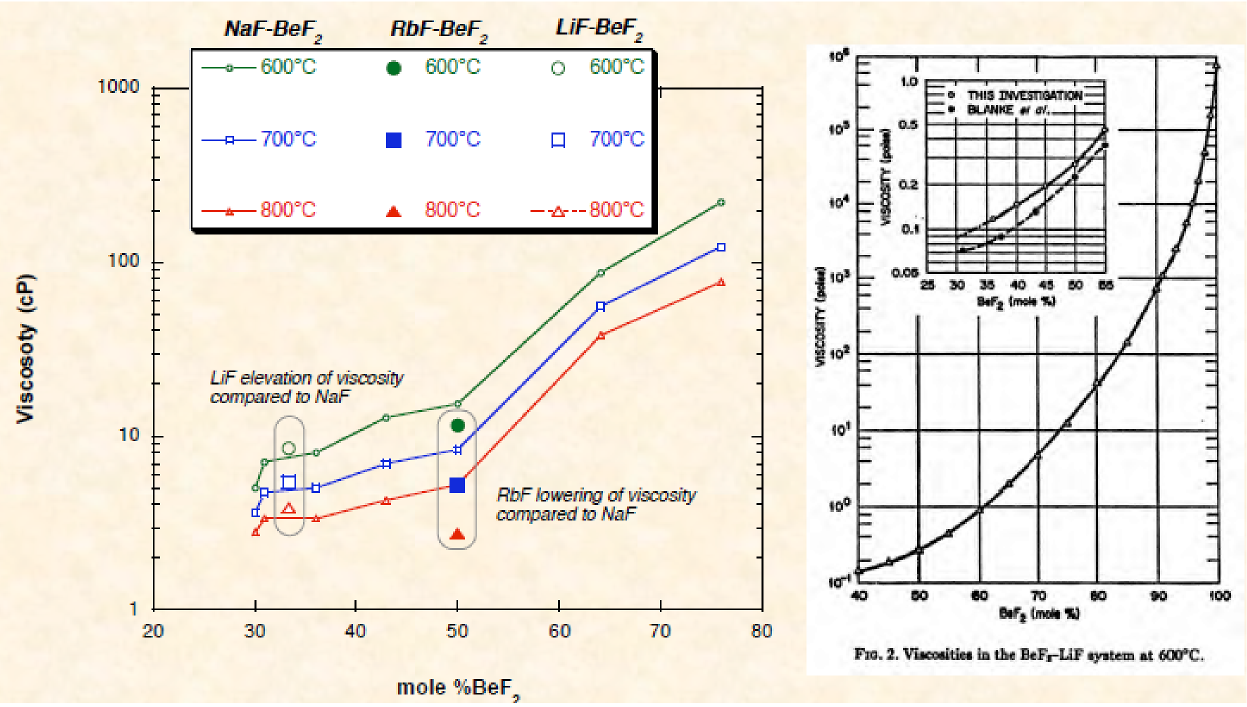


FIG. 2. Viscosities in the BeF$_2$–LiF system at 600°C.

Figure 11. Viscosity of salts containing BeF2. (Williams[iii, iv])

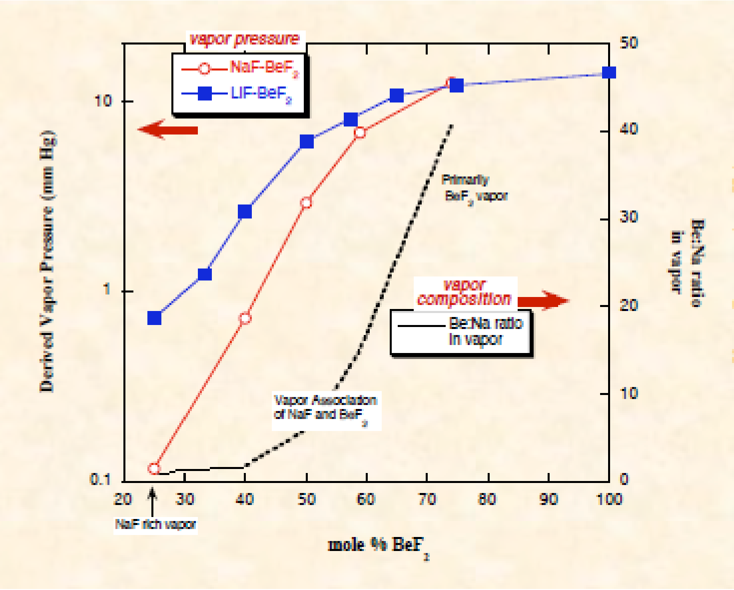


Figure 12. Vapor pressure of salts containing BeF2. (Williams[iii, iv])

