



# Molten fluoride salt and liquid metal multistage extraction model



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## ABSTRACT

A multistage extraction model based on the distribution of actinides and rare earths between two phases of lithium activated bismuth and molten LiF–BeF<sub>2</sub> (66 mole % LiF) has been developed. The model shows that the distribution across the cascade is affected by the concentration of Li in the metal phase, system temperature, flow rates of each phase, and the presence and concentration of other elements in the molten salt phase. Based on the model, it is predicted that an online molten salt coolant purification system could be used to separate both rare earths and actinides from the primary salt coolant in fluoride salt-cooled high-temperature reactors (FHRs). Additionally, the results provide sufficient evidence that this extraction method can separate primarily actinides prior to extraction of other rare earth elements, which would allow for fission products and other reactor poisons to be discarded, while fuel materials (U and Pu) can be recycled back into a reactor system.

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## 1. Introduction

The fluoride salt-cooled high-temperature reactor, FHR, has acquired interest as a GEN IV reactor candidate with potential to be manufactured as a commercial power reactor. The conceptual design and research objectives of FHR technology have been previously reported (Holcomb et al., 2013a). A major concern for FHR development is the likelihood of contamination in the primary coolant. Uranium, alkali metals, alkaline earths, and rare earth elements all form stable fluoride compounds, as such, salt-seeking elements from leaking fuel would contaminate the primary coolant (Yoder et al., 2014; Holcomb et al., 2013b). Therefore, a continuous online cleanup system is necessary to ensure the continued operation of the reactor, while also minimizing the volume of salt coolant waste. Leaked fission products and transuranic materials from the fuel are a major source of this contamination (Yoder et al., 2014; Holcomb et al., 2013b). The use of a liquid metal reducing agent, such as bismuth with dissolved lithium, has been identified as a good removal technology in Molten Salt Breeder Reactors, and has been proposed as a clean-up method for FHR primary coolant (Grimes, 1970; Delpech et al., 2009).

A previously developed distribution model for the removal of actinides and rare earths from chloride salt using lithium activated

bismuth has been modified and adapted as part of this study (Wu, 2016). A new model has been developed to simulate a multistage extraction system for the removal of actinides and rare earths from a eutectic mixture of LiF–BeF<sub>2</sub> (66% LiF) salt using the same reductive extractant. The model predicts the distribution of actinides and rare earths between the fluoride salt and liquid metal at each stage using experimentally determined data for the apparent potential and activity coefficients of each contaminant in both phases. All stages are assumed to have a residence time large enough for equilibrium to be reached and electrochemical kinetics are therefore not considered. However, previous experiments and studies show that the time scale for reaching equilibration in a batch system is on the order of a few hours to a couple days (Zagnit'ko and Ignat'ev; Moriyama et al., 1984). This is a significant challenge that will need to be addressed in order for the continuous extraction process described in this paper to be advantageous. The development of equipment to decrease the equilibration time will be necessary. Possible solutions could be to use a series of centrifugal contactors or pulse columns (Law and Todd, 2008) to mix the liquids during the separation. The centrifugal contactor and the pulse column have been successfully applied in liquid-liquid separation in PUREX for used fuel reprocessing.

The salt-seeking elements include actinides and rare earths, such as U, Pu, Y, La, Ce, Pr, Nd, Pm, Gd, Tb, Dy, Ho, Er, Zr, Sm, Eu, Sr, Ba, Rb, and Cs (Yoder et al., 2014). However, based on limitations of available electrochemical data in fluoride salt, the model can

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currently predict the distribution across any number of stages for a combination of up to two actinides (U and Pu) and three rare earths (La, Ce, and Sm). The model has the capability to be expanded to include additional elements, if necessary data becomes available in the future. The remainder of this paper will discuss the methods and equations used in the development of the model and the efficacy and plausibility of this multistage extraction system based on the results.

## 2. Molten salt/liquid metal distribution

### 2.1. Equilibrium model for one stage

In a molten salt/liquid metal system, reductive extraction can be applied to remove metal elements from the salt phase. For the case of an FHR using LiF–BeF<sub>2</sub> as the primary coolant, lithium activated bismuth can be used to reduce metallic fluorides through the reaction shown below.



where  $M$  denotes the metal species being reduced and  $n$  is the oxidation state of the oxidized metal. The Nernst equation can be used to describe the equilibrium potential of the reaction

$$E_{eq} = E_{M^{n+}}^{ap} + \frac{RT}{nF} \ln \left( \frac{X_{M^{n+}}}{\gamma_M Y_M} \right) \quad (2)$$

where  $E_{eq}$  and  $E_{M^{n+}}^{ap}$  are the equilibrium potential and the apparent standard potential, respectively,  $R$  is the gas constant,  $F$  is Faraday's constant,  $X_{M^{n+}}$  is the molar fraction of the metallic fluoride in the molten salt,  $\gamma_M$  is the activity coefficient of metal  $M$  in bismuth and  $Y_M$  is the molar fraction of the metal in the liquid metal.

