

**DEVELOPMENT OF PLUTONIUM RECOVERY PROCESS
BY MOLTEN SALT ELECTROREFINING WITH LIQUID CADMIUM CATHODE**

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Abstract

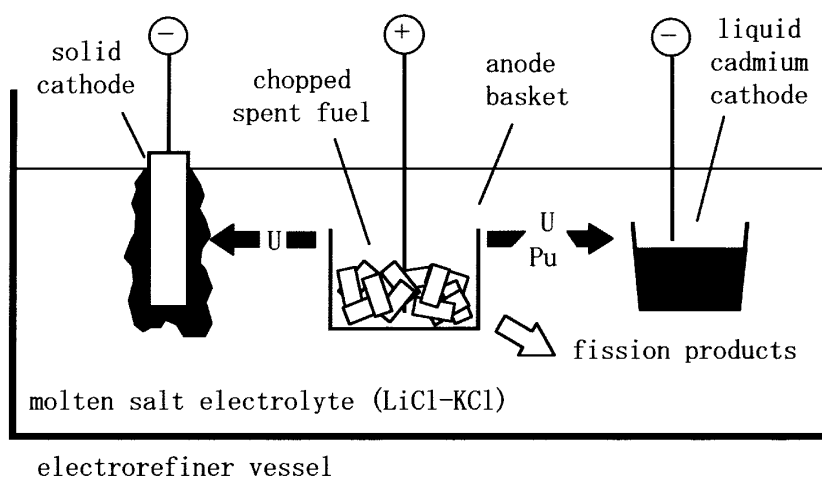
The effects of electrochemical conditions on the behaviour of plutonium and adequate conditions for recovery at liquid cadmium cathode (LCC) used in pyrometallurgical reprocessing were studied with small, not stirred electrodes. Cathodic current density adequate for plutonium collection at LCC was considered to be controlled by diffusion plutonium ion in molten salt and proportional to its concentration. It was shown that plutonium collected at the LCC beyond saturation formed intermetallic compound PuCd_6 and accumulated at the bottom of the LCC. This behaviour of coexisting americium was reasonably explained by the local equilibrium model between plutonium and americium at the surface of the LCC. The plutonium collection rate in practical electrorefining equipment estimated by extrapolation of experimental results was satisfactorily high in designing practical equipment and process.

1. Introduction

Metallic fuel cycle which consists of a metal (U-Zr or U-Pu-Zr) fuelled fast reactor and pyrometallurgical reprocessing has been proposed originally by Argonne National Laboratory (ANL) as an innovative nuclear fuel cycle technology [1]. The metallic fuel cycle has an excellent safety potential aspect originating from high thermal conductivity of the metal fuel [2]. It also has economic advantage because a pyrometallurgical reprocessing plant is estimated to be smaller than conventional aqueous reprocessing plants due to fewer steps and smaller equipments [3].

The main step in the pyrometallurgical process is molten salt electrorefining [4], where the actinide elements are recovered and decontaminated from the fission products. Figure 1 shows a schematic flow of the normal operation of this electrorefining step. The spent fuel is cut into small pieces, loaded in a steel basket, and immersed into molten chloride electrolyte. Almost all of the actinide elements in the spent fuel are anodically dissolved. Noble metal fission products are left in the anode basket by controlling the anode potential. Chemically active fission products such as alkali, alkaline earth, and rare earth metals exchange with the actinide chlorides in the electrolyte and accumulate in the molten salt in the form of their chlorides. Two kinds of cathodes are used to obtain different streams of products. One is a solid cathode made of iron and the other is a liquid cadmium cathode (LCC). At the solid cathode, uranium is selectively collected because the free energy change of chloride formation for uranium is negatively less than those of the other actinide elements. On the other hand, free energy changes of the actinide elements are close to each other at LCC because the transuranium elements (plutonium, neptunium, americium and curium) are stabilised in the LCC due to their very low activity coefficients in liquid cadmium [5,6]. Therefore, transuranium elements can be collected at LCC together with uranium.

Figure 1. Schematic flow of routine operation of the electrorefining step



The use of LCC is the most important technology in the pyrometallurgical process, where plutonium is recovered, roughly separated from uranium, and decontaminated from fission products. Because performance of LCC significantly influences the feasibility of the pyrometallurgical reprocessing, ANL studied plutonium recovery with LCC in depth with laboratory scale equipment [7-10]. Central Research Institute of Electric Power Industry (CRIEPI) has also reported on the LCCs, especially focusing on the formation of dendritic uranium deposit [11,12]. In those studies, it was shown that stirring in cathode cadmium with vertical paddles is effective to restrain growth of the

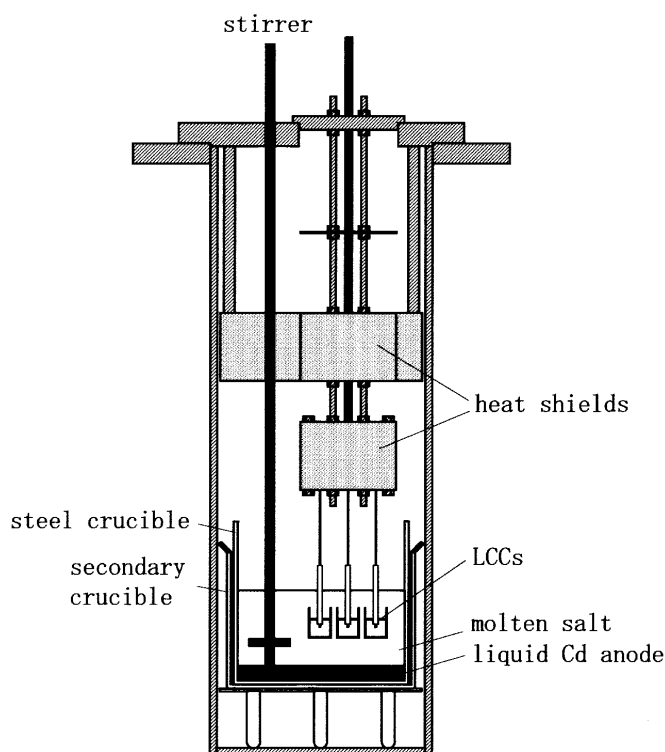
uranium dendrite and that uranium can be collected into LCCs at a cathodic current density of 0.2 A/cm^2 up to about 10 wt% in the cathode without dendrite formation [12]. In addition to the uranium studies, we have launched a joint research program with Japan Atomic Energy Research Institute (JAERI) on pyrometallurgical processes for the actinide elements. In 1999, a plutonium electrorefining apparatus equipped with a LCC assembly was fabricated and installed in a glove box. In this study, fundamental plutonium electrotransport experiments were carried out in order to understand the effects of electrochemical conditions on the behaviour of plutonium at LCC preceding investigation of engineering factors like stirring method.

2. Experiment

2.1 Apparatus

All the experiments were carried out in a high purity argon atmosphere glove box. Both oxygen and moisture levels in the atmosphere were kept less than two ppm during the tests. Figure 2 is a schematic view of the experimental apparatus. Inner diameter and depth of the container for molten salt were 124 mm and 120 mm, respectively. The amount of lithium chloride-potassium chloride (LiCl-KCl) eutectic mixture loaded in this container was about 1 200 grams. Under the molten salt electrolyte, a liquid cadmium layer was placed and used as an anode which supplied plutonium in electrotransport experiments. The amount of the anode cadmium was about 1 400 grams. The salt and anode cadmium were heated with an electric furnace and the temperature of the system was kept to $773 \pm 1 \text{ K}$.

Figure 2. Schematic view of experimental apparatus



The electrorefining apparatus and the cathode assembly were originally designed to accommodate a LCC of 50 mm outer diameter, which would be stirred to facilitate the mass transfer of plutonium. In this study, however, much smaller cathodes were used because the study aimed to understand the effects of fundamental electrochemical conditions on the behaviour of plutonium at LCC proceeding to investigate engineering factors like stirring method. The size of the cathode crucible used in this study was 9 mm in diameter and 16 mm in depth. About 3 to 5 grams of cadmium was loaded in the crucible. A silver-silver chloride (1 wt% AgCl in LiCl-KCl) reference electrode contained in a thin Pyrex glass tube was used as a reference electrode.

2.2 Chemicals

The chlorides (LiCl-KCl, CdCl₂ and AgCl) were purchased from Anderson Physical Laboratory. Because their purity was no less than 99.99% and their moisture content was extremely low, they were used with no additional purification procedure. Cadmium metal of more than 99.9999% purity for the anode and the cathode was purchased from Rare Metallic Corporation. Because the cadmium had been packed under vacuum just after production to avoid oxidation by the air, it was not washed or polished before use. PuO₂ used in this study contained about 2% of americium which was generated by (n, γ) reaction of Pu²³⁹ and β -decay.

