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An Experimental Test Plan for the Characterization of Molten Salt Thermochemical Properties in Heat Transport Systems

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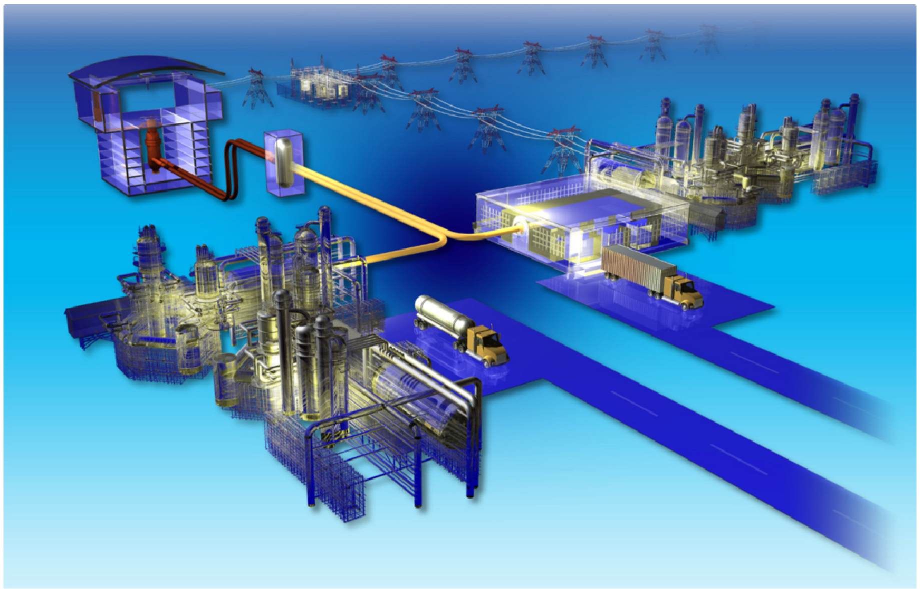

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ABSTRACT

Molten salts are considered within the Very High Temperature Reactor program as heat transfer media because of their intrinsically favorable thermophysical properties at temperatures starting from 300°C and extending up to 1200°C. In this context, two main applications of molten salt are considered, both involving fluoride-based materials: as primary coolants for a heterogeneous fuel reactor core and as secondary heat transport medium to a helium power cycle for electricity generation or other processing plants, such as hydrogen production. The reference design concept here considered is the Advanced High Temperature Reactor (AHTR), which is a large passively safe reactor that uses solid graphite-matrix coated-particle fuel (similar to that used in gas-cooled reactors) and a molten salt primary and secondary coolant with peak temperatures between 700 and 1000°C, depending upon the application. However, the considerations included in this report apply to any high temperature system employing fluoride salts as heat transfer fluid, including intermediate heat exchangers for gas-cooled reactor concepts and homogenous molten salt concepts, and extending also to fast reactors, accelerator-driven systems, and fusion energy systems.

The purpose of this report is to identify the technical issues related to the thermophysical and thermochemical properties of the molten salts that would require experimental characterization in order to proceed with a credible design of heat transfer systems and their subsequent safety evaluation and licensing. In particular, the report outlines an experimental research and development test plan that would have to be incorporated as part of the design and operation of an engineering-scaled facility aimed at validating molten salt heat transfer components, such as intermediate heat exchangers.

This report builds on a previous review of thermophysical properties and thermochemical characteristics of candidate molten salt coolants generated as part of the same project. However, this work focuses on two materials: the LiF-BeF2 eutectic (67 and 33 mol%, respectively, also known as flibe) as primary coolant and the LiF-NaF-KF eutectic (46.5, 11.5, and 52 mol%, respectively, also known as flinak) as secondary heat transport fluid. Common issues are identified involving the preparation and purification of the materials as well as the development of suitable diagnostics. Issues specific to each material and its application are then considered, focusing on the compatibility with structural materials and the extension of the existing properties database.

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FIGURES

TABLES

ACRONYMS

AHTR	Advanced High Temperature Reactor
ARE	Aircraft Reactor Experiment
BeF2	beryllium di-fluoride
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectroscopy
LiF	lithium fluoride
Lif-NaF-KF	lithium, sodium and potassium fluoride
MSRE	Molten Salt Reactor Experiment
ORNL	Oak Ridge National Laboratory
R&D	research and development
VHTR	Very High Temperature Reactor

An Experimental Test Plan for the Characterization of Molten Salt Thermochemical Properties in Heat Transport Systems

1. INTRODUCTION

Molten salt technology has been used for many decades in industrial process heat transfer, thermal storage, and materials processing applications.[1] The potential utility of molten salts as heat transfer agents was also demonstrated for nuclear reactors, as the liquid fuel in the Aircraft Reactor Experiment (ARE) and the Molten Salt Reactor Experiment (MSRE) programs. The behavior and material compatibility of various molten salts was studied extensively by Oak Ridge National Laboratory (ORNL) from the 1950s through the 1970s in support of the MSRE and the Molten Salt Breeder Reactor programs.[,2,3,4,5,6,7,8,9,10,11,12,13]

More recently, molten salts are considered within the Very High Temperature Reactor (VHTR) program as heat transfer media because of their intrinsically favorable thermophysical properties at temperatures starting from 300°C and extending up to 1200°C.[14,15,16,17] Those include:

- Chemical stability at high temperatures
- Radiolytic stability in a high radiation environment
- Relatively low melting point
- Large specific heat and thermal conductivity
- Low vapor pressures
- High compatibility with high-temperature materials, alloys, graphite, and ceramics.

In this context, two main applications of molten salts as heat transfer fluid are considered: as primary coolants for a heterogeneous fuel reactor core (described in detail in Section 0) and as secondary heat transport medium to high efficiency power cycles for electricity generation (helium Brayton or super-critical CO_2) or other processing plants, such as hydrogen production. For the latter, molten-salt-heat transport systems offer several advantages for systems operating at temperature above 600°C, including:

- *Size*: The size of a molten-salt heat-transport loop is only a small fraction of those using helium and is small relative to those for other coolants.[18] The pipe diameter of a molten-salt system will typically be one-fifth of a high-pressure helium system.
- *Design freedom*: While the vapor pressure of proposed molten salts is below 1-atmosphere, a molten-salt heat-transport system can be operated at any pressure by using a pressurizer with a small amount of inert gas. For example, the heat transport loop can be operated at a pressure level between that of the chemical plant and that of the reactor to minimize stresses on heat exchangers and minimize long-term creep.
- *Safety*: Molten salts are effectively incompressible; consequently, a heat exchanger failure in the chemical plant will not pressurize the plant, thus minimizing the risk associated with the release of toxic chemicals that drift off-site to populated areas. In contrast, if helium or other gases are used in the heat transport systems, a heat-exchanger failure can pressurize the chemical plant with the potential for large releases of toxic materials.

- *Performance*: The performance of liquid heat-transport systems is superior to gas heat-transport systems in terms of minimizing temperature drops across heat exchangers and minimizing pumping costs. The power required to overcome heat-exchanger pressure drops in a molten-salt system is typically about one-twentieth that of a helium system.

This work builds on a previous review of thermophysical properties and thermochemical characteristics of candidate molten salt coolants.[19] The review identified the main physical and chemical properties of the materials that impact their heat transfer performance, as well as limitations in the existing properties database. The purpose of this report is to outline an experimental test plan that would allow the characterization and control of those physical and chemical properties as well as the extension of the database to the temperature range relevant to VHTR applications for safety analysis and licensing purposes. Such test plan would have to be incorporated as part of any research and development (R&D) program aimed at the design of molten salt heat transfer components, such as a VHTR intermediate heat exchanger.

1.1 Molten Salt Composition

The most widely considered salt in nuclear applications is the lithium fluoride (LiF) and beryllium di-fluoride (BeF_2) eutectic. The binary mixture phase diagram is shown in Figure 1.[20] A liquid phase eutectic composition exists in equilibrium with the solid with melting point as low as 363.5°C. However, since the eutectic viscosity rapidly increases with the BeF_2 content (and consequently the pumping power for forced convection loops) the reference composition adopted is the 67 mol% LiF and 33 mol% BeF_2, also known as flibe. In the MSRE and related experiments (see Figure 2), flibe was the solvent matrix carrying the homogenously distributed fuel as well as the heat transfer media in the intermediate heat exchanger.

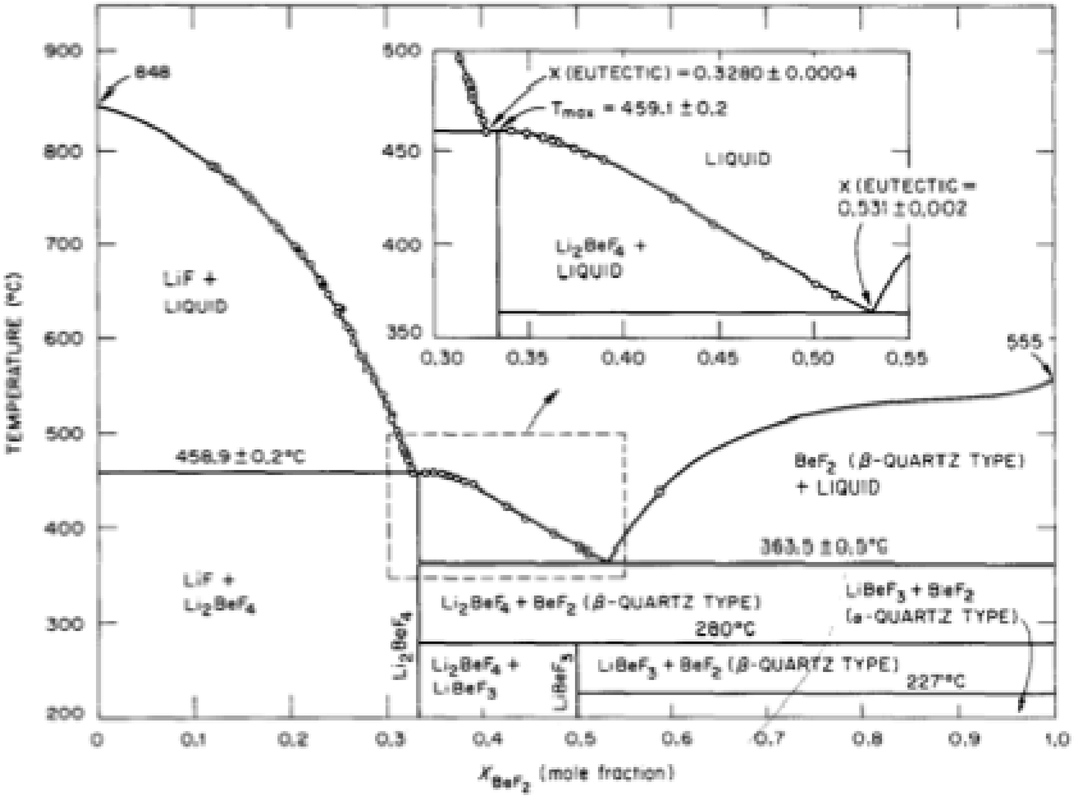


Figure 1. Lithium fluoride (LiF) and beryllium di-fluoride (BeF_2) eutectic phase diagram.20[,21]

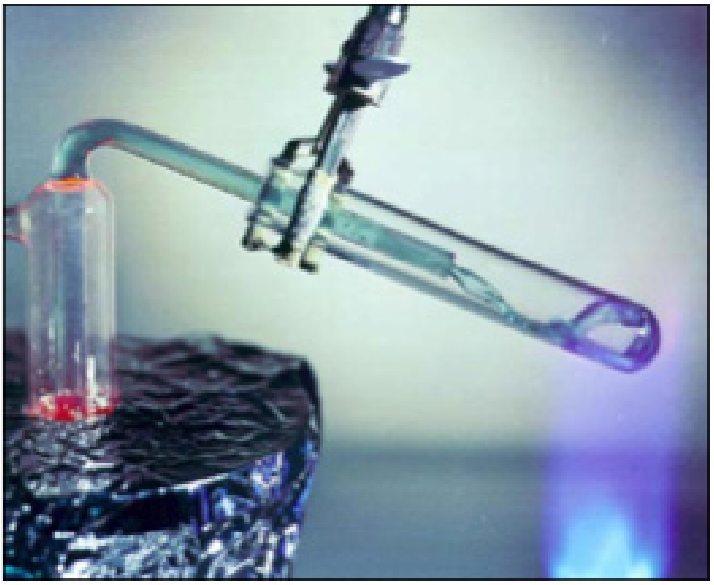


Figure 2. Flibe handling during MSRE related experiments at ORNL.

Recent studies have evaluated alternative salt compositions to flibe for various nuclear applications.[14-17] No credible alternative was identified as coolant material for the core, or primary circuit, even for heterogeneous fuel concepts in which the molten salt is only used as a heat transfer media. The main shortcomings of flibe are the: increased sensibility of regulatory agencies to the toxicity of beryllium (and related licensing issues and handling costs); high Li content (resulting in the generation of large amount of tritium), and high cost of fluoride raw materials. However, the neutronic properties of flibe are so favorable when compared to other mixtures or chloride based salts that flibe remains the main candidate material for reactor core cooling. On the other hand, several alternatives have been identified as heat transfer fluids in the secondary loop, which offer selected advantages with respect to some of the flibe shortcomings. Of those, the ternary fluoride eutectic LiF-NaF-KF (46.5-11.5-42 mol% respectively), also known as flinak, emerged as main alternative because of its low toxicity, excellent heat transfer properties, and chemical properties similar to those of flibe. This work therefore focuses on those two salt compositions, although many of the general considerations would apply to other materials.

1.2 The Advanced High Temperature Reactor as Reference Design Concept

The purpose of this report is to indentify technical issues related to molten salt thermochemical properties that would have to be considered in R&D programs aimed at using the materials in heat transfer systems. As such, the arguments contained herein are not relevant to a specific application or design. However, in order to provide bounds for parameters windows, such as operating temperature, pressure, etc., it is useful to indicate a design concept as reference. The Advanced High Temperature Reactor (AHTR) is the reactor concept selected, since it most closely relates to the objectives of the report because it has adopted molten salt cooling for both the primary and secondary loop, and it envisions operating conditions of up to 1000°C outlet temperatures.

The AHTR is a new reactor concept that has three technical characteristics: high temperature, passive safety, and a large power output. The high temperature is required to produce hydrogen and efficiently produce electricity. The passive safety features are required to reduce operating costs and improve public acceptance. The large power output, passive safety features, and high efficiency of electricity production (a consequence of high temperatures) are the enabling technologies to improve economics. The development is a joint effort of ORNL, Sandia National Laboratories, and the University of California at Berkeley.[21]

The AHTR uses coated-particle graphite-matrix fuels and a molten-fluoride-salt coolant. The fuel is the same type used in modular high temperature gas-cooled reactors, with fuel failure temperatures in excess of 1600°C. The optically transparent molten salt coolant is a mixture of fluoride salts with freezing points near 400°C and atmospheric boiling points of ~1400°C. As mentioned in the previous section, several different salts are being evaluated as the primary coolant with flibe as the main candidate. The reactor operates at near-atmospheric pressure. At operating conditions, the molten-salt heat-transfer properties are similar to those of water. Heat is transferred from the reactor core by the primary molten-salt coolant to an intermediate heat-transfer loop. The intermediate heat-transfer loop uses a secondary molten-salt coolant to move the heat to the turbine hall. In the turbine hall, the heat is transferred to a multireheat nitrogen or helium Brayton cycle power conversion system. For hydrogen production, the heat is transferred to the thermochemical hydrogen production facility, which converts water and high-temperature heat to hydrogen and oxygen. A schematic of the AHTR system is shown in Figure 3, while the main operating parameters are listed in Table 1.

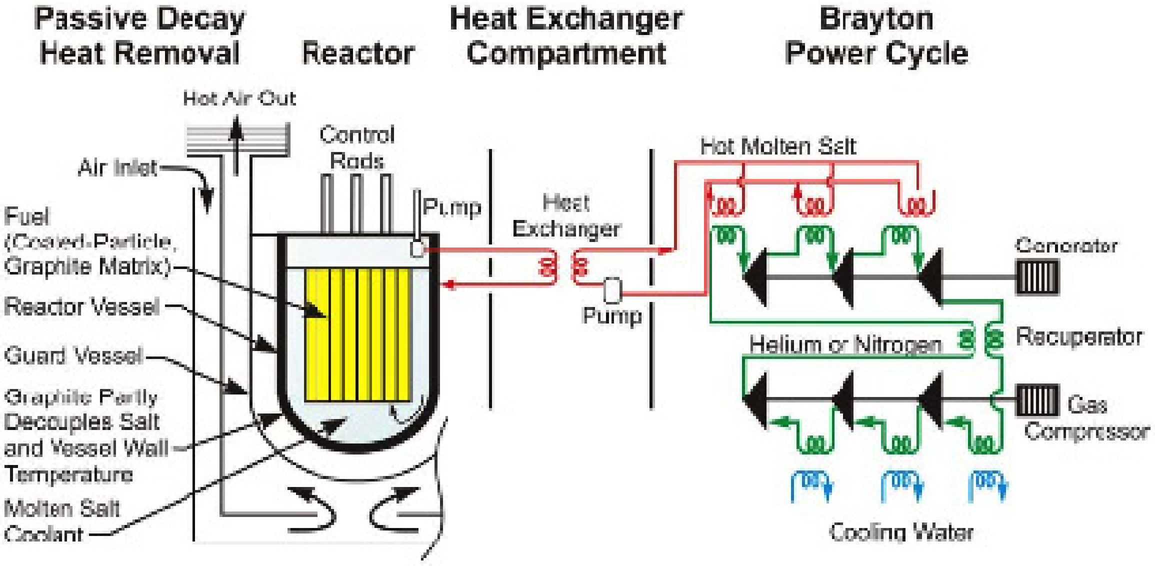


Figure 3. AHTR system schematic.[21]

Table 1. AHTR main operating parameters.[21]

Power level	2400 MW(t)	Power cycle	3-stage multi-reheat Brayton
Core inlet/outlet temperature	900°C / 1000°C	Electricity	1357 MW(e) at 1000°C
	700°C / 800°C		1235 MWe at 800°C
	670°C / 705°C		1151 MWe at 705°C
Coolant	2 LiF - BeF_2	Power cycle working fluid	Nitrogen (Helium longer-term option)
	NaF – ZrF_4	Power cycle working fluid	Nitrogen (Helium longer-term option)
Fuel		Vessel	
Kernel	Uranium carbide / oxide	Diameter	9.2 m
Enrichment	10.36 wt% ^{235}U	Height	19.5 m
Form	Prismatic	Reactor core	
Block diam.	0.36 m (across flats)	Shape	Annular
Block height	0.79 m	Diameter	7.8 m
Columns	324	Height	7.9 m
Decay heat system	Air cooled	Fuel annulus	2.3
Volumetric flow rate	5.54 m^3/s	Power density	8.3 W/cm^3
Coolant velocity	2.32 m/s	Reflector (outer)	138 fuel columns
		Reflector (inner)	55 fuel columns

2. EXTENSION OF DATABASE OF PHYSICAL PROPERTIES RELEVANT TO HEAT TRANSFER APPLICATIONS

Heat transfer characteristics of molten salts depend on their thermophysical properties. The fundamental properties for heat transfer applications are those considered in the nondimensional analysis leading to engineering correlations for heat transfer based on the following Nusselt, Reynolds, and Prandtl numbers:

- Density, ρ, expressed in kg/m^3
- Specific heat capacity, Cp, expressed in J/kg·K
- Viscosity, μ, expressed in Pa·s
- Surface tension, γ, expressed in N/m
- Thermal conductivity, k, expressed in W/m·K.

