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Investigation of Frozen Chemistry for Molten Salt Reactors (MSRs)

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ABSTRACT

Understanding accident progression and the potential/conditions for fission product release from fuel is necessary to evaluate safety for any nuclear reactor system. Molten Salt Reactors (MSRs) under development need such analysis to support safety evaluations. Fission product chemistry specific to MSR concepts is a critical area that introduces distinct considerations relative to the current state-of-knowledge in reactor safety, primarily developed for water-moderated nuclear reactor systems. In Light Water Reactor (LWR) systems, it is necessary to capture the chemical interaction of fission products with the reactor evironment, containment and confinement systems. The overall effects at this point are relatively well understood for the purposes of performing safety evaluations. A key insight from LWR studies is that fission product chemical behavior can be reasonably captured by modeling approaches where the chemistry is "frozen". These modeling approaches assume that radionuclide reaction and speciation can be represented by chemical classes, each with characteristic transport behavior that is invariant under a broad range of thermochemical conditions. However, radionuclides can exhibit a range of behavior in the liquid salt-melt phase of the coolant used in MSRs. Radionuclides, salt, and the metal containment surfaces (i.e. pipes) can co-exist in dynamic equilibrium that could evolve with small system mass changes. A detailed investigation to the degree the equilibrium state can dynamically evolve with changes in the conditions of the molten salt mixture has not been previously conducted. It is currently not well understood where frozen chemistry assumptions are valid. Expanding the state-of-knowledge in this regard is relevant to better assessing the range of chemical effects that should be incorporated as part of MSR safety assessments.

This investigation used the Oak Ridge Isotope GENeration (ORIGEN) module of the Standardized Computer-Analysis for Licensing Evaluation (SCALE) code to generate simulated radionuclide inventories for the MSR Experiment (MSRE) and then modeled reactor chemical speciation using the Molten Salt Thermodynamic Database – Thermochemical (MSTDB-TC) coupled with Thermochimica. The effect of composition variation during decay of fission product inventory in a molten salt over a period of 500 days prolonged post- at multiple temperatures was studied. Mass fractions for fluorine and berilium were varied in order to probe the effects of free fluorine control. Finally, speciation of fluoride reactors were showed by comparing MSRE readionuclide inventories with a FLiBe based molten salt breeder reactor (MSBR).

The results showed that fission product mass change has little effect on phase mass changes and vapor pressures for fluoride species, but differ with varying carrier and fuel salt compositions. However, iodine species were found to have a vapor pressure not only dependent on temperature, but also the free fluorine potential, releasing iodine when the free fluorine potential is equal to the iodine inventory. This observation, however, arose under free fluorine potentials that are very unlikely to be realized in typical molten salt mixtures. Despite this observation, temperature was found to be the dominant parameter that drove phase change and fission product species vapor pressure. The results indicate that the current frozen chemistry approach is adequate for MSR analysis.

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ACKNOWLEDGEMENT

The authors would like to acknowledge the help of both Dr. Juliano Schorne-Pinto and Prof. Theodore Besmann at the University of South Carolina for assistance with using the Molten Salt Thermodynamic Database - Thermochimical (MSTDB-TC) and to help ensure that the calculation results are reliable.

Donny Hartanto and Friederike Bostelmann of Oak Ridge National Laboratories (ORNL) performed the MSRE SCALE analyses that provided the radionuclide decay for the MSBR calculations.

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ACRONYMS & DEFINITIONS

CALPHAD Calculation of Phase Diagram

FM3M Solid state solution composed of alkali metals

GEM Gibbs Energy Minimizer

LWR Light Water Reactor

MSBR Molten Salt Breeder Reactor

MSFL Molten Salt Fluoride Liquid

MSR Molten Salt Reactor

MSRE Molten Salt Reactor Experiment

MSTDB-TC Molten Salt Thermodynamic Database - Thermochemical

ORIGEN Oak Ridge Isotope Generation

SCALE Standardized Computer Analysis for Licensing Evaluation

P3c1 Solid state solution composed of actinide and lanthanide metals

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1. INTRODUCTION

The need to supply carbon-free electricity at terawatt capacity has driven a resurgence in nuclear energy innovation, renewing interest in non-Light Water Reactor (non-LWR) design concepts. These are typically denoted as Generation IV reactor concepts. These types of advanced reactors introduce unique features relative to earlier designs and include more compact facilities, higher temperature fluids, and the use of passive safety features. These types of features make these design concepts attractive for a broad range of applications requiring energy beyond just electricity. However, the behavior of new reactor designs introduce new physical and chemical processes that must be characterized in order to understand system behavior under operational and accident conditions.

The phenomenological characterization of LWR operation and accident behavior has evolved due to multiple decades of research, from lab-scale to reactor-scale. The occurrence of abnormal operational occurrences, and a range of accidents of varying degrees of severity in LWRs has further expanded understanding system behavior. The understanding of reactor-scale behavior has been valuable to advanced the state-of-knowledge of LWR behavior relevant to safety evaluations. The insights from reactor-scale events have enabled understanding of how a broad range of accident phenomena that interact under the harsh conditions and are realized during a reactor accident.

The basis for understanding non-LWR system behavior under operational and accident conditions remains largely limited to experiments at research facilities and reactors. The breadth of operational experience that exists for LWRs is largely not present for many of the non-LWR concepts, though substantial knowledge has developed due to past research efforts. For molten salt reactors (MSRs), the molten salt reactor experiment (MSRE)[8, 9, 12] remains an invaluable source of data highlighting system-level behavior. It also can elucidate the types of operational challenges that arise at system-scale, which have in the past served as important information to precursor conditions that can progress to system states that have an enhanced potential for fission product release beyond the primary retention barrier (i.e., the molten salt).

In the absence of more extensive operational experience for these unique reactor designs relying on passive safety measures, it is difficult to directly apply Probabilistic Risk Assessment (PRA) methods to identify and quantify likely accident scenarios that could occur. While PRA comprises a range of methods that enable the systematic identification of fault scenarios, the methods have a heritage in assessing systems developed to implement a safety philosophy relying on active safety systems. In this type of safety philosophy, high levels of safety function availability are achieved through redundancy, diversity, and independence in conjunction with multiple layers of defense-in-depth. The adoption of passive safety systems is likely to make nuclear power plants safer through the fact that these systems have high degrees of reliability and availability – i.e., they are much less likely to randomly fail on demand.

However, these enhanced levels of safety are generally relevant when considering traditional engineering safety design for nuclear power plants – the assurance of high availability of safety functions when the loss of engineered functions cause a power plant to enter an abnormal state in which one or more safety functions must be restored through backup safety measures (i.e., nuclear safety systems). These types of events are typically considered to be *internal events*, in which engineered systems are lost primarily due to random occurrences. There are perturbations to a nuclear power plant that can cause it to enter an abnormal state that are not encompassed within the set of internal events. These *external events* typically involve hazards that arise from natural phenomena, such as an earthquake or severe weather disturbance.

Also, incipient processes that occur over long times during power plant operations that could degrade structures, systems, and components (SSCs). An example relevant to MSRs is the ongoing corrosion of reactor vessel structures during operation. The loss of structural integrity due to such corrosion is the primary means by which reactor vessel failure is postulated to occur in an MSR[2]. This failure leads to what is typically considered a maximum hypothetical salt spill accident. This type of accident was assessed conservatively as part for the MSRE safety basis. Failure of SSCs as a result of these incipient processes could establish the conditions for faults progressing to safety-significant events.

A broader range of scenarios arising from intentional acts to damage the nuclear power plant represent an extension of these external events. A more extensive understanding of how external events and intentional acts impair or degrade safety functions provided by passive safety designs may be relevant to understanding of advanced reactor safety and approaches to manage residual risk.

The system response under a broad range of perturbations becomes more important to represent for passive safety concepts. Advanced reactor systems are very likely to exhibit high levels of safety under more traditional internal event contributors to risk. The manner that other perturbations disrupt passive safety system dynamics represents a sensitive coupling between external factors and the intrinsic dynamics of the power plant. Modeling and simulation methods are thus evolving to ensure adequate resolution to understand a broader range of fault scenarios. These may represent a more dominant contribution to residual risk.

Of particular interest for MSR concepts are the conditions that could lead to an enhanced mobilization of fission products outside of the molten salt. The release from molten salt to atmospheres in different regions of the plant establishes the extent to which hazardous material exists in a state in which they can more readily transport to on-site workers or the off-site public. For example, LWRs traditionally exhibit an enhanced potential for fission product release to the environment when fuel is at elevated temperatures. MSRs, however, have the potential to reach sufficiently elevated temperatures without promoting greater mobilization of fission products from the liquid fuel. This is often considered an important advantage of the MSR concept. However, loss of structural integrity could release salt into configurations that promote more extensive mechanical release of radionuclides. There may also be a potential for disturbance of the control of the working fluid chemistry to create chemical states yielding a greater vaporization of fission products from salt in high radiation fields[12].

This report investigates the applicability of frozen chemistry to model MSR accidents. Radionuclide inventories were calculated using the Oak Ridge Isotope Generation (ORIGEN) module in the SCALE (Standardized Computer-Analysis for Licensing Evaluation) for a 500 day prolonged shutdown of the MSRE[7]. Speciation of the calculated radionuclide inventories was then calculated using the Thermochimica Gibbs energy minimizer[11, 10, 6] (GEM) with the Molten Salt Thermodynamic Database - Thermochemical (MSTDB-TC)[4, 3, 5]. Frozen chemistry was investigated by permuting temperature, free-fluorine and carrier salt mass fractions to see how fission product speciation and their thermochemical properties changed. Free-fluorine and beryllium mass fraction was perturbed to explore the limits that would cause fission product release. Finally, impact of carrier and fuel salt composition was compared by comparing MSRE speciation to that of the MSBR. The results show that frozen chemistry is applicable for a wide range of MSR operation ranges.

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2. BACKGROUND

There are many chemical concepts and reactions that can occur in an MSR. This chapter describes possible chemical phenomenology of interest and approaches to modeling MSR fission product speciation.

