Numerical and Experimental Approaches for Residual Actinide Recovery Process Development

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1. Introduction

The management of spent nuclear wastes is one of important issues for sustainable utilization of nuclear power. Pyrochemical process is one of the favorable candidates for partitioning of actinide elements and long-lived fission products (LLFPs) from waste stream in virtue of its proliferation-resistance, economic competitiveness and compactness. The separation performance of total pyrochemical process, represented by decontamination factor (DF), should be increased to reduce final waste toxicity and volume. It is verified experimentally that about 99.9% of actinide elements (DF = 1000) can be recovered from the nuclear waste by combining chopping, voloxidation, electrolytic reduction, electrorefining (ER), and electrowinning (EW) [1,2]. Several researches are on going to recover more actinide elements through additional processes.

The goal of this study is development of residual actinide recovery (RAR) process using both numerical and experimental approach.

2. Approach and results

2.1. Residual Actinide Recovery

To maximize the decontamination factor of actinide elements, all the actinide elements in the waste stream should be minimized. About 0.1% of actinide elements is still remained in final wastes after ER and EW. RAR process is being developed to recover more actinide elements from the molten salt, which is contaminated by rare earth elements.

Reductive extraction method is one of the candidates for RAR process. Different reduction tendency between actinide and rare earth elements is used to extract actinide elements from molten salt into liquid metal. Rare earth elements, remained in molten salt, are removed from molten salt as its oxide form by reaction with air. Actinide elements, extracted into liquid metal, are re-circulated to EW by exchange reaction with oxidant such as $CdCl_2$ and $BiCl_3$.

Selective oxidation method is also being studied as alternative. Before selective oxidation step, both actinide and rare earth elements are reduced into liquid metal by electrolysis. Different oxidation tendency is used to extract rare earth element from liquid metal into molten salt. Rare earth elements are removed from molten salt by reaction with air. Actinide elements in liquid metal are contained in fast reactor fresh fuel by distillation of liquid metal or re-circulated to electrowinning by exchange reaction with oxidant. Fig 1 shows the flowsheet of reductive extraction and selective oxidation.
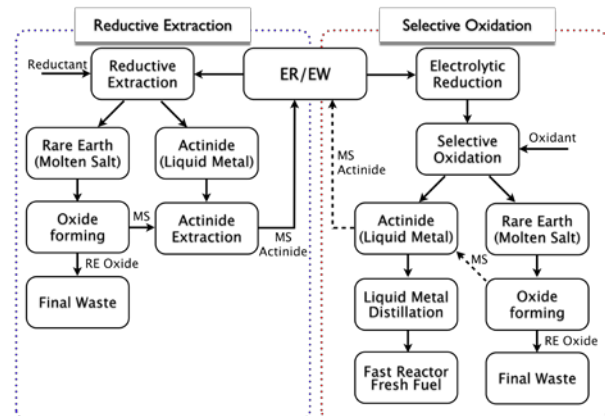

Fig. 1. Flowsheet of reductive extraction and selective oxidation

2.2. Calculation Result of Multi-stage Reductive Extraction

If the concentrations of actinide and rare earth elements are determined, each element distribute to molten salt and liquid metal at a specific ratio due to the difference of reduction tendency. The ratio of distributed elements to salt and liquid metal is defined as a distribution coefficient. At a specific temperature, the relative ratio of the distribution coefficient is defined as a separation factor. This value was used to simulate the process numerically, because this factor does not change much though the concentration of each elements are changes.

Multi-stage reductive extraction process is considered to increase the DF. And recovery yield of this process is calculated by changing the number of constituting stages. However, simulation of con-current extraction system shows separation efficiency get worse as the number of stages is increased. To increase the efficiency, counter-current extraction method was suggested and developed [3,4].

Figure 3 shows schematics of multi-stage counter-current reductive extraction process for RAR. Spent salt from ER/EW process contains small amount of TRU & RE as a form of chloride. Remaining TRU is selectively extracted to contacted liquid metal (e.g. Bi/Cd) by addition of lithium as a reducing agent.
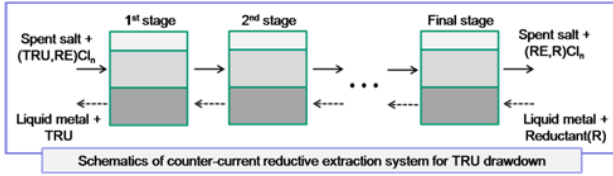

Fig. 2. Schematic of counter-current reductive extraction system for residual TRU recovery.

Previous reductive extraction research shows that bismuth is better than cadmium for separation of TRU and RE, because the ratio of separation factor of each elements of Bi is bigger than Cd. Therefore, in this study, Bi is selected as a liquid metal for the simulation. Table I shows the calculated recovery yield of counter-current reductive extraction when initial concentrations of each elements are assumed same with the value of Kinoshita's work [5]. The result shows over 99.9% of actinides are recovered even in 3 stages extraction (DF=1,000).

Table I : Expected Recovery Yield of Counter-current Reductive Extraction

Recovery Yield [%]			
Elements	2 stages	3 stages	4 stages
U	99.99976	99.99999966	99.99999999
Np	99.98561	99.99983545	99.99999811
Pu	99.96815	99.99945714	99.99999073
Am	99.87715	99.99586504	99.99986059
Pr	28.50892	28.30503614	28.18009275
Ce	28.80722	28.64376113	28.53589354
Nd	32.11181	32.46418015	32.60166812
La	9.56794	8.92449747	8.80613917
Gd	2.09572	2.02301214	2.01748524
Y	0.03482	0.03455888	0.03451451

The result of multi-stage counter-current extraction system also shows good separation efficiency even if the number of stages is increased as shown in Table II.

Table II : Weight Ratios of TRUs to REs

Weight Ratio [TRUs/ Res]	
2 stage extraction	0.33978
3 stage extraction	0.39853
4 stage extraction	0.39854
5 stage extraction	0.39855

Although, the simulation was performed only based on the thermodynamic equilibrium of each element, the simulation of counter-current extraction shows that expected DF value of 1,000 could be achieved only single step of additional recovery process. For more reliability, modification of model for the simulation by including kinetic effects will be done as a future work.

2.3. Experimental Approaches

Basic understanding about molten salt/liquid metal system is important to enhance the performance of proposed processes. Experimental approaches will be tried to measure thermodynamic and kinetic parameters at molten salt system from this point of view. Both electrochemical (e.g. cyclic voltammetry, normal pulse voltammetry) and spectrophotometric (e.g. electronic absorption spectroscopy, Raman spectroscopy) techniques are considered to achieve these goals. The performance of RAR process will be also evaluated using these techniques.

3. Summary and future work

Numerical and experimental approach is being studied about pyrochemical process, especially RAR process. Numerical study result shows that TRU decontamination factor of RAR process can be reached above 10^3 by multi-stage counter current reductive extraction (over 3 stages). Experimental approach is on going to verify this calculation result and measure basic thermodynamic and kinetic parameters at molten salt/liquid metal system. The separation performance of selective oxidation method will be also evaluated using both numerical and experimental approaches.

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