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Actinides recovery from molten salt/liquid metal system by electrochemical methods

Masatoshi Iizuka [a,*], Tadafumi Koyama [a], Naruhito Kondo [a,1], Reiko Fujita [b], Hiroshi Tanaka [a]

[a] *Nuclear Fuel Cycle Department, Central Research Institute of Electric Power Industry, Komae-shi, Tokyo 201, Japan*
[b] *Nuclear Engineering Laboratory, Toshiba Corporation, Kawasaki-ku, Kawasaki 210, Japan*

Abstract

Electrochemical methods were examined for the recovery of actinides from the electrorefiner which is used in pyrometallurgical reprocessing of spent metal fuel for fast reactors. Uranium was successfully collected at the solid steel cathode from both liquid cadmium and molten salt solvents. In electrotransport from liquid cadmium, the behavior of uranium and rare earths was as expected by a computer simulation code based on the diffusion layer model at the interface between the electrolyte and the electrodes. In electroreduction from the molten salt electrolyte, a considerable amount of uranium was reduced at the Cd–Li anode by direct chemical reduction with lithium, especially at a lower anodic current density. The decrease in collection efficiency of uranium due to the direct chemical reduction would be avoided by maintaining the anode potential higher than the deposition potential of uranium. © 1997 Elsevier Science B.V.

1. Introduction

The Central Research Institute of Electric Power Industry (CRIEPI) has been developing metallic fuel cycle technology which has excellent potential in economics, safety and non-proliferation. The concept of the metallic fuel cycle consists of a metal (U–Zr or U–Pu–Zr) fueled fast reactor and pyrometallurgical reprocessing of spent fuel. The most important step in the pyrometallurgical reprocessing is electrorefining [1] (Fig. 1), where (i) spent fuel containing fissile materials and fission product elements (FPs) are anodically dissolved in molten salt electrolyte, (ii) uranium is selectively recovered on the solid steel cathode due to the differences in the formation energies of chlorides and (iii) other actinide elements (plutonium, neptunium, americium and curium) are recovered into the liquid cadmium cathode together with uranium due to their small activity coefficients in liquid cadmium.

According to many batches of spent fuel are processed, a large amount of FPs accumulate in the solvents; noble metals (Ru, Mo, etc.) in the liquid cadmium layer at the bottom of the electrorefiner and chemically more active elements (Nd, Ba, Cs, etc.) in the molten salt electrolyte. Before these solvents are sent to a waste treatment process, actinides which also exist in them have to be collected to attain a high recovery ratio.

For the recovery of actinides from these solvents, electrochemical methods have been proposed because they might require less additional equipment. The electrochemical recovery of actinides from the electrorefiner is considered to be done in two steps: (i) electrotransport from the liquid cadmium layer and (ii) electroreduction from the molten salt electrolyte. In this report, both methods were

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[*] Corresponding author. Tel.: +81-3 3480 2111; fax: +81-3 3480 7956; e-mail: iizuka@criepi.denken.or.jp.

[1] Present address; Advanced Reactor Engineering Department, Toshiba Corporation, Isogo-ku, Yokohama, 235, Japan.

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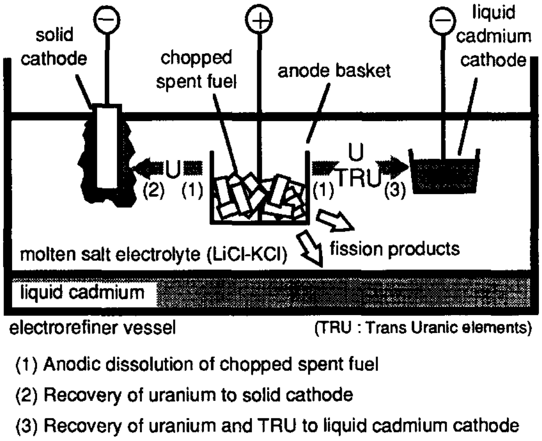

Fig. 1. Electrorefining of spent metal fuel.

experimentally examined and the behavior of uranium and rare earth elements in these processes was investigated.

