Separation behaviors of actinides from rare-earths in molten salt electrorefining using saturated liquid cadmium cathode

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Abstract

Electrorefining in the molten LiCl–KCl eutectic salt containing actinide (An) and rare-earth (RE) elements was conducted to recover An elements up to 10 wt% into liquid cadmium (Cd) cathode, which is much higher than the solubility of the An elements in liquid Cd at the experimental temperature of 773 K. In the saturated Cd cathode, the An and RE elements were recovered forming a $PuCd_{11}$ type compound, MCd_{11} (M = An and RE elements). The separation factors of element M against Pu defined as [M/Pu in Cd alloy (cathode)]/[M/Pu in molten salt] were calculated for the saturated Cd cathode including MCd_{11}. The separation factors were 0.011, 0.044, 0.064, and 0.064 for La, Ce, Pr, and Nd, respectively. These values were a little differed from 0.014, 0.038, 0.044, and 0.043 for the equilibrium unsaturated liquid Cd, respectively. The above slight differences were considered to be caused by the solid phase formation in the saturated Cd cathode and the electrochemical transfer of the An and RE elements in the molten salt.
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PACS: 28.41.Bm; 82.45.Qr; 81.20.Ym; 81.05.Bx

1. Introduction

Central Research Institute of Electric Power Industry (CRIEPI) and Japan Atomic Energy Agency (JAEA) have been developing pyrometallurgical processing technology for spent metallic and nitride fuels [1,2]. Electrorefining in the molten lithium chloride–potassium chloride (LiCl–KCl) eutectic at 773 K is employed for the recovery of actinides (An) elements, i.e. U, Pu, and minor actinides, separated from fission products [3–7]. The spent fuel is placed in an anode basket, and then An elements in the spent fuels dissolve anodically into the molten salt. At cathode, the An elements dissolved in the molten salt are reduced to metal. The behavior of the other elements can be estimated from their red-ox potentials in the molten salt

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[8–11]. Alkali metals, alkaline-earth metals, and rare-earth (RE) elements in the spent fuel also dissolve into the salt, while noble metals remain undissolved in the anode basket. The solid cathode is used for efficient recovery of U, of which content in the spent fuel is more than 70%. The deposit on the solid cathode is U metal isolated from the other elements, since the red-ox potential of U is relatively positive away from those of the other cations in the salt. The use of the liquid cadmium (Cd) cathode allows recovering U, Pu, and minor actinides together. Their red-ox potentials on the liquid Cd cathode are so close, because the activity coefficients of Pu and minor actinides in liquid Cd are much smaller than that of U. Some amounts of RE elements enter into the Cd cathode together with the An elements because of the small activity coefficients of RE elements, while alkali and alkaline earth metals remain in the molten salt.

Equilibrium distribution of An and RE elements in the molten LiCl–KCl eutectic/liquid Cd system has been examined to measure the separation factors [12–15]. The separation factor of element M against element N was defined as [M/N ratio in Cd]/[M/N ratio in salt], where M and N are An or RE elements distributing in the salt and liquid Cd. The separation factors were measured at relatively low concentrations of the An and RE elements in the liquids, where the solute An and RE elements obeyed Henry's law, so that the separation factors were regarded as constant over the wide composition ranges of the salt and Cd liquids [12–15].

However, the molten LiCl–KCl eutectic/liquid Cd system used for the previous separation factor measurements is different from the molten salt bath/liquid Cd cathode system for the actual electrorefining process. The request for the high efficiency of the separation process is that the concentrations of the An elements in the cathode are set to be much higher than those in the liquid Cd phase for the separation factor measurements in order to diminish the amount of Cd that need be separated from An elements by distillation in the following stage [16]. Thus, the authors intend to recover the An elements up to 10 wt% in the Cd cathode [5,6]. Since the solubility of An elements is approximately 4 wt% in liquid Cd at 773 K of the operation temperature [5,6], the electrorefining proceeds forming some solid precipitate in the saturated Cd cathode. In addition, the transfer of the An and RE elements during the electrorefining generate concentration gradient in the molten salt,

causing that the concentrations in the salt on the cathode surface vary from those in the bulk salt [17].

In this study, some electrorefining experiments in molten salt containing An and RE elements were carried out to recover the An elements up to 10 wt% in liquid Cd cathode. The amounts of An and RE elements electrodeposited in the saturated Cd cathodes were analyzed to examine the distribution behavior in the molten salt bath/liquid Cd cathode system. Moreover, in order to clarify the effect of Cd saturation and concentration gradients in the salt on the distribution of the An and RE elements, a part of the saturated Cd cathode was annealed in the molten salt bath, and after equilibrated with the molten salt, their concentrations were analyzed and compared.

2. Experimental

The electrorefining was carried out at 773 K using a small-scale apparatus in an argon atmosphere glove box. Fig. 1 shows the electrorefining apparatus schematically. The molten salt of about 90 g was contained in an alumina crucible with 40 mm inner diameter. The solvent salt of LiCl–KCl eutectic was purchased from Anderson Physics
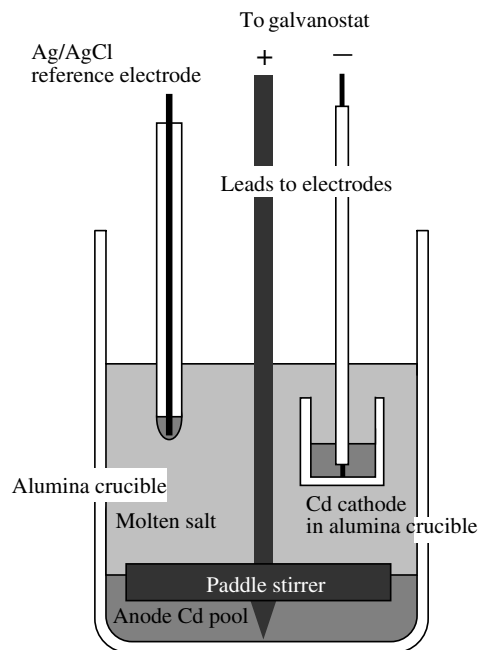

Fig. 1. Apparatus for electrorefining experiments using liquid Cd cathode.

Table 1
Concentration of An and RE elements in molten salt and passed charge in electrorefining experiments

| RUN no.	Concentration in molten salt (wt%)						Passed charge (wt% An elements in cathode)
	U	Pu	Nd	La	Ce	Pr	
Pu-1b	1.5	4.8	–	–	–	–	10.3
Nd-1a	1.4	5.1	0.94	–	–	–	3.3
Nd-1b	1.4	4.6	0.88	–	–	–	10.3
La-1b	1.5	4.8	0.90	0.31	–	–	10.3
La-2a	1.4	4.3	1.6	0.61	–	–	3.3
La-2b	1.5	4.6	1.7	0.63	–	–	10.3
La-3a	1.6	4.4	2.6	0.98	–	–	3.3
La-3b	1.5	4.3	2.6	0.95	–	–	10.3
Ce-1b	1.4	4.4	2.5	0.90	1.5	1.0	10.3

– : Not added.

Laboratory. Table 1 indicates the initial concentrations of the An and RE elements in the molten salt used in the respective runs. Plutonium chloride in the molten salt was prepared from the original material of plutonium oxide powder, PuO_2, as previously mentioned elsewhere [4]. Uranium was introduced into the molten salt by anodic dissolution of U metal lumps. The concentrations of U and Pu in the molten salt were around 1.5 wt% and 4.5 wt%, respectively, which were almost same in all the runs. The ratio of U/Pu of about 1/3 is close to the process design value for the metallic fuel recycle system reported by Sato et al. [18]. The molten salt contained a small amount of Am-241 generated by the decay of Pu-241. The concentration of Am was not determined but the Am/Pu ratio of radiation was measured to obtain the separation factor of Am against Pu.

Rare-earth elements added in the molten salt were La, Ce, Pr, and Nd, which are formed with highest yields in RE fission products. The total yield of the above four elements is higher than 80% of the entire RE fission products [10]. Also, the separation factors of La, Ce, Pr, and Nd against Pu were reported to be larger than those of the other RE elements [12–15]. It means that the separation of the four RE elements from Pu is relatively difficult compared with the other RE elements. Thus, the major RE elements in the Cd cathode must be La, Ce, Pr, and Nd. In order to carry out the electrorefining experiments with various ratios of the RE elements to Pu in the molten salt, the high purity RE chlorides purchased from Anderson Physics Laboratory were added run by run. The ratio of these RE elements in RUN Ce-1b of Table 1 was close to that in the spent fuel, i.e. around La:Ce:Pr:Nd = 1:2:1:4 [10].

As shown in Fig. 1, the Cd pool was situated at the bottom of the alumina crucible. Prior to the electrorefining experiments, a part of the An and RE elements in the molten salt were reduced to metals and extracted into the Cd pool by adding Cd–Li alloy in the Cd pool as a reducing agent [4,14,15]. During electrorefining experiments, the An and RE elements in the Cd pool dissolved anodically into the molten salt as to use the Cd pool for the anode instead of the metallic fuel alloy in the actual reprocessing. The total content of the An and RE elements was about 1 wt% in the Cd pool of about 100 g. The respective concentrations of the An and RE elements were determined so as to obey the separation factor depending on the salt composition indicated in Table 1. A paddle stirrer rotating at less than 10 rpm agitated the Cd pool to avoid lack of An and RE elements in the vicinity of the anode surface, which would cause anodic dissolution of Cd. The iron shaft of the stirrer was also used as the electric lead to the Cd pool. The cathode was 4 g of Cd contained in a small alumina crucible with 9 mm inner diameter and 15 mm depth. A silver/silver chloride (Ag/AgCl) reference electrode was used to measure the cathode potential during the electrorefining experiments [8,19].

The electrorefining experiments were conducted with a constant current of 30 mA controlled by EG & G Princeton Applied Research potentiostat/galvanostat Model 263A-2. The current of 30 mA adopted is corresponding to 47 mA/cm^2 of the cathodic current density. The passed electric charge was calculated on the basis of the cathodic reaction of Eq. (1) to be equivalent to the recovery of 3 wt% or 10 wt% of An elements in the cathode as shown in Table 1.

$$\text{An}^{3+} \text{ (in molten salt)} + 3 \cdot \text{e}^-$$
$$\rightarrow \text{An (in liquid Cd cathode)} \qquad (1)$$
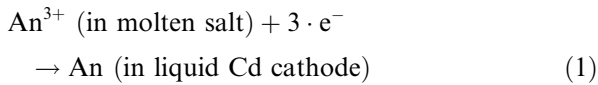
The concentration of 3 wt% An elements is below their solubility, 4 wt% in liquid Cd at 773 K. On the other hand, the Cd cathode containing 10 wt% of An elements should include solid precipitates. In the respective electrorefining runs, the amount of An and RE elements transferring into the Cd cathode was less than 0.5 g, which is a small amount compared with the content of the An and RE elements in the molten salt or the Cd pool. Thus, the composition of the salt was estimated to remain almost unchanged during the electrorefining run.

After the completion of each run, the cathode crucible with the Cd alloy was pulled up above the salt level, and then cooled in the furnace to room temperature. The cathode crucible was broken to take out the Cd ingot. The ingot was separated from the salt and weighed for the mass balance. The sample was taken from the ingot for the composition determination. The ingot with 3 wt% An elements was re-melted at 773 K and then a small amount of the sample melt was siphoned into a Pyrex glass tube fitted with a syringe. Because the siphoned melt only give the An concentrations in the Cd liquid phase, as shown in the previous experiments [5–7], the ingot with 10 wt% An elements were cut into a few pieces and one of them was melted with a fresh Cd metal to decrease the concentration of An elements in the melt below the solubility prior to siphoning the sample melt. The ingots were cut vertically so as to take representative pieces with respect to the precipitates in the bottom part of the ingots.

The small pieces of the cathode Cd ingots of RUN Pu-1b and Ce-1b were used to determine the separation factors for the saturated Cd alloy in which the Cd liquid phase and the solid precipitates were in equilibrium with the molten salt. The alloy was put in an alumina crucible and annealed in the molten salt bath that had been used in RUN Ce-1b. The An and RE elements redistribute between the molten salt and the Cd alloy saturated with 10 wt% An elements. In equilibrium, the same separation factors should be obtained for each of the elements in the two alloys, of which the initial compositions were different. After the annealing at 773 K for one week, the crucibles with the Cd alloys were picked up out of the furnace for quick cooling. The compositions of the Cd alloys were determined according to the procedure for the ingot containing 10 wt% An elements as mentioned above.

The quantitative analysis of U, Pu, and RE elements was carried out by means of inductively coupled plasma-atomic emission spectroscopy (ICP–AES; Shimadzu GEW-170). The samples of the Cd alloy were dissolved in 1 M HNO_3. The measured wavelengths were 385.96 nm, 297.25 nm, 408.65 nm, 418.65 nm, 390.84 nm, and 401.23 nm for U, Pu, La, Ce, Pr, and Nd, respectively. The calibration curves were obtained by using the standard solutions containing these elements individually. Since the intensity detected at some of the wavelengths was increased linearly with increasing concentrations of the other elements as well as that of the object elements, it was corrected by subtraction. The applicability of the correction was checked by measuring a trial sample, in which the concentrations of the An and RE elements were known and simulated to those in the actual samples. Table 2 shows the measured concentrations together with the known concentrations of the trial sample. The concentrations of all the elements were corrected into good agreement with the known values within ±5% of error.

The ratio of Am/Pu was measured by γ-ray spectrometry with a high-purity germanium detector and a multichannel analyzer (Seiko EG&G ORTEC MCA7700). The structural property of An and RE elements in the Cd cathode was characterized by using X-ray diffractometer (XRD;

Table 2
Correction in concentration analysis using ICP–AES

Element	Known concentration (ppm)	Measured concentration(ppm)		Corrected/known
		Uncorrected	Corrected	
U	90.7	101	88.9	0.98
Pu	205	220	210	1.02
La	0.900	1.54	0.862	0.96
Ce	4.71	7.02	4.66	0.99
Pr	2.43	7.37	2.49	1.02
Nd	9.39	12.5	9.58	1.02

Rigaku Geigerflex) with CuKα radiation and using electron probe microanalyzer (EPMA; Shimadzu ASM-SX).

3. Results and discussion

3.1. Contents of actinide and rare-earth elements in Cd cathode

The cathode potentials vs. the reference electrode were measured during the electrorefining. The potential curves of RUN La-2b and La-3b are shown as a typical result in Fig. 2. The horizontal axis means the passed charge, which was converted to the weight percent of An elements in the cathode on the assumption that the charge fully contributed to the reduction of the An elements into metals by Eq. (1). The gradual descent of the potential was observed in an early stage, and then an almost constant potential was kept. The similar trend had already been observed in the previous electrorefining studies [5,6]. Since the composition of the molten salt did not vary significantly during the electrorefining experiments as expected, the descent is considered to be caused by the increase of the concentration of An elements in the liquid Cd cathode with increasing passed charge. The constant potential indicates that the concentration of the An elements was constant in the liquid Cd phase because of the saturation of the An elements. The potential did not change with the concentration above 4 or 5 wt% An elements. Therefore, at the concentration of 3 wt% An elements, where the potential is still varying, no An solid phases should be included in the Cd cathodes.

Fig. 3 shows the cathode Cd ingot taken after RUN La-3b. All the ingots gave similar appearance of lump, which could be separated easily from the salt and the crucible material. The current efficiencies and the contents of the An and RE elements
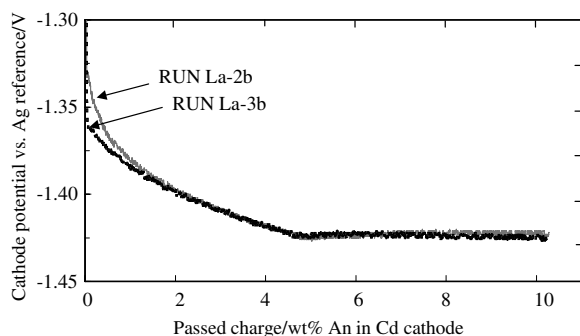

Ingot diameter:approx. 9 mm

Fig. 3. Cathode Cd ingot taken after RUN La-3b.

in the ingots are summarized in Table 3. The current efficiency was defined as [equivalent electric charge to the recovered An and RE elements]/[passed charge] × 100 (%). The equivalent electric charge was calculated for the recovery of the trivalent An and RE cations in the molten salt. The current efficiencies were close to 100%. The result shows that the passed charge fully contributed to the recovery of An and RE elements by electrodeposition into the cathode, and that the compositions of the saturated as well as the unsaturated Cd alloys can be determined appropriately. The weight ratios of RE elements/Pu in the cathode ranged from 1/100 to 1/15, which are appropriate to examine practical recovery behavior of An and RE elements, because the conceptual process design estimates about 1/30 of the ratio [18]. Fig. 4 indicates the content of An and RE elements in the cathode Cd ingots as a function of passed charge. The figure shows the results of RUN La-3a and La-3b, which were conducted with almost the same composition of the molten salt. The amounts of all four elements kept increasing after the saturation of An elements in the liquid Cd cathode. All these elements are considered to have solid precipitates formed in the Cd cathode above the saturation concentrations.

3.2. Chemical form of actinide and rare-earth elements in Cd cathode

In order to characterize the solid phases in the saturated Cd cathode, the cathode ingots were observed using EPMA. The ingots were cut into several pieces and polished. Fig. 5 shows the cross section of the ingot of RUN La-3b as a typical image.

Fig. 2. Change of cathode potentials during electrorefining.

Table 3
Current efficiency and content in cathode Cd ingot

RUN no.	Current efficiency/%	Content of cathode Cd alloy (wt%)						Weight ratio of RE elements to Pu
		U	Pu	Nd	La	Ce	Pr	
Pu-1b	100	3.8	6.3	–	–	–	–	0
Nd-1a	104	1.1	2.3	0.018	–	–	–	1/130
Nd-1b	99	3.2	6.8	0.072	–	–	–	1/94
La-1b	97	3.4	6.3	0.072	0.0058	–	–	1/81
La-2a	101	1.1	2.2	0.031	0.0032	–	–	1/63
La-2b	97	3.1	6.4	0.14	0.011	–	–	1/42
La-3a	101	1.2	2.0	0.050	0.0054	–	–	1/37
La-3b	97	2.8	6.5	0.28	0.017	–	–	1/22
Ce-1b	103	2.9	6.9	0.25	0.016	0.10	0.11	1/15

– : Not added.
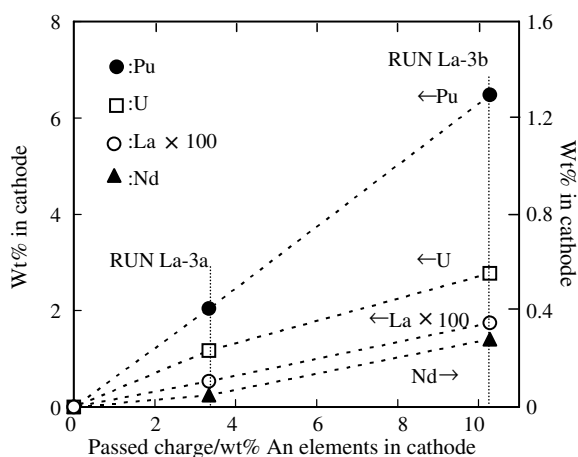
Fig. 4. Content of An and RE elements in Cd cathodes as a function of passed charge.

Fig. 5(a) is the back scattering electron image, in which the dark regions and light inclusions are observed. Cadmium was distributed in both area and that in the dark regions did not contain An and RE elements, since no characteristic X-ray of the other elements was detected. Fig. 5(b) and (c) are the characteristic X-ray images of U and Pu, respectively. Most of U and Pu existed in the inclusions giving virtually the same distribution in the EPMA images. The cathode ingots were also examined using XRD. Fig. 6 shows the XRD pattern of the ingot of RUN La-3b. Since $PuCd_{11}$, which is iso-structural with UCd_{11} [20,21], was identified [22], the inclusion should be a solid solution of UCd_{11} and $PuCd_{11}$, i.e. MCd_{11}. That was the same behavior as observed in the previous electrorefining experiments, which were carried out without using RE elements [5,6]. Thus, it is considered that regardless of RE

coexisting, U and Pu are recovered as MCd_{11} after the saturation of the liquid Cd cathode.

The characteristic X-rays of Nd were detected in the inclusion of RUN La-3b. Fig. 7 is a part of the characteristic X-ray spectrum from the inclusion. An apparent peak was observed at 0.237 nm, which is the wavelength of the X-ray of Nd–$L\alpha_1$. The other RE elements were difficult to detect because of their smaller content in the cathode ingot. However, they should also be contained in the inclusion because they form the intermetallic compounds of the same crystal structure as $PuCd_{11}$ as shown in the binary phase diagrams with Cd [23]. It is considered that the RE elements are recovered as the solid solution MCd_{11} together with An elements after the saturation of the liquid Cd cathode.

The behavior of RE elements observed in this study was different from that in the previous experiments to electrodeposit U and RE elements into Cd cathodes, where deposition of RE elements no more proceeded though U was continuously recovered in the saturated cathode with the increase of the passed charge [3]. The difference seems to be due to the solid phase formed in the saturated Cd cathode. In the previous electrorefining work where Pu was not contained, U contributed to most of the electro-reaction on the cathode. According to the phase diagram of the U–Cd binary system, which shows that UCd_{11} decomposes above 743 K [23], the U metal phase must be formed in the saturated liquid Cd at the experimental temperature of 773 K. The uranium metal phase included almost no RE elements as in the U deposition on the solid cathode, where the activity coefficients of RE elements would be much larger than those in liquid Cd or compounds with Cd.
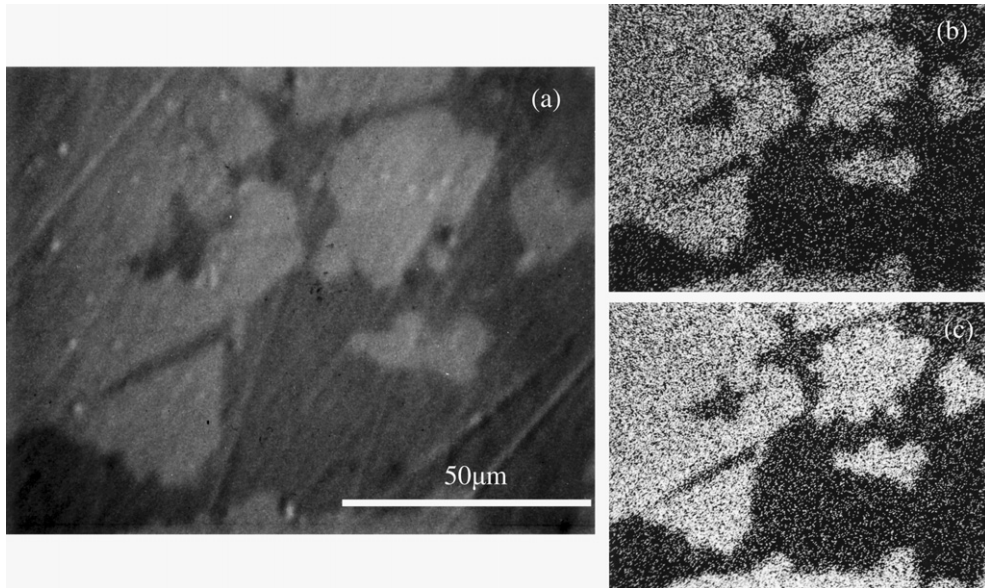
Fig. 5. EPMA image of the cathode Cd ingot obtained after RUN La-3b: (a) Back scattering electron image, (b) Characteristic X-ray image of U, and (c) Characteristic X-ray image of Pu. Dark region in the back scattering electron image consists of Cd without containing An and RE elements.
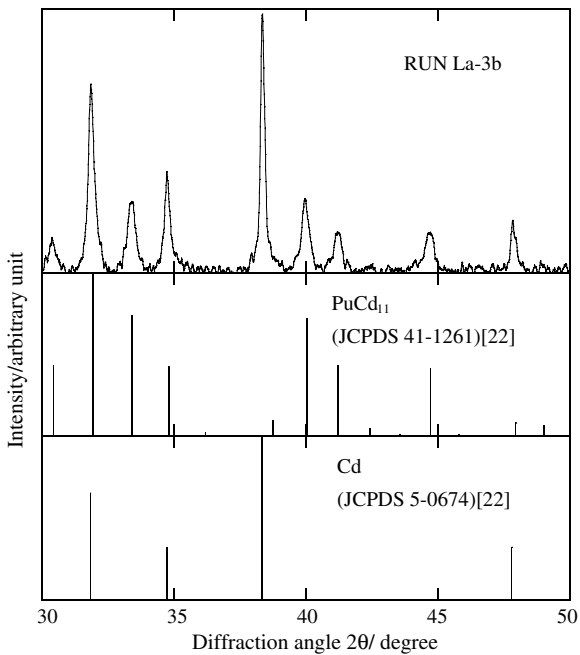

Fig. 6. X-ray diffraction pattern of the Cd cathode cooled after RUN La-3b.

Fig. 7. Characteristic X-ray spectrum of MCd_{11} phase in the cathode Cd ingot (RUN La-3b).

The formation of the U metal phase in the saturated liquid Cd cathode was also found in the preceding electrorefining study us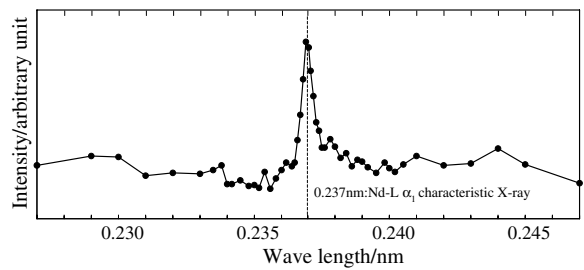ing U, Pu and Am [5]. The electrorefining experiment was conducted in the molten salt with the U/Pu ratio around 1/2, which was richer for U than 1/3 in this study. The recovery of Pu and Am did not proceed after the saturation of the Cd cathode, and then U metal was observed in the cathode ingot by using EPMA. The behavior of Pu and Am should be caused by the U metal deposition in the saturated Cd cathode, which rejects further recovery of Pu and Am, as mentioned above. The formation condition of U metal in the saturated Cd cathode is concerned with the U–Pu–Cd ternary phase diagram [5]. The ternary phase diagram, especially the phase relationship in the liquid Cd, U metal, and MCd_{11}, should be examined for further discussion on the deposition of An and RE elements in the saturated Cd cathode.

3.3. Separation factors

The separation factor in the molten salt/saturated Cd alloy system was calculated by Eq. (2), where $SF_{M/N}$ denotes the separation factor of element M against element N.

$$SF_{M/N} = [M/N \text{ ratio in Cd alloy(cathode)}]$$
$$/[M/N \text{ ratio in molten salt}]. \quad (2)$$

Table 4 indicates the separation factors against Pu for the saturated Cd alloy of RUN Ce-1b, which was conducted to recover An elements up to 10 wt% in the liquid Cd cathode. The values denoted by 'Annealed' in the table are those obtained for the Cd alloy of RUN Ce-1b annealed in the molten salt. These values of the respective elements were in good agreement with those for the other annealed Cd alloy of RUN Pu-1b, as expected. Thus, the separation factors can be determined properly for the saturated Cd alloy consisting of the saturated liquid Cd and the solid precipitate phases that were in equilibrium with the molten salt. The values for La, Ce, and Pr in the 'Annealed' column were a little smaller than the equilibrium values for unsaturated liquid Cd shown together in Table 4 [12].

The saturated Cd cathode of RUN Ce-1b was also analyzed without annealing in order to obