Computational Benchmark on Reductive Extraction Process in LiCl-KCl/Bi System

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1. Introduction

Pyrochemical process which is one of the innovative technologies for recycling spent nuclear fuel has been researched worldwide. In pyroprocess, there are some processes in system which is composed of molten LiCl-KCl eutectic salt and liquid metal. One of them is the process for separating transuranic elements (TRUs) from lanthanides (Lns) so that purify the waste salt from electrorefing and electrowinning. Two elements are usually considered as a liquid metal, one is cadmium (Cd) and the other is bismuth (Bi). As for main characteristics with those two metals, cadmium has a higher solubility on TRUs but a lower selectivity than bismuth [1, 2]. For that reason, researchers have been variously investigating extraction behaviors for TRUs and Lns in molten salt/Cd or Bi system .

In Republic of Korea, however, it is hard to handle not only spent nuclear fuel (SNF) so people conduct pyroprocess experiments by using depleted uranium and surrogate materials. Therefore, computational modeling is important to predict and evaluate process conditions for reducing experimental risks. REFIN, one dimensional time-dependent electrochemical simulation code, have been used pyroprocess modeling. It is verified by benchmarking electrolytic experiments such as electrorefining [4].

In this study, it is conducted that benchmark on reductive extraction system with liquid Bi in order to verify REFIN for the system in which current is not given.

2. Methods and Results

2.1 Benchmark object

In 1999, CRIEPI had multistage extraction experiment on LiCl-KCl/Bi system to separate actinides from rare earth elements [6]. They investigated to measure distribution coefficient as a preliminary experiment for multistage extraction. In this experiment, molten salt includes uranium (U), TRUs and neodymium (Nd) as chloride form and liquid Bi includes lithium (Li) as a metal alloy.

Li is used as a reducing agent, so that a number of U, TRUs and Nd can be extracted to liquid Bi as following equation.

$$Li + MCl_3 \rightarrow 3LiCl + M \quad (1)$$

CRIEPI examined reductive extraction behavior according to amount of Li reductant from 0 to about 6mg. Initial amounts and concentrations of LiCl-KCl and Bi phase are as shown in Table I. Also mass balance curves of U, Np, Pu and Am in molten salt and liquid metal phase are as shown in Figure 1.

Table I. Initial amounts and concentrations of experiment

Element	Weight [g]	Mole Fraction in Salt
Bi	48.675	-
LiCl-KCl	10.042	-
U	0.0076	1.767E-4
Np	0.0220	5.137E-3
Pu	0.0245	5.556 E-4
Am	0.0273	6.217 E-4
Nd	0.0058	2.224 E-4

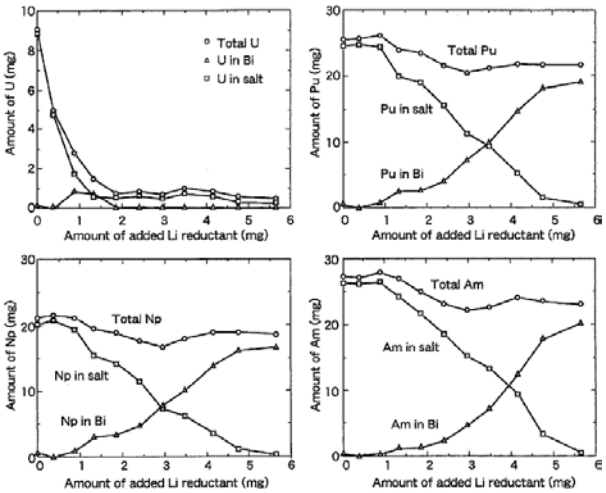

Figure 1. Mass balance curves of U, Np, Pu and Am

2.2 REFIN simulation for reductive extraction

REFIN calculates current density, potential distribution and material concentration variation at each phase in multi-species electrochemical system. Therefore, mass balance curves in Figure 1 can be produced. Properties of ions used in this simulation are represented in Table II. Standard reduction potential is referred to 1wt% Ag/AgCl and diffusion coefficient is assumed by Stokes-Einstein equation. Also, exchange current density and transfer coefficient are assumed with same value.

