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Development of transuranium elements recovery from high-level radioactive liquid waste

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Abstract

The Transuranium Elements (TRUs) recovery process from High-Level Liquid Waste (HLLW) at a Purex reprocessing plant requires both simple processes and a high yield of TRUs recovery. This paper outlines a new TRUs recovery process which combines an aqueous process and a pyrochemical process. In the first step, TRUs and Rare Earth elements (REs) are precipitated from HLLW to separate alkali metal elements because the HLLW is an aqueous solution. It is difficult for TRUs to be separated simply from REs in the aqueous solution. A pyrochemical process is more effective to separate TRUs than an aqueous one. TRUs are separated from REs with an electrorefining process in molten salt in the final step. A tracer of Am was experimentally separated from a simulated HLLW at more than 99.5% yield in the oxalate precipitation. After the simulated HLLW was treated with the oxalate precipitation process, the precipitates were converted to their chlorides with hydrochloric acid and hydrogen peroxide below 100°C in 99.4% yield. Finally, Ce used to simulate TRUs was deposited on the cathode in order to study the separation from La used for REs with the electrorefining process in molten salt. The separation factor of TRUs from REs is estimated to be about 70.

Keywords: Oxalate precipitation; Electrorefining; Transuranium elements; Rare earth elements

1. Introduction

The High-Level Liquid Waste (HLLW) at the Purex reprocessing plant contains long-lived Fission Products (FPs) such as I-129, Tc-99 and transuranium elements TRUs. At present, the HLLW is treated and formed into a vitrified form, which contains the long-lived FPs and TRUs, is deeply buried and must be controlled for several tens of thousands of years. TRUs must be recovered from HLLW and transmuted into short-lived TRUs. The separation processes for TRUs from HLLW are classified into two categories: wet processes, such as processes using an ion exchanger, solvent extraction [1] or precipitation in aqueous solution, and dry processes, that is pyrochemical processes [2]. The wet processes have the capability of separating TRUs from REs but are complicated because the separation processes requires many steps, whereas the dry processes have small decontamination factors (DFs) for FPs but are simple. What is required is a new TRUs recovery process that is both simple and realizes high separability of TRUs from REs.HLLW has the following features:

1. It is an aqueous solution.
2. It contains a small amount of TRUs and a large amount of FPs which include REs.

A new TRUs recovery process from HLLW requires a combination of simplicity and a high yield of TRUs recovery. This paper outlines a new TRUs recovery process which combines an aqueous process and a pyrochemical process.

2. Aqua-Pyro partitioning process

A new TRUs recovery process named ‘Aqua-Pyro partitioning process’ is shown in Fig. 1. In the first step, TRUs and Rare Earth elements (REs) are precipitated from HLLW to separate alkali metal elements because HLLW is an aqueous solution. Simple separation of TRUs from REs in the aqueous solution is difficult to be achieved. A pyrochemical process is more effective for separating

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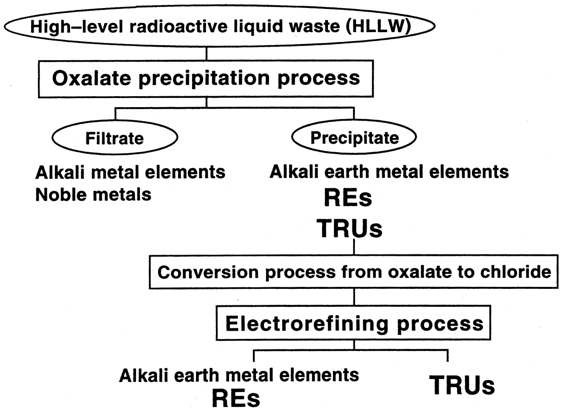

Fig. 1. Process flow of the 'Aqua-Pyro partitioning process'.

TRUs from REs than an aqueous one. TRUs are separated from REs by electrorefining in molten salt in the final step.

3. Experimental details

3.1. Oxalate precipitation process

Regarding the oxalate precipitation process, we examined various nitric acid concentrations, ionic concentrations, amount of oxalic acid added, and reaction temperatures. The simulated HLLW used is shown in Table 1 [3]. Nd is used for the simulated TRUs. A tracer of Am is also used for oxalate precipitation tests.

3.2. Conversion process from TRU oxalate precipitates to the corresponding chloride

After hydrochloric acid is added to the TRU oxalate precipitates, TRU ions are converted to TRU chloride. The TRU oxalate was simulated with cerium oxalate. The excess of oxalic ions of cerium oxalate in hydrochloric acid were decomposed by hydrogen peroxide. Ce^{3+} in hydrochloric acid was recovered as cerium chloride after the hydrochloric acid was dried under an argon or air atmosphere.

Table 1
Chemical composition of simulated HLLW [3]

Element	Concentration (M)
Fe	0.038
Cr	0.0091
Ni	0.0060
Na	0.076
Mo	0.069
Sr	0.0165
Ba	0.0207
Cs	0.0371
Rb	0.0074
Zr	0.069
Ru	0.034
Rh	0.0080
Pd	0.018
Te	0.0068
Nd	0.127
H^+	2.0

3.3. Separation of TRUs from REs by electrorefining process

TRU ions in TRU chloride are deposited on the cathode made of low carbon steel. On the other hand, RE ions in RE chloride remain in the molten salt after electrorefining. Ce and Nd were employed for the simulated TRUs in electrorefining tests. La was used for REs. The small difference of redox potential between TRUs and REs, which is 259 mV, was simulated with a 42 mV [4] difference in redox potential between Ce and La (Table 2). Cerium chloride and lanthanum chloride, as well as neodymium chloride and the same lanthanum chloride in KCl–LiCl eutectic molten salt were electrorefined at a constant potential. We examined various electrorefining potentials and ratios of $LaCl_3$ to $CeCl_3$ in KCl–LiCl eutectic molten salt.

3.4. Measurements

The amounts of Nd, Ce,and La in nitric acid solution, hydrochloric acid solution and molten salt were measured by inductively-coupled plasma spectrometry (ICP). A tracer of Am was detected by a liquid scintillation counter. The oxalate ion concentration was measured by ion chromatography. Cerium chloride after conversion tests was measured by the X-ray diffraction method. Neodymium chloride in KCl–LiCl eutectic molten salt before and after electrorefining was measured by cyclic voltammetry.

4. Results and discussion

4.1. Oxalate precipitation process

Fig. 2 shows the effect of the amount of oxalic acid on the Nd and Am recovery yield in the case that the simulated HLLW is diluted twice at a reaction temperature of 90°C. More than about 99.5% of Nd was recovered in the case that more than 1.0 M of oxalic acid was added (namely, about 3 g added to 50 cm^3 solution). More than 99.5% of Am was also recovered under the same precipitation conditions as Nd.

Table 2
Standard REDOX potentials and separation factors (SF)

Elements	REDOX potential (V)[a]	Potential difference (V)	Separation factor[b]
REs			
Eu/Eu^{3+}	−2.076		
Sm/Sm^{3+}	−2.004		
La/La^{3+}	−1.714	0.022	5.9
Ce/Ce^{3+}	−1.692	0.042	3.9
Pr/Pr^{3+}	−1.689		
Nd/Nd^{3+}	−1.672	0.259	
Gd/Gd^{3+}			(69.4)[c]
TRUs			
Cm/Cm^{3+}	−1.413		
Am/Am^{3+}	−1.409		
Pu/Pu^{3+}			
Np/Np^{3+}	−1.402		
U/U^{3+}	−1.399		

[a] Calculated value based on the literature [4].
[b] Separation Factor (SF) = [TRU/RE] of deposit on the cathode/[TRU/RE] in KCl–LiCl eutectic molten salt.
[c] Calculated value based on this paper.

4.2. Conversion process from TRU oxalate precipitates to the corresponding chloride

The cerium oxalate was converted to cerium chloride in 99.4% yield, which was measured by ICP analysis. Fig. 3 shows the X-ray diffraction patterns of the products after a conversion test under argon and air atmospheres. Under the air atmosphere, the peaks for both $CeCl_3H_2O$ and Ce_6O_{11} are visible. Ce oxide (Ce_6O_{11}) remained in the conversion product. On the other hand, the peaks for Ce_6O_{11} disappeared under the argon atmosphere. The peaks for $CeCl_3xH_2O$ (x = 1, 4 and 6) are visible.