2.1. General MSR Chemistry

MSRs are actively being developed by several countries and pursued designs are typically, but not limited to, a solid-fueled liquid-cooled or liquid-fueled liquid cooled design. The MSRE ran from 1965 to 1969 and was of the latter design. The experimental reactor, and the broader research effort book-ending the reactor's operation, provided critical insights from reported observations that reveal the complex chemistry that occurs within an MSR system. Chemical reactions can occur in all aspects of an MSR. Besides the corrosion of metals by the carrier salt, oxidation and reduction of fission products metals continuously occurs in the salt melt from addition of additives that control the free fluorine potential[5]. Fission-product distribution in the MSRE having a large varied distribution across the reactor[8, 12, 9]. For instance, noble metals can plate out across the fuel pipe, the off-gas system and in the graphite moderator[9].

2.1.1. Metal Oxidation and Reduction

Oxidation and reduction reactions involve the exchange of electrons between elements. The exchange of electrons is involved with a reaction energy that may or may not be favorable, known as oxidation and reduction potentials, and is known for many elemental species under standard conditions. The general oxidation-reduction reaction can be expressed as:

$$M^0 \leftrightarrow M^{+}+e^{-} \tag{2.1}$$

Salts, such as LiF, in the liquid phase will be present in their ionic state. While most elements used as carrier salts have fixed elemental oxidation states, the metals used as fuel or form as fission products have multiple stable charge states. The exchange of electrons from salt ions to neutral metal alloy species can cause corrosion of metal piping or plating out of noble metal fission products. These reactions are highly dependent on the chemistry environment that is ever changing due to fission product decay. Therefore, it is unknown to what degree one needs the accuracy for modeling such reactions within an MSR.

2.1.2. Free-Fluorine/Halogen Potential

$$M^{4+} - F_4 \rightarrow M^{3+} - F_3 + F^{-} \rightarrow M^{2+} - F_2 + F^{-} \rightarrow M^{+} - F + F^{-} \tag{2.2}$$

The free halogen potential, or free fluorine potential in this context, refers to the amount of unpaired F^{-} present in the salt melt. Initially, all F^{-} is balanced by cation elements in the fuel and carrier salts. During operation, fuel cation elements decay into lower valent species (i.e., reducing the number of bonds that are available to form with F atoms), creating free F^{-}. This reaction is illustrated in 2.2. The reactions with free fluoride can be predicted through Ellingham diagrams, which plot formation of fluorides based on the free fluorine potential. The presence of free fluorine typically leads to the formation of fluoride corrosion products but can also react with fission products to form fluorides.

$$2Be + 2F^{-} + 2U^{4+} - 8F^{-} \leftrightarrow 2U^{3+} - 6F^{-} + 2Be^{2+} - 4F^{-} \tag{2.3}$$

Uranium fueled reactors use the U^{3+} to U^{4+} as a measure of fluorine potential. As free fluorine forms, the ratio for the two species will decrease (Eq 2.3). A reducing reagent is usually added during reactor operation, Be metal in MSRE, to shift equilibrium of Eq. 2.3 to the right, capturing the free fluorine[12]. As this occurs, the free fluorine reduces and shifts formation of fluoride fission products. Therefore, free fluorine potential could have significant impact on fission product release.

2.1.3. Liquid-Vapor Equilibrium

Liquids are in natural equilibrium with their vapor counterparts, called partial pressures. Each pure liquid substance has a partial pressure. The vapor pressure, and therefore the contents of a vapor phase directly depends on liquid composition. The complexity of an MSR may make it hard to calculate the vapor phase and therefore determine mass transfer to the off-gas system and source term.

2.1.4. Solid Crystallization

Although both fuel and carrier salts will be in a liquid form, it is possible for solid fluorides to form at operational temperatures[12]. Formation of solids could happen in two ways: formation of insoluble products that are dispersed in the carrier salt and raising of the carrier salt melting point through change of their colligative properties. Fluorides of corrosion products can form and will be insoluble at operational temperatures, and can be transported by the liquid salt melt and deposited in different areas of the reactor[12]. Formation of these solids can *lock up* free fluorine as discussed in the previous subsections.

Crystalization in MSRs not only occurs with the formation of insoluble fission and corrosion product fluorides, but also occurs in the the bulk salt melt. Addition of soluble fission products generally increase the melting point of the bulk salt melt[3]. This could promote further crystallization of species to separate out of the melt or to cause pipe clogging. However, to the degree of impact fission products will have on the bulk melt is subject to investigation in this report and the driving thermodynamics for formation of solids competes with the reaction and mass transport rate. This is further discussed in the next topic.

2.1.5. Kinetics and Thermodynamics

$$BeF_2\texttt{(l)+}H_2O\texttt{(l)} \rightarrow Be(OH)_2\texttt{(s)+}2HF\texttt{(g)} \tag{2.4}$$

$$BeF_2\texttt{(g)+}H_2O\texttt{(g)} \rightarrow BeO\texttt{(s)+}2HF\texttt{(g)} \tag{2.5}$$

Generally, thermodynamics refers to the energetic stability of a compound and kinetics refers to the rate at which a reaction occurs. Thermodynamics is often easier to model than kinetics, as the reaction enthalpy between two reactants will be the sum of bond making and bond breaking energies, with the most stable substituent being formed. Kinetics modeling requires additional knowledge of species concentration that participate in a reaction. Although thermodynamics may predict the formation of a compound from two reactants, a product will not form if a reactant mass is carried away at a rate faster than the reaction rate constant. For modeling MSR accident scenarios, where salt melts flow around loops and gases are separated, reactions where the rate constant is considerably less than the mass transport rate can use thermodynamic calculations (i.e. Eq 2.4, $K = 10^{-5}s$)[1]. If the reaction rate constant is beyond the time frame of interest or the mass transfer rate is quicker than than the reaction rate, then the chemical reaction will not need to be considered (i.e. Eq 2.5 $K = 10^{5}s$)[1]. Many chemical reactions will have a rate constant on the order of Eq 2.4, but those that have rate constants larger than the mass transfer coefficient will need to be identified.

2.2. CALculation of PHAse Diagrams (CALPHAD) and the Molten Salt Thermodynamic Database (MSTDB-TC)

Nuclear fuels for LWRs have been previously modeled using the CALculation of PHAse Diagrams (CALPHAD) method. This approach uses databases of Gibbs energy functions to model complex system equilibrium in partner with a GEM[6, 11, 10]. As the name suggests, a GEM minimizes the set of Gibbs energies for an input of species and their masses for thermodynamic equilibrium. Therefore, important kinetics used by this approach may not be captured. However, modeled reactions are limited to those in the database as well as experiments used for fitting. The Molten Salt Thermodynamic Database-Thermochemical (MSTDB-TC) is a database that has been designed to model MSR chemistry and has been used to study corrosion in molten salt fuels[4, 3, 5]. The created MSTDB-TC database captures thermodynamically the reactions described above and continues to be developed to include systems based on community feedback.

2.3. Decay and Radionuclide Inventory Generation

During reactor operation, fuel salts will decay into other elements, naturally. The amount of fission products produced will depend on reactor fuel and reactor operation. The Oak Ridge Isotope GENeration (ORIGEN) module of the Standardized Computer-Analysis for Licensing Evaluation (SCALE) has developed a module to simulate MSRE operation under different power and time conditions for calculation of radionuclide inventory[7].

2.4. LWR Chemistry Modeling

Fission product migration and chemistry for LWRs typically uses physics-based mass transfer formulas. Due to reactor design, locations of key chemical reactions are limited to the core and off-gas system. For reactor systems in which solid fuel is used, fission products are retained in the solid fuel matrix under most conditions. Fission gases that form in the solid fuel and migrate out of the fuel matrix, intact fuel cladding prevents their migration into the reactor coolant.

Fission products, like xenon gas can migrate out of the fuel and enter the off gas system. Because the chemistry is well defined and and occurs instantaneous with regards to time scales used to model nuclear accidents, using approximations like the Antoine equation for vapor pressures are well suited. We call this ”frozen” chemistry and define it in detail in the following section.

2.5. Frozen Chemistry

We define ”frozen chemistry” in this section as to why and where physics based mass transfer and estimates work for capturing LWR chemistry and the criteria needed for it to be applied to MSRs. First, we assume that **fission products are only in trace amounts**. If the mass of a fission product is only present such that it composes of less than 0.01 mole%. At this composition point, fission product species change as a function of temperature. At this concentration, **any changes in fission product species has negligent effect on the bulk carrier and fuel salt**.

Second, **chemical reactions occur on time-scales below or longer than the investigated time-scale**. If the chemical reactions occur below the time scale being analyzed, then reactions will occur instantaneous either at $t = 0$ or between a time step, allowing mass fractions to shift between different classes and/or species. Reactions with rate constants greater than investigated are not needed for consideration. There may be reactions that will occur on the timescale that an accident scenario is investigated. Frozen chemistry will not be applicable in these places and sufficient models will need to be used.

Finally, **fission products do not interact with each other**. Any reactions that occur with fission products will likely be a reaction between the carrier, fuel salt, or any element that will not be in trace concentrations. This assumption is also used in guiding optimization of chemical systems in the MSTDB-TC. Any reaction that would occur would also follow the previous point and result in shifting mass fraction of an element to another class/species.

2.6. Conclusion

This section provided the chemical and mathematical background for MSR chemistry. The defined processes and equations will be investigated and used in the following sections to explore if frozen chemistry can be applied to MSRs.

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3. METHODOLOGY AND ASSUMPTIONS

All chemical analysis was carried out using Thermochimica[11, 10, 6], an open-source GEM. The MSTDB-TC v. 3.0 was used to provide Gibbs energy models for chemical analysis. Coupling Thermochimica with MSTDB-TC has been previously demonstrated to accurately model thermochemical and thermophysical properties of molten salt systems[4, 3, 5]. Three hypotheses were tested through Thermochimica calculations: 1) How does radionuclide inventory change MSR thermochemical properties, 2) Can radionuclide inventories be grouped, and 3) are there chemical conditions that can drive fission product release? Frozen chemistry is deemed to be acceptable if speciation changed independent of fission product concentrations and linearly with the chosen variables.