2. Reactions in actinides recovery processes

2.1. Electrotransport of actinides from liquid cadmium

The liquid cadmium layer at the bottom of the electrorefiner is made anodic and a current is passed between it and a solid steel cathode suspended in a molten salt electrolyte (Fig. 2).

At the anode, actinides and rare earths are anodically dissolved:

$$\mathrm{An}_{\mathrm{in\,Cd}} = \mathrm{An}^{3+}_{\mathrm{in\,salt}} + 3e^- \quad (\mathrm{An: actinides}), \tag{1}$$

$$\mathrm{RE}_{\mathrm{in\,Cd}} = \mathrm{RE}^{3+}_{\mathrm{in\,salt}} + 3e^- \quad (\mathrm{RE: rare\ earths}). \tag{2}$$

After these elements are exhausted from the anode, solvent cadmium would be then dissolved into the salt:

$$\mathrm{Cd} = \mathrm{Cd}_{\mathrm{in\,salt}} + 2e^-. \tag{3}$$

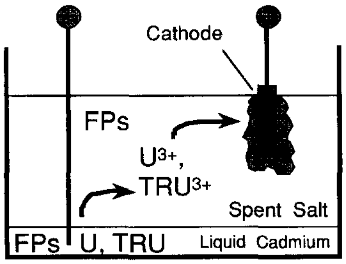

Fig. 2. Electrotransport of actinides from liquid cadmium.

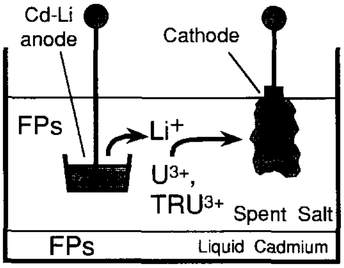

Fig. 3. Electroreduction of actinides from molten salt electrolyte.

At the cathodes, actinides or rare earths are reduced unless the concentrations of these elements are not very low:

$$\mathrm{An}^{3+}_{\mathrm{in\,salt}} + 3e^- = \mathrm{An}, \tag{4}$$

$$\mathrm{RE}^{3+}_{\mathrm{in\,salt}} + 3e^- = \mathrm{RE}. \tag{5}$$

These reactions are affected by mechanical factors such as the geometric structure of the electrorefiner and the intensity of stirring as well as by electrochemical factors like the composition of the solutions and current density. Their reaction rates are expected to be estimated approximately by the diffusion layer model using redox potentials, diffusion coefficients and the effective thickness of the diffusion layers [2].

2.2. Electroreduction of actinides from molten salt electrolyte

In electroreduction of actinides from a molten salt electrolyte (Fig. 3), reductive material like a Cd–Li alloy is used as an anode in order to avoid the evolution of corrosive chlorine gas and to generate a stable oxidation product which does not affect the decontamination at the cathode.

At the anode, direct chemical reduction of actinides and rare earths in the electrolyte with lithium metal is expected to occur,

$$\mathrm{An}^{3+}_{\mathrm{in\,salt}} + 3\mathrm{Li}_{\mathrm{in\,anode}} = \mathrm{An} + 3\mathrm{Li}^{+}_{\mathrm{in\,salt}}, \tag{6}$$

$$\mathrm{RE}^{3+}_{\mathrm{in\,salt}} + 3\mathrm{Li}_{\mathrm{in\,anode}} = \mathrm{RE} + 3\mathrm{Li}^{+}_{\mathrm{in\,salt}}, \tag{7}$$

in addition to anodic dissolution of lithium:

$$\mathrm{Li}_{\mathrm{in\,anode}} = \mathrm{Li}^{+}_{\mathrm{insalt}} + e^-. \tag{8}$$

At the cathode, actinides and rare earths are reduced first. After the concentration of these elements gets lower, lithium can be reduced:

$$\mathrm{Li}^{+}_{\mathrm{in\,salt}} + e^- = \mathrm{Li}. \tag{9}$$

The Argonne National Laboratory (ANL) has studied this process [3]. They reported that most of the uranium was reduced from the salt with a low contamination of cathode