In the MSRE, all metallic surfaces wetted by the salt were fabricated of low Cr, solid solution-strengthened Ni-based alloy INOR-8 (developed at ORNL and now commercially available as Hastelloy™-N or Alloy N). Several hundred thousand hours of corrosion experience with Hastelloy™-N and fluoride salts were obtained in thermal convection loop tests,[v] [vi] [vii] and pumped loop tests[viii] in addition to experience in the MSRE. The results of ORNL's work for the MSRE showed that Hastelloy-N corrosion was manifest as void formation in the base metal due to Cr diffusion to the salt metal interface where it was oxidized by impurities in the salt or by UF_4. The latter effect, oxidation by UF_4, was controlled in the MSRE by the use of Be metal. Hastelloy-N exposed to the fuel salt was subject to intergranular cracking and irradiation damage caused due to the presence of the Te fission product generated in the fuel salt. These embrittlement issues were, for the most part, alleviated by modifying the composition of Alloy N with approximately 2% Nb (**Error! Reference source not found.**).[ix] [x] Additional control of cracking was obtained by control of the redox potential of the molten salt (**Error! Reference source not found.**).[xi] Redox control was obtained in the MSRE by controlling the U(IV)/U(III) ratio (redox buffer system). In addition, as elaborated in another section, in a non-isothermal system, corrosion can occur due to thermal gradient mass transfer if the chemical potential of the corrosion product fluoride, at a given concentration, is a strong function of temperature.

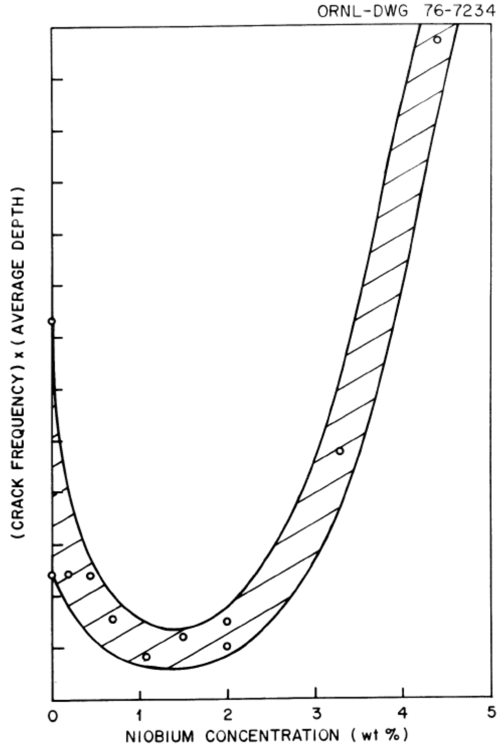


Figure 13. Effect of niobium in modified Hastelloy™-N on grain boundary cracking in salt-Cr3Te4 + Cr5Te6 for 250 h at 700°C. (Keiser11)