Table II. Ion properties [5]

Ion	U(III) /U	Np(III)/ Np	Pu(III)/ Pu	Am(III) /Am	Nd(III)/ Nd
Standard reduction potential [V]	-1.249	-1.684	-1.833	-2.12	-2.358
Diffusion coefficient in molten salt [cm^2/s]	1.70 E-5	1.70 E-5	1.70 E-5	1.70 E-5	1.61 E-05
Diffusion coefficient in liquid Bi [cm^2/s]	2.70 E-5	2.70 E-5	2.70 E-5	2.70 E-5	2.55 E-5
Exchange current density [A/cm^2]	1E-6	1E-6	1E-6	1E-6	1E-6
Transfer coefficient	0.5	0.5	0.5	0.5	0.5

When it is considered that initial condition in Table I which is specified in the paper, the mass balance curves in Figure 1 cannot be reproduced at all because it is lost that approximately 90% of initial amount for U and 10% of initial amount of TRUs. So this work carries out as assuming the loss initial amount.

Figure 2 shows the computational mass balance curves of U, Np, Pu and Am. Compared with experimental data, a tendency is similar, however, there is some differences. In computational result, A number of Np is extracted at small amount of Li and saturated at about 2mg of Li. Pu is saturated at about 4mg of Li and Am is not fully extracted when about 5.6mg of Li is added.

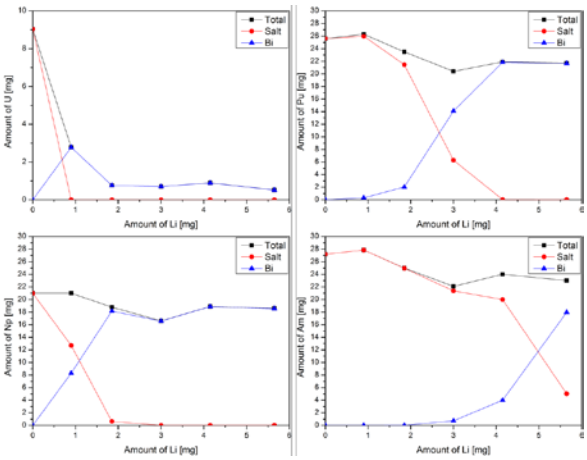

Figure 2. Mass balance curves of U, Np, Pu and Am from computational benchmark

But in experimental result, huge amount of Np and Pu is extracted to Bi but not all. That is because ion properties of TRU are assumed with same values. It means standard potential only effect to amount of extraction and that is the reason that computational and experimental result has differences.

3. Conclusions

It is investigated that computational benchmark on reductive extraction process which is not by electrolytic method but by chemical agent. Though the experimental result is not completely ideal due to material loss of initial amount, the computational result shows that tendency between the two results matches up by considering material loss in experiment. But there are some discrepancies and it seems that those come from assumed properties such as diffusion coefficient. Also stirring effect should have been considered. Therefore, if properties and other variables can be reliably determined, process modeling by REFIN will result in more accurate prediction.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science, ICT and Future Planning, Republic of Korea (MSIP). (NRF-2011-0031839, NRF-2011-0031890)

REFERENCES

[1] Y. Sakamura et al., Actinide, Lanthanide and Zirconium Chemistry in Pyrometallurgical Reprocessing, Proceedings of Nuclear Material Conference, NuMat 2012, 22-25 October, Osaka, Japan, 2012.
[2] M. Kurata, Distribution behavior of uranium, neptunium, rare-earth elements (Y, La, Ce, Nd, Sm, Eu, Gd) and alkaline-earth metals (Sr,Ba) between molten LiC1-KC1 eutectic salt and liquid cadmium or bismuth, Journal of Nuclear Materials, 227, 110-121, 1995.
[3] Sungyeol Choi, Jaeyeong Park, Robert O. Hoover b, Supathorn Phongikaroon, Michael F. Simpson, Kwang-Rag Kim, Il Soon Hwang, Uncertainty studies of real anode surface area in computational analysis for molten salt electrorefining, Journal of Nuclear Materials, 416, 318-326, 2011.
[4] K. Kinoshita, Separation of Uranium and Transuranic Elements from Rare Earth Elements by Means of Multistage Extraction in LiCl-KCl/Bi System, Journal of Nuclear Science and Technology, Vol. 36, No. 2, 189-197, 1999.
[5] R.K. Ahluwalia, Electrotransport of Uranium from a Liquid Cadmium Anode to a Solid Cathode, Nuclear Technology, Vol. 140, 2002.