Radionuclide inventories were generated using an ORIGEN module that was developed by ORNL for simulating the MSRE[7]. A calculation for both 500-day shutdown and 24-hr after start-up for MSRE was carried out and were used as mass inputs for Thermochimica. The 500-day shutdown scenario had the greatest RN inventory changes with time, while the 24hr calculation remained constant. Therefore, the 500-day shutdown inventory was used to investigate how RN speciation evolves with decay while the 24 hr run would be used to test how speciation changes with temperature, beryllium and fluorine content.ORIGEN/SCALE calculations for 4-year operation of a 60-30-10 percent LiF-BeF_2-UF_4 percent MSBR were also carried out.

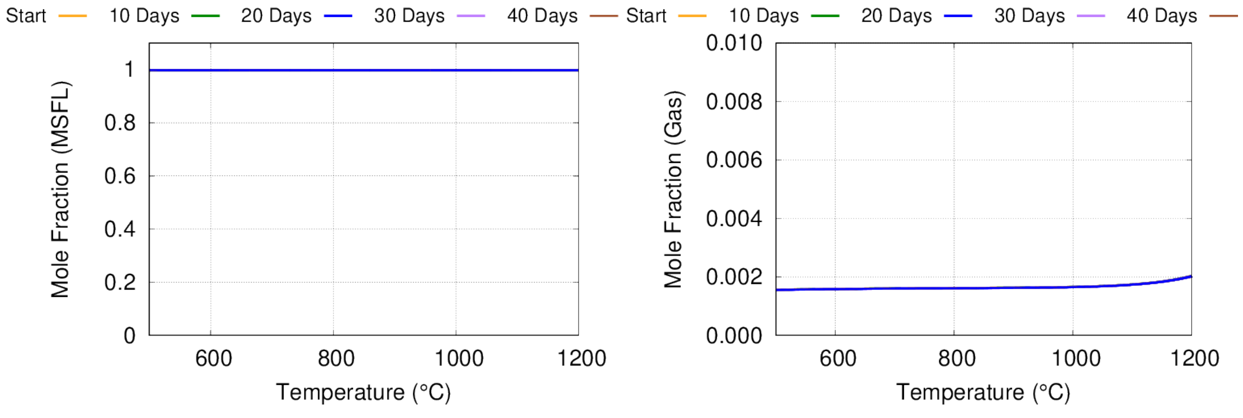
For the first set of calculations, an initial set of Thermochemica calculations using ORIGEN/SCALE calculations directly in Thermochimica as a function of temperature gives a baseline for chemical speciation, but without iodine. A second set of calculations balance excess fluorine by adding beryllium and chromium. One mole of iodine was then added to analyze fluorine-iodine equilibrium as a function of temperature. Finally, different fission product grouping and inventories were tested. Although the MSTDB-TC contains many salt systems, not all possible MSR applicable systems are available. System substitution assumptions were made for Eu, Hf, Mo, Np, Sm and Pm. fission products less than 10 g was assumed to be negligible for thermophysical changes. Ce and Nd masses had the greatest changes, and thus variation of those elements was first tested with varying elemental groupings. Temperature was varied from 350 °C to 1300 °C in 10 °C increments.

The second set of calculations holds radionuclide inventory constant. First, phase change and species vapor pressures are plotted as a function of beryllium and fluorine mass fraction at 650 °C. Second, similar calculations were carried out varying fluorine mass fraction and temperature from 350 °C to 1300 °C in 10 °C increments. All sets were calculated first without an iodine inventory, then with one mol of iodine added to investigate affects of iodine-fluorine equilibrium to chemical speciation.

The third set of calculations compared solid, liquid and vapor compounds of MSRE to MSBR to compare how carrier and fuel salt speciation. Vapor pressures for both systems were also compared.

4. ASSESSMENT OF FROZEN CHEMISTRY APPROXIMATION

4.1. Baseline Results



(a) (b)

Figure 4-1. The mol fraction of a) the molten salt phase and b) the gas phase as a function of temperature for the MSRE 500 days after shut down.

Using straight MSRE SCALE results as Thermochimica inputs results in the formation of two stable phases, the molten salt fluoride liquid phase (MSFL) and the gas phase above 500 °C. Solid state phases exist below 500 °C, with thirteen solid state phases forming at 350 °C. The mol fractions of the liquid and gas phases are presented in Figure 4-1. The largest changes occur as temperature change, exchanging mass between the salt melt and the vapor phase. Gas phase analysis shows that as much as 99 percent of the composition is F_2 (Figure 4-2). This occurs because depletion of U^{4+} to lower valent elements (3+, 2+, 1+) causes the free-fluorine to become a non-negligible mass fraction. At the point where all metals have been oxidized to their highest valent state, the excess fluorine is placed in the gas phase. Solid Be was added during MSRE operation to control the free fluorine potential and was not accounted for in the mass fraction. The next section evaluates how balancing excess free-fluorine with a metal affects chemical speciation.

4.2. Balancing Uranium Decay with Be and Cr Additions

Excess fluorine was balanced in the calculations by adding 1,491 mol of Be. It is assumed that added chromium will go in to a 3+ oxidation state, so fluorine was balanced with the addition of 994 mol chromium. The changing inventory during the 500 days changes the oxidation state balance

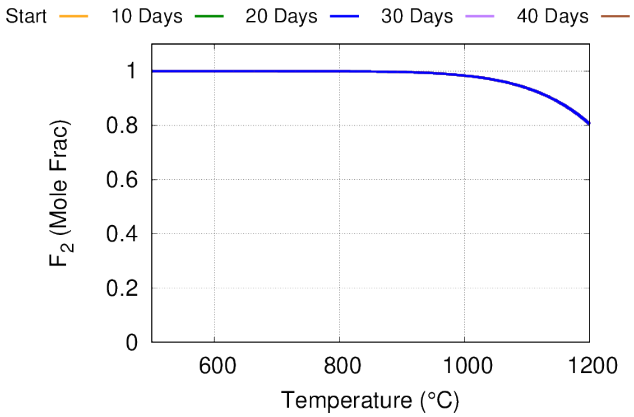


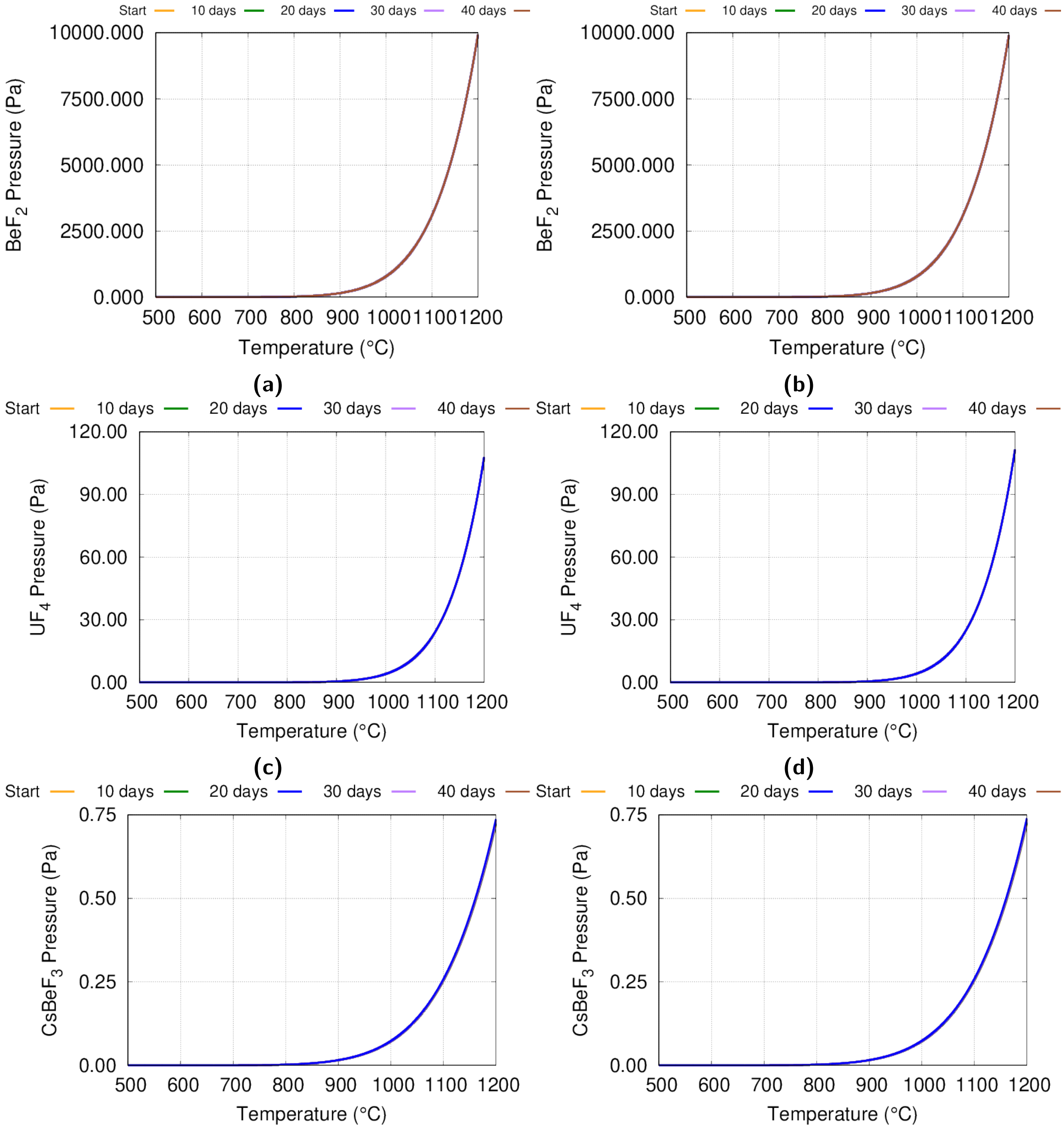
Figure 4-2. The mole fraction of F_2 as a function of temperature for the MSRE 500 days after shutdown.

with the production of radionuclides like Nd^{3+}. In order to keep the fluorine potential near zero, Be and Cr was proportionally balanced for each 10 day time step. Both calculations resulted in loss of the gas phase.

The addition of either Cr or Be results in similar vapor pressures for BeF_2 (Figure 4-3a and 4-3b). This is likewise for UF_4 (Figure 4-3c and 4-3d). Differences occur when looking at the secondary chemical property U^3/U^{4+}. Cr balanced calculations show small changes in the oxidation ratio with respect to temperature (Figure 4-4b), similar to vapor pressure changes. Be balanced calculations show that U^{3+}/U^{4+} changes not with temperature, but with fission product decay (Figure 4-4a). This result matches observations from the MSRE. Cr and Be additions show different results because Cr and U^{3+} were assumed to be minor constituents during MSTDB-TC development and does not contain any CrF_x-UF_3 models. Therefore, addition of Cr would have only minor affect on U^{3+}/U^{4+}. This will result in differences for modeling iodine.

One mole of iodine was added to both salt systems. The addition of iodine does not change vapor pressures for any of the fluorine species, with no changes in BeF_2 or $CsBeF_3$ vapor pressures. Both systems do differ in the dominant iodine species. LiI is the dominant species for Be balanced systems, while I_2 is dominant for Cr added. Again, the available database models explain the differences between dominant iodine species. Cr does not have any iodine systems implemented in our used version of MSTDB-TC, but it contains the BeF_2-BeI_2 pseudo binary. There is therefore a chemical mechanism that influences iodine equilibrium. For the Cr balanced system, all excess fluorine coordinates with Cr and does not have an iodine model to affect speciation. Since the added iodine does not have a cation to coordinate to and fluorine has greater electronegativity than iodine, iodine does not coordinate with any cation and forms I_2.

In this section, we have shown that it is essential to balance the free-fluorine and carrier salt masses in order to properly model MSR speciation. The choice of element used for balancing free-fluorine formation changes the results and depends on the systems implemented in MSTDB-TC. Although the choice of either Be or Cr did not affect properties like melting point or fluoride vapor pressures, it did affect modeling of U^{3+}/U^{4+} and iodine vapor pressures. This is because Be is a major constituent in the MSRE and is reflected in the database makeup, while Cr is expected to be a minor constituent with corrosion products forming. These considerations should be kept in kind when



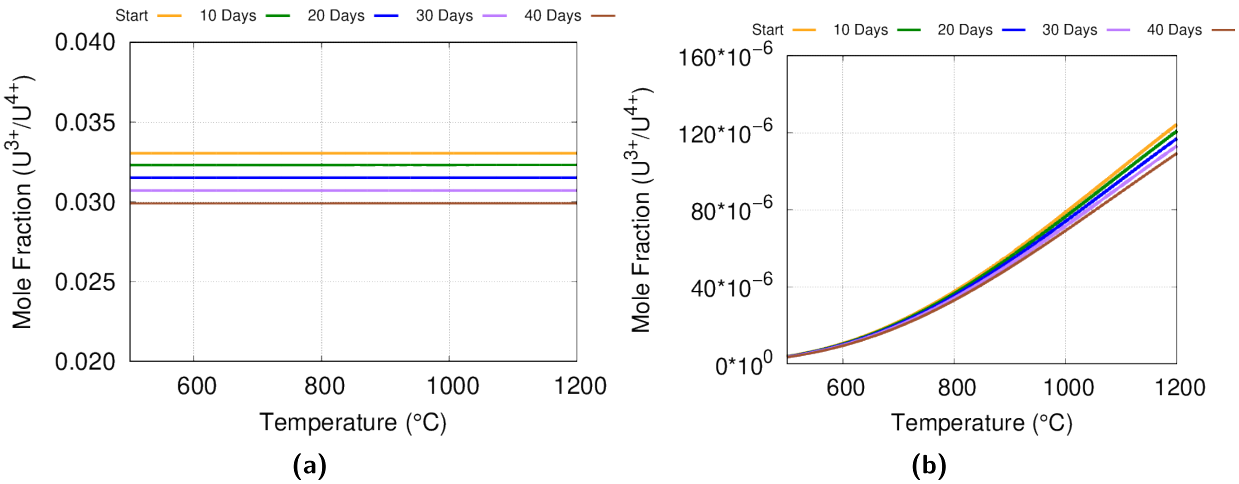
(a) (b)

(c) (d)

(e) (f)

Figure 4-3. Partial pressures for a-b) BeF_2, c-d) UF_4 and e-f) $CsBeF_3$ for a,c,e) Be and b,d,f) Cr.

modeling molten salt speciation. The results also showed that vapor pressures and phase changes were largely independent of radionuclide mass changes, showing that temperature is the primary driver.



(a) (b)

Figure 4-4. Different U^{3+}/U^{4+} profiles occur for c) Be and d) Cr addition

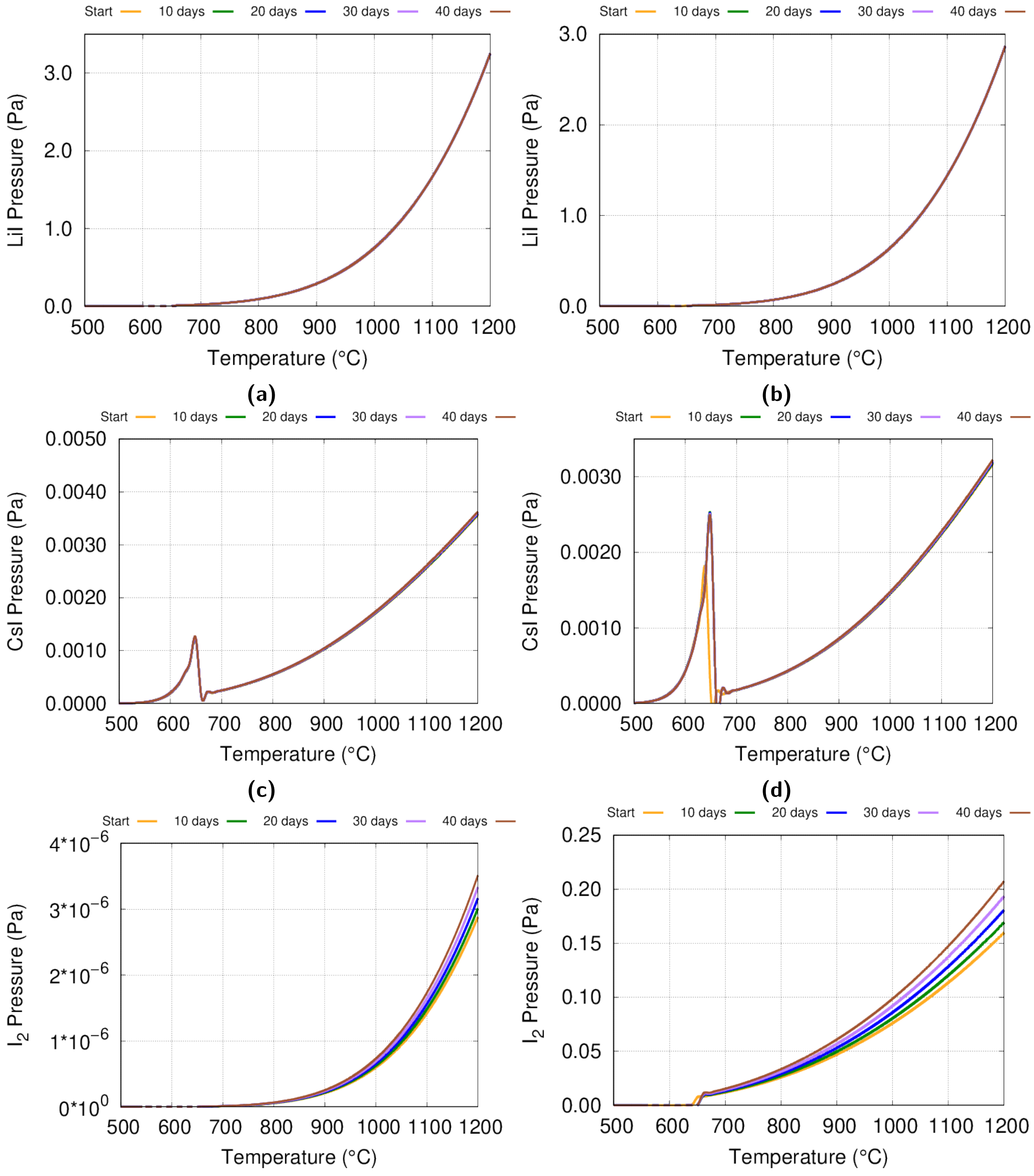
4.3. MSR Phases as a Function of Elemental Grouping

In order to simplify calculations in MELCOR, representative classes are set, then propagated through the system. For instance, CeF_3 may be used to to represent the mass transport of LaF_3, EuF_3 and NdF_3. This is the foundation of MELCOR's class system. We therefore explore how combining and reducing mass inventory. Although our mass inventory now differs, we again ensure that the free fluorine potential remains as close to zero as possible (Figure 4-6) but only performed calculations using Be to balance fluorine. The calculated partial pressures for BeF_2, UF_4, $CsBeF_3$ and LiI are presented in Figure 4-7. Vapor pressures are nearly the same, except for the slightly higher vapor pressure from $CsBeF_3$ from adding proportional Rb mass to Cs. Therefore, modeled vapor pressures for fluoride species are not likely to change with small mass permutations with respect to the carrier salt. These results indicate that grouping radionuclides into chemical classes, when done correctly, will have a minimal impact on modeling MSR chemical speciation.

4.4. Conclusion

In this chapter, we reviewed how elemental inventories change vapor pressures for important species in an MSRE radionuclide inventory for 500 days after shut down. The results showed that the depletion of uranium into lower valent elements creates excess free fluorine that is then pushed into the vapor phase. Compensating excess fluorine with another element, Be or Cr, eliminated the vapor phase, but had similar vapor pressures for fluoride species. However, vapor pressures differed for iodine species. Simplifying elemental inventory had little effect on vapor pressures. Overall, the results suggest that phase and vapor pressures change little with radionuclide inventory, but are strongly temperature dependent.

The results point to the sensitivities of vapor pressure calculations to models implemented in MSTDB-TC. Fluorine species vapor pressures were not sensitive to changing fission product inventory because masses of fluoride carrier salts are much greater than the evolving fission products.



(a) (b) (c) (d) (e) (f)

Figure 4-5. Partial pressures for a-b) LiI, c-d) CsI and e-f) I_2 for a,c,e) Be and b,d,f) Cr.

Therefore, it would take a significant amount of fission products to shift fluorine equilibrium. However, iodine masses are significantly less than fluorine and small changes in fission products can have large changes on the iodine equilibrium. However, this may change as MSTDB-TC adds additional iodine species, particularly those corresponding to fuel and carrier salts. The results

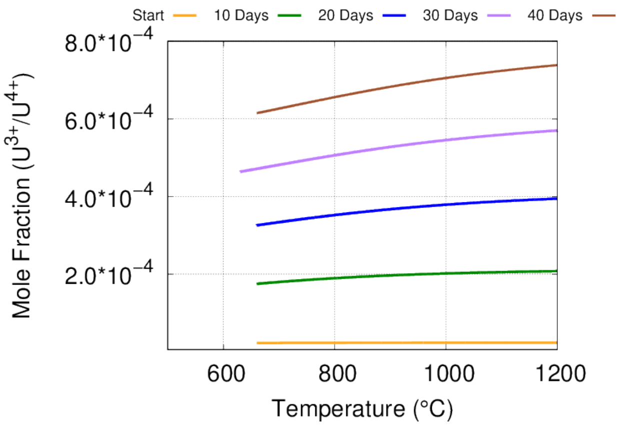
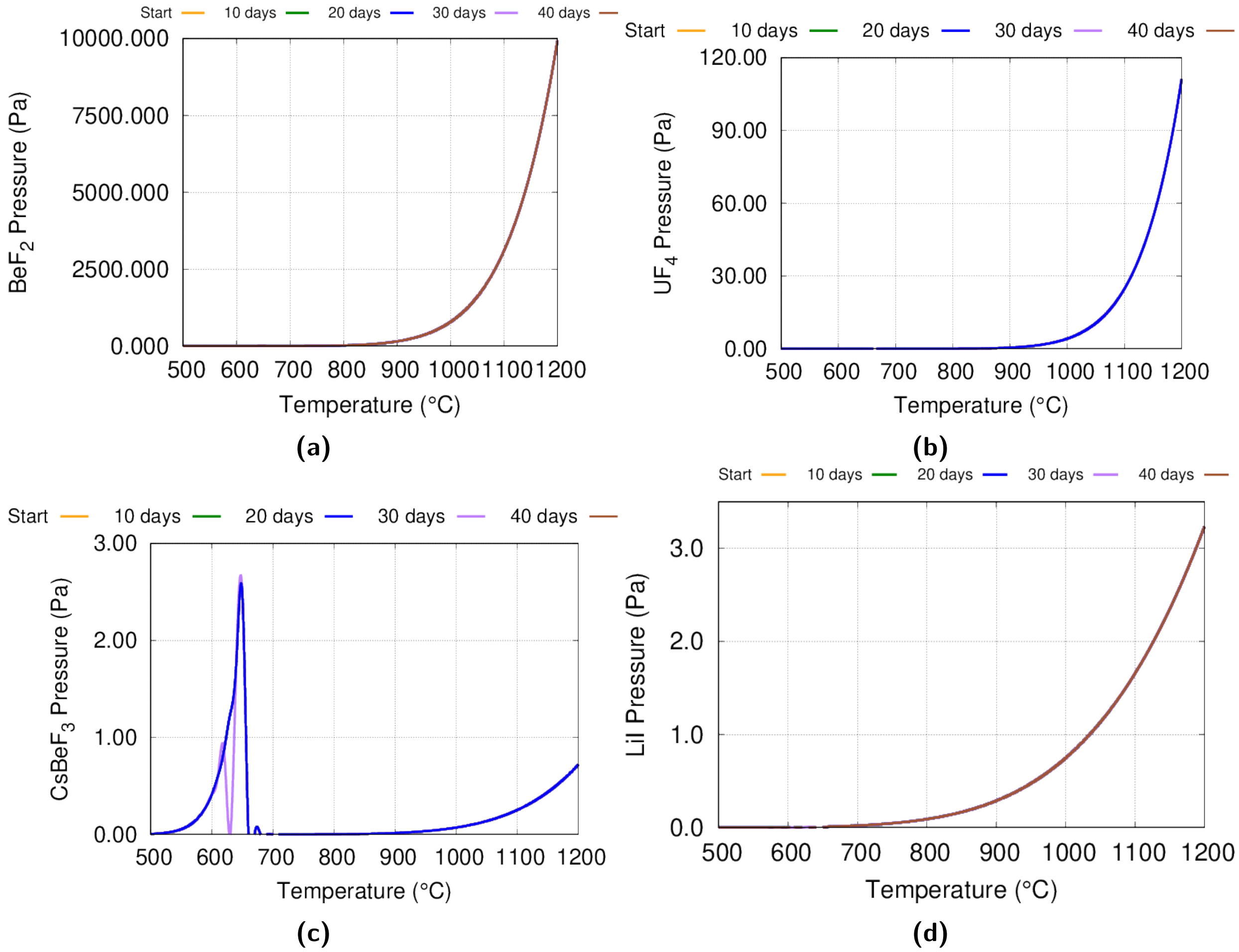


Figure 4-6. U^{3+}/U^{4+} profile for the simplified inventory calculation.



(a) (b)

(c) (d)

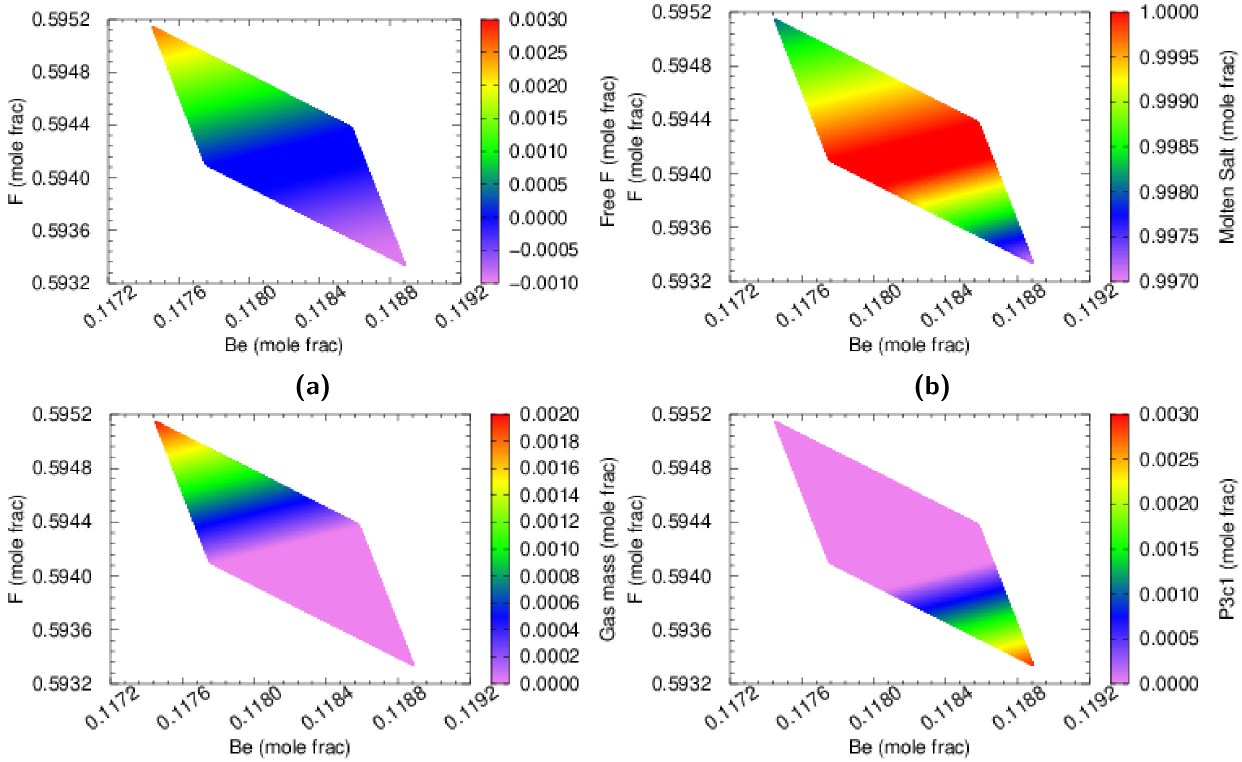
Figure 4-7. Partial pressures for a) BeF_2, b) UF_4, c) $CsBeF_3$ and d) LiI for the simplified radionuclide inventory.

suggest that those modeling MSR speciation using MSTDB-TC should be aware of what elements are being perturbed and the available corresponding models.

5. TWO PARAMETER TESTING

In this chapter, we freeze time and radionuclide inventory to see how species change with three major variables: fluorine, beryllium (oxidizing agent) and temperature. Like in the previous section, we investigate the parameters with and without iodine in order to investigate it's effect on species equilibrium.

5.1. Fluorine vs Beryllium at Constant Temperature



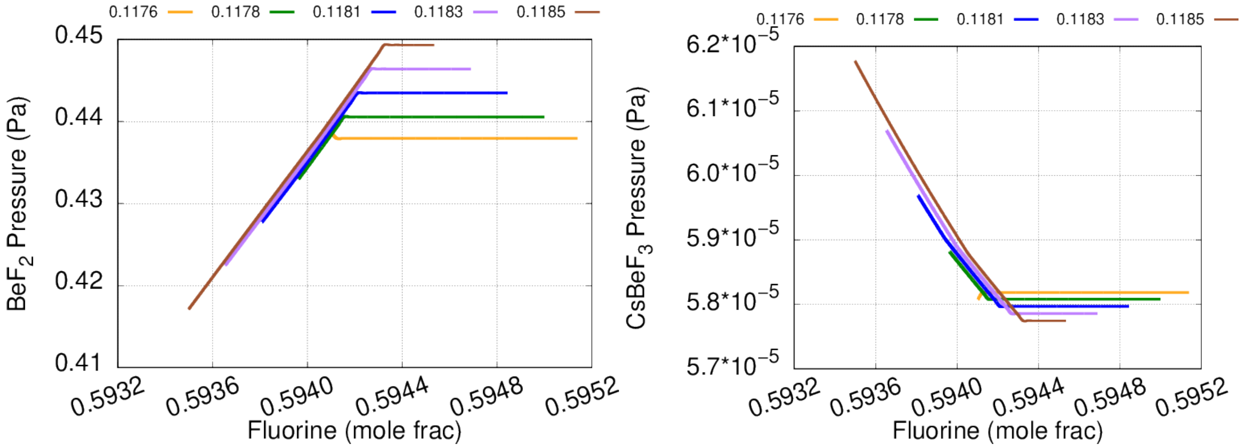
(a) (b) (c) (d)

Figure 5-1. Plots for beryllium vs fluorine for a) free fluorine, b) molten salt fluid liquid phase, c) gas phase, and d) solid P3c1 phase that contains M^{3+} metals such as U, Pu and La.

Plots for phase changes as a function of fluorine and beryllium held at 650 °C are presented in Figure 5-1. All plots are rhomboidal where the upper triangular is fluorine rich and the lower triangular is fluorine depleted. The diagonal of the graph is where beryllium is equal to fluorine and the free fluorine potential is equal to zero (Figure 5-1a). The lower diagonal is less sensitive, because multivalent metals, such as uranium, reduce to higher valent states to balance the fluorine.

Eventually, all metals have been reduced and the free fluorine mass fraction decreases to less than zero.

The free fluorine mass fraction shows a close relationship to the three dominant phases in the system: the MSFL, the gas and the solid P3c1 phase. Figure 5-1b shows that the molten salt melt phase remains dominate in excess or the depleted free fluorine conditions. The lowest mass fraction for the molten salt melt is 0.997. Therefore, the molten salt phase will still be the dominate phase, provided that the temperature remains sufficiently above the melt temperature.



(a) **(b)**

Figure 5-2. Vapor pressures for a) BeF_2 and b) $CsBeF_3$ as a function of fluorine mass fraction for different beryllium fraction.

Figures 5-1c and 5-1d show how the upper and lower triangular for free-fluorine affect the phase formation. A gas phase is produced when excess fluorine is present, consisting primarily of F_2, as seen in the previous section. The lower diagonal produces a dominant P3c1 solid phase. As fluorine is removed, the metals reduce to lower valent state. Eventually, fluorine is sufficiently depleted that a solid phase is formed containing uranium, plutonium and lanthanum (P3c1).

Vapor pressures for BeF_2 and $CsBeF_3$, shown in Figure 5-2, show that at a constant temperature, vapor pressures change little across chemical space, unlike phase changes. BeF_2 shows small vapor phase change with variation of 0.01 Pa, decreasing in the fluorine deficient lower half and increasing slightly in the upper half. There is not a detectable change in $CsBeF_3$, likely because Cs mass is held constant for these sets of calculations.

All iodine enters the gas phase at the diagonal where the iodine mass fraction is equal to the free fluorine mass fraction. The dominant species at this point is I_2 (Figure 5-5b). I_2 partial pressure decreases as fluorine increases not because the mass of iodine in the gas phrase decreases, but because the mass fraction of iodine in the gas phase decreases quickly due to the formation of fluorine in the gas phase. The results yield an important limit for iodine release in MSRs: the inventory of iodine in a salt melt will be released when the mass fraction of excess fluorine is equal to the mass fraction of iodine. However, this limit is likely not to be reached in operating MSRs. The mass of free fluorine required to saturate the system is equivalent to thousands of kilograms, an unrealistic amount. MSRs are not likely to come close to this limit because of fluorine control

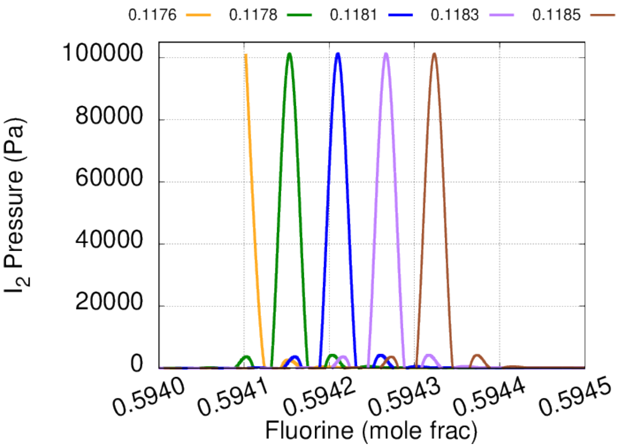


Figure 5-3. I_2 **vapor pressures for different Be mass fractions.**

practices and fluorine reaction with other constituents not modeled in these calculations, like corrosion products. Nonetheless, this is an important hypotheitcal limit.

5.2. Fluorine Mass vs Temperature with Constant Fission Product Masses

This section investigates how fluorine and temperature affect both phase and equilibrium partial pressures for dominant cesium and iodine species. Temperature is plotted for 700 °C to 1200 °C in °C increments, which was chosen to remove solid formation at the low temperature range. Figure 5-4 shows how the free fluorine, molten salt, gas and P3c1 mass fraction change with temperature and fluorine mass fraction. Speciation is sensitive to fluorine mass fraction when cation mass is held constant, changing phases in smaller increments than when balanced by beryllium. Figure 5-4a shows that the temperature of the salt mixture has no demonstrable affect on free fluorine, only being a function of the mass fraction. Likewise, fluorine mass fraction is now the dominant driver for phase changes. Mass fraction for the molten salt phase decreases when either gas or P3c1 phase forms. The P3c1 phase has temperature dependence, as increased mass presence requires higher temperatures to full melt the solid. Temperature dependence only appears when excess fluorine appears.

Figure 5-5 shows the vapor pressure of BeF_2 and $CsBeF_3$ as a function of fluorine mass fraction and temperature. Both species show no affect to fluorine mass fraction, but only changes as a function of temperature. This is because the addition of fluorine changes the oxidation states of the multi-valent metals, seen in the fraction of U^{3+}/U^{4+}. It forms F_2 after fluorine saturation.

However, the vapor pressure for fluorides are not perturbed, as seen in $CsBeF_3$ (Figure 5-6b). Iodine vapor pressures show that there is fluorine dependent speciation. LiI dominates in the fluorine depleted region and has only temperature dependency for the vapor pressure (Figure 5-6a). At the fluorine saturation limit, Lii starts to decrease with fluorine mass fraction and I_2 increases. When free fluorine mass equals iodine, all iodine enters the vapor phase as I_2 (Figure 5-6d), similar

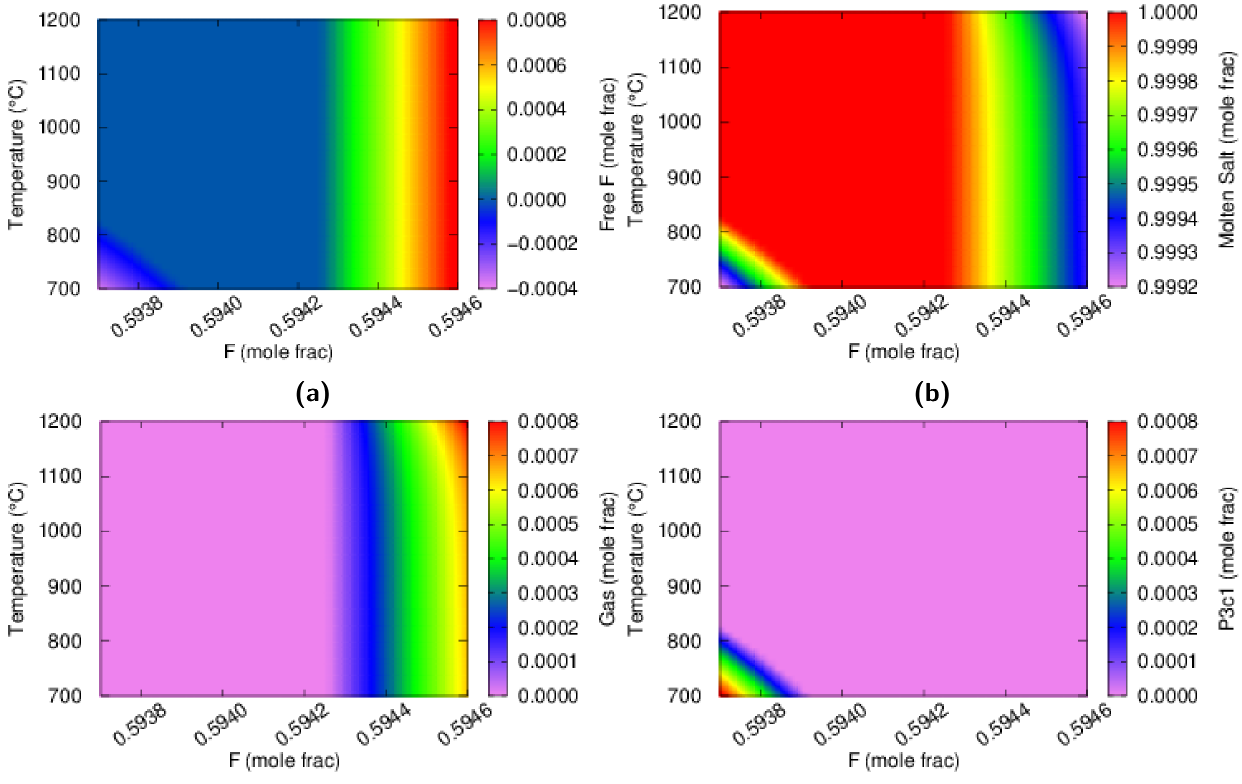


Figure 5-4. Plots for fluorine vs temperature for a) free fluorine, b) molten salt phase, c) gas phase, and d) solid P3c1 phase that contains M^{3+} metals such as U, Pu and La.

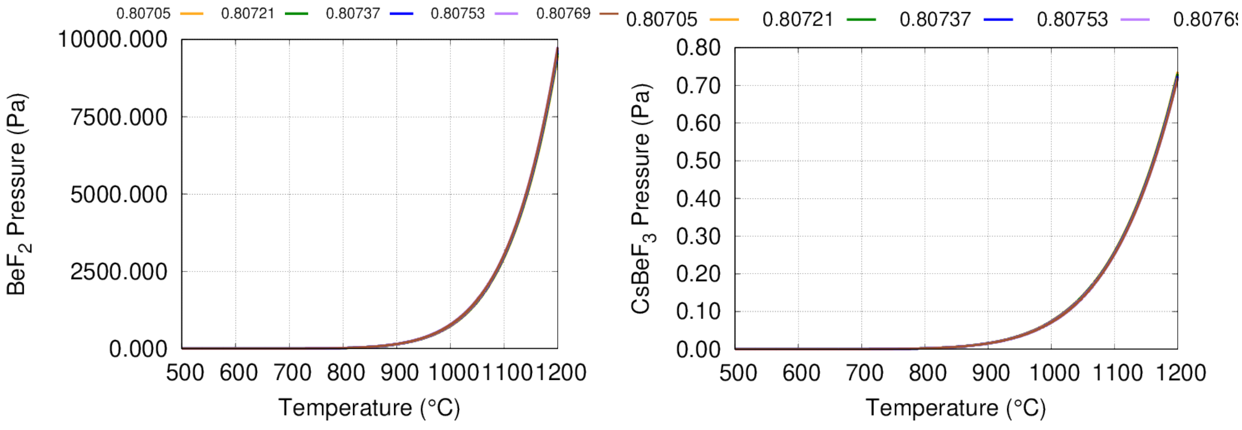
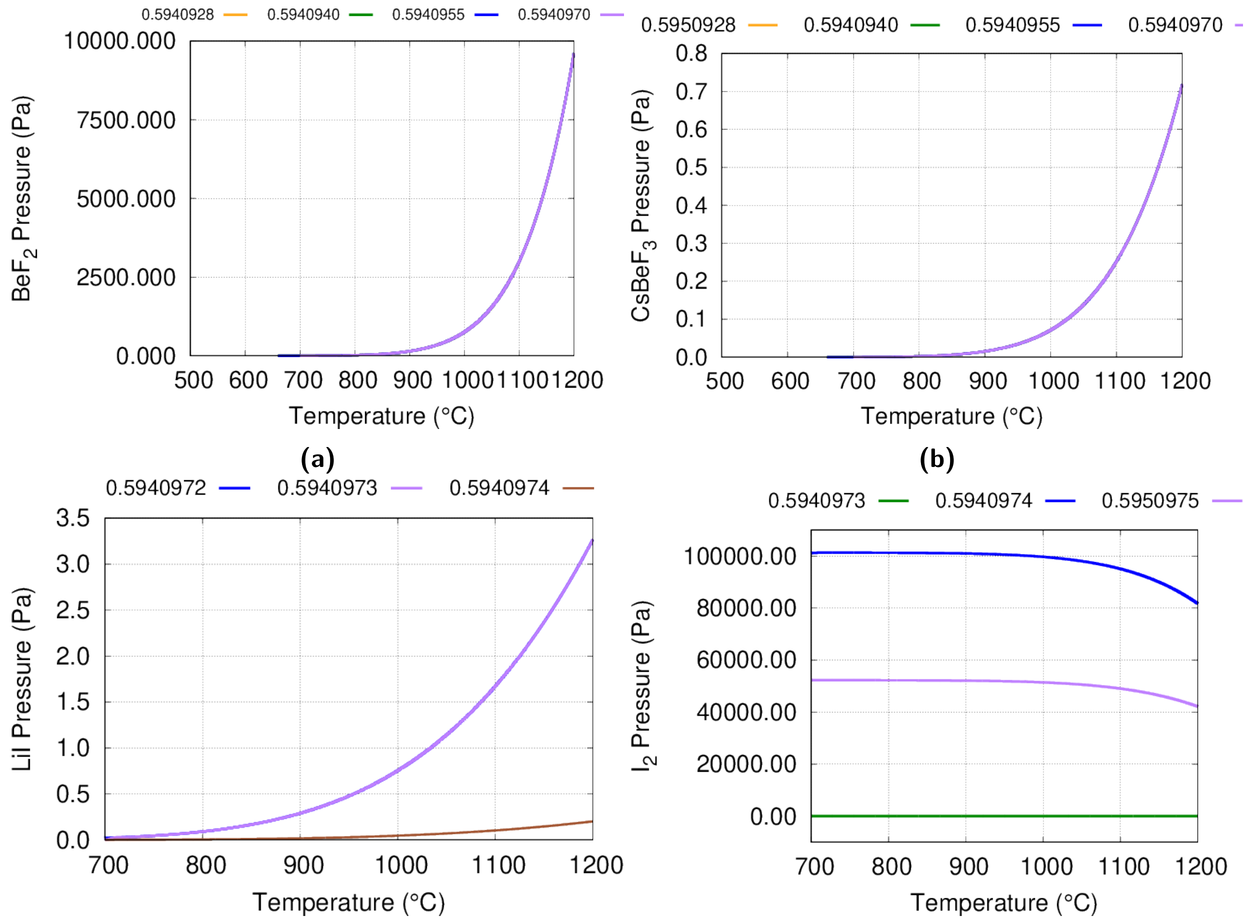


Figure 5-5. Vapor pressures for a) BeF_2 and b) $CsBeF_3$ as a function of temperature for different fluorine mass fractions.

to what was seen in the Be vs F calculations. This, again, yields a limit should be noted for severe accidents.



(a) (b)

(c) (d)

Figure 5-6. Vapor pressures for a) BeF$_2$, b) CsBeF$_3$, c) LiI and d) I$_2$ as a function of temperature for different fluorine mass fractions.

5.3. Conclusion

This chapter explored how phase and vapor species changed with fluorine and beryllium mass fractions, and with temperature. The results showed that the molten salt liquid phase is stable in fluoride depleted states to the ability to reduce multi-valent metals to lower charged states, balancing the reduced fluorine mass content. Eventually, the system becomes too depleted and forms the dominant P3c1 solid mixture that contains 3+ valent metals. The fluorine rich system produces a gas phase of F$_2$, similar to the previous chapter. Fluorine vapor pressures were shown to be independent of beryllium and fluorine mass fractions. However, iodine was shown to have mass fraction dependency, with I$_2$ entering the gas phase when free-fluorine mass fraction equals iodine mass fraction.

Plotting fluorine verses mass fraction shows that phases are free fluorine dependent near the saturation point , with little temperature dependency. Phases become both temperature and free fluorine dependency at the lower fraction. Fluorine vapor pressures were shown to be only temperature dependent, having no dependency on fluorine mass fraction. Iodine vapor species were found to have fluoride dependent dominant species. At low fluorine content, LiI dominated and had only a temperature dependency. A complex equilibrium between LiI and I_2 was shown near the fluoride saturation point, at which, all iodine entered the gas phase as I_2.

These results provide a crucial understanding with regards to fission product species vapor pressures. Fluoride species are largely mass independent, having only temperature dependency, indicating that chemical changes would likely not lead to a release to a fluoride species. However, iodine was shown to have predicted species dependent on the fluorine mass fraction, where all iodine mass will enter the gas phase when the free fluorine mass fraction equals the iodine mass fraction. This is not likely to occur as the mass of free fluorine iodine would need to be quite large and would be mitigated by oxidation control measures or react to form species like corrosion products.

6. EVALUATION OF FISSION PRODUCT SPECIATION FOR DIFFERENT CARRIER AND FUEL SALT COMPOSITIONS

We have explored in the previous chapters how mass composition does and does not change chemical properties of the molten salt melt. The results have shown that changes to carrier salt mass fractions can affect speciation, implying that the largest change to speciation will come from differences in carrier and fuel salt composition. We compare the previous MSRE Thermochimica calculations to a four year inventory of a 60-30-10 percent composition of LiF-BeF_2-UF_4 fuel for an MSBR.

6.1. Fission Product Speciation for MSRE and MSBR

Table 6-1. Mass fraction of different elements in the MSRE and MSBR calculations.

Element	MSRE	MSBR
Ce	$8.80 \cdot 10^{-6}$	$1.48 \cdot 10^{-4}$
Cs	$3.85 \cdot 10^{-6}$	$6.32 \cdot 10^{-4}$
I	$7.43 \cdot 10^{-4}$	$6.22 \cdot 10^{-8}$
La	$3.00 \cdot 10^{-6}$	$2.67 \cdot 10^{-5}$
Nd	$1.09 \cdot 10^{-5}$	$1.75 \cdot 10^{-4}$
Pu	$8.88 \cdot 10^{-6}$	$4.04 \cdot 10^{-4}$
Rb	$1.11 \cdot 10^{-6}$	$1.53 \cdot 10^{-7}$
Y	$2.36 \cdot 10^{-6}$	$9.22 \cdot 10^{-6}$
Zr	$2.02 \cdot 10^{-2}$	$2.10 \cdot 10^{-4}$
F	0.59	0.61
Li	0.26	0.23
Be	0.19	0.12
U	$3.09 \cdot 10^{-3}$	$3.71 \cdot 10^{-2}$

The mass for both MSRE and MSBR are presented in Appendix A and B. First pass will show that the mass input for MSBR is significantly higher than MSRE. The mass fractions for key fission products are listed in Table 6-1 and show that the metal fission product mass fraction is higher in MSBR than MSRE. However, MSRE has higher mass fractions for iodine and zirconium, the latter due to the use of ZrF_4 as a carrier salt.

Thermochimica calculations for MSRE and MSBR at 350 °C are presented in Table 6-2. There is no liquid state at this temperature and all elements are present in a solid speciation. Although the mass for each species differs, the species overlap with each other, with the exception of the two

Table 6-2. Solid species and solid solutions calculated by Thermochimica for MSRE and MSBR at 350 °C. SS denotes that it is a solid solution.

MSRE	MSBR
P3c1 (SS)	P3c1 (SS)
FM3M (SS)	FM3M (SS)
Li_2BeF_4	Li_2BeF_4
Li_2ZrF_6	Li_2ZrF_6
BeF_2	BeF_2
LiU_4F17	LiU_4F17
NdF_3	NdF_3
$CsBe_2F_5$	$CsBe_2F_5$
$LiYF_4$	$LiYF_4$
SrF2	
$LiBaF_3$	

rubidium-plutonium fluorides. MSRE also contains Sr, Ba and Pr compounds that are not present in MSBR because those elements were incorporated into other elements in the calculation.

Table 6-3. Top vapor pressures in Pa calculated by Thermochimica for MSRE and MSBR at 1,000 °C.

Species	MSRE	MSBR
BeF_2	780	1,009
$LiBeF_3$	83	89
LiF	11	9
$LiUF_5$	0.22	1.72
Li_2ZrF_6	1.01	$1.22 \cdot 10^{-2}$
UF_4	4.04	39
ZrF_4	790	14

Vapor pressures for species at 1000 °C are presented in Table 6-3 and show the differences between the vapor pressures. MSBR has higher vapor pressure for beryllium and uranium species while MSRE has higher vapor pressure species for Zr species. This shows that the largest vapor species will be of the carrier and fuel salts. Vapor pressures for the top iodine and cesium species are also in Figure 6-1. Like in the previous section, the top species contains elements of the carrier salt, $CsBeF_3$ and LiI, although the vapor pressures are significantly smaller than the carrier and fuel salt vapor pressures.

6.2. Conclusion

We have investigated in this chapter how fuel and carrier salt composition changes speciation of properties for two FLiBe based MSRs, MSRE and MSBr. Although the radionuclide mass fraction differs between the two reactor fuels, they show similar speciation for both solid and vapor phases. Vapor pressures were shown to largely depend on the carrier and fuel salt mass fraction,

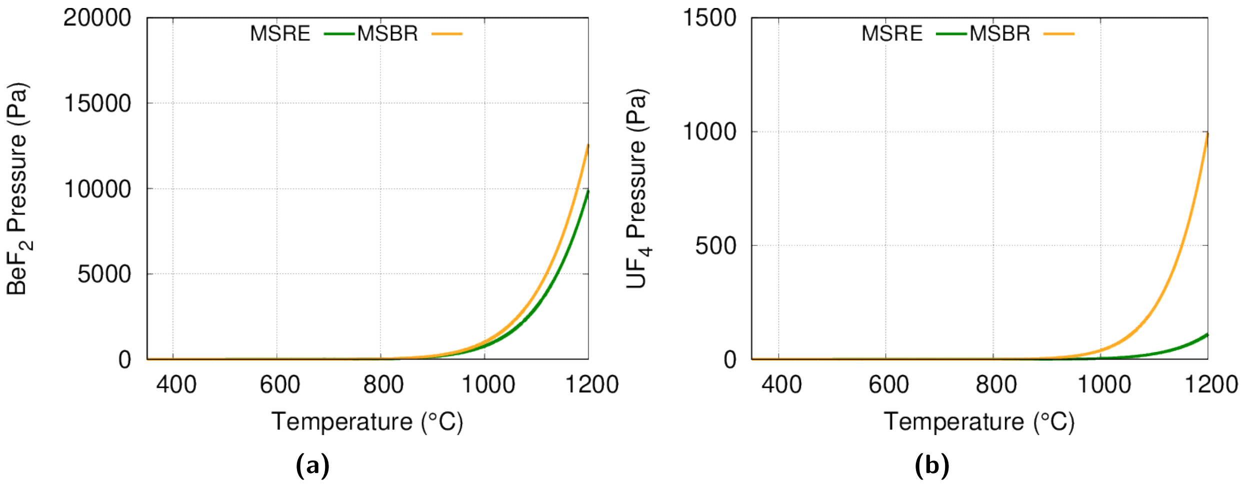


Figure 6-1. Vapor pressures for a) BeF_2 and b) UF_4 for MSRE and MSBR systems.

having different temperature profiles. This shows that although speciation overlaps between reactor carrier/fuel compositions, they will likely have different mass transfer rates, specifically for the vapor phase.

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7. DISCUSSION

This report contains three sections that discusses how MSR properties change with respect to radionuclide inventory. It is discussed in the context of fission product decay, operation parameters (fluorine, beryllium and temperature changes) and in carrier/fuel salt compositions. The results have shown that small mass fraction changes from fission product decay does not change speciation or vapor pressures. Temperature was shown to be the primary driver for speciation changes, specifically for vapor pressures. Carrier and fuel salt composition were also shown to effect speciation and vapor pressures. The following is a discussion of modeling MSR chemistry in context of the results.

7.1. Applicability of Frozen Chemistry

The concept of frozen chemistry was outlined in Section 2.5. Frozen chemistry is applicable if mass change has little effect on macroscopic properties. The results in Chapter 4 verified our assumptions that mass changes less than 0.01 mole % do not change macroscopic properties, such as a melting point and vapor pressures. Large mass fraction changes, those greater than 0.01 mole % can and do change system properties (Chapters 5 and 6). This shows that we can pre-set mass transfer coefficients and vapor pressure correlations for a known fuel and carrier composition.

One major assumption that is not answered in this report is that of kinetics. A major assumption in the use of frozen chemistry is that the kinetic rate constant for species formation is much quicker than the time-step being investigated. This means that any mass change instantaneously forms the thermodynamic product. To that, additional research will need to be carried out. As long as the reaction rate constant is quicker than the evaluated time-step, frozen chemistry can be used for a given carrier and fuel salt composition.

7.2. Insights into Speciation Variation with Varying Salt Composition

Chapter 6 looked at the speciation differences between MSRE and MSBR fuel compositions. Although both systems are FLiBe based, the two reactors differ by their contents of Zr (in the form of ZrF_4 in MSRE) and UF_4 (0.9% verses 10%). Speciation was found to be similar, demonstrating that set species classes can be set amongst carrier and fuel salt compositions.

Although speciation is similar between MSRE and MSBR for all phases, melting point and vapor pressures differed between the two systems, entailing that fitted parameters, such as Antoine coefficients, should be reassessed for differing carrier and fuel salt compositions. Temperature was again was shown to be the primary driver for vapor pressure.

7.3. Dependence on MSTDB-TC Models

This investigation used the MSTDB-TC as the basis for species determination. Therfore, all results are strongly tied to systems implemented in the database. The database has a comprehensive set of pseudo-binary fluorides, the list of possible species is not exhaustive. Although the database contains many binary and ternary compounds and it is possible that higher order species can form or that dilute species (i.e. fission products) may be incorporated as defects into other solid crystals. Such incorporation would be present in the form of solid-solutions, of which MSTDB-TC includes many examples, such as the actinide/lanthanide P3c1 solid-solution, but again, is not exhaustive. Due to the complex nature of solid-reformation of salt melt with fission products, it can be assessed that MSRs behave ideally at higher temperatures, and need to be investigated more at the lower temperature.

MSTDB-TC is constantly adding additional models. The version used here is 3.0 and in the process released 3.1 that includes additional iodine models. Inclusion of additional models may change the representative species, though will likely not change the conclusions found here in this report.

8. CONCLUSION

We present here a computational study of FP speciation in molten salts to validate usage of frozen chemistry for severe nuclear accidents for MSRs. Fission product inventory was calculated for two MSRE operation scenarios using the SCALE computational program, which was then used as input to determine speciation using Thermochimica coupled to the MSTDB-TC. Elemental grouping, fluorine/beryllium mass and temperature sensitivity was tested, in addition to comparing MSRE and MSBR speciation.

The results showed that speciation was invariant to radionuclide inventory change and that fluorine species are invariant to chemical changes. However, iodine species were found to be more sensitive to inventory changes due to the much smaller mass fractions in the melt. However, this may change as MSTDB-TC adds additional iodine species, particularly those corresponding to fuel and carrier salts. The results suggest that those modeling MSR speciation using MSTDB-TC should be aware of what elements are being perturbed and the available corresponding models.

Changing the mass fraction of beryllium and fluorine can change the phase fraction at a given temperature. Solid solution can form when fluorine is depleted and fluorine gas forms in an excess fluorine environment. However, fluorine species vapor pressures are invariant. Iodine, again, is more sensitive to large changes. All iodine enters the vapor phase when the system is saturated and iodine cannot coordinate with any cations. Before this limit, iodine obeys primarily temperature dependent behavior.

Finally, speciation and vapor pressure curves for MSRE were compared to MSBR and showed that speciation is similar for both systems. However, there were differences in the vapor pressure curves. This suggests that vapor pressure species and coefficients will need to be reconfigured for a given carrier/fuel salt composition.

The general assumptions required to use frozen chemistry for MSRs were generally shown to hold. The primary drivers for changes were temperature and carrier/fuel salt initial composition. Generalized mass transfer formulas and parameters can be determined given these conditions.

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APPENDIX A. MSRE Thermochimica Input

```
! Initialize variables:
pressure = 1
temperature = 350.000000
mass(9) = 800263.0831199999
mass(3) = 354339.9210000000
mass(4) = 160125.645740
mass(94) = 11.9549
mass(58) = 10.330835
mass(55) = 5.066967
mass(56) = 4.317625
mass(57) = 4.04479
mass(59) = 3.400260
mass(38) = 5.592418
mass(39) = 3.184940
mass(37) = 1.50494
mass(24) = 0.036538
mass(60) = 13.357739
mass(40) = 27256.917
mass(92) = 4152.939

temperature unit = C
pressure unit = atm
mass unit = mol
data file = MSTDB-TC-V3.0-Fluorides.dat
```

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APPENDIX B. MSBR Thermochimica Input

```
Initialize variables:
pressure = 1
temperature = 350.000000
mass(3) = 1122203.481
mass(9) = 2960473.684
mass(60) = 845.3889585
mass(94) = 1947.474275
mass(58) = 716.1751760000000
mass(55) = 30.47404
mass(4) = 555219.3372000001
mass(53) = 0.304967162
mass(57) = 128.8135211
mass(37) = 0.738473207
mass(92) = 179081.6862
mass(39) = 44.43825304
mass(40) = 1012.966124

temperature unit = C
pressure unit = atm
mass unit = mol
data file = MSTDB-TC-V3.0-Fluorides.dat
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