Importance of Computer Model Validation in Pyroprocessing Technology Development

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1. Introduction

Molten salt-based pyroprocessing technology is being examined internationally as an alternative to treat spent nuclear fuel over aqueous technology. The central process in pyroprocessing is electrorefining(ER) which separates uranium from transuranic elements and fission products present in spent nuclear fuel. ER is a widely used process in the minerals industry to purify impure metals. Studies of ER by using actual spent nuclear fuel materials are problematic for both technical and political reasons. Therefore, the initial effort for ER process optimization is made by using computer models. A number of models have been developed for this purpose. But as validation of these models is incomplete and often times problematic, the simulation results from these models are inherently uncertain.

In this research, we developed a plan for experimental validation of one of the computer models developed for ER process modeling, i.e., the ERAD code [1]. Several candidate surrogate materials are selected for the experiment considering the chemical and physical properties.

2. Need for model validation

In the current investigations on pyroprocessing, one of the main issues is to improve the efficiency of materials separation. Increased separation efficiency is important for economic efficiency of nuclear materials recycling. In this regard, the effort to improve separation efficiency deals with design optimization of electrorefining(ER), the step to separate uranium from transuranic elements and fission products in the spent nuclear fuel.

Process optimization of ER by using actual spent nuclear fuel materials is problematic. Therefore, initial effort to improve the efficiency of materials separation can be performed by using computer models. Availability of a well-developed computer model provides a good basis for actual process design and optimization.

When models are developed, validation work is also needed to evaluate the accuracy of the models. Due to general lack of relevant experimental data, and due to the variation in required input parameters, validation of the developed model is difficult. One of our previous work attempted to use cyclic voltammetry experimental data for model validation [2]. In this work, our effort is focused on developing experimental data to validate computer model for mass transport analysis in ER. Plans are developed for generation of experimental data for model validation with surrogate metals.

3. Plan for model validation

When model was developed, many phenomena which occur in electrochemical cell were considered and these phenomena were expressed as equations. The ERAD code [1], being used in this study for the simulation of mass transport in ER as an extension of REFIN [3], considers several phenomena. One of them is based on thermodynamics which describes how easily metals form metal chloride. It is determined by the Nernst equation which is a function of standard electrode potential(redox potential). Another is the rate of reaction which is called kinetics. It is expressed by Butler-Volmer equation which determines exchange current density.

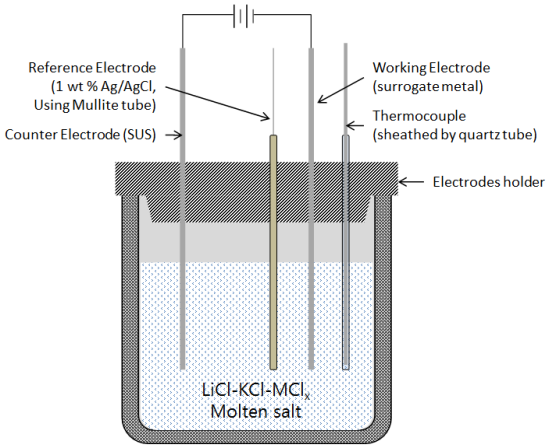

Fig. 1. Electrochemical cell design for experiment

To generate experimental data, a small-scale electrorefiner was set up in a glove box. The electrochemical cell used in the present work is shown in Fig. 1. Experiments are to be carried out in a glove box under a high purity argon atmosphere(99.999%) with moisture and oxygen concentration less than 5 ppm. The molten salt are at around 773 K(±3.0 K) measured by K-type(chromel-alumel) thermocouple, composed of 59-41 wt% LiCl-KCl and 5 wt% metal chloride as starting materials. Selected surrogate metals will be used as working electrode and stainless steel is used as counter electrode. Ag/AgCl electrode made by using mullite tube is used as reference electrode. It consisted of 1 wt% Ag in LiCl-KCl eutectic mixture in which 1 mm diameter silver wire is immersed. The diameter of

Table I: The properties of Uranium, Plutonium and Surrogate materials.[4,5]

	U	Pu	Al	Zr	La
M.W. [g/mol]	238.029	244.064	26.982	91.224	138.905
Common oxidation states*	6, 5, 4, 3	6, 5, 4, 3	3	4	3
Atomic radius (Ionic radius) [pm]	241 (102.5)	243 (100)	184 (53.5)	223 (72)	243 (103.2)
Redox potential(standard state)	-1.66	-2.0	-1.676	-1.55	-2.38
Gibbs free energy of MCl_x [kcal/mol]	-189.92	-213.30	-166.49	-230.24	-253.20
Electronegativity (Pauling scale)	1.700	1.300	1.610	1.33	1.100

*The Oxidation state of U and Pu :3

each electrode is 5 mm and thermocouple is also inside the cell by sheathing it in quartz tube whose diameter is also 5 mm. The potentiostat/galvanostat(Biologic, SP-150, France) will be used as power supplier for electrochemical studies along with the use of EC-lab software. Throughout the experiments, the concentration of electrolyte and counter electrode will be determined by inductively coupled plasma mass spectroscopy(ICP-MS). This result will be compared with the result of ERAD simulation.

To make this experiment validation reliable, the choice of surrogate metals is very important. As we cannot use U and Pu, the surrogate metals used in the experiment affect the accuracy and reliability of the validation. Candidate metals are selected by considering their chemical and physical properties. For example, in electrochemical cell, because all reactants are ions, it is necessary to consider the size and atomic mass of materials. U and Pu are big and heavy ions, so elements with similar properties need to be chosen. Other properties which affect electrolysis performance such as valence(oxidation state), redox potential, exchange current density etc. are to be considered. Initially, Aluminum, Zirconium and Lanthanum are chosen as candidate surrogate metals based on these considerations along with cost consideration. The properties of these metals are shown in Table I.

For a well-working ER progress, stability of the molten salt system is also important as the composition of molten salt system has an effect on the efficiency of ER. The molten salt used in ER for nuclear spent fuel treatment is LiCl-KCl eutectic salt with 5 wt% UCl_3. Thus, when surrogate metal, M, is used, 5 wt% MCl_x need to be added. Fig. 2 shows the results of molten salt system stability simulation by using the HSC software [4] for the selected surrogate metals. The simulation was based on the equilibrium composition from 25 ^oC to 500 ^oC. The case (a) was for 59-41 wt% LiCl-KCl with 5 wt% UCl_3. The (b), (c) and (d) are the case of using surrogate metal, Al, Zr and La, respectively. Each case includes 5 wt% $AlCl_3$, $ZrCl_4$ and $LaCl_3$ respectively. As shown in the case of (a) and (d), the concentration of each metal chloride were stable. But in the case of (b) and (c), some transitions were observed in the LiCl-KCl-$AlCl_3$ and LiCl-KCl-$ZrCl_4$ system.

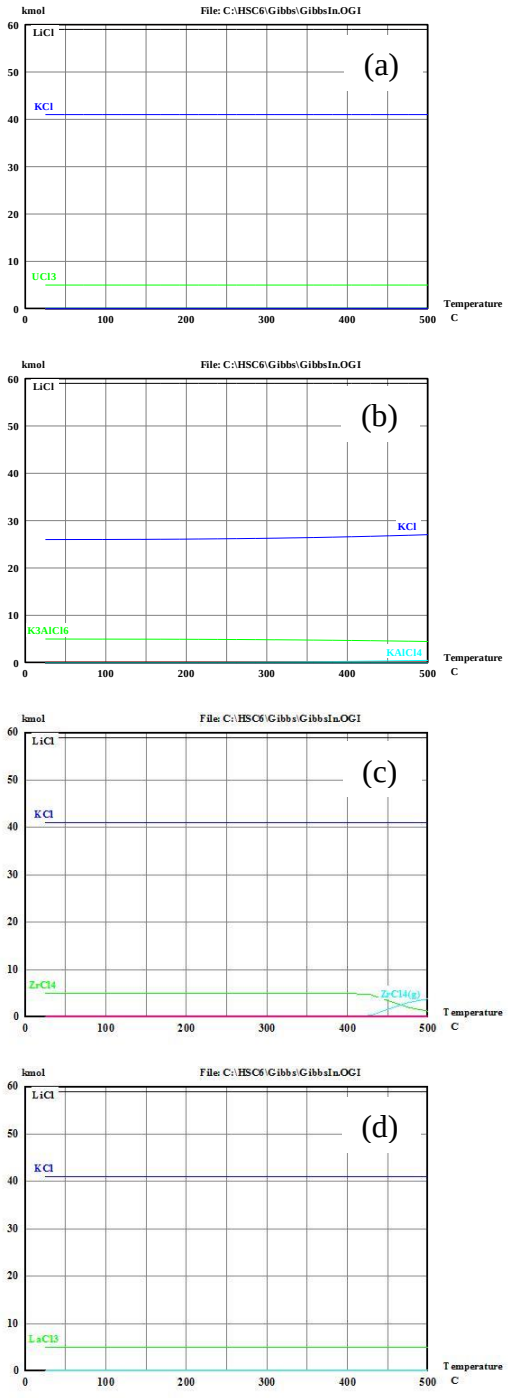

Fig. 2. The equilibrium composition for LiCl-KCl molten salt system with 5 wt% (a)UCl_3, (b)$AlCl_3$, (c)$ZrCl_4$ and (d)$LaCl_3$.

In the case of Al(case (b)), compounds such as K_3AlCl_6 and $KAlCl_4$ were formed which may be due to the low melting and boiling temperature of $AlCl_3$. In (c), in the LiCl-KCl-$ZrCl_4$ system, $ZrCl_4$ state was changed to a gaseous form after around 430 ^oC. Formation of such compounds would cause some problem during the operation and have an adverse effect on the ER processing.

4. Future work

Using the selected surrogate metals, experiment will be carried out with the focus on developing data to describe mass transport from anodic dissolution to cathodic deposition in electrorefining. To ensure the reliability and the accuracy, a series of experiments with different surrogate metals will be conducted and the results will be compared and analyzed according to the difference of surrogate metals. Also alloys will be selected as surrogate anode for the experimental situation to be closer to the ER modeling condition.

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