In ideal conditions for each eutectic composition those properties are a function of the temperature only (expressed in K). However, for molten salt their experimental determination presents unique challenges when compared to traditional heat transfer fluids.[1] The major challenges include:

- High temperature range, often incompatible with commercial instruments
- Limited material compatibility to contact salts liquid or vapor phase
- Difficulty to control composition, both in terms of eutectic mixture and of impurities concentrations, particularly for small batches.

Those handling challenges and the necessity of developing ad hoc instruments result in limited accuracy and repeatability of the measurements. The already cited report developed as part of this project provides a complete assessment of the available database of measured properties and citations to available references for several salt compositions.[19] Summary plots for flibe and flinak are reported here from Figures 4 through 9. The main reason is to identify the limitation of the existing database, particularly in the higher temperature range of interest for VHTR applications. Based on this assessment, an experimental test plan aimed at developing molten salt heat transfer components would have to include the capability of measuring the salt's thermophysical properties to the upper temperature range of interest. In particular, experimental needs are as follows:

- Extend properties database to high temperature range.
- Investigate temperature dependence and establish correlation for design studies across a wider operating range: some properties, especially thermal conductivity, were assumed constant across the small temperature range of MSRE operations, and the assumption is commonly extrapolated to higher temperatures. However, experimental verification is required because conductivity is the single most important physical property for heat transfer analysis.
- Improve accuracy and repeatability of measurements by diagnostic system development. A renewed effort has to be made to test the accuracy of properties data with improved and more accurate measuring instrumentation that can take advantage of technological improvements since MSRE operation.
- Consider the effect of salt mixture composition variation on thermophysical properties. Heat transfer components are part of complex system with interfaces to process fluids, pumping equipment, etc. Because of material compatibility issues or impurities contamination, the salt composition in such systems is dynamically changing; the average composition is maintained by chemistry control. However, local or transient variation in composition is expected. It is therefore necessary to evaluate

heat transfer properties not only for the reference salt composition, but also within the composition variations expected in a real system.

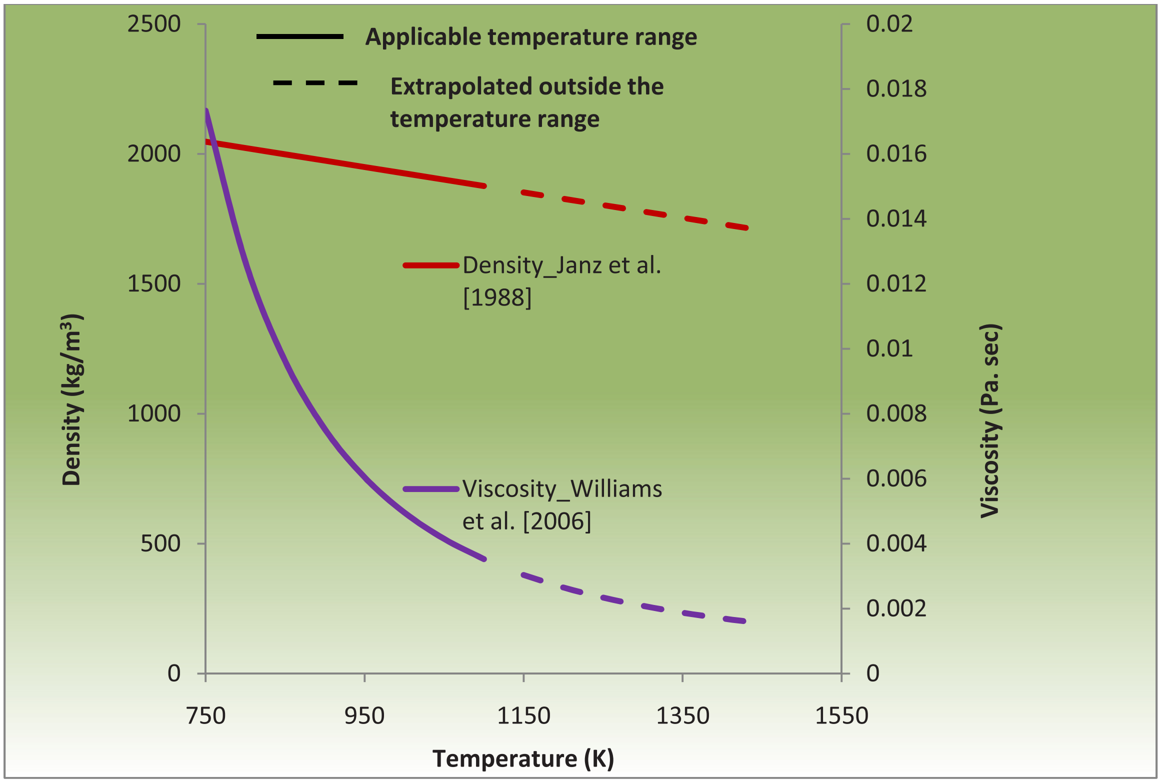


Figure 4. Flibe density and viscosity.

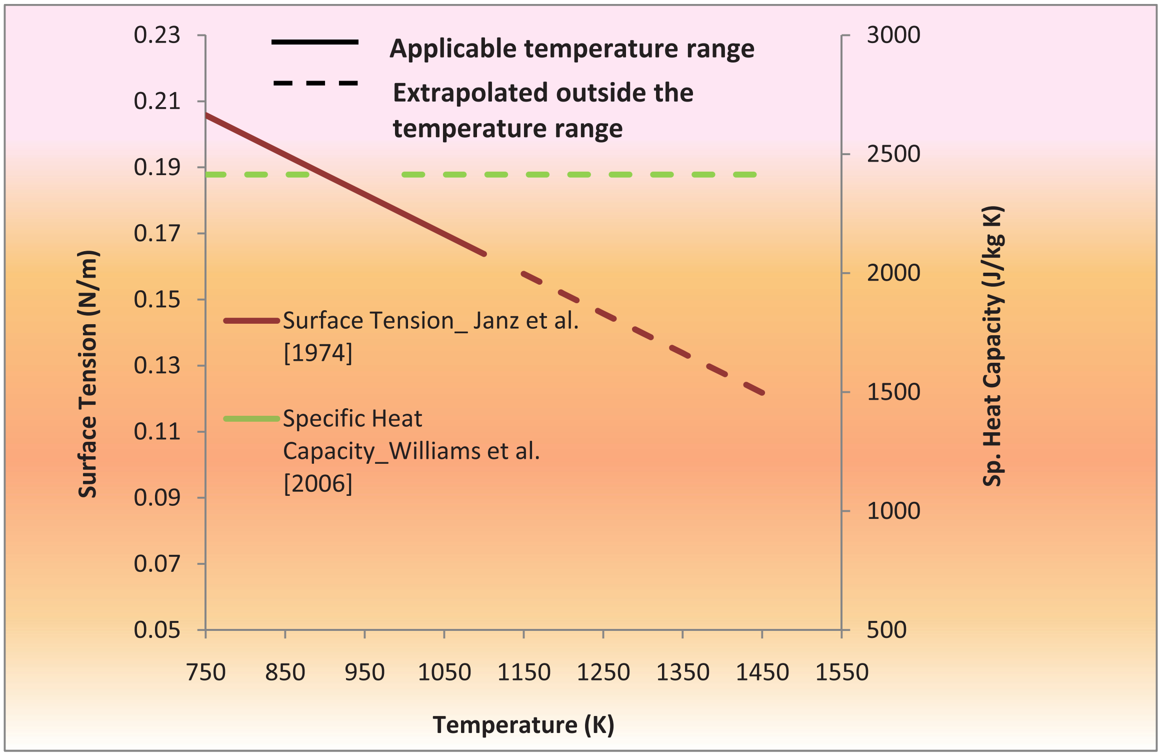


Figure 5. Flibe surface tension and specific heat capacity.