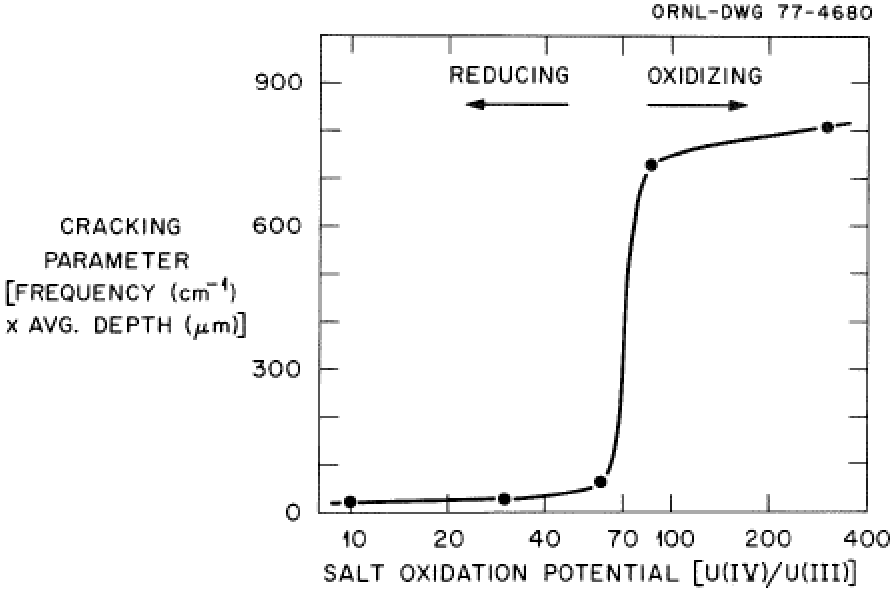


Figure 14. Effect of redox potential on cracking behavior of INOR-8 exposed 260 h at 700°C in salt containing CrTe1.266. (Keiser11)

Tritium

Tritium production was addressed for the various molten salt reactors. The calculated tritium production rate for the MSRE was 54 Ci/day. Approximately, 80% of the production rate could be accounted for: 48% discharged from fuel off-gas system, 2% discharged from coolant off-gas system, 7% discharged in coolant radiator air, 9% appeared in the cell atmosphere, and 14% migrated into the core graphite. It was speculated that the majority of the remaining production was retained in oil residues in the fuel off-gas systems. Unlike the relatively low tritium production rate of the MSRE, the proposed 1000-MW(e) Molten-Salt Breeder Reactor (MSBR) was expected to produce 2420 Ci/full-power day of tritium. At the MSBR operating temperatures of 426 to 704°C, it was estimated that approximately 60% of the tritium produced could have been transported to the reactor steam system (assuming no retention by the secondary coolant salt), where it would be released to the environment.[xii] Various studies were undertaken, both technical and economical on approaches to manage and concentrate the tritium.

The Coolant-Salt Technology Facility (CSTF) was developed at ORNL to examine the potential of sodium fluoroborate, the proposed coolant salt for an MSBR, to sequester tritium. Results of testing in the CSTF indicated that sodium fluoroborate was effective in trapping tritium in that over 90% of tritium added at steady-state conditions was trapped by the sodium fluoroborate and appeared in the off-gas system in a chemically combined (water-soluble) form, and that a total of 98% of the tritium added at steady-state conditions was removed through the off-gas system. Extrapolation of the results to an operating MSBR showed that less than 10 Ci/day of tritium would be transported to the reactor steam system, within the existing guidelines for release of tritium to the environment.[xii] An economic evaluation of tritium removal from the MSBR assumed that the tritium could be removed from the fuel stream by a hydrogen-helium purge and that the helium could be separated from the hydrogen for recycle via a palladium membrane. Various systems were conceptualized, designed, and economically evaluated to concentrate or store the hydrogen and tritium including storage of unconcentrated tritiated water, water distillation, gaseous thermal diffusion and cryogenic distillation of liquid hydrogen. Cryogenic distillation was shown to be the most economical. [xiii]

Implications for Use of FLiBe in Fusion Systems

In molten fluoride salts, containment alloys must be thermodynamically stable, or react very slowly with, the salt. Two general mechanisms of corrosion, metal dissolution and oxidation of metal to ions, can occur in molten salt systems. Because of low solubilities of most structural metals in salt systems, the first mechanism, metal dissolution due to solubility in the melt, is not a common form of attack. The second mechanism, oxidation of metal to ions, is more likely. As molten salts are electronic as well as ionic conductors, reduction reactions can occur in the melt as well as at the metal-melt interface. In many molten salt systems the rate controlling step is ion diffusion into the bulk solution, not the charge transfer that is typical of aqueous systems.

Thermodynamic stability of the fluoride salt components versus alloy constituents is quite important because molten-salt corrosion is usually induced by reduction/oxidation (redox) reactions. In work leading to the MSRE, ORNL demonstrated the excellent compatibility of