PuCl₃ was prepared in the following two steps. (a) carbothermic reduction of PuO₂ to produce PuN [13], and (b) exchange reaction between PuN and cadmium chloride (CdCl₂) in LiCl-KCl. Pu in the liquid cadmium anode layer was prepared by reduction of PuCl₃ by addition of Cd-Li alloy. After these procedures were completed, concentrations of plutonium in the molten salt and in the liquid cadmium anode were 2.28 wt% and 1.72 wt%, respectively.

2.3 Analytical procedures

EG&G Princeton Applied Research potentiostat/galvanostat Model 273A and EG&G 270/250 Research Electrochemistry Software were used for both electrochemical measurement and constant-current electrotransport. The concentrations of plutonium and cadmium in the molten salt were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) of the samples. Cathode products were analysed by scanning electron microscope (SEM) and electron probe microanalyser (EPMA). An X-ray diffract meter (XRD) was also used to determine the chemical form of the cathode deposit.

3. Results and discussion

In order to understand the relationship between the behaviour of plutonium at LCC and its reduction rate, electrotransport experiments were carried out at various cathodic current densities. Major results are summarised in Table 1 with experimental conditions.

Table 1. Conditions and results of Pu electrotransport experiments with LCCs

Run no.	Pu concentration in molten (wt %)	Cathodic current density (mA/cm ²)	Electrotransport-time (s)	Electricity passed in experiment (C)	Initial amount of cathode (g)	Increase of cathode weight (g)	Collection efficiency (%)	Final Pu concentration in cathode (wt %)
1	2.28	33	12 000	240	4.036	0.1983	100	4.68
2	2.11	41	11 870	297	2.918	0.245	105	7.75
3	2.28	50	7 800	234	4.899	0.1555	80.6	3.08
4	2.11	66	6 500	260	3.406	0.0023	1.07	0.07
5	4.6	66	7 200	288	4.0287	N/A	N/A	N/A
6	4.6	82	5 400	270	4.0056	N/A	N/A	N/A
7	4.6	100	5 400	324	4.024	N/A	N/A	N/A

3.1 Time course of LCC potential and plutonium recovery efficiency

Changes of LCC potential in the electrotransport tests at plutonium concentration of about 2 wt% in the molten salt are shown in Figure 3. At cathodic current density of 33 to 41 mA/cm², cathode potential was kept between -1.4 V and -1.55 V after a slight shift to the lower direction at the beginning. In this range of the potential, reduction of plutonium followed by dissolution to liquid cadmium or formation of an intermetallic compound is expected to occur from the result of the CV measurement [14]. The moderate change of the cathode potential indicated that plutonium was smoothly collected in the LCC without abrupt growth of solid phase at the interface. Collection efficiencies for plutonium calculated from increase of cathode weight and electric charge passed between the electrodes were nearly 100% in these conditions. This result supports the above consideration. Figure 4 is a photograph of the cathode cadmium ingot taken out of the crucible in Run 2 where plutonium was collected up to 7.75 wt% in cadmium at cathodic current density of 41 mA/cm². Although there was a little inequality on the surface of the LCC, no growth of dendritic deposit was found.

Figure 3. Change of LCC potential in Pu electro-transport tests

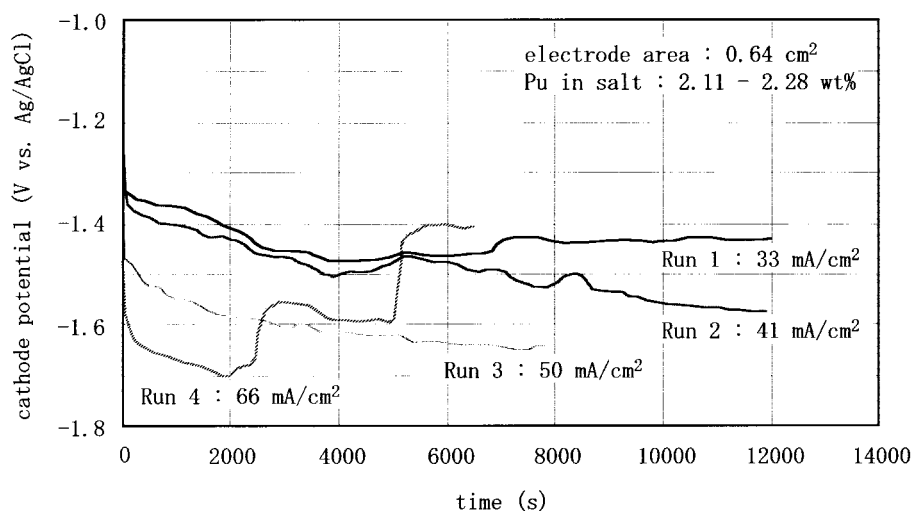
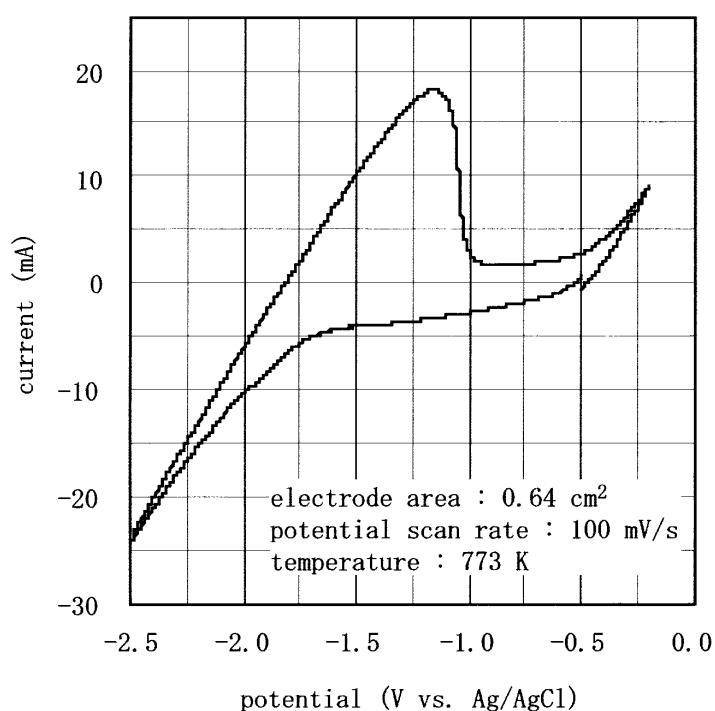


Figure 4. Cathode Cd ingot obtained after Pu electro-transport test at cathodic current density of 41 mA/cm²



Cathode potential went down to -1.65 V at cathodic current density of 50 mA/cm². The solidified salt on the top of the cathode cadmium in Run 3 was white although the bulk salt containing about 2 wt% of plutonium is usually light blue in colour. Collection efficiency for plutonium was about 80%, a little lower than in the preceding case. These results indicate that lithium in the electrolyte was reduced at the LCC at -1.6 V and that the reduced lithium reacted with plutonium tri-chloride near the cathode after the electrotransport. Although lithium forms a very stable chloride which has more than 0.6 V lower standard potential than that of plutonium at an inert electrode, its metal is stabilised in liquid cadmium due to the very low activity coefficient [15]. Figure 5 shows a CV measured for blank LiCl-KCl with a liquid cadmium electrode. It can be seen that reduction current for lithium increases from about -1.6 V, suggesting the validity of the above consideration.

Figure 5. Cyclic voltammogram for blank LiCl-KCl with liquid cadmium electrode



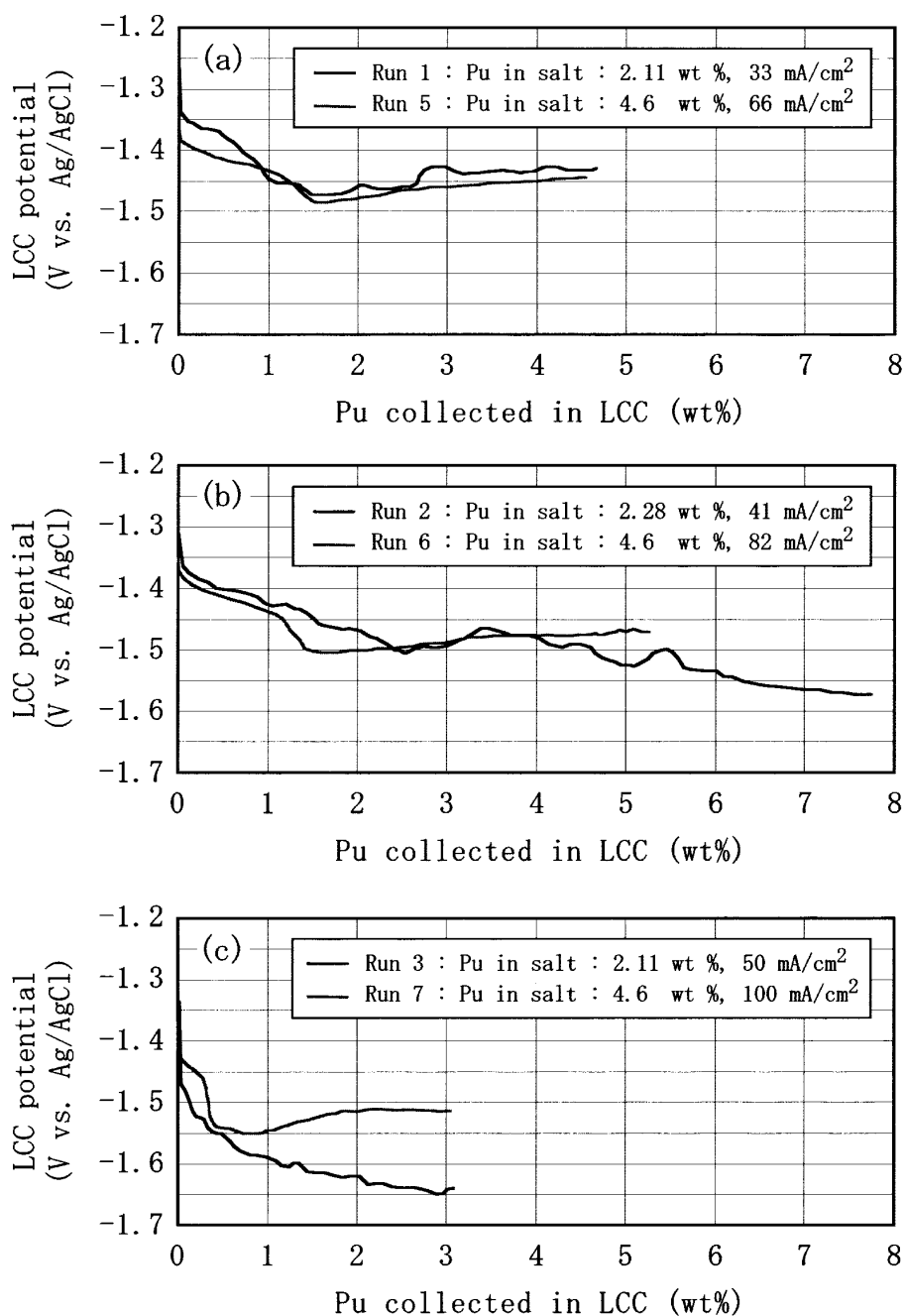
When cathodic current density was increased to 66 mA/cm², cathode potential descended to -1.7 V at first and subsequently ascended in two steps. After the experiment, the cathode was visually inspected. The lower part of the alumina insulator sheath of the electric lead for the LCC had turned black and a deposit with metallic gloss was found on that region. XRD analysis showed that the major portion of this deposit was PuCd₆. At such low potential and higher cathodic current density, it is expected that the reduction rate and the LCC surface concentration of lithium were increased and that the lithium reacted with the alumina sheath. It is very likely that the alumina sheath was wetted much more easily with liquid cadmium due to the reaction with lithium. This is considered the reason why the alumina sheath worked as a thin LCC and PuCd₆ was deposited there. The very low collection efficiency for plutonium (25%) in Run 3 should be due to the PuCd₆ formation out of the LCC.

3.2 Plutonium concentration dependence of optimum cathodic current density

Electrotransport experiments were carried out at higher plutonium concentration in molten salt in order to investigate the effect of plutonium concentration on the reduction behavior of plutonium at LCC. The concentration of plutonium in the molten salt was adjusted to 4.6 wt% by the procedure described above. The results were compared with those at lower concentrations in Figure 6(a) to (c). In Figure 6(a) and (b), it is clear that the overall trends of the charts at approximately same ratio between plutonium concentration in the molten salt and cathodic current density can be closely correlated. It indicates that cathodic current density at which plutonium can be smoothly collected into LCC is proportional to the plutonium concentration in molten salt at least in the range of this study. A distinct difference was found in two charts in Figure 6(c). In Run 3, cathode potential went down to -1.65 V and lithium in the solvent was considered to be reduced. In Run 7, on the other hand, cathode potential was kept higher than -1.55 V at which it was expected that plutonium was selectively reduced at the LCC. As mentioned above, the ratio between cathodic current density and the plutonium concentration in molten salt was a little higher in Run 3 ($24 \text{ mA/cm}^2 \cdot \text{wt}\% \text{-Pu}$) compared to Run 7 ($22 \text{ mA/cm}^2 \cdot \text{wt}\% \text{-Pu}$). It is thought that a limitation in the mass transfer rate of plutonium by diffusion in molten salt in a not stirred system lies between those conditions. Conversely, selective and smooth plutonium reduction at the LCC would be expected at a cathodic current density proportional to the concentration of plutonium in molten salt at a ratio of $22 \text{ mA/cm}^2 \cdot \text{wt}\% \text{-Pu}$ at least.

Throughout the plutonium electrotransport experiments with LCCs in this study, the highest cathodic current density at which plutonium was recovered selectively and stably was 100 mA/cm^2 at plutonium concentration of 4.6 wt% in the molten salt.

Figure 6. Change of LCC potential in electrotransport tests (effect of cathodic current density and Pu concentration in molten salt)



3.4 Behaviour of plutonium and americium in LCC

The LCC ingot recovered after the electrotransport was analysed in order to evaluate the behaviour and distribution of plutonium in the cathode. Figure 7 is a SEM image of the intersection of the LCC ingot obtained in Run 2, where plutonium was collected into the cathode up to 7.75 wt% at cathodic current density of 41 mA/cm². There is a layer near the bottom of the LCC containing a

crystallized phase in high density. Figure 8 is a characteristic X-ray image of plutonium of this layer. It is clearly shown that the crystallised phase in this region contains a high concentration of plutonium and that only a small amount of plutonium exists in the bulk. The plutonium-rich phase was identified to be PuCd_6 by quantitative EPMA analysis.

Figure 7. SEM image of the LCC ingot shown in Figure 4 (near the bottom)

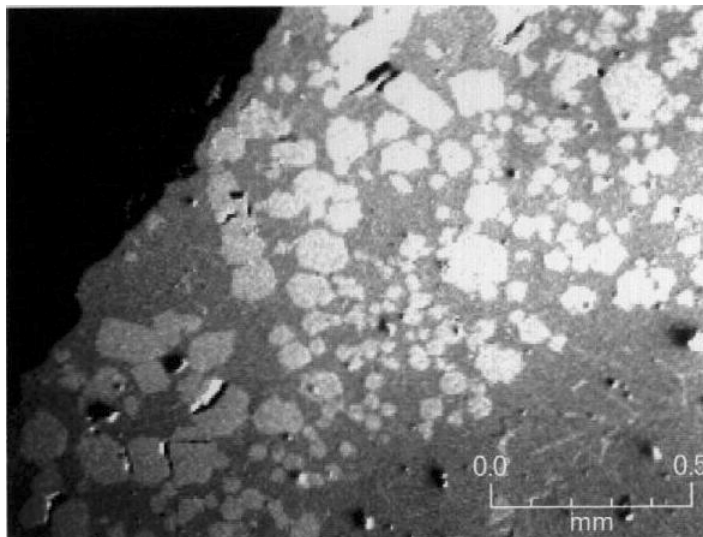
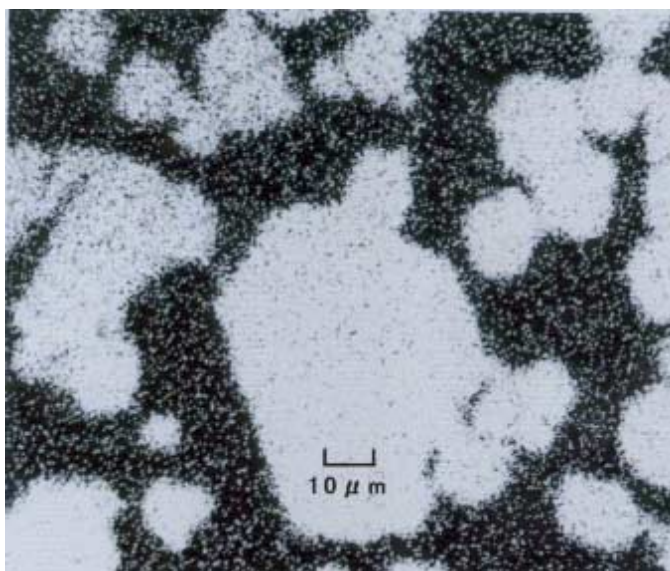
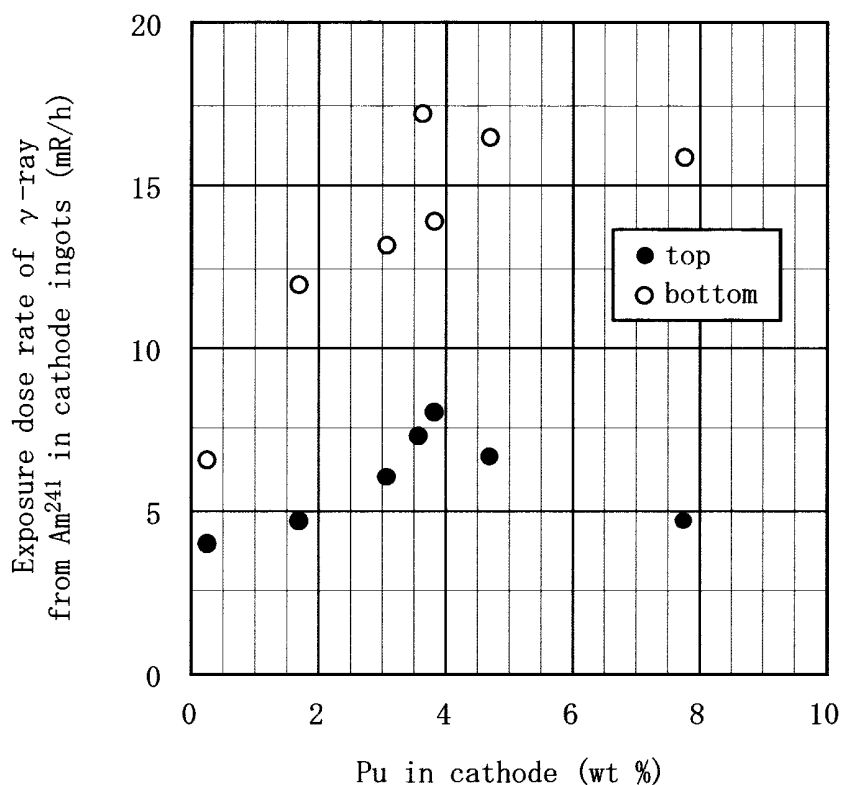


Figure 8. Characteristic X-ray image of Pu at bottom region of LCC ingot



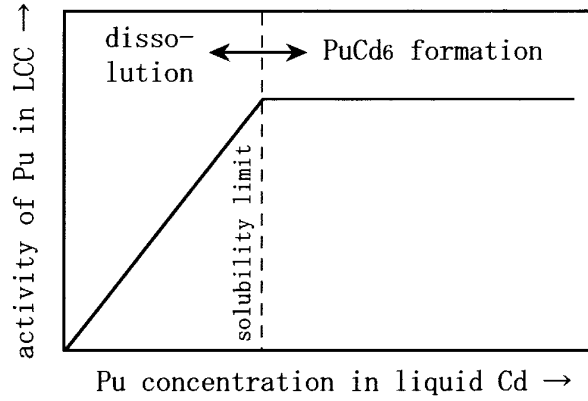
From these results, it seems most likely that plutonium reduced at the LCC beyond its solubility limit in liquid cadmium instantly forms PuCd_6 at the surface of the LCC and settled down to the bottom of the cathode. It is still possible, however, that the segregation of PuCd_6 was caused by vertical temperature gradient in the LCC, because it was cooled very slowly after the experiments. Further tests are needed to elucidate the mechanism of PuCd_6 accumulation at the bottom of the LCC.

Figure 9. Relation between Pu concentration in LCCs and γ -ray from cathode ingots



The exposure dose rate of γ -ray from Am^{241} in the LCC ingots was plotted in Figure 9 versus the concentration of plutonium collected in the cathodes. The dose rate was measured for both top and bottom of the ingots by a GM survey meter placed outside of the glove box at a distance of about 2 mm from the ingots. These plots have a distinctive tendency. At low concentrations of plutonium in the LCCs, the dose rate at either top or bottom of the ingots increased according as the electrotransport proceeded. When the concentration of plutonium in the LCCs reached its solubility limit, however, the increase of the dose rate simultaneously stopped. In our previous LCC study with uranium and lanthanide elements, similar behaviour was observed [16]. While the concentration of uranium in the LCC increased linearly to the electricity, deposition of gadolinium and neodymium stopped before uranium saturation and their concentrations remained almost constant. Such behaviour of americium and lanthanides can be explained by the following consideration based on a local equilibrium model. Assume that electrode reactions of plutonium and americium at the LCC are reversible, that is, a local equilibrium relationship between the two elements at the cathode cadmium/molten salt interface described in equation in Figure 10 is established at every moment. Activity of plutonium in the LCC increases with its concentration before it reaches solubility limit. After saturation, plutonium forms intermetallic compound PuCd_6 . Because PuCd_6 is solid at 773 K, the activity of plutonium in the LCC does not change although a larger amount of plutonium may be collected beyond its solubility limit. Under this condition, deposition of americium would be restrained so that the local equilibrium would be maintained.

Figure 10. Concept of Pu activity change in liquid cadmium and local equilibrium at the surface of LCC



$$\frac{a(\text{AmCl}_3 \text{ salt/Cd})}{a(\text{Am Cd/salt})} = K \frac{a(\text{PuCl}_3 \text{ salt/Cd})}{a(\text{Pu Cd/salt})}$$

where

$a()$ represents activity of each species at the molten salt/LCC interface, and

AmCl₃ salt/Cd : AmCl₃ in molten salt
 Am Cd/salt : Am in LCC
 PuCl₃ salt/Cd : PuCl₃ in molten salt
 Pu Cd/salt : Pu in LCC
 K : equilibrium constant

3.5 Expectation of plutonium recovery rate at a practical electrorefiner

From the results of the electrotransport experiments with LCCs, it was found that lithium was reduced after exhaustion of plutonium in the salt at higher cathodic current densities, and that cathodic current density adequate for smooth plutonium collection is proportional to its concentration in the molten salt at least in the range of this study. Therefore, it is reasonable to assume that plutonium reduction current at the LCC is controlled by diffusion of plutonium ion and is proportional to its concentration in the molten salt. It is also proper to assume that plutonium reduction current is proportional to the surface area of the LCC, although this relationship should be significantly influenced by the geometric design of the electrorefining equipment.

Based on the above consideration, plutonium collection rate at LCC in practical electrorefining equipment was estimated as follows. The sum of the concentrations of all actinides in the molten salt is planned to be adjusted to 2 mol% (about 8 wt%) in the practical operation of electrorefining step [16]. In LCC operation, the plutonium / uranium ratio in molten salt will be set considerably high in order to avoid formation of uranium dendrite. This ratio was assumed to be 7/1 in this calculation. Cathodic current density adequate for smooth plutonium collection was assumed to be proportional to the concentration of plutonium in molten salt at a ratio of 20 mA/cm²·wt%-Pu based on the

consideration described in the preceding section. The inner diameter of a practical scale LCC was supposed to be 30 cm. Consequently, reduction current for plutonium at one LCC was evaluated as:

$$0.02 (\text{A}/\text{cm}^2 \cdot \text{wt}\%) * 7 (\text{wt}\%) * 15^2 \pi (\text{cm}^2) = 99.0 (\text{A})$$

This is equivalent to a collection rate of 294 grams of plutonium per hour. This performance is considered high enough in designing a practical electrorefiner and pyrometallurgical process.

4. Conclusion

Plutonium was smoothly collected into a LCC even without cathode stirring. At plutonium concentration of 2.11 wt% in molten LiCl-KCl and cathodic current density of 41 mA/cm², the collection efficiency of plutonium was nearly 100% and maximum plutonium loading into the LCC was 7.75 wt%. At higher cathodic current densities, lithium and plutonium metals were generated at the surface of the LCC and reacted with ceramic LCC parts. Collection efficiency was decreased due to these reactions.

Cathodic current density adequate for smooth plutonium collection was proportional to its concentration in molten salt at a ratio of about 20 mA/cm²·wt%-Pu at least in the range of this study. At plutonium concentration of 4.6 wt% in molten salt, cathodic current density of 100 mA/cm² was attained without any trouble such as solid deposit growth or descent of cathode potential indicating reduction of lithium.

It was considered that plutonium collected into the LCC after saturation formed intermetallic compound PuCd₆ and accumulated at the bottom of the LCC based on EPMA analysis of the LCC ingot. It is still possible, however, that segregation of PuCd₆ was caused by a vertical temperature gradient in the LCC in the course of the slow cooling process.

Increase of γ -ray count from Am²⁴¹ in the LCC ingots stopped coincident with saturation with plutonium. This behaviour was reasonably explained with the local equilibrium model between plutonium and americium at the surface of the LCC.

Plutonium collection rate in practical electrorefining equipment was estimated to be 294 grams per hour for one LCC based on the assumption that the collection rate is proportional to the plutonium concentration in the molten salt and the surface area of the LCC. This performance is considered sufficient in designing a practical electrorefiner and pyrometallurgical process.

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