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Electrochemical behaviors of uranium and plutonium at simultaneous recoveries into liquid cadmium cathodes

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Abstract

Experiments were conducted on simultaneous recovery of uranium and plutonium electrochemically into laboratory scale liquid cadmium cathodes (LCCs) at different U/Pu ratios in the salt phase, and the influence of the salt composition on the recovered amounts of uranium and plutonium, the morphologies of uranium and plutonium in the LCC, and the behavior of americium, which is present as a decay product of plutonium-241, were examined. As a result, it was shown that there is a threshold in the U/Pu ratio in the salt phase between 1/4.3 and 1/1.73 for the successful simultaneous recovery of uranium and plutonium up to 10 wt% in the LCC at high current efficiencies. In the LCC, uranium and plutonium existed in the forms of intermetallic compounds, (U, Pu)Cd_6 and (U, Pu)Cd_{11}, and also pure uranium metal. It was also revealed that americium associates with plutonium according to the separation factor during the LCC operation.

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1. Introduction

The fuel cycle in the next generation requires reasonable economy, enhanced safety, proliferation resistance, and environmental friendliness. In order to satisfy these requirements, actinide recycling by simply designed pyrometallurgical processes offers a promising solution. Since the early 1980s, Central Research Institute of Electric Power Industry (CRIEPI) has been engaged in establishing the pyrometallurgical fuel cycle technology that adapts metallic fuel fast breeding reactors [1], which is shown in Fig. 1. The major steps in the process include electrorefining and reductive extraction for recovering actinides in molten chloride/liquid metal systems. As is shown in Fig. 1, the pyrometallurgical fuel cycle includes not only the metallic fuel cycle for fast reactors but also pyrometallurgical technologies combining the LWR fuel cycle, i.e., the reduction of spent oxide fuel to metallic form and the pyrometallurgical partitioning of actinide elements from the high level liquid wastes of Purex reprocessing. Thus the pyrometallurgical technology has high potential for establishing a nuclear fuel cycle using fissile materials effectively in fast reactors.

One of the main steps in the pyrometallurgical process is electrorefining using molten salt as an electrolyte, where the actinide elements are recovered and decontaminated from the fission products [2]. Fig. 2 shows a schematic flow of the regular procedure of the electrorefining step. The spent metallic fuel is cut into small pieces, loaded into a metallic basket, and immersed in

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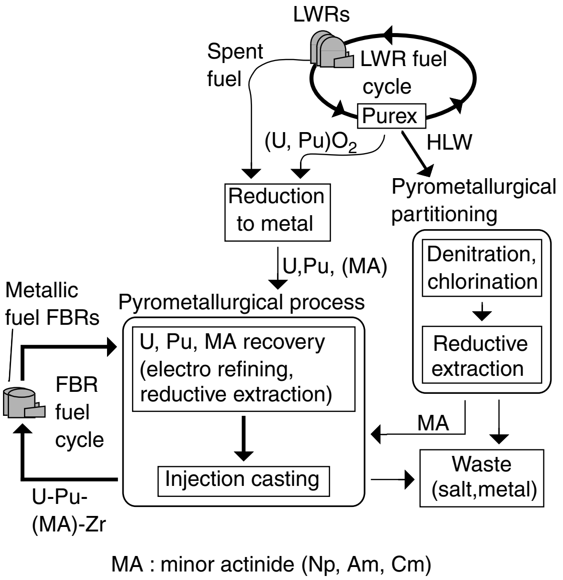


Fig. 1. Pyrometallurgical fuel cycle process proposed by CRIEPI.

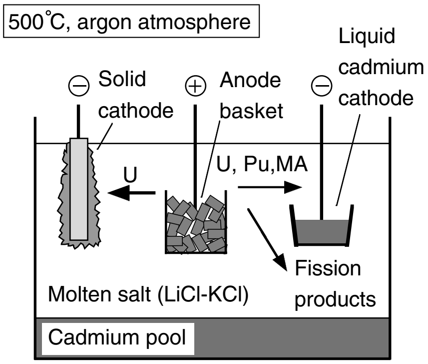


Fig. 2. Electrorefining step.

molten LiCl–KCl eutectic electrolyte. Almost all of the actinide elements in the spent fuel are dissolved anodically in the form of actinide chlorides. Chemically active fission products such as alkali, alkaline-earth, and rare-earth elements are also converted to their chlorides and accumulate in the salt phase. Fission products nobler than uranium are retained in the anode basket by controlling the anode potential.