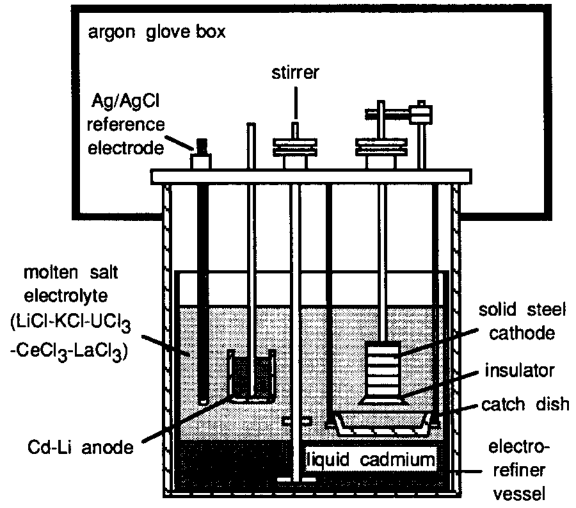

Fig. 4. Schematic view of experimental apparatus.

Table 2
Initial composition of electrolyte salt and cadmium layer in electrotransport tests

	U	Ce	La
Concentration in the salt (wt%)	0.14	2.91	1.48
Concentration in the cadmium (wt%)	0.45	0.17	0.03

products by rare earths. In their report, however, no discussions were found on the reactions at the Cd–Li anode nor the electrochemical parameters like the electrode potentials, although these are significantly important points considering the collection efficiency of actinides at the cathode.

3. Experimental

The experimental apparatus is schematically shown in Fig. 4.

All the experiments were carried out in an argon-atmosphere glove box. Oxygen and moisture in the glove box were kept below 20 ppm, respectively.

The size of the electrorefiner vessel was 180 mm in diameter and 200 mm in depth. It was heated by an electric furnace to keep its temperature at 773 K. About 3 kg of salt (LiCl–KCl eutectic) and ~ 6 kg of cadmium metal were loaded into the vessel. The surface area of the liquid cadmium layer was approximately 240 cm^2.

Cd–Li anodes used in the electroreduction tests were prepared in another glove box. Lithium metal was added into liquid cadmium to make about 6 wt% Cd–Li alloy at 973 K. The alloy, once cooled, was broken into small pieces. Before use, they were melted in zirconia crucibles and cooled again to be loaded into the electrorefiner.

The steel cathode was 30 mm in diameter and 50 mm in immersed length. It was rotated at about 20 rpm to obtain a uniform deposit. A zirconia dish was located under the cathode to collect the cathode product which slipped off the cathode.

The reference electrode was a Ag/AgCl (0.1 wt% AgCl–LiCl–KCl) electrode which was contained in a Pyrex tube.

The electrolyte salt and liquid cadmium layer were agitated with a paddle-shaped stirrer.

All the chlorides and metals used in these tests were of more than 99.9% purity. The electrolyte salt (LiCl–KCl) was heated in the electrorefiner vessel to remove trace amounts of moisture before it was melted. Cadmium was used after washing with diluted sulphuric acid. Uranium, lanthanum and cerium metal were polished to remove oxides on the surface before use.

These metals were at first dissolved in the liquid cadmium layer at the bottom of the electrorefiner. Then they were oxidized by addition of $CdCl_2$ to adjust the initial composition of the liquid cadmium and the electrolyte salt.

During the tests, the current was kept at a desirable value and the anode/cathode potentials were recorded. Samples were taken from the salt and the cadmium phases at an interval of 15 or 30 min.