Hastelloy-N with fluoride salts containing LiF, BeF_2, ThF_4, and UF_4. If the salt is pure and the metal clean, UF_4 is the strongest oxidant in a fuel-salt system. The reaction,

$$UF_4\ (d) + \tfrac{1}{2}\ Cr\ (s) \leftrightarrows UF_3\ (d) + \tfrac{1}{2}\ CrF_2\ (d),$$

has a favorable free energy of formation at 500 - 800°C. Since CrF_2 is one of the most stable structural metal fluorides, Cr can selectively react with extraneous (impurity) oxidants (fluorides) in the system. Because of the unusually high stability of alkali metal and beryllium fluorides, the corrosion potential of melts without uranium is likely controlled by redox equilibria involving impurities in the melt or gas phase. Gradients in the chemical activities of constituents caused by temperature differences can result in dissolution of metal in one region of the system with subsequent deposition in other portions of the system. The amount of attack will depend on the driving force and dissolution or deposition kinetics for reactions that result in transporting the corroding species to a different part of a circuit where they might deposit. In single material systems (e.g., capsule tests) at constant temperature, there would be no activity gradient and the amount of attack would be a function of the relative solubility of the respective corrosion product in the salt or, if the product is volatile, the partial pressure in the atmosphere immediately above the salt. Thus, equilibrium solubility principles would limit the amount of solute and degree of corrosive attack in this type of system. However, a non-isothermal system could also be subject to corrosion from thermal gradient mass transfer if the chemical potential of the corrosion product fluoride, at a given concentration, is a strong function of temperature, and deposition of the corrosion species occurs in the cooler regions of a loop operating with a relatively high temperature differential. Although equilibrium solubility principles limit the amount of solute in a specific volume of salt in a closed system (capsule test) at constant temperature, continued transport of material can occur to the cold leg of a non-isothermal system.

Mass transfer can also occur when dissimilar structural materials are included in the same system. The dissimilar materials do not have to be electrically coupled. Two things are required for dissimilar material mass transfer to be a factor. First, an element contained in one of the materials has to have a strong tendency to form an alloy or compound with the second material. More importantly, an element in one of the materials must be subject to oxidative attack or suffer dissolution within the salt solution. The oxidative attack can be either by reaction with impurities or, if a reactive element, with the salt constituents. In either event, once the element goes into solution, it can then migrate through the solution and form the required product if the chemical driving force (activity gradient) is sufficient. If the product does form, this will allow the mechanisms of corrosive attack or dissolution to continue (i.e., favorable thermodynamics) although kinetics may be limited by solid state diffusion. If the attack is solely by reaction with impurities, the problem may dramatically slow with time. However, the reaction will not stop if there is solubility in the salt for a specific element.

In the case of previous fluoride corrosion studies at ORNL, the containment system was generally monometallic, and dissimilar metal effects were not encountered. However, graphite was a major nonstructural component in the reactor system and there was no evidence of graphite interaction with the structural materials at Molten Salt Reactor (MSR) temperatures.

Even if redox reactions with major salt constituents are limited, materials can interact with oxidizing impurities present in the salt or in the system (capsule or loop). The presence of HF within the salt, which is used for impurity removal in the purification process, as well as moisture or oxides residing on the container or loop walls, can all lead to adverse corrosive reactions. HF can react either directly with the material forming a fluoride as noted in Equation (1) or indirectly with oxides present on the wall of the container as noted in Equations (2-4). All of these reactions should cease when the impurities are consumed.

$$HF + metal \rightarrow metal\ fluoride\ (dissolve\ in\ melt) + H_2\ , \qquad (1)$$

$$HF\ (gas) + oxide\ (wall) \rightarrow H_2\ (gas) + F\ (wall)\ , \qquad (2)$$

$$H_2O\ (gas) + alkali\ F\ (melt) \rightarrow HF\ (gas) + alkali\ OH\ (melt),\ and \qquad (3)$$

$$Alkali\ OH + metal \rightarrow alkali\ oxide + metal\ OH\ . \qquad (4)$$

As alluded to earlier, oxidation of one of the constituents of the material by the reduction of a less stable impurity metal fluoride initially in the salt, such as Fe or Ni fluoride, can occur. Examples of this include:

$$Cr + FeF_2 \rightarrow CrF_2 + Fe \text{, and} \quad (5)$$

$$Zr + 2FeF_2 \rightarrow ZrF_4 + 2Fe\ . \quad (6)$$

In order to control the redox potential of the fluoride salt in the MSRE, the melt chemistry was made slightly reducing by the addition of a small amount of Be metal that reduced approximately 1% of the UF_4 solute to UF_3:

$$Be + 2UF_4 \leftrightarrows BeF_2 + 2UF_3. \quad (7)$$

As a result of this addition, the 100/1 ratio of UF_4/UF_3 minimized the corrosion of Hastelloy-N by UF_4 (where Cr is the most active metal present and therefore the first to be oxidized) because of the equilibrium between the Cr and U components:

$$Cr + 2UF_4 \leftrightarrows CrF_2 + 2UF_3. \quad (8)$$

The redox potential of systems that do not contain U may be controlled in another fashion – by addition of a small amount of solute that can exist in two oxidation states, by addition of a sparge gas that is set at the proper redox potential, or by electrochemically setting an applied potential equivalent to the desired redox potential. A redox solute mix of choice would be Ce (IV/III) fluorides which would function very much the same as the uranium redox equilibrium of above, namely

$$Cr + 2CeF_4 \leftrightarrows CrF_2 + 2CeF_3. \quad (9)$$

However, an even simpler means of controlling the redox potential is frequently used in the laboratory to prevent corrosion of metal containers during the hydrofluorination purification process, which is intended to remove oxide and S contaminants:

$$Cr + 2HF \leftrightarrows CrF_2 + H_2. \quad (10)$$

If the ratio of H_2/HF is set at approximately 10/1, the redox potential is suitable for preventing the corrosion of the container, and the reaction,

$$BeO + 2HF \leftrightarrows BeF_2 + H_2O, \quad (11)$$

is used to convert dissolved oxides (and similarly hydroxides) to water vapor which is swept from the system in the flowing sparge gas. (When the laboratory container is made of nickel, this less reactive metal allows a lower H_2/HF ratio to be used and thus hasten the oxide purification process.) Reaction (11) is of particular interest for fusion, where addition of excess Be may in any case be required to improve the tritium breeding ratio of a FLiBe blanket.

In the high neutron flux of the fusion reactor, use of Ni-based alloys is highly problematic due to Ni alloys' susceptibility to radiation damage and their long-lived neutron activation products. Although it is known that Cr and Ti and to much less extent, V and Fe, tend to partition into molten fluoride salts[vii] (**Error! Reference source not found.**), ferritic steels with Cr content (8-9 wt.%) and V alloy V-4Cr-4Ti may offer useful service lives. However, extensive evaluation of the alloy(s) long-term mechanical properties, radiation effects, and compatibility with FLiBe is necessary. It is highly likely that a redox control strategy can be implemented that will ameliorate corrosion effects. Redox buffer systems would need to be developed[xiv] and electrochemical techniques including those that were under consideration for use in the MSRE will be needed. As with all fluoride salt cooled systems, purity of the salt, thermodynamic stability of the salt with respect to the materials of containment, and redox control are the first lines of defense for corrosion prevention. As can be inferred from the above equations, redox control can also be employed to aid in the removal of F and HF resulting from Li burnup probably, as an on-line side-stream clean-up process.

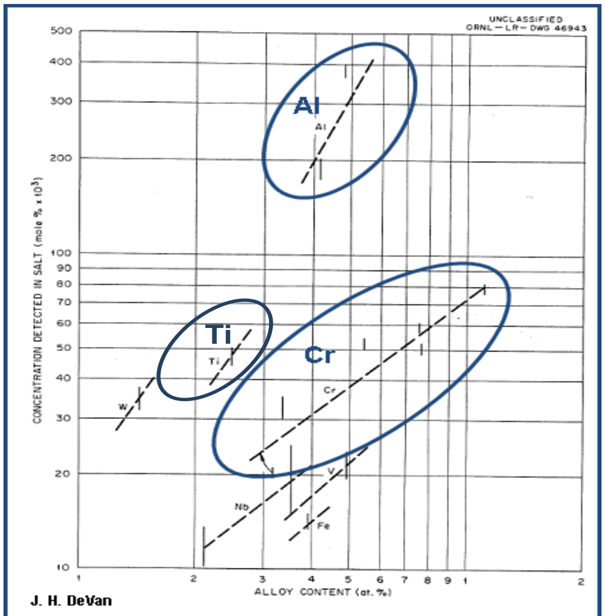


Figure 15. Comparison of corrosion-product concentrations formed in Salt 107 by various alloying additions as a function of alloy content.

Figure 15. Alloying element concentration in the salt as a function of its content in the alloy. Much higher concentrations of Ti and Cr as compared to V and Fe in the salt. (DeVan7)

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