Two kinds of cathodes are used in the electrorefining. One is a solid cathode made of iron and the other is a liquid cadmium cathode (LCC). On the solid cathode, uranium is selectively collected because the reduction potential for uranium is more than 200 mV positive than those for the other actinide and lanthanide elements [3]. On the other hand, the reduction potentials for the actinide elements are close to each other on the LCC because transuranic elements (plutonium, neptunium, americium, and curium) are stabilized in the LCC due to their very low activity coefficients in liquid cadmium [4–6]. Therefore, transuranic elements can be collected into the LCC together with uranium. Since no additional process is necessary for collecting minor actinides (MA; neptunium, americium, and curium), the pyrometallurgical process has an advantage for recycling MA as fuel along with plutonium. Although small amounts of lanthanide fission products appear in the LCC product along with the actinide elements due to the low activity coefficients of lanthanide elements in liquid cadmium, this does not affect the performance of a fast reactor loaded with the recycled fuel [7,8]. The unavoidable coexistence of fission products in the recycled fuel is actually an advantage in terms of non-proliferation. Since the operation of the LCC significantly influences the feasibility of pyrometallurgical reprocessing, it is crucial to evaluate the performance of the LCC.

For development of the pyrometallurgical reprocess, a joint research program has been conducted by CRIEPI and Japan Atomic Energy Research Institute (JAERI). Under the program, an electrorefining apparatus equipped with an LCC assembly was fabricated and installed in an argon atmosphere glove box. By using the apparatus, up to 8 wt% of plutonium has already been transported into small LCCs (3–5 g, 9 mm ∅ – i.d.) and it was found that the maximum cathodic current density suitable for plutonium recovery is proportional to the plutonium concentration in the molten salt in the relation of 22 $\text{mA/cm}^2 \times \text{wt\%-Pu}$ in salt, in the range of 2.1 and 4.6 wt%-Pu in the salt [3].

Next, it is necessary to study the behaviors of uranium and plutonium during simultaneous recovery into the LCC. Particularly, separation factor of uranium to plutonium (SF(U/Pu)), which is defined as (U/Pu ratio in the cathode product)/(U/Pu ratio in the salt), is necessary for estimating the mass flow of uranium and plutonium during the LCC operation. However, there are few detailed reports on the simultaneous recovery of uranium and plutonium. For the system of molten LiCl–KCl eutectic salt/unsaturated liquid cadmium, SF(U/Pu), which is defined as (U/Pu ratio in the cadmium)/(U/Pu ratio in the salt) in the equilibrium state, is reported to be 1.88 at the temperature of the electrorefining operation; 773 K [9]. Since our tentative target is to collect up to 10 wt% of uranium and plutonium into the LCC, the cathode cadmium must be saturated with uranium and plutonium, because the solubility limits of uranium and plutonium in liquid cadmium at 773 K are reported to be 2.35 and 3.62 wt%, respectively [10]. However, there is no information on the separation factors for collecting uranium and plutonium into the LCC that is saturated with uranium and plutonium. After the saturation, formation of solid materials in the forms of uranium metal and $PuCd_6$ is expected in the LCC based on the U–Cd and Pu–Cd binary phase diagrams [11]. However, there is no report on the morphology of uranium and plutonium recovered in the LCC.

Additionally, uranium has a tendency to form dendritic deposits on a cathode [12]. The uranium dendrite formed on the LCC may cause an electrical short circuit with cell components, and may also act as a solid cathode that collects only uranium. Thus, the formation of such dendritic deposit should be prevented during the LCC operation. Therefore, it must be verified that uranium and plutonium can be recovered simultaneously into the LCC up to 10 wt%.

In the present work, several experiments were conducted on recovering uranium and plutonium simultaneously into 120 g LCCs, which are estimated to be roughly 1/300 of the practical LCC in weight, at different U/Pu ratios in the salt phase, and the influence of the salt composition on the recovered amounts of both elements and their morphology in the LCC were studied. Then separation factors of uranium to plutonium during the simultaneous recovery were obtained. Additionally, the behavior of americium, which amounts for 70% of the entire MA in the spent fuel and is contained in the present experimental system as a decay product of plutonium-241, was also examined.

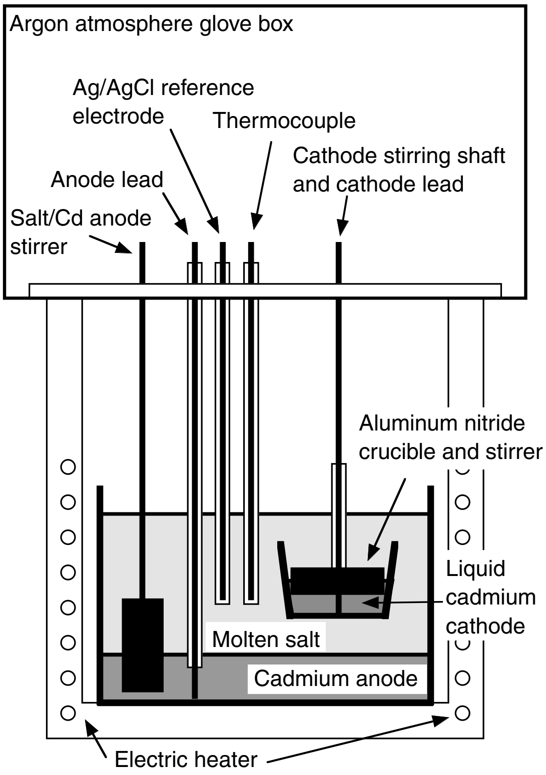


Fig. 3. Experimental apparatus.