The electrorefining analysis code 'TRAIL', which is based on the diffusion layer model [2], was used for comparison between the experimental and calculated re-

Table 1
Thermodynamic data and parameters used in calculation

	U	Ce	La
Standard potential (V versus Ag/0.1 wt% AgCl–LiCl–KCl)	− 1.10	− 1.69	− 1.71
Activity coefficient in salt (−)	1.00	1.00	1.00
Diffusion coefficient in salt (cm^2/s)	1.00×10^4	1.00×10^4	1.00×10^4
Activity coefficient in cadmium (−)	88.7	1.13×10^{-5}	1.13×10^{-8}
Diffusion coefficient in cadmium (cm^2/s)	1.50×10^{-5}	1.50×10^{-5}	1.50×10^{-5}
	Anode cadmium		Steel cathode
Thickness of diffusion layer (cm)	in salt, 0.020	in Cd, 0.002	in salt, 0.020

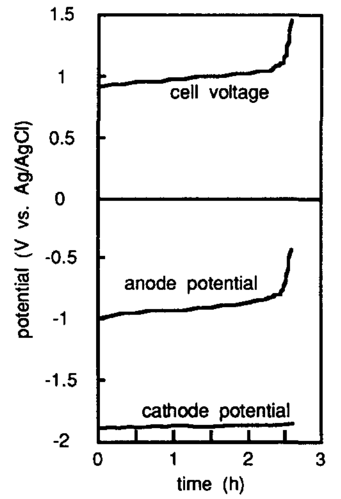

Fig. 5. Change of electrode potentials in electrotransport tests.

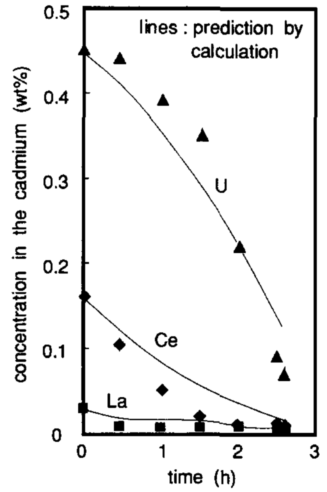

Fig. 6. Change of composition of liquid cadmium layer in electrotransport tests.

sults. The thermodynamic data and parameters used in this report are shown in Table 1.

4. Results and discussion

4.1. Electrotransport of actinides from liquid cadmium layer

Uranium and rare earths in the liquid cadmium layer at the bottom of the electrorefiner were electrotransported to the solid steel cathode. The initial composition of the salt and the cadmium are shown in Table 2. The current density was 0.02 A/cm^2 at the anode and 0.1 A/cm^2 at the cathode, respectively.

The change of the electrode potentials and the composition of the cadmium layer are shown in Figs. 5 and 6, respectively. The anode potential rose suddenly about 2.5 h after the start of the test. By that time, the uranium concentration in the cadmium had decreased to about 0.1 wt%. From this result, it is expected that the cadmium anode was polarized due to the exhaustion of uranium. Electrotransport of uranium from the cadmium could not occur after this point because cadmium would be dominantly oxidized on such conditions. The cathode product in this test contained approximately equal amounts of uranium and cerium. This ratio is about one third of that in the cadmium anode and more than twenty times larger than that in the salt at the beginning of the test.

The calculated results, which are also shown in Fig. 6, indicate that the behavior of uranium, lanthanum and cerium in electrotransport can be well explained by a diffusion layer model.

4.2. Electroreduction of actinides from molten salt electrolyte

The Cd–Li anode contained in the zirconia crucible and the steel cathode were used. The anodic current density was changed as a parameter. The initial composition of the salt and the cadmium are shown in Table 3 with the anodic current density. Each test was divided into three runs. These three runs were carried out in the same system but the electrorefiner was cooled down after each run.

Table 3
Initial composition of electrolyte salt and cadmium layer in electroreduction tests

Run no.	Anodic current density (A/cm^2)	U		Ce		La	
		in the salt	in the Cd	in the salt	in the Cd	in the salt	in the Cd
5	0.293	0.45	0.16	0.35	< 0.01	0.49	< 0.01
6	0.293	0.12	0.20	0.31	< 0.01	0.48	< 0.01
7	0.293	0.008	0.17	0.20	0.04	0.40	0.03
8	0.195	0.51	0.19	0.39	< 0.01	0.51	< 0.01
9	0.195	0.05	0.25	0.31	0.02	0.46	0.01
10	0.195	0.009	0.23	0.17	0.04	0.34	0.04

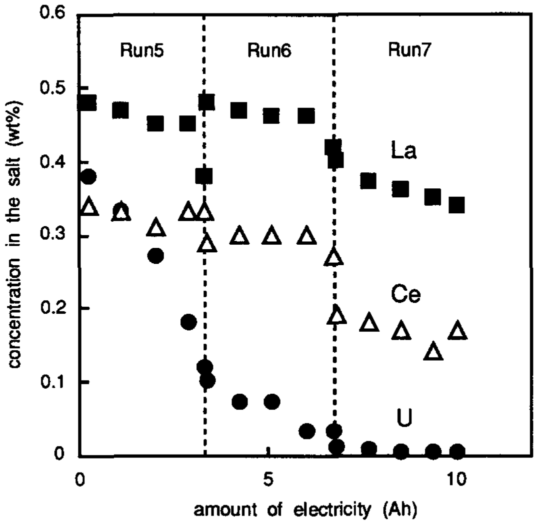

Fig. 7. Change of composition of molten salt electrolyte in electroreduction tests (anodic current density = 0.293 A/cm^2).

Table 4
Analytical result of cathode products in electroreduction tests

Run No.	Weight (g)	U (wt%)	Ce (wt%)	La (wt%)
5	95.11	14.14	0.38	0.58
6	18.82	1.72	7.50	8.99
7	4.52	1.00	13.69	25.36
8	89.24	8.7	1.00	0.66
9	23.77	0.58	8.49	8.18
10	4.39	0.81	12.46	25.32

4.2.1. Electroreduction at higher anodic current density (0.293 A / cm^2)

Fig. 7 shows the change of the salt composition in the test at higher anodic current density. It can be seen that uranium was removed from the salt at first and then cerium and lanthanum followed it.

The change of the electrode potentials in the same runs are shown in Fig. 8. A very low (about −2.5 V) cathode potential in run 6 and 7 suggests that rare earths or lithium were reduced dominantly after the uranium concentration in the salt decreased to about 0.1 wt%. Results from the chemical analysis of the cathode products in these runs (Table 4) clearly showed that the major constituent of the cathode deposit changed from uranium to rare earths. Thus, it was found difficult to recover uranium from the salt by electroreduction at a lower concentration than 0.1 wt% due to the contamination of the cathode product by rare earths.

Mass balances of uranium, cerium and lanthanum in

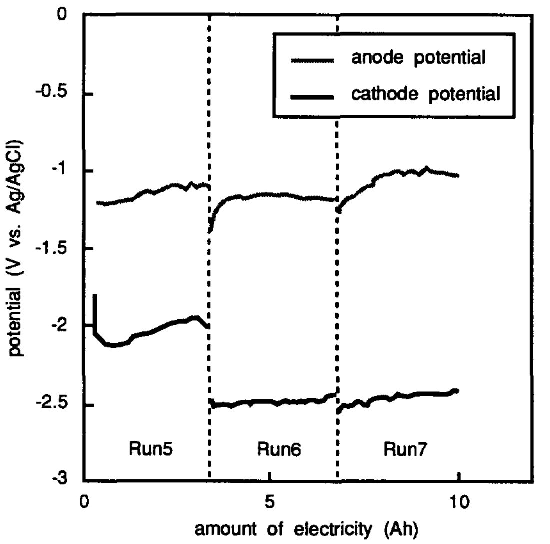

Fig. 8. Change of electrode potentials in electroreduction tests (anodic current density = 0.293 A/cm^2).

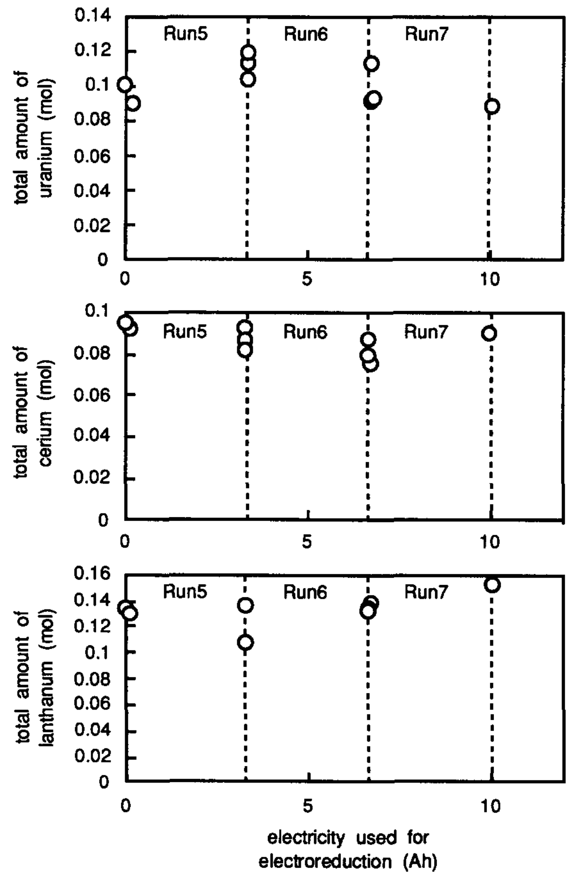

Fig. 9. Mass balance of uranium, cerium and lanthanum in electroreduction tests (anodic current density = 0.293 A/cm^2).

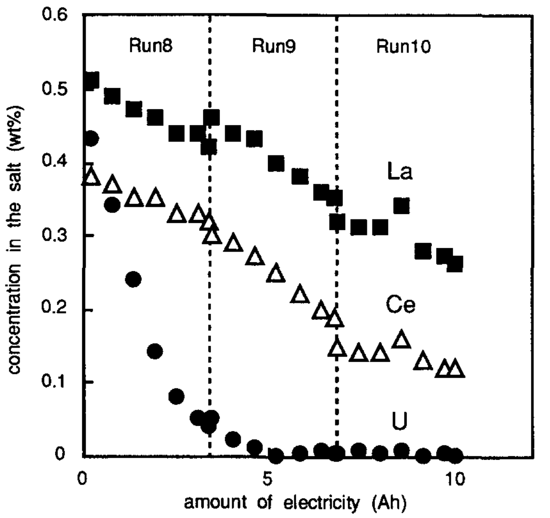

Fig. 10. Change of composition of molten salt electrolyte in electroreduction tests (anodic current density = 0.195 A/cm^2).

these runs are shown in Fig. 9. Total amounts plotted in Fig. 9 are sums of those in the liquid cadmium layer at the bottom of the electrorefiner, in the salt and in the cathode products. It can be seen that the mass balances of these elements were well kept throughout the runs within the range of errors in sampling and chemical analysis.

4.2.2. Electroreduction at lower anodic current density (0.195 A/cm^2)

Fig. 10 shows the change of the salt composition in the test at lower anodic current density. It can be seen that uranium, cerium and lanthanum in the salt decreased faster than in the case at a higher anodic current density (shown in Fig. 7). This is thought to be caused by the direct chemical reduction of these elements at the Cd–Li anode (see below). The composition of the cathode products (Table 4) showed that uranium was mainly reduced at the cathode in run 8 and that rare earths and lithium were dominantly reduced in run 9 and 10. Fig. 11 shows mass balances of uranium, cerium and lanthanum in these runs. The total amount of uranium was clearly decreased while essentially no changes were found in those of cerium and lanthanum. This is also expected to be due to the direct chemical reduction at the Cd–Li anode.

4.2.3. Direct chemical reduction at the anode

The sum of the amount of uranium, cerium and lanthanum in the salt in the electroreduction tests is plotted in Fig. 12. At a lower anodic current density, the amount of these elements decreased faster than calculated with the amount of the electric charge (Fig. 12A). This difference is expected to be caused by the direct chemical reduction with lithium metal at the anode. In fact, a paste-like product which contained high concentrations of uranium was found on the anode crucibles after most of runs. The content of the elements could not be determined because those products are easily dispersed in the salt and involved a large amount of the electrolyte salt.

Because of these undesirable characteristics of the anode product, it is preferable to collect actinides only at the cathode. To investigate conditions which restrain the direct chemical reduction at the anode, the anode potential in the electroreduction tests was compared with a value calculated with Nernst equations with the concentration of uranium in the bulk salt (Fig. 13). At a higher anodic current density, the anode potential was higher than the calculated value almost throughout the tests, indicating that uranium tended to be oxidized at the anode. On the other hand, the anode potential was occasionally lower than the calculated value at a lower anodic current density. Under

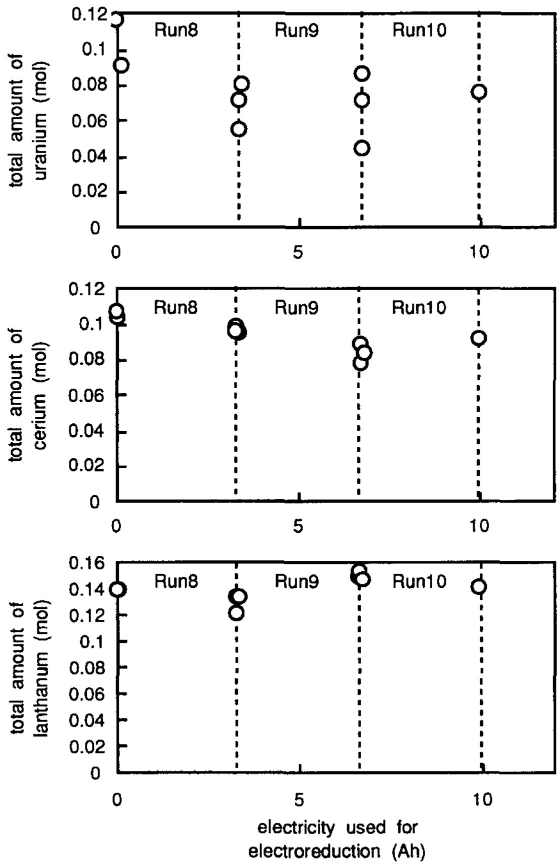

Fig. 11. Mass balance of uranium, cerium and lanthanum in electroreduction tests (anodic current density = 0.195 A/cm^2).

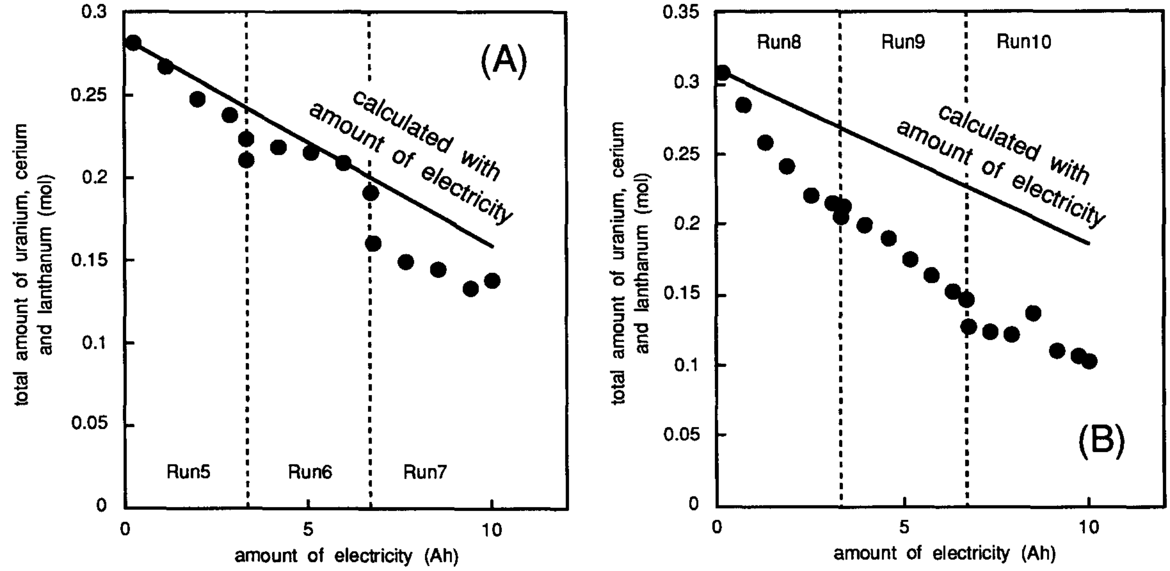

Fig. 12. Total amount of uranium, cerium and lanthanum in salt in electroreduction tests. (A) Anodic current density = 0.293 A/cm^2 and (B) anodic current density = 0.195 A/cm^2.

this condition, the direct chemical reduction of uranium at the anode was likely to occur to produce a large amount of anode product.

From these results, the direct chemical reduction of uranium at the anode in electroreduction could be avoided by monitoring the anode potential and keeping it higher than the deposition potential of uranium calculated with the composition of the bulk salt.

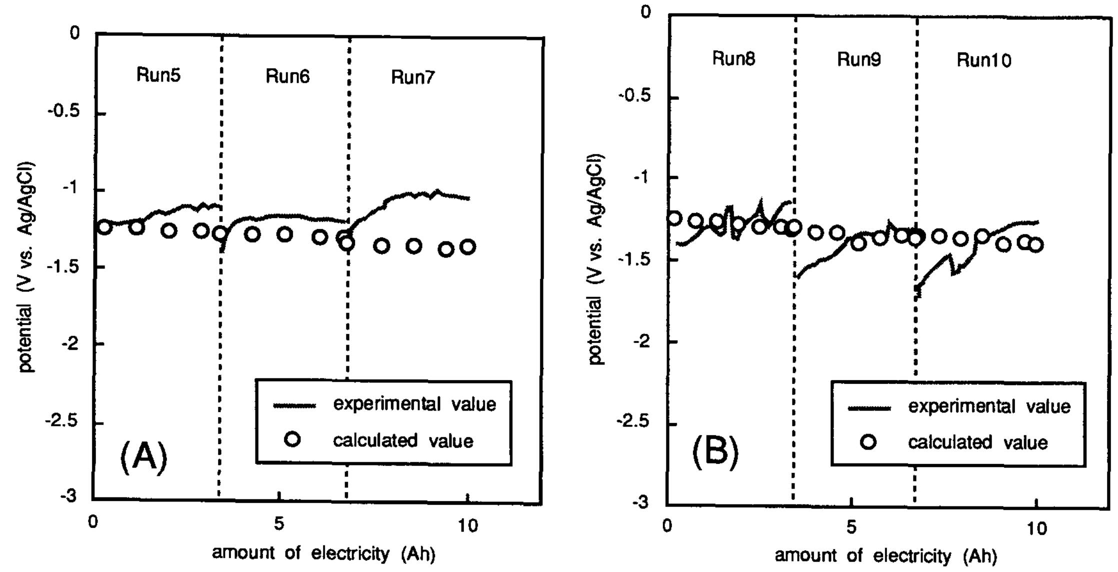

Fig. 13. Change of anode potential in electroreduction tests. (A) Anodic current density = 0.293 A/cm^2 and (B) anodic current density = 0.195 A/cm^2.

5. Summary

For the recovery of actinides from a molten salt/liquid cadmium system: (1) the electrotransport of uranium from a liquid cadmium layer and (2) the electroreduction of uranium from a molten salt electrolyte were examined. Uranium was successfully recovered from both a liquid cadmium and a molten salt electrolyte. At a uranium concentration lower than 0.1 wt%, recovery was difficult from either liquid cadmium or molten salt due to the polarization of the anode or contamination of the cathode product by rare earths. A diffusion layer model well explains the behavior of the electrotransport from the liquid cadmium anode. In electroreduction from molten salt, direct chemical reduction occurred at the anode especially at a lower anodic current density. It can be avoided by maintaining the anode potential higher than the deposition potential of uranium.

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