The distribution coefficient can be defined as the ratio of the concentration of metal  $M$  in the salt phase ( $X_{M^{n+}}$ ) to the concentration of metal  $M$  in the metal phase ( $Y_M$ ). Rearranging the above equation gives

$$D_M = \frac{X_{M^{n+}}}{Y_M} = \gamma_M \exp \left( \frac{nF}{RT} (E_{eq} - E_{M^{n+}}^{ap}) \right) \quad (3)$$

For a multi-contaminant system with multiple metallic fluorides dissolved in the molten salt, the equilibrium potential,  $E_{eq}$ , must be equal for all species. Therefore, the distribution coefficient for each rare earth and actinide is driven by the concentrations of all other elements within the molten salt/liquid metal system. Molar balances across a single stage are shown below, assuming that there are initially no rare earths or actinides in the liquid metal phase and that the change in volume of the molten salt and liquid metal phases as ions are transferred is negligible.

$$Bi_{feed} Y_{M_i} + Salt_{feed} X_{M_i^{n_i+}} = Salt_{feed} X_{M_i^{n_i+}}^I \quad (4)$$

$$Bi_{feed} Y_{Li} + Salt_{feed} X_{Li^+} = Salt_{feed} X_{Li^+}^I + Bi_{feed} Y_{Li}^I \quad (5)$$

$$\sum_{i=1}^m Bi_{feed} n_i Y_{M_i} = Bi_{feed} Y_{Li}^I - Bi_{feed} Y_{Li} \quad (6)$$

where  $Bi_{feed}$  and  $Salt_{feed}$  are the volumetric flow rates of the liquid bismuth phase and molten fluoride salt phase, respectively, the superscript "I" denotes the initial concentration, and  $m$  is the total number of metal elements in the system. Combining the molar balance equations with the first half of the equation for distribution coefficient gives:

$$\sum_{i=1}^m \frac{n_i X_{M_i^{n_i+}}^I}{Bi_{feed} + Salt_{feed} D_{M_i}} = \frac{Y_{Li}^I D_{Li} - X_{Li^+}^I}{Bi_{feed} + Salt_{feed} D_{Li}} \quad (7)$$

With specified initial concentrations for each element (including lithium), the only unknown variables are the corresponding distribution coefficients at equilibrium. The previously shown equation for distribution coefficient shows that for a specified temperature, the equilibrium potential,  $E_{eq}$ , is the only unknown. Since the equilibrium potential is constant within the system for all present elements at every stage, the above equation has only one unknown variable.

### 2.2. Apparent potential in LiF–BeF<sub>2</sub> molten salt

In order to accurately predict the distribution of rare earths and actinide elements, the apparent potential of each element in the salt phase must be known. The apparent potential has been shown to be dependent on temperature in previous studies and can be expressed in the form shown below.

$$E_{M^{n+}}^{ap} = A + BT \quad (8)$$

where  $A$  and  $B$  are experimental constants and  $T$  is temperature in Kelvin. Data has been collected from previous experiments and are reported in Table 1. All literature data is valid for LiF–BeF<sub>2</sub> (66% LiF) within the temperature range of 600–800 °C.

### 2.3. Activity coefficient in Bi liquid metal

In addition to the apparent potential in the salt phase, the activity coefficient in the liquid metal phase must also be known. The activity coefficient, which is also temperature dependent, can be expressed using the equation below.

$$\ln \gamma = A - \frac{B}{T} \quad (9)$$

where  $A$  and  $B$  are experimental constants and  $T$  is temperature in Kelvin. Data has been collected from previous experiments and are reported in Table 2. As with apparent potential literature data, all activity coefficient data is valid for liquid bismuth metal within the temperature range of 600–800 °C.

The activity coefficient of lithium in bismuth has also been reported in literature (Foster et al, 1964). However, the activity coefficient does not follow the form used above for LiF–BeF<sub>2</sub> salt. The expression for activity coefficient can be seen below and is reported to be valid within the temperature range of 775–1100 K (approximately 500–825 °C).

$$\ln(\gamma_{Li}) = -4.262 + .787T - 4.72*10^{-4}T^2 + (307.72 - .842T + 2.94*10^{-4}T^2)*Y_{Li} \quad (10)$$

Based on the expression, along with temperature, concentration of Li is also significant contributing factor in the activity coefficient in liquid bismuth.

## 3. Multistage extraction model

A continuous multistage extraction model is the proposed method for online primary coolant reprocessing. The described process will include multiple equilibrium stages with a fresh liquid metal stream at each stage. The product molten salt stream from

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