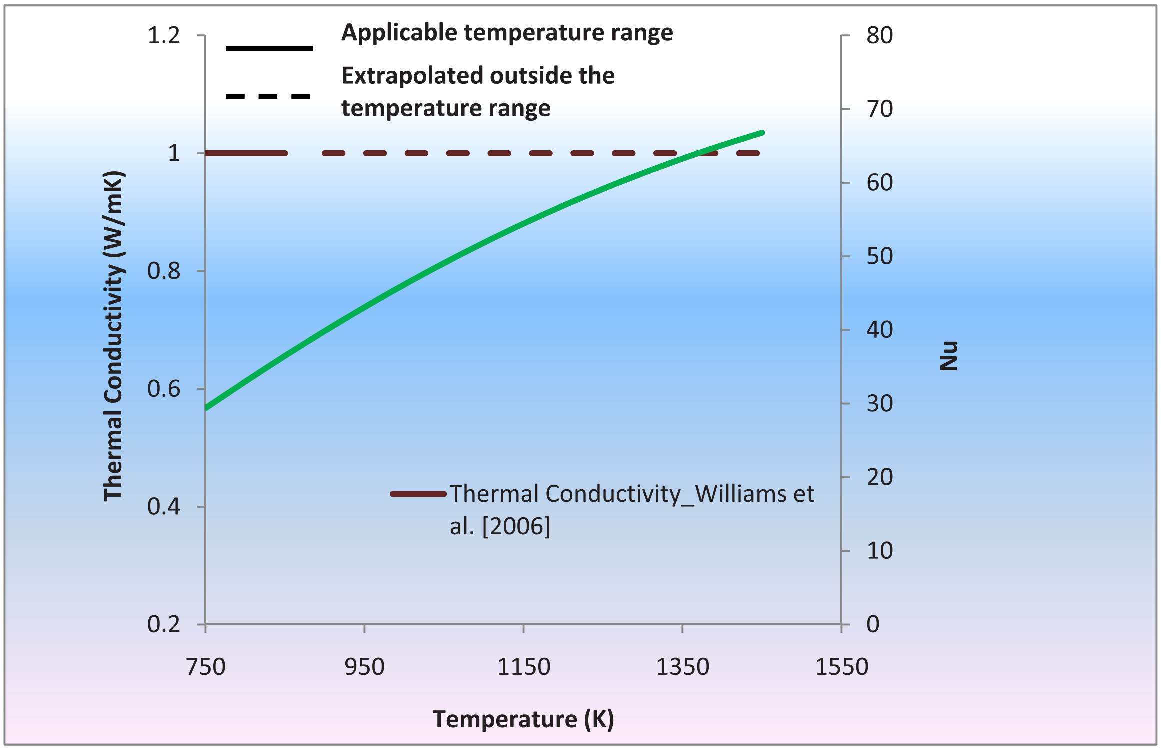


Figure 6. Flibe thermal conductivity and Nusselt number according to Dittus Boelter correlation.

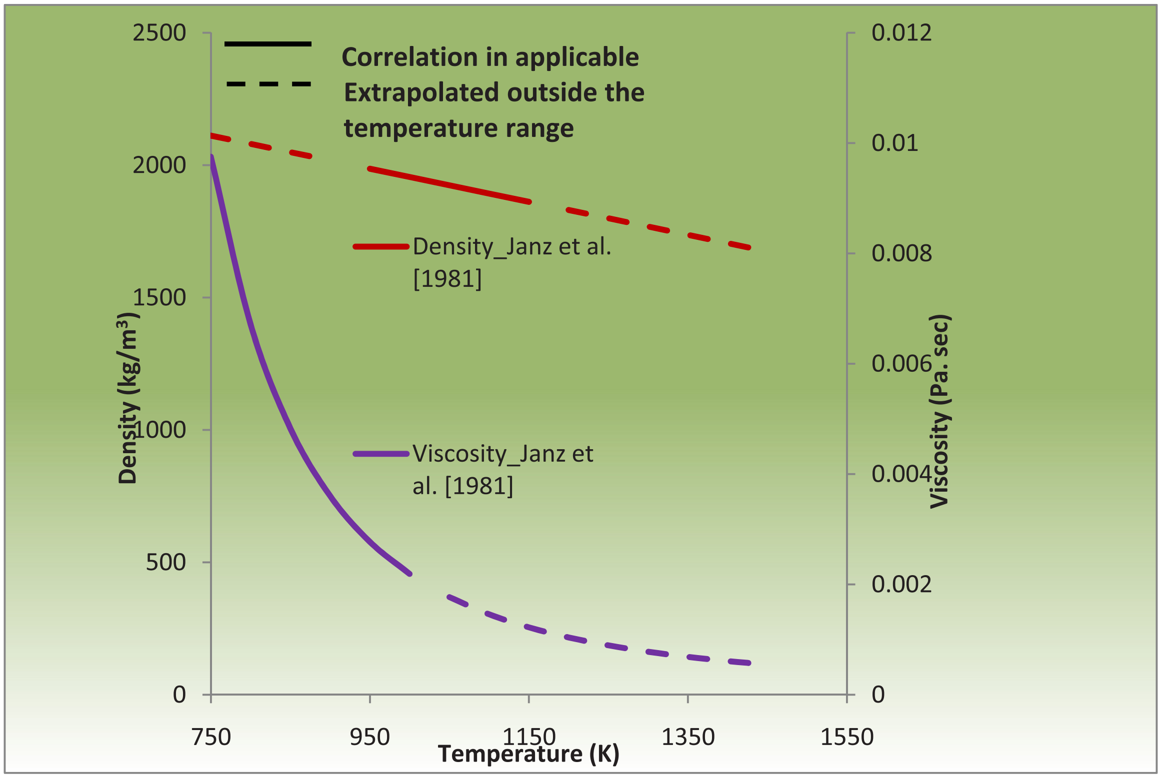


Figure 7. Flinak density and viscosity.

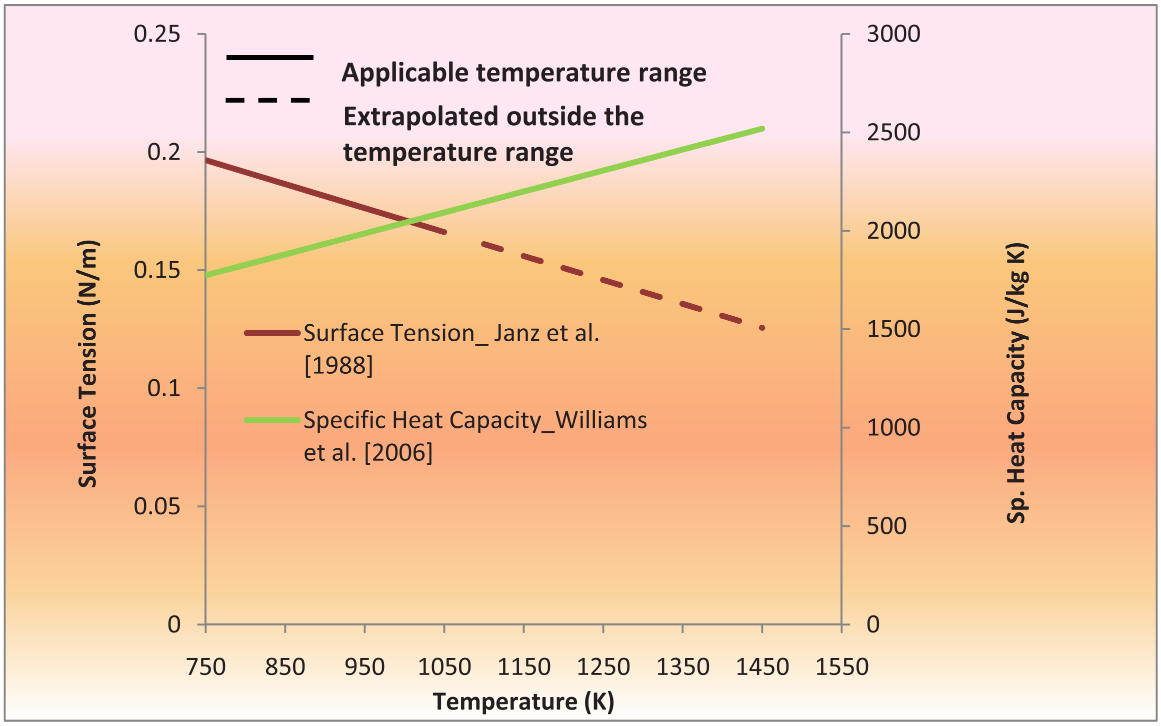


Figure 8. Flinak surface tension and specific heat capacity.

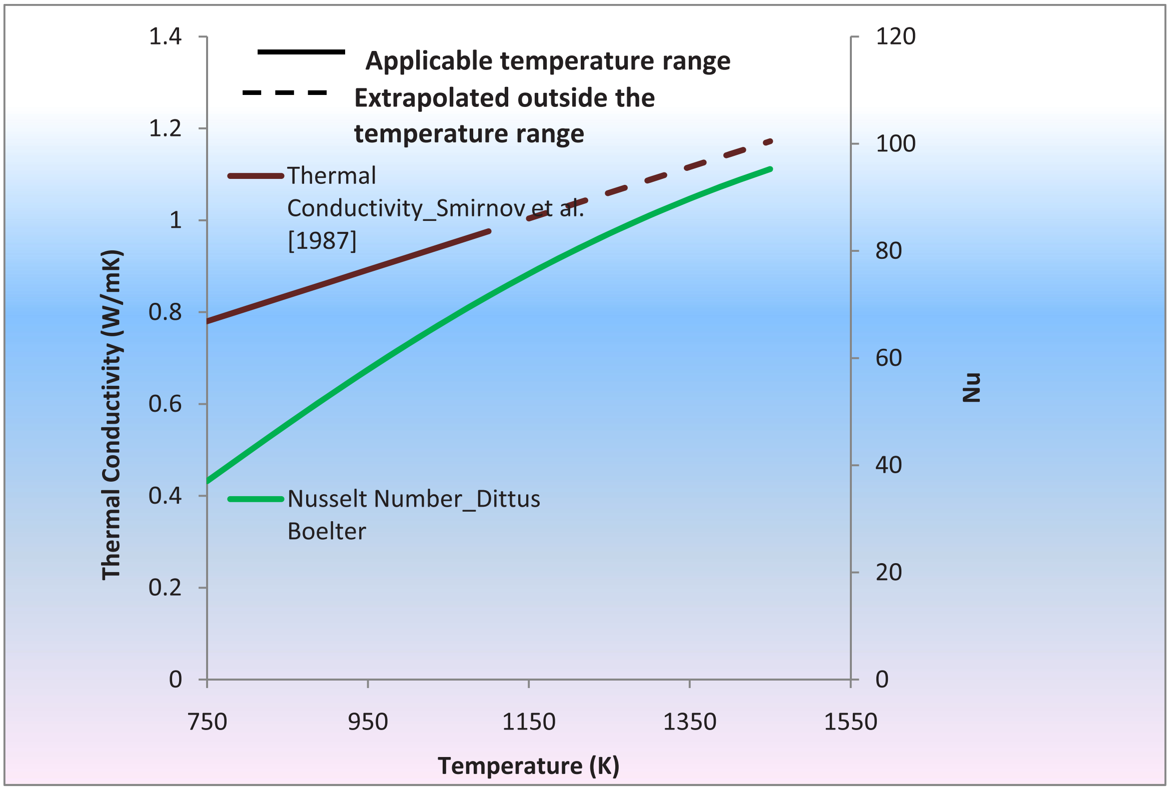


Figure 9. Flinak thermal conductivity and Nusselt number according to Dittus Boelter correlation.

3. DETECTION AND CONTROL OF MELT CHEMICAL COMPOSITION IN A HEAT TRANSFER TEST FACILITY

3.1 Purification

The level of impurities present in the molten salt can directly affect heat transfer thermophysical properties, and must therefore be considered in the analysis of fundamental properties measurements. But more importantly, impurities strongly affect the design and operation of any test facility because they dominate physical and chemical processes related to the control of molten salt composition (eutectic title) and material compatibility such as corrosion of structural materials, deposition in cold leg and flow restrictions and response to electrochemical analytical instruments. The design and operation of any molten salt test facility must include an R&D test plan aimed at the characterization and control of impurities present in the system.

3.1.1 Purification by Chemical Processing

Initial impurities in a molten salt largely stem from the purity of the starting powders (oxide and sulfate levels) and the amount of hydration that occurs in the salts, particularly the LiF because of its hygroscopic nature. Typically, powders of mixed salts are baked-out under vacuum or reduced pressure to remove the moisture. In the case of flibe, because of the toxicity and complications stemming from handling the BeF_2 salt, it is often preferred to heat the individual salts to around 450°C while being purged with a He/H_2 gas mixture at a flow rate of 100 to 200 sccm. This will drive off hydrated and absorbed moisture, allowing more accurately weighed amounts of the LiF and BeF_2 salts for use in obtaining targeted compositions.

The reduction of the oxides of (Be, Ni, Fe, and Cr), and also fluorides of these metals from corrosion processes has been accomplished by purging the molten salt bath with H_2/HF gas mixtures. This process has been well described by Shaffer.[22,23] By controlling the ratio of H_2 to HF in the gas mixture to approximately a factor of10, a balance may be achieved between the rates of the reduction of impurities and corrosion to the containment materials. Oxide ions from metal oxides are reduced providing water and fluoride ions by the following reaction.

$$O^{2-} + 2HF \leftrightarrow 2F^{-} + H_2O \qquad (1)$$

When HF reacts with the container material it produces fluorides from the alloy constituents during the corrosion process according to reaction Equation (2), where M represents Ni, Fe, and Cr. The Ni and Fe fluorides can be effectively reduced during a final H_2 purge. Metallic chromium can also replace the Ni and Fe from the fluorides from reaction Equation (2). The CrF_2 formed by these mechanisms is not so easily reduced by an H_2 purge. It requires reduction by a more reactive metal addition, e.g., Be or Zr. In addition to oxides inherently introduced from the salts, oxides existing on the container material will be converted into fluorides. Additional Cr can thus be displaced from the structural alloy. In fact, reaction Equation (1) demonstrates the ineffectiveness of oxide layers toward achieving corrosion resistance.

$$2HF + M \leftrightarrow MF_2 + H_2 \qquad (2)$$

Sulfur impurity can exist as a sulfate in BeF_2 and can be a problem. The sulfate can be reduced to sulfide using metallic Be turnings or powder. The sulfide in turn can be reduced with a H_2/HF sparging treatment. This treatment produces H_2S that can enhance corrosion to the container material and downstream components. Shaffer points out however that the reductions can be accomplished successfully if sufficiently high H_2 to H_2S ratios are maintained.

3.1.2 Purification by Electrochemical Methods

The chemical purification process removes most anion impurities from the melt. The metallic impurities will still remain dissolved in the molten salt or perhaps weakly adhered onto the surfaces of the container. White[24,25] provides excellent reviews of electrochemical applications to remove metallic and, to some extent, anionic impurities from molten halide systems. Basically, electroactive impurity species are transported between two electrodes and deposited by applying a potential. Choices of electrode potential, current density, cell parameters, (e.g., electrode geometry and material), and other parameters such as mixing will vary for the particular application to obtain suitable efficiency. Low levels of impurities (e.g., 10^{-2} to 10^{-3} M) and their low diffusivities (10^{-5} cm^2-sec^{-1}) often limit current density to 10^{-3} to 10^{-2} A/cm^2. Deposition or removal of impurities within a reasonable time frame may thus be promoted by mixing or stirring the melt and using a deposition electrode with a large surface area. The electrodes can be a choice of several different types of inert materials, e.g., carbonaceous (vitreous or glassy carbon) or a metal such as Pt, W, Ta, or Mo. White mentions that lithium from the salts can sometimes be intercalated or absorbed into carbonaceous materials. In such cases tungsten was a suitable alternative. Example parameters given by White for the electrolytic purification in a FliNaK mixture at 750°C were a tungsten cathode, a vitreous carbon anode, and voltage control at about 3 V. This resulted in current densities of about 5×10^{-3} A/cm^2. This author states that metallic impurities can be reduced below 2 mM by such electrochemical purification. Removal of water or hydroxide ions are more difficult but may be accomplished using a carbon anode. The oxygen reacts to form either CO or CO_2. These gases must be swept away by either vigorous purging or a reduced pressure or vacuum over the bath to keep the electrode from becoming polarized.

3.2 Electrochemical Analytical Methods

To control molten salt composition and impurities concentration it is necessary to develop accurate and reliable diagnostics, and electrochemical analysis is the most promising method. Several potential electrochemical analytical methods are reviewed in this section. This review identifies which methods might be mostly readily applied and which might have the most sensitive detection limits. Not all the methods need to be developed as part of this program, but diagnostic development must be part of the R&D test plan for any molten salt test facility.

3.2.1 Electrical Conductivity

Applications of measuring the resistance and obtaining specific conductance in molten salts (flibe) have been thoroughly explored by ORNL during the MSRE Program.[26] The major difference between electrical resistivity measurements in molten salts and aqueous solutions is the much higher conductivity of the salts. The resistance or capacitance encountered at electrodes become significant compared to that of the bulk solution for molten salt. Electrode contributions are manifested with frequency dependencies. The use of electrodes with a capillary design that provided a long path length and small area increased the resistance through the molten solutions. Influences from electrode capacitance can also be distinguished and identified by using a variable capacitance bank within the balancing circuit. As an example, Bamberger and Baes provided well characterized plots of specific conductance versus temperatures for molten LiF-BeF_2 mixtures.[27] This type of measurement provides a relatively quick benchmark as to the purity levels, but it would not provide information on the specific type of impurities present. The established database, a rigid retractable probe, and no need for a reference electrode would be reasons to consider this method for characterizing the molten flibe.

3.2.2 Potentiometry-EMF Measurement

Measurements of cell potentials of a molten salt may be obtained between an inert electrode and a reference electrode. Such measurements may be used to show concentrations differences of a solely existing known ionic species in both the reference cell and the test solution. With several different types of ionic species present, the cell potential can represent the overall oxidizing/reducing power of the melt. For dilute solutions with assumed equilibrium, cell potentials may theoretically be expressed by the Nernst equation shown by

$$E_{cell} = E^{o}_{O/R} + RT/nF \ln C^{i}_{O}/C^{i}_{R} - E_{ref.electrode} + E_{junction} \qquad (3)$$

where the concentrations C^{i}_{O} and C^{i}_{R} represent the concentrations of each component that has a redox reaction expressed as: O + n e- → R. The terms $E^{o}_{O/R}$, $E_{\text{ref electrode}}$, and E_{junction}, represent the standard potential for the redox reaction, the potential of the reference electrode, and potentials at electrode and boundary interfaces.

Effects from chemical interactions at electrodes, transition of electrodes to nonstandard state, isothermal conditions, and electrode polarization imbedded in the latter term may cause deviations from theoretical expectations. However, emf measurements can be used as rough estimates of the oxidizing power of flibe melts. Tables of emf series, from both experimental and theoretical studies for single and mixed halide salts are also available as a gauge for emf measurements.[28,29] Applications of this method could involve determinations of changes to cell emf, as minor controlled amounts of additives are charged to a purified bath. The biggest challenge for this technique is obtaining a reference electrode that provides long-term stability and resistance to the aggressive molten salt environments. The issue of an appropriate reference electrode is further discussed in Section 3.2.5.

3.2.3 Various Methods of Voltammetry

Various methods of voltammetry may be applied to identify the presence and quantity of different electroactive species. Included are methods of linear sweep, cyclic, stripping, and square wave voltammetry, and chronopotentiometry. These methods and their capabilities and detection limits are discussed in turn. All methods use three electrodes setup with a working electrode, a counter electrode, and a reference electrode. Similar problems of a stable reference electrode exist as discussed above. However, the rapid nature and short exposures associated with some of these tests make them more amenable to using certain refractory metals as quasi-reference electrodes.

3.2.3.1 Linear Sweep Voltammetry

This method linearly ramps up potential relative to the reference electrode while the current between the working and counter electrode is measured. As the reduction potential of a given electroactive species is reached, the species contributes to the current carrying capacity of the solution at the working electrode. A step up in current occurs as the potential progresses through the range for the electroactive species. An ideal case for the detection of several impurities in 0.05 M aqueous solution of KCl is shown in Figure 10. The distinction and height of the peaks depend upon such variables as impurity concentration, sweep rate (mV/s), electrode size and type, and the proximity of reduction potentials of different species. Faster sweep rates results in higher step heights. The onset (potential) at each step with available emf series is used to provide information as to which impurities are present. Quantitative measurements require calibrations performed by spiking known quantities of a given impurity into a purified salt.

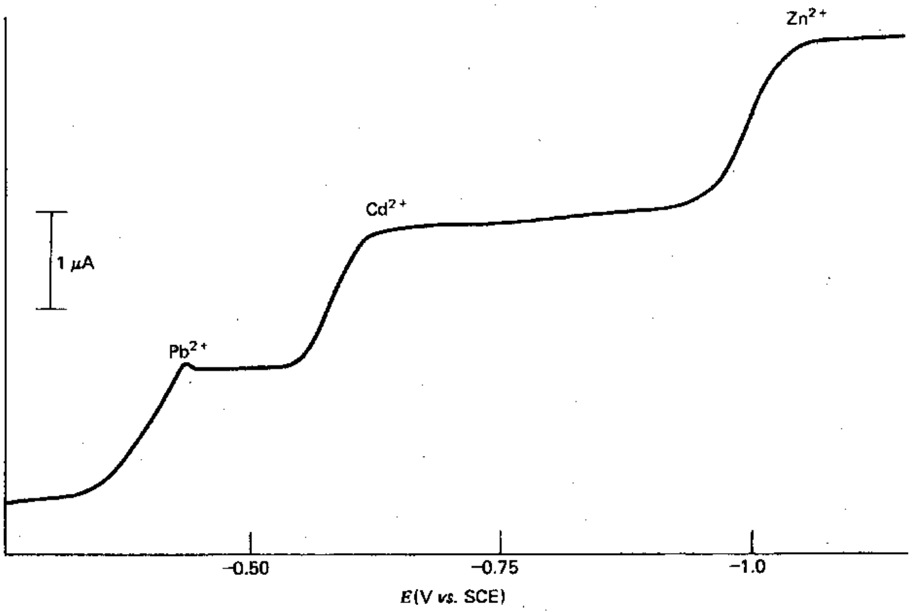


Figure 10. Plateaus shown for 0.2 nM Pb^{2+}, Cd^{2+}, and Zn^{2+} in 0.05 M KCl solution.

Another analytical approach develops a series of voltagrams run at different (faster) scan rates than portrayed above. Several studies provide illustrations of this approach.[30,31,32,33] The scans in Figure 11(a) show voltagrams from flinak. Peaks in the current versus potential curves form when the electrode reaction process involves a simple reversible charge transfer. This process is quite rapid and the current then becomes limited by a mass transfer diffusion process in the solution after peak currents are achieved. The peaks in the current increase in proportion to the square root of the voltage scan rate and can be expressed by the Randles-Sevick equation

$$i_p = 1.67x10^5 n^{3/2} A D^{1/2} v^{1/2} C \tag{4}$$

where i_p is the peak current (Amp), n is the electron charge involved in the redox reaction, C is the concentration, (moles/cm^3), A is the electrode area (cm^2), D is the diffusion coefficient (cm^2/s), and v is the scan rate (volts/s). Linear plots of i_p versus $v^{1/2}$, as shown in Figure 11(b), confirm that the process is diffusion controlled. The slope provides a means of obtaining the diffusion coefficient of a given ionic species in the molten salt. Please note the similarities in approach and the type of information that can be extracted from the rapid cyclic voltammetry tests and the chronopotentiometry (constant current) tests presented in Section 3.2.4.

Often a small or even micro electrode is used for the working electrode in cyclic voltammetry. This will limit the amount of the active species plated-out during a test and prevent significant changes to the bulk concentration during the course of an investigation. Manning and Mamantov[30,32] used platinum wires and rods 0.5 to 3 mm in diameter and pyrolytic graphite for electrodes. One of the platinum electrodes was used as a “quasi-reference” electrode.

This is the preferred method to apply for initial electroanalytical analyses following the H_2/HF purification. The use of platinum as a quasi-reference electrode provides a much simpler system than other types of reference electrodes. The brief nature of the analysis negates problems from some potential drift at the Pt electrode. Reversed current could also be used to clean or refresh the surface before the tests. Figure 11 shows results when only a single active species is present. Multiple impurities would result in several steps in cyclic voltagrams. This could cause some interference between different species and uncertainty in the application of Equation (4). Procedures whereby known impurities are added to a purified salt must be applied to provide a calibration for the current versus potential curves.

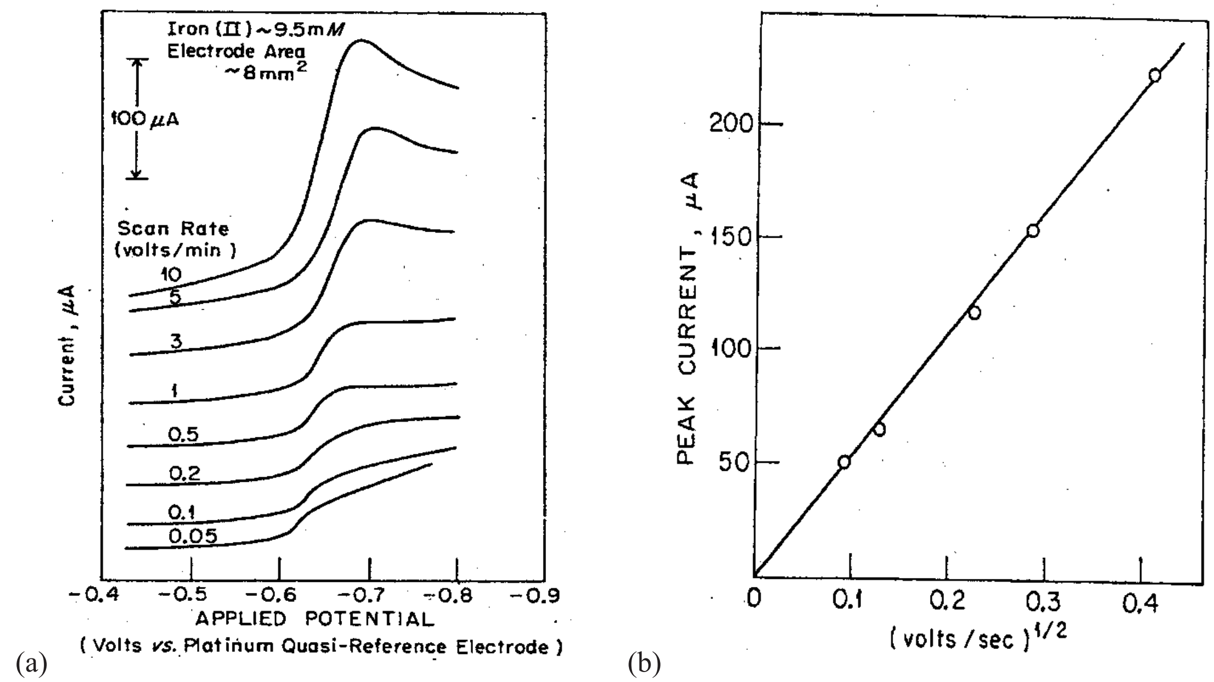


Figure 11. Current-potential curves from various scan rates and peak current versus square root scan rate plot for iron impurity in flinak.

3.2.3.2 Cyclic Voltammetry

Cyclic voltammetry is an extension of the rapid linear sweep method. The potential scan is reversed over the same potential range while current is measured. Reference 30 provides an example of such scans that provide the same information as described above. Such cyclic tests also checks for reversible conditions at the electrode and to the redox reactions. Bioanalytical Systems, Inc. provides information on detection limits for cyclic voltammetry. They point out that a potential difference of 60 to 70 mV is usually observed between the oxidation peak and reduction peak for reversible reactions (the theoretical is about 58 to 59 mV). Charging currents are also often associated at the electrolyte working electrode interface. These contribute to the background current and render detection limits by cyclic voltammetry to about 10^{-5} M.

3.2.3.3 Stripping Voltammetry

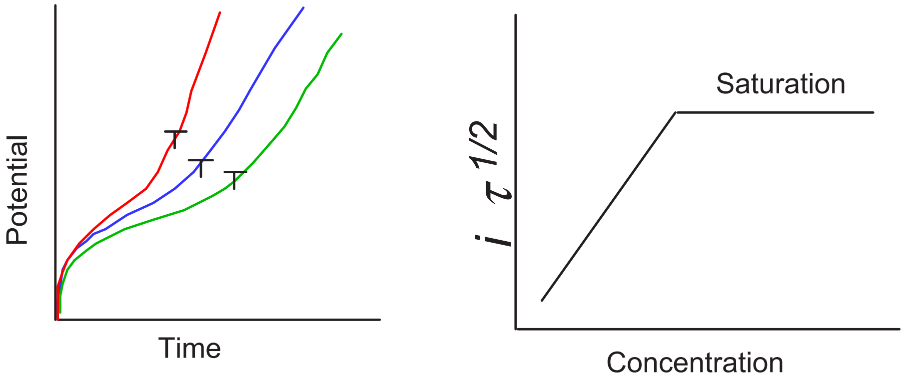
Stripping voltammetry uses a combination of voltage control phases to provide more sensitive current versus potential plots from very dilute solutions. A constant voltage is applied for a given period (e.g., 2 to 15 minutes) to concentrate or deposit metal ions at a cathode. According to Bard and Faulkner[15] concentration factors of 100 to 1000 may be obtained. The potential is then reversed with a more rapid rate typical of those discussed for cyclic voltammetry above, e.g., scan rate of 10 to 100 mV/sec. The anodic currents produced by stripping the impurity from the electrode will provide more distinct peaks for analyses than those obtained from linear voltammetry. Bard and Faulkner report that this technique can detect solutions as dilute as 10^{-10} to 10^{-11} M. BAS information also indicates that stripping techniques can provide quantitative measurements down to low (ppb) concentrations. Such sensitivities are likely those achievable for a cell that uses droplets such as Hg or a molten metal that have refreshed surfaces and can more closely represent ideal electrode conditions. Detection limits using solid metal or glassy carbon electrodes are likely not quite as low. However, an electrode such as Pt as a quasi-reference electrode would probable work satisfactorily for this method. This would make this approach a very viable method for analysis of very dilute impurities in solution in the molten salts.

3.2.3.4 Square Wave Voltammetry

There are also some pulsed or square-wave, potential controlled methods, e.g., Osteryoung or Barker square wave voltammetry, that provide increased sensitivity. Descriptions and applications of these techniques are provided in References 34. BAS reports that detection limits of 10^{-7} to 10^{-8} M may be obtained with such differential pulsed-voltammetry methods. This is a factor of 100 to 1000 more sensitive than the cyclic voltammetry discussed above. Claußen and Rüssel[35] report that they used pulses of 50 to 200 mV applied at frequencies between 5 to 500 Hz in their study in molten glass. They used 1-mm diameter platinum wire for the working electrode and a platinum plate for the counter electrode. A zirconia probe with an air purge was used for the reference electrode. Such a probe may be good for the oxygen-bearing glasses but not appropriate for molten fluorides that need to be maintained essentially oxygen-free. To apply this technique an appropriate reference electrode would need to be developed as discussed in Section 3.2.5.

3.2.4 Chronopotentiometry

Other electrochemical methods involving various types of current controlled experiments, i.e., chronopotentiometry, have been used to obtain concentrations, saturation limits, and diffusion coefficients of impurities in molten salts. Van Norman, et al.,[36,37] provide examples of methods that can be used to measure the solubility of metals in their chloride and bromide solutions. The concept behind this method of chronopotentiometry is quite simple. A constant current is applied across two electrodes in a homogeneous unstirred solution. The potential is recorded with time as conditions of the electroactive metal ion change at the working electrode to accommodate the current. Initially the concentration of the ion, M^{n+} is initially uniform throughout the solution and at the electrode. When a current is imposed diffusion by a semi-infinite planar diffusion mode may be assumed to provide the mass transport from the solution to the electrode. The potential will change with time as polarization occurs at the electrode. The transition time has been identified as the time from the onset of the application of the current to the point where significant polarization occurs, which in turn causes a dramatic increase in the potential. A series of potential versus time plots for a set of different currents is obtained as shown in Figure 12. A more rapid onset of the transition time correlates with higher current densities.



(a) (b)

Figure 12. (a) Schematic illustration of anodic chronopotentiograms at different current densities and (b) corresponding plot of iτ1/2 vs. concentration to determine solubility.

3.2.5 Reference Electrodes for Electrochemical Analysis

The choice of an appropriate reference electrode is very important in electrochemical analysis. The electrode should provide a stable reference potential and also resist corrosive attack from the molten salt environments. Molten fluoride systems are particularly aggressive and place even additional requirements upon the containment material compared to molten chloride systems. Minh and Redey[38] provide a comprehensive review of requirements and electrodes developed for various systems. These authors express the critical need of a stable electrode with known potential for studies into the thermodynamic properties of molten salt systems. The requirements for kinetic studies using voltammetric or chronopotentiometric methods are not as critical. They state that various metals, such as, Pt, Ni, Mo, W, Ta, and even graphite may be used as a quasi-reference electrode. They reference the report by Mamantov and Manning[30] where potential variation of only 10 to 20 mV were observed over a weekly period from a Pt electrode.

These are several common requirements for a suitable stable reference electrode. The media with the known redox potential must be isolated from the test solution, however a bridge or membrane must exist allowing an electrolytic junction between the compartments. The bridge may allow limited diffusion through a porous media such as a frit or graphite, or it can be a solid ionic conducting compound. The container material should also be resistant to the fluoride salt mixture to prevent contamination. There have been several reports showing the development of various reference electrodes during the MSRE program.[39,40] The development can be traced though the following basic designs:

- A design with boron nitride as the outer container (thinned to serve as the bridge at the bottom). The internal half-cell was a Ni electrode in a known molten fluoride. This electrode was reported to remain within ±3 mV over several days. This cell was reported as usable up to 800°C. However, other reports indicate susceptibility to chemical attack and thermal cycling.
- A design that used a silica or BeO tube to contain a mixture of flibe saturated with NiO or BeO. Ni was again used as the internal electrode. This assembly was housed in a perforated Ni jacket.
- Advanced designs used single crystals of LaF_3 for the ionic conductor. A pool of molten fluoride (flibe saturated with NiF_2, with a Ni electrode) was used for the internal component. This cell was contained in nickel and boron nitride components. A nickel frit was used for a porous junction. These were the types of cells that operated for several months in the flowing loops with emf potential drifts of only a few mV.

A recent report presented an alternative to the types of reference cells described above[41] in response to some of the problems with the reference cell discussed above. These include the availability of the LaF_3 used in the third type of cell and the susceptibility of boron nitride to thermal shock, which resulted in probes reported to survive only a few cycles. The alternative design used similar internal components; either a Ni or Ag wire electrode in flinak saturated with either NiF_2 or AgF contained in a closed bottom graphite cell. However, pyrolytic boron nitride was coated onto the outer diameter of the graphite cell while the bottom was left uncoated to provide the porous membrane for the salt mixture. The probe showed good reversibility, and response time was actually improved with additional thermal cycling.

3.3 Sampling and chemical analysis

The capability to add and remove samples repeatedly during the course of long-term operations of a heat transfer test facility is fundamental. Bamberger[42] describes experimental hardware (flanges, bellows, seals, and valves) needed for such operations based on a sample exchange chamber. Sampling is done with a rod through a gas tight fitting with a gasket such as teflon, graphnol, or lavite that can withstand the temperature on the risers extending from the top lid of the test vessel. The rod is lowered to dip a sample and then raised into an inert gas chamber above the test cell. The chamber has a lower valve to isolate it from the bath, allowing sample removal and the attachment of a new sampling cup. The chamber is purged with helium to reestablish a high purity environment in the sampling chamber between operations. Such a system is also required in order to add material to the melt, either for composition control (eutectic title) or to provide known concentrations for the calibration of electrochemical analysis instruments.

Chemical analysis is performed on collected sample to determine their composition using inductively coupled plasma atomic emission spectroscopy (ICP-AES) or inductively coupled plasma mass spectroscopy (ICP-MS) for metallic elements and Leco analytical systems for oxygen, nitrogen, and carbon. ICP-MS has better detection limits for some elements but the system is not tolerant to strong acidic solutions. Detection limits reported for ICP-AES for impurities such as Fe, Cr, and Ni range from 2 to 4 μg/L. This allows detection of these impurities at near ppm levels, depending upon the final procedures used for sample dissolution.

4. MATERIAL COMPATIBILITY ISSUES RELEVANT TO A HEAT TRANSFER TEST FACILITY

Material compatibility issues are likely not within the scope of an experimental test plan aimed at investigating the heat transfer properties of molten salts. However, any heat transfer test facility would likely involve a forced convection loop whose design and operation would inevitably have to consider material compatibility issues, such as corrosion, and the prevention or detection of component performance degradation.

The discussion on melt composition measurement in the previous chapter already addressed the issue of corrosion detection. The discussion that follows on structural materials compatibility has the main objective of providing guidance for the design of a heat transfer test facility aimed at minimizing the effect of corrosion on the system's performance. It will also introduce limitations in the available properties database that may require the addition of specific R&D tasks related to material compatibility of the test plan.

Available options for the active control of corrosion processes through the fluoride potential are also discussed. Although their development and characterization will not be part of the test plan, one or more methods may be employed in a heat transfer test facility, depending on the choice of materials adopted for system structures and components and other operation parameters such as temperature.

4.1 Definition of Corrosion in Fluoride Molten Salts

In high-temperature nonaqueous systems, the redox state is a measure of the propensity for corrosion of the container metals.[43] Redox is a generalized term that is made specific according to the anion X that is exchanged between two valence states of a cation M. The redox condition is referred to as the *potential* of the anion species. Since the anion species is usually an elemental gas in its normal state, the potential is defined in terms of its partial pressure. The redox condition or potential fixes the ratio of the high and low valence states of a cation that is simultaneously present, or vice versa. The "X-potential" is defined in terms of the partial molar Gibbs free energy of the diatomic gas X_2, where X = O, S, F, Cl,…:

$$\Delta\overline{G}_{X_2} \equiv RT\ln p_{X_2} \tag{5}$$

This particular definition follows from the equilibrium expression of the generalized oxidation reaction:

$$MX_n + \tfrac{1}{2}X_2(g) = MX_{n+1} \tag{6}$$

where $0 \le n \le 4$.

The most common redox potential is the oxygen potential, where X = O. This potential is an important thermodynamic property of oxide systems containing multivalent cations such as U and Pu in nuclear fuels. The multivalent cation can be contained in a gas (e.g., M = H_2 or CO, n = 0), a metal (e.g., M = Ca, n = 0), or an oxide (e.g., M = Ti, n = 1). It is not necessary that the gas X_2 be physically present in the system; a metal and its oxide can be enclosed in a gas-free container yet still exhibit the potential for generating an oxygen pressure. In the case where the cation is a gas, the equilibrium partial pressure of X_2 may be too small to include in material balances; many metal to metal oxide systems generate oxygen pressures of 10^{-25} atm or less.

In flibe and flinak, it is clear that X = F, and the redox condition is properly termed the *fluorine potential* based on

$$\Delta\overline{G}_{F_2} \equiv RT\ln p_{F_2}\,. \tag{7}$$

The fluorine potential controls the equilibrium concentrations of structural metals dissolved in the fluoride-based salts. As such, it provides a quantitative description of the corrosion process at the solid/liquid interface.

Various phenomena can alter the fluorine potential, either in the system as a whole or at a specific location, thus affecting the corrosion process. Those are sometimes identified as corrosion *mechanisms* and differentiate to what is then referred to as *intrinsic* corrosion, which is the unaltered equilibrium condition defined above. All those mechanisms can quantitatively be referred to a variation in the fluorine potential as expressed by Equation 7. They include:

- *Corrosion by impurities*: Addition of oxidizing contaminants, such as HF or H_2O, residual oxides of metals, and polyvalent metal ions can have a strong effect on the fluorine potential of the relative element.
- *Temperature gradients*: Steady or transient temperature gradients affect the fluorine potential of dissolved element. This mechanism is usually described in terms of solubility, which is a more familiar concept generally applied in the macroscopic description of aqueous solutions.
- *Galvanic effects*: The application of an external electromotive force (an applied electrical potential) between two interfaces in contact with the liquid results in the variation of the fluorine potential for elements present in the solid phases. Small electrical forces can locally arise from the presence of dissimilar materials, such as in welds. Large forces can be controlled by applying an external potential to two or more electrodes, which is the theoretical basis for electrochemical purification methods described in the previous section.

The effect of the mechanism described above on structural materials for flibe and flinak systems has been summarized in the cited database evaluation report.[1] This qualitative evaluation, along with the quantitative measurement of the fluorine potential in thermodynamic equilibrium for relevant elements (expressed by the free energy of formation at a specific temperature), constitute the basis for the choice of structural materials in molten salt systems. An example of how such information can be employed for design studies is illustrated in Figure 13.

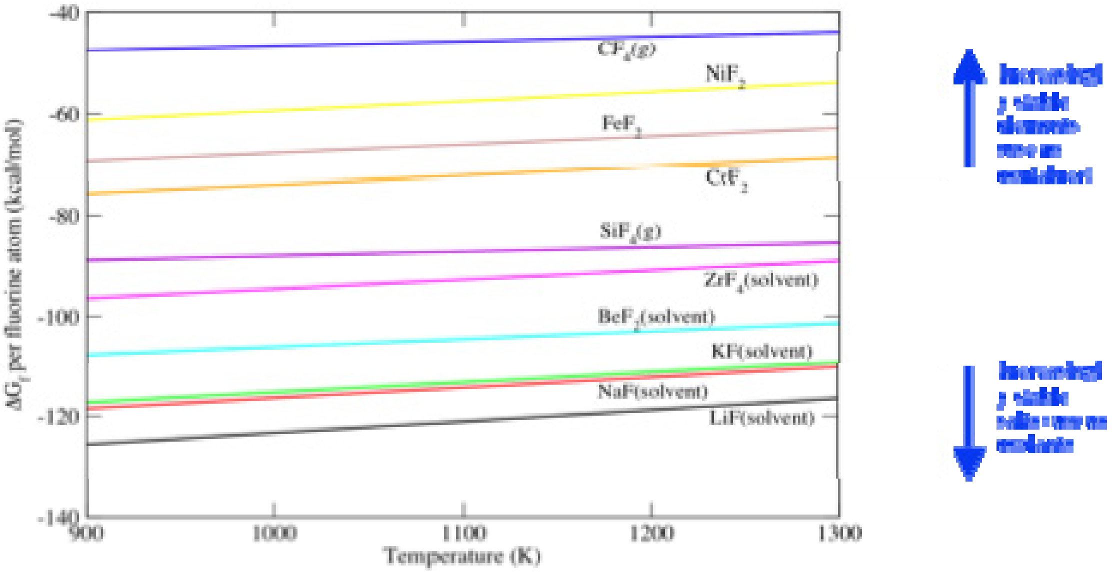


Figure 13. Comparison of the stability of structural alloy elements with respect to fluoride corrosion [laurant thesis].

4.2 Limitations in Available Database of Structural Materials Corrosion in Molten Salt

A few general observations can be drawn from the existing but limited data.[1] Ni and alloys with dense Ni coatings are effectively inert to corrosion in fluoride salts. Of the chromium containing alloys, Hastelloy N appears to have the best corrosion resistance. In general, alloys with increasing carbon and chromium content are increasingly subject to corrosion by the fluoride salts flibe and flinak because of attack and dissolution of the intergranular chromium carbide.

In general, flinak caused extensive intergranular corrosion in most of the alloys, producing substantial void structure at the grain boundaries that developed rapidly and extended deeply in susceptible alloys. In some cases, intergranular corrosion progressed to open, connected porosity with salt intrusion into the degraded alloy. On the other hand, flibe caused more moderate intergranular corrosion. Based on a single test on reduced activation martensitic steel developed in Japan for fusion applications (JLF-1)[44] and Incoloy 800H,[45] flinak appears to be much more corrosive than flibe.

Finally, thermal gradients and galvanic couples in the molten salts can enhance corrosion rates by one to two orders of magnitude relative to corrosion by residual contaminants in the molten salts. However, correlations of corrosion rate as a function of contaminant type, concentration, and temperature are not available for a quantitative comparison for many elements.

The existing data on material compatibility as a whole are insufficient to serve as a basis for reliable selection of containment materials. This stems from the fact that the large database available from MSRE operation was obtained for salts with dissolved fuel elements, not for the pure salts envisioned for heat transfer applications. The corrosion data are limited in terms of coolant composition and the structural alloys tested. Comprehensive parametric investigation (for example, a range of impurities concentration at a specific temperature) is even more limited, and so are single-effect tests designed to focus on a single corrosion mechanism. Finally, quantification of corrosion data rely mostly on mass loss measurements from exposed specimens, which might not represent a realistic measure of the effects of corrosion because intergranular corrosion could severely degrade the mechanical characteristics and cause premature failure in alloys, even at low mass loss values.

All the above limitations need to be overcome by a new experimental R&D program on material compatibility focused on flibe and flinak as heat transfer media. Such an effort is likely to start in parallel with the evaluation of heat transfer performance, which is the subject of this report. The extent of material compatibility testing necessary before the design of a heat transfer test facility will be determined by available funds, project schedule, and risk analysis, and is beyond the scope of this report.

5. CONCLUSION

This report identifies technical issues related to the thermophysical and thermochemical properties of the molten salts that would require experimental characterization in order to proceed with a credible design of heat transfer systems and their subsequent safety evaluation and licensing. In particular, it outlines an experimental R&D test plan that would have to be incorporated as part of the design and operation of an engineering scaled facility aimed at validating molten salt heat transfer components, such as intermediate heat exchangers.

The preparation and purification of the materials is discussed, focusing on the development of suitable diagnostics to detect material composition and impurities concentration. Issues specific to each material and its application are also considered, focusing on the compatibility with structural materials and the extension of the existing properties database.

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