2. Experimental

2.1. Apparatus

All the experiments were carried out in a high-purity argon-atmosphere glove box. Both oxygen and moisture concentrations in the argon atmosphere were maintained at less than 2 ppm during the experiments. Fig. 3 shows a schematic view of the experimental apparatus. About 1200 g of LiCl–KCl eutectic salt was loaded in a containing vessel, which was made of iron. Under the molten salt electrolyte, 1400–1540 g of liquid cadmium was placed and used as an anode that supplied uranium and plutonium during the experiments. The salt and anode cadmium were held at 773 ± 2 K using an electric furnace.

At the start of each experiment, 120 g of cadmium was contained in a cathode crucible, which was made of aluminum nitride. The cathode surface diameter was 42 mm. For stirring the boundary of cathode cadmium and molten salt phases, a stirrer made of aluminum nitride was used at a rotation speed of 40 rpm. An iron shaft lead through the cathode stirrer was used as a rotation drive, and also as an electrical contact to the cathode. Another stirrer made of iron was placed in the containing vessel and used for mixing the molten salt and the cadmium anode phases. A tungsten rod was used as an anode contact. An Ag/AgCl reference electrode (1 wt% AgCl in LiCl–KCl) contained in a thin Pyrex glass tube was used for monitoring the cathode potential. To control the electrotransport, EG&G Princeton Applied Research potentiostat/galvanostat model 273A was used.

Samples of the molten salt, anode cadmium, and cathode cadmium were taken by drawing them into a small diameter Pyrex glass tube fitted with a syringe. After solidification, the samples were weighed and then dissolved in nitric acid. The concentrations of uranium and plutonium in the solutions were determined using an inductively coupled plasma-atomic emission spectroscope (ICP-AES). The concentrations of americium in the solutions were measured using a high-purity germanium γ-ray detector and a multi-channel analyzer, by detecting the 59.5 keV gamma ray emitted from Am-241. A maximum error of approximately 10% was expected for the sample analysis, based on the random errors ascribed to sample collection, weighing, solution preparation, and instrumental analysis. In order to identify the phase compositions containing uranium and plutonium in the cathodes after experiments, small pieces cut from the cathode products were analyzed using an electron probe microanalyzer (EPMA).

Table 1
Conditions of U and Pu recovery experiments

Run #	Starting salt composition in weight			Cathode Cd (g)	Cathode current density (mA/cm^2)	Passed charge (coulomb)
	U (%)	Pu (%)	U/Pu ratio			
Run 1	–	4.6	–	120.0	23.4 → 19.5	1.96×10^4
Run 2	0.36	4.4	1/12.2	120.1	23.4	1.89×10^4
Run 3-1	0.67	5.0	1/7.4	120.1	23.4	1.92×10^4
Run 3-2	0.62	5.0	1/8.0	120.0	23.4	1.85×10^4
Run 4-1	1.07	4.7	1/4.4	120.0	23.4	1.90×10^4
Run 4-2	1.11	4.8	1/4.3	120.1	23.4 → 19.5	1.91×10^4
Run 5	2.6	4.5	1/1.73	120.1	23.4	1.88×10^4

2.2. Chemicals

The purities of chlorides (LiCl–KCl eutectic, $CdCl_2$, and AgCl) were no less than 99.99%. For the anode and the cathodes, cadmium metal of 99.9999% purity was used. Purities of the other electrode materials, such as tungsten rod and silver wire, were no less than 99.95%.

2.3. Experimental conditions

In the present study, seven experiments were conducted at roughly five different salt compositions including a case of containing no uranium. The starting compositions of the molten salt for all experiments are listed in Table 1. The U/Pu weight ratios in the starting salt phase ranged between 0 and 1/1.73. Usually, each electrotransport was conducted at a constant current with the cathode current density of 23.4 mA/cm^2. The total electric charge passed in each experiment was 1.85×10^4–1.96×10^4 coulombs, which corresponded to 15.3–16.2 g of plutonium or 11–12 wt% of actinides in the LCC, assuming a current efficiency of 100%.

3. Results and discussion

3.1. LCC potentials during experiments

The LCC potential relative to the reference electrode during each experiment is shown in Fig. 4(A) and (B). In all cases, the LCC potentials gradually shifted to the negative direction, with deviations of about 60 mV, until the LCCs were saturated with uranium and plutonium. After the saturation, the LCC potentials remained almost constant or showed small rises. The sudden rises in LCC potentials in Runs 1 and 4-2 were caused by the reduction in cathode current density from 23.4 to 19.5 mA/cm^2. Additionally, the Ag/AgCl reference electrode was replaced at the current reduction in Run 4-2. As shown in these figures, the LCC potentials before the saturation were not significantly affected by the salt phase composition. After the saturation, the LCC potential profiles were somewhat different. As explained later, the rise in LCC potential after the LCC saturation seems to have some relation to the cathode appearance.

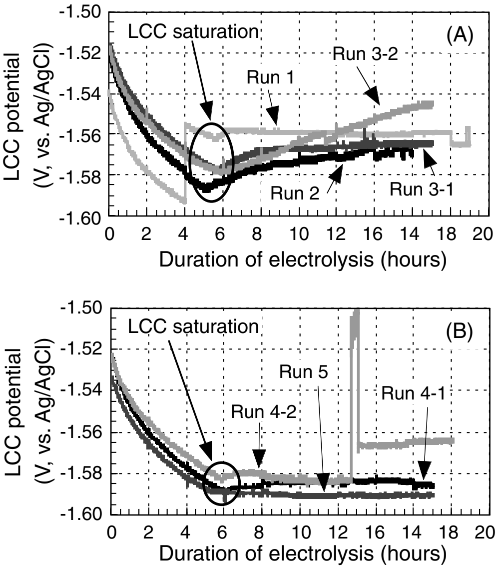


Fig. 4. LCC potential profiles in present experiments for (A) Runs 1, 2, 3-1, 3-2 and (B) Runs 4-1, 4-2, and 5. Current densities during experiments were 23.4 mA/cm^2, with the exception of 19.5 mA/cm^2 for Run 1 after 4 h and Run 4-2 after 13 h. Potential rise between 12.5 and 13 h in Run 4-2 was due to damage of reference electrode.

It was reported that dendritic deposit formation was indicated by a sharp LCC potential deviation in the case of collecting uranium into LCC [12]. In the present experiments, no such significant deviation was observed.

3.2. Appearance of cathodes

After each experiment, the solidified cathode cadmium ingot was removed from the aluminum nitride crucible. Although no dendritic deposit formation was indicated by the LCC potential profile, the surface of the Run 2 cathode ingot was highly uneven as seen in

Fig. 5(A). One particular part projected upwards by about 19 mm, and was significantly higher than the remaining parts. In the case of Run 3-1, the cathode ingot had a smooth surface but contained about 5 g of salt dispersed inside the ingot, which seemed to have occurred due to mixing of the cathode surface. In the case of Run 3-2, which was conducted without cathode stirrer rotation to confirm the effect of cathode mixing, the cathode showed a smooth surface. However, approximately 30 g of deposit was found on the stirrer in Run 3-2. On the other hand, the cathode ingots of Runs 1, 4-1, 4-2, and 5 showed smooth surfaces and contained no salt. The cathode ingot of Run 4-1 is shown in Fig. 5(B).

In the cases that the LCC potentials were constant after the LCC saturation, as shown in Fig. 4(A) and (B), smooth surface cathodes were obtained. The rises in LCC potentials observed in Runs 2 and 3-2 can be explained by the shortening of the mass transfer pass and increase in LCC surface area, due to projection formation in Run 2 and deposit formation on the LCC stirrer in Run 3-2. Accordingly, the LCC potential profile after the LCC must have some relation with the cathode appearance.

3.3. Content of uranium and plutonium in LCC

The amounts of elements collected in each cathode are listed in Tables 2 and 3. Based on the increase in cathode weight throughout the experiments, it was estimated that 14.35–15.33 g of uranium and plutonium were recovered into LCCs. According to these values,

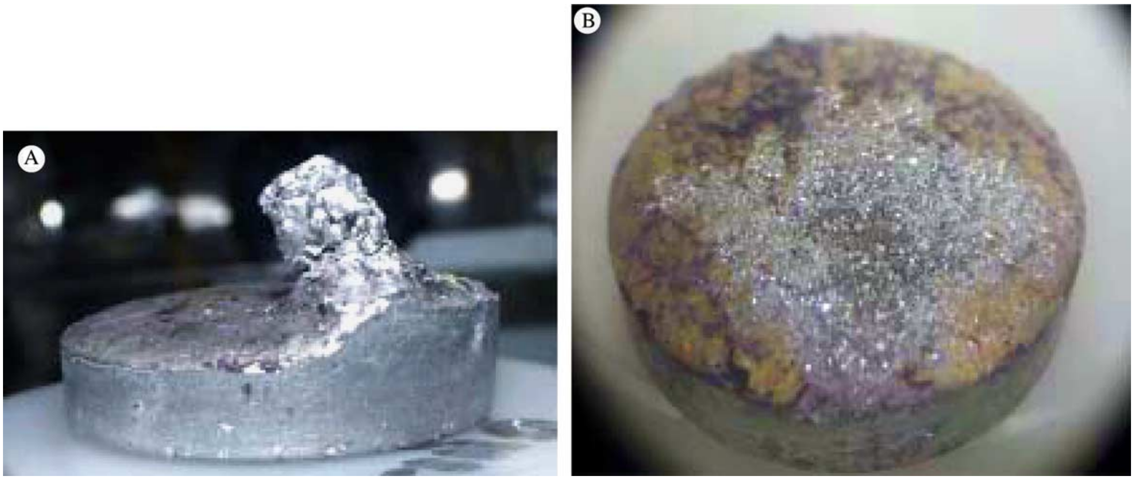


Fig. 5. Cathode ingot recovered in (A) Run 2 and (B) Run 4-1.

Table 2
Major results of U and Pu recovery experiments

Run no.	Based on increase of cathode weight			Based on cathode sample			
	Amount of U + Pu in cathode (g)	U + Pu weight ratio (%)	Current efficiency (%)	Weight ratio in saturated liquid Cd			SF before saturation[a]
				U (%)	Pu (%)	U + Pu (%)	
Run 1	15.05	11.1	93	–	3.8	3.8	–
Run 2	14.35	10.7	92	0.58	3.3	3.8	2.2
Run 3-1	N/A[b]	N/A	N/A	0.83	3.1	4.0	2.1
Run 3-2	N/A[c]	N/A	N/A	0.73	3.1	3.8	1.9
Run 4-1	14.67	10.9	93	1.28	2.8	4.1	2.0
Run 4-2	14.72	10.9	93	1.21	2.7	3.9	1.8
Run 5	15.33	11.3	99	1.81	2.2	4.0	1.5

[a] (U/Pu ratio dissolved in liquid Cd in saturated cathode)/(U/Pu ratio in salt).

[b] Unmeasurable because of salt dispersion in cathode.

[c] Unmeasurable because of deposit formation on stirrer.

Table 3
Major results of U and Pu recovery experiments

Run no.	Based on mass balance					Based on ingot analysis			
	Weight ratio in cathode		Total SF[a]	SF after saturation[b]	Current efficiency	Weight ratio in cathode		Total SF[a]	Current efficiency (%)
	U (%)	Pu (%)				U (%)	Pu (%)		
Run 1	–	N/A	–	–	N/A	–	N/A	–	N/A
Run 2	1.26	9.1	1.6	1.4	87	N/A	N/A	N/A	N/A
Run 3-1	1.76	9.3	1.4	1.1	93	N/A	N/A	N/A	N/A
Run 3-2	1.23	7.9	1.2	0.8	80	N/A	N/A	N/A	N/A
Run 4-1	3.4	8.6	1.7	1.6	102	2.9	8.3	1.5	95
Run 4-2	3.3	7.1	2.0	2.1	89	N/A	N/A	N/A	N/A
Run 5	9.0	1.75	10	–[c]	92	9.0	2.2	8.0	96

[a] (U/Pu ratio in cathode product)/(U/Pu ratio in salt).

[b] (U/Pu ratio in cathode solid material)/(U/Pu ratio in salt).

[c] Unable to calculate.

weight ratios of uranium and plutonium in LCCs reached 10.7–11.3 wt%, which exceeded the tentative target; 10 wt%. In cases of Runs 3-1 and 3-2, the increase in cathode weight was not measured due to the salt dispersion in the cathode or the deposit formation on the cathode stirrer.

Changes in the uranium and plutonium contents in cathodes of Runs 2, 4-1, and 5 are plotted in Fig. 6(A)–(C). The uranium and plutonium concentrations in the cathode samples drawn by Pyrex tubes showed almost constant values on the way of electrorecovery, indicating that the cathode samples showed concentrations of uranium and plutonium dissolved in the liquid cadmium phase. As shown in Table 2, concentrations of uranium and plutonium in the saturated cathode samples were almost constant at 3.8–4.1 wt% in the present study.

Separation factors of uranium to plutonium (= SF(U/Pu)) before the saturation of cathodes, which were defined as (U/Pu ratio dissolved in liquid cadmium phase in the saturated cathode)/(U/Pu ratio in the salt), were calculated to be 1.5–2.2 as listed in Table 2. These values roughly agreed with the SF(U/Pu) value in LiCl–KCl eutectic salt/unsaturated liquid cadmium system in equilibrium state; 1.88 [9]. In the present study, uranium and plutonium behaved as thermodynamically expected before the saturation of LCC.

In order to estimate the amounts of uranium and plutonium collected into each cathode from the mass balance in the system, the decrease of these elements in the molten salt and the anode cadmium phases were calculated by the sample analysis. Since recovered amounts of uranium and plutonium based on their mass balance in the system (□ in the figures) showed good agreement with the weight increase of cathodes (× in the figures), as shown in Fig. 6(A)–(C), this method based on the mass balance was considered to be reliable. The result of the mass balance method is summarized in Table 3. According to the mass balances, the current efficiencies for the experiments were higher than 80%. The total SF(U/Pu), defined as (U/Pu ratios in the cathode products)/(U/Pu ratio in the salt), ranged between 1.2 and 2.0 except for Run 5. These values were slightly smaller than corresponding values before the saturation of cathodes, because the SF(U/Pu) while solid materials were being generated after the saturation of cathodes were closer to 1.0. In the case of Run 5, the weight ratio of plutonium in the cathode estimated from the mass balance was close to the values in the samples taken from the cathode after saturation. This means that plutonium was not contained in the solid phase and not recovered after the cathode saturation in Run 5.

Additionally, the recovered amounts of uranium and plutonium for Runs 4-1 and 5 were directly estimated by the following method. Fan-shaped samples were cut from the cathode products and melted with LiCl–KCl eutectic salt and CdCl$_2$ to extract the uranium and plutonium contained in the samples into the salt phase. By analyzing the concentrations of uranium and plutonium in the extraction salt, the amounts of uranium and plutonium in the entire cathodes were estimated. The results of this estimation, named as ‘ingot analysis’, are also shown in Table 3 and Fig. 6(B) and (C). The ingot analysis values were very close to the final values based on mass balances in the system, indicating that the values obtained by the two methods were both reliable.

From these results, it is concluded that under the conditions that the U/Pu ratio in the salt phase were less than 1/4.3, uranium and plutonium were recovered into LCCs up to 10 wt% with SF(U/Pu) ranging between 1.2 and 2.0. Though the obtained total SF(U/Pu) values have somewhat large deviations, it may be concluded that uranium and plutonium were collected according to an almost constant SF(U/Pu) value. When the U/Pu ratio in the salt phase was 1/1.73, only uranium was

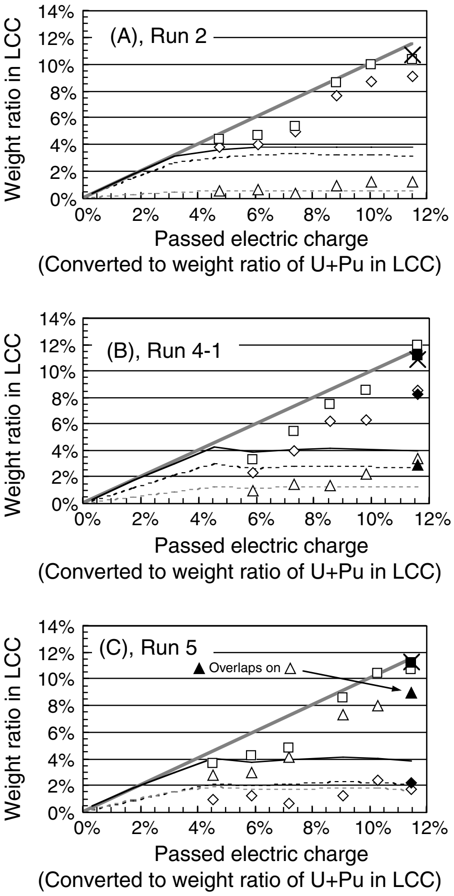


Fig. 6. Change of U and Pu contents in LCC in (A) Run 2, (B) Run 4-1, and (C) Run 5. Based on LCC sample analysis: (- - - - - -) U; (- - -) Pu; (—) U + Pu. Based on mass balances in system: (△) U; (◇) Pu; (□) U + Pu. Based on cathode ingot analysis: (▲) U; (◆) Pu; (■) U + Pu. (×) U + Pu, based on cathode weight gain; (————) U + Pu, 100% current efficiency.

collected into the LCC after the saturation. Accordingly, it is indicated that there is a threshold for the U/Pu ratio of the salt phase between 1/4.3 and 1/1.73 for collecting uranium and plutonium simultaneously.

3.4. Morphology of cathode products

Cross sections of Runs 2, 4-1, and 5 cathodes were analyzed by EPMA to investigate the chemical forms of uranium and plutonium in the LCCs. The back scattering electron images on the cathodes are shown in Fig. 7(A)–(C). The chemical composition of each phase containing uranium or plutonium is summarized in Table 4, including the result of plutonium recovery experiment into small LCCs [3]. In the case of Run 2, the cathode consisted of a pure cadmium phase and a U–Pu–Cd ternary intermetallic compound phase with mole ratio of U:Pu:Cd = 0.11:0.89:5.3. Since it is known that $PuCd_6$ is stable at 500 °C [11], the recovered uranium and plutonium appear to have formed an (U, Pu)Cd_6-type intermetallic compound including a small fraction of uranium in the place of plutonium in $PuCd_6$.

In the case of Run 4-1, the cathode consisted of a pure cadmium phase and two kinds of U–Pu–Cd ternary intermetallic compound phases. The mole compositions of these intermetallic phases were U:Pu:Cd = 0.24:0.76:5.2 and U:Pu:Cd = 0.24:0.76:9.2, respectively.

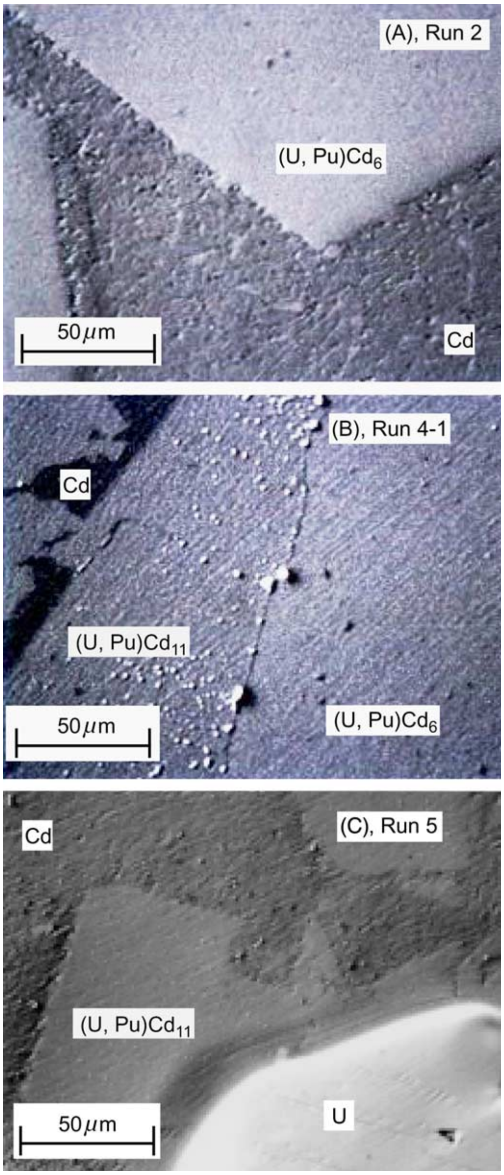


Fig. 7. Back scattering electron images of cathode cross sections after (A) Run 2, (B) Run 4-1, and (C) Run 5.

Table 4
Compositions of U and Pu in cathodes found by EPMA

Run #	U/Pu ratio in initial salt	(U, Pu)Cd_6 phase composition as UxPuyCdz $(x+y=1)$				(U, Pu)Cd_{11} phase composition as UxPuyCdz $(x+y=1)$				Metallic uranium phase
		x	y	z	x/y	x	y	z	x/y	
Small LCC [3]	No uranium	–	1	6.1	–	Not found				–
Run 2	1/12.2	0.11	0.89	5.3	1/8.1	Not found				Not found
Run 4-1	1/4.4	0.24	0.76	5.2	1/3.2	0.24	0.76	9.2	1/3.2	Not found
Run 5	1/1.73	Not found				0–0.6	0.4–1	10	0–1.5	Pu, Cd < detection limit

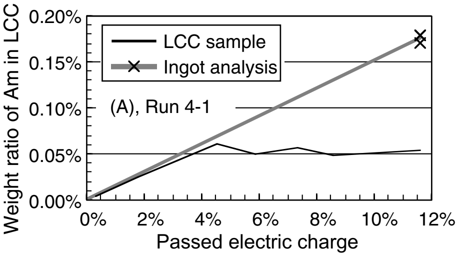
The latter compound was much more abundant than the former one. Considering the analytical errors in EPMA analysis, these two phases seem to be (U, Pu)Cd_6- and (U, Pu)Cd_{11}-type ternary intermetallic compounds, because it is known that both uranium and plutonium form intermetallic compounds with cadmium, UCd_{11} and $PuCd_{11}$, which decompose at 746 and 683 K, respectively. Depending on the Cd–U and Cd–Pu binary phase diagrams [11], it had been predicted that uranium and plutonium recovered into LCC form pure uranium metal and $PuCd_6$, respectively. On the contrary, no metallic uranium phase was found in the Run 2 and Run 4-1 cathodes. Since the cathodes were not quenched in the present experiments, these intermetallic compound phases might have formed during the cooling. However, if uranium metal existed in the LCC at 773 K, the uranium metal phase must have remained in the solidified cathode ingot. Thus, it is considered that the actual behavior of uranium and plutonium in simultaneous recovery differs from the expected one.

In Run 5, besides pure cadmium and (U, Pu)Cd_{11}-type ternary intermetallic compound phases, an uranium phase containing little amount of cadmium or plutonium was found. The existence of the uranium phase means that the activity of uranium in the LCC was unity independent of the amount of uranium in the LCC, which means that uranium can be recovered without increasing its activity. Therefore the uranium phase formation must be the reason for the selective collection of uranium in Run 5 after the saturation of LCC.

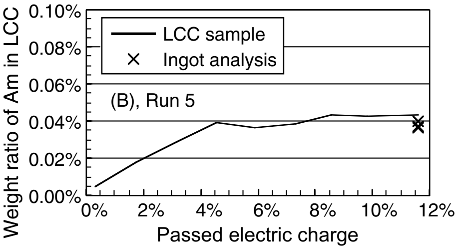
3.5. Behavior of americium

In the cases of Runs 4-1 and 5, the behavior of americium during the electrotransport was studied. As shown in Fig. 8(A) and (B), the concentrations of americium in the samples drawn from the LCCs became constant during electrotransport in both runs. In contrast, the weight ratio of americium in the final cathode cadmium of Run 4-1 estimated by the ingot analysis method was much higher than in the samples drawn from the LCC. The weight ratios of americium estimated by the ingot analysis method agreed well with the extrapolated concentrations of americium in the samples drawn directly from the Run 4-1 cathode before the saturation of LCC. Therefore, americium was recovered at almost a constant rate in Run 4-1. Since the concentration of americium in the salt phase was almost constant throughout the experiment, it is indicated that the electrotransport of americium was not affected by the saturation of uranium and plutonium in the cathode cadmium. Since concentrations of americium in the LCC samples were constant after the saturation, americium seems to have been involved in the U–Pu–Cd intermetallic compound.

In the case of Run 5, the weight ratios of americium estimated by the ingot analysis method agreed with the concentrations of americium in the samples drawn directly from the Run 5 cathode after the saturation of



(A) (Converted to weight ratio of U+Pu in LCC)



(B) (Converted to weight ratio of U+Pu in LCC)

Fig. 8. Change of Am content in LCC in (A) Run 4-1 and (B) Run 5.

LCC. This means that americium was not collected into the LCC after the saturation and its behavior was similar to that of plutonium.

The separation factor of americium to plutonium (= SF(Am/Pu)) before the saturation of cathodes, which was defined as (Am/Pu ratio in the samples taken from the saturated cathode)/(Am/Pu ratio in the salt), was calculated to be 0.70 for Run 4-1 and 0.66 for Run 5. These values roughly agreed with the separation factor of 0.61 for americium to plutonium in the LiCl–KCl/unsaturated liquid cadmium system in the equilibrium states [9]. In Run 4-1, SF(Am/Pu) while the solid material was being formed was 0.81. The total SF(Am/Pu), defined as (Am/Pu ratio in the cathode product)/(Am/Pu ratio in the salt), was 0.78 for Run 4-1. Although the Am/Pu ratio in the LCC product was reduced to 0.78 of that in the salt phase, it can be concluded that most of the americium is co-recovered in the LCC along with plutonium.

These results on the behavior of americium do not agree with those in a previous report [3], which concluded that the recovery of americium was controlled after the saturation of the liquid cadmium phase with plutonium in the cases of plutonium recovery into small LCCs from the salt containing no uranium. In the previous study, the recovered amounts of americium in the product cathode ingots were estimated from the γ-ray dose measured by a GM survey meter. The method using the GM survey meter might have counted the γ-ray that was not emitted from Am-241. Furthermore, the previous results might have been affected by the self-shielding of the γ-ray in the cathode ingots. In the present study, the γ-ray used for the americium content estimation was confirmed to be emitted from Am-241 by measuring the energy of the γ-ray. Since the proportion of the γ-ray counts to the concentration of americium in the solute was also verified by using the standard solutions including much more americium concentrated one than the actual samples, the self-shielding of the γ-ray was negligible. Therefore, the conclusion drawn from the present study is much more reliable.

4. Summary

In order to study the salt composition dependence of the behavior of uranium and plutonium in simultaneous recovery into liquid cadmium cathodes (LCCs), several experiments were conducted to recover uranium and plutonium electrochemically into LCCs at different U/Pu ratios in the salt phase.

The major results were as follows: (1) The weight ratios of uranium and plutonium in 120 g LCCs reached more than 10 wt% (the tentative target), with current efficiencies higher than 80%. Under the conditions of U/Pu ratios in the initial salt phase less than 1/4.3, the amounts of recovered uranium and plutonium were proportional to the passed electric charges, with the separation factors of uranium to plutonium (= (U/Pu ration in the recovered product)/(U/Pu ratio in the salt)) ranging between 1.2 and 2.0. Thus, uranium and plutonium were successfully recovered into LCC. On the other hand, under the condition of U/Pu ratio in the initial salt phase of 1/1.73, only uranium was recovered into the LCC after the saturation of the liquid cadmium phase in the LCC with uranium and plutonium. Accordingly, it was indicated that there is a threshold in the U/Pu ratio in the salt phase between 1/4.3 and 1/1.73 for the simultaneous recovery of uranium and plutonium. (2) The recovered uranium and plutonium formed ternary intermetallic compounds in the forms of (U, Pu)Cd_6 for the cases that the U/Pu ratios in the salt phase were 1/12.2 and 1/4.4 and (U, Pu)Cd_{11} for the cases that the U/Pu ratios in the salt phase were 1/4.4 and 1/1.73. Furthermore, an almost pure uranium metal phase was found in the case that the U/Pu ratio in the initial salt phase was 1/1.73. Since the formation of U–Pu–Cd ternary intermetallic compounds had not been estimated previously, the actual mechanisms of uranium and plutonium recovery were revealed to be more complicated than elucidated in the previous model that includes only the formation of $PuCd_6$ and uranium metal. (3) Though americium was recovered constantly into LCC when the U/Pu ratio in the salt phase was 1/4.4, the recovery of americium was controlled after the saturation of LCC when the U/Pu ratio in the salt phase was 1/1.73. The behavior was similar to that of plutonium. When the U/Pu ratio in the salt phase was 1/4.4, the separation factors of americium to plutonium (= (Am/Pu ration in the recovered product)/(Am/Pu ratio in the salt)) was 0.78, which means that most of the americium is co-recovered in LCC along with plutonium.

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