4.3. Separation of TRUs from REs by electrorefining process

The effect of the ratio of $LaCl_3$ to $CeCl_3$ in KCl–LiCl eutectic molten salt on the separation factor when the initial ratio of La concentration to Ce is varied from 1–11 is shown in Fig. 4. Separation factor is defined by the following formula:

$$\text{Separation factor} = \frac{[\text{Ce}]/[\text{La}]\ \text{of deposit on the cathode}}{[\text{Ce/La}]\ \text{in KCl} - \text{LiCl eutectic molten salt}} \quad (1)$$

As a result, the separation factor of Ce to La is almost 5.0 because the separation factor is independent of the ratio of $LaCl_3$ to $CeCl_3$ in the molten salt.

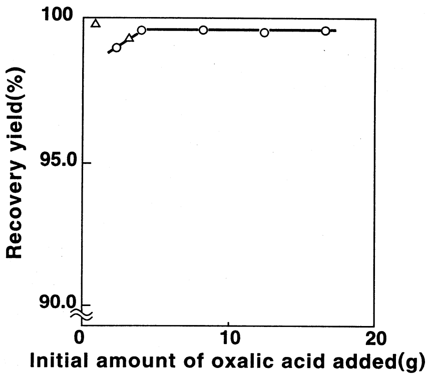

Fig. 2. Effect of the amount of oxalic acid initially added to 50 cm^3 solution. ○, Nd recovery yield (%); △, Am recovery yield (%).

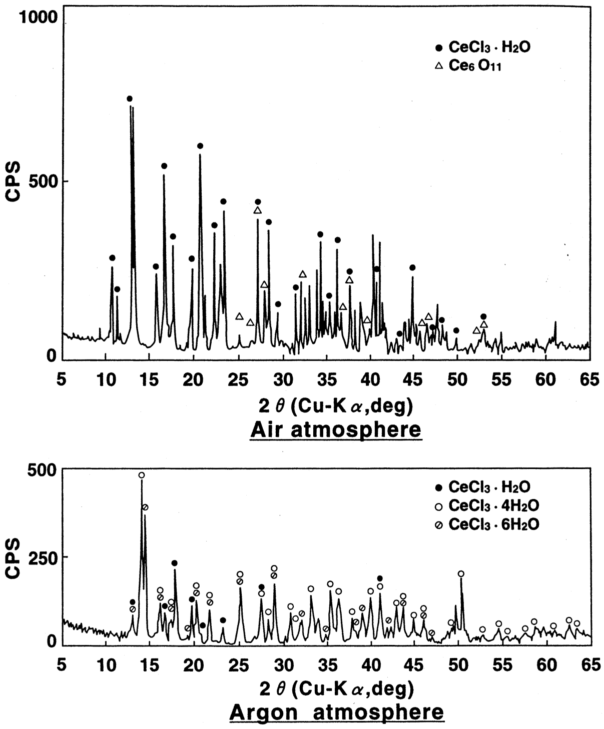

Fig. 3. X-ray diffraction patterns of conversion products.

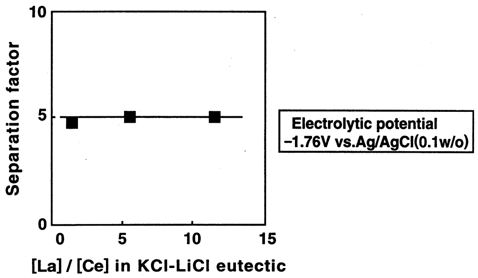

Fig. 4. Effect of the ratio of La/Ce concentration in KCl–LiCl eutectic molten salt on the separation factor.

Fig. 5 shows the effects of electrorefining potential on the separation factor in each 1.5 wt% of Ce and La in KCl–LiCl eutectic molten salt. Electrorefining potentials were varied from −1760 to −1830 mV vs. Ag/AgCl (0.1 wt%). The separation factor is almost 5.9 at a potential more positive than −1.800 mV. The separation factor of Ce to La increases in accordance with increasingly positive electrorefining potential. On the other hand, the separation factor of Nd from La was 3.9 when the initial ratio of Nd to La was equal to 1.0 (Fig. 5). The separation factor of Nd from La was smaller than that of Ce from La in spite of larger potential difference between Nd and La than that between Ce and La.

Fig. 6 shows the cyclic voltammograms of $NdCl_x$ in the KCl–LiCl eutectic molten salt before and after electrorefining. After the electrorefining, other peaks of Nd^{x+}/Nd than Nd^{3+}/Nd were visible. These peaks are considered to contribute to Nd^{2+}/Nd, and therefore the heterogeneous reaction results in the following formula [5]:

$$Nd + 2NdCl_3 \rightleftarrows 3NdCl_2 \quad (2)$$

Where Nd is the simulated TRUs, the simulated TRUs recovery is very difficult because Nd is more stable in KCl–LiCl eutectic molten salt. Where Nd is used for real REs, Nd is not deposited on the cathode. The estimated separation factor of TRUs from REs is shown in Table 2. The separation factor of TRUs from REs is estimated to be 69.4. Other REs are estimated to have larger separation factors because some REs such as Nd are at RE^{2+} which is more stable than RE^{3+}.

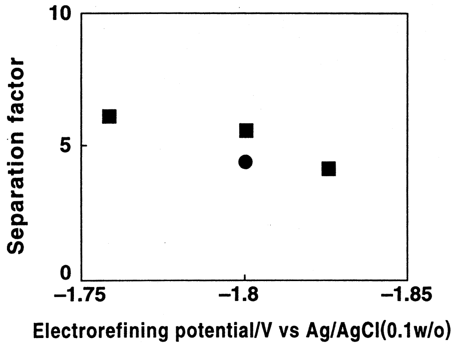

Fig. 5. Effect of electrorefining potential on separation factor in KCl-LiCl eutectic molten salt. ■, $CeCl_3$ 1.5 wt%, $LaCl_3$ 1.5 wt% (initial concentration); ●, $NdCl_3$ 1.5 wt%, $LaCl_3$ 1.5 wt% (initial concentration).

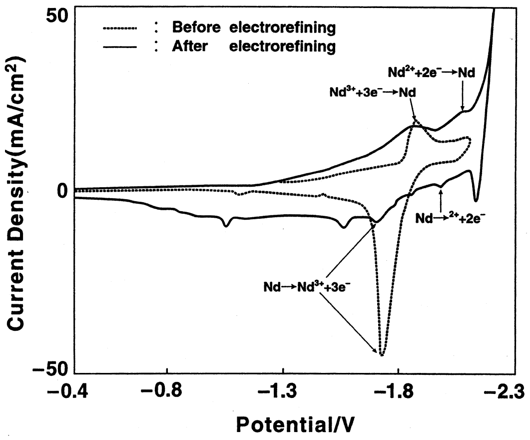

Fig. 6. Cyclic voltammograms of $NdCl_x$ in KCl–LiCl eutectic molten salt before and after electrorefining.

5. Conclusions

The new partitioning process which is composed of 3 processes, that is, the oxalate precipitation process, the conversion process from oxalate to chloride and the electrorefining process, was experimentally confirmed.

1. In the oxalate precipitation process, more than 99.5% of Am was experimentally recovered from the simulated HLLW with more than 99.5% of Nd.
2. When cerium oxalate was used as the simulated TRU oxalate, hydrochloric acid was added to convert it to cerium chloride. The conversion to chloride was confirmed by the X-ray diffraction pattern after decomposition of oxalic acid by hydrogen peroxide and drying the chloride under argon atmosphere.
3. When Ce was the simulated TRUs,it was separated from La as REs by electrorefining at a separation factor of more than 5.0 despite the small difference of 42 mV in redox potential. The separation factor of TRUs from REs is estimated to be about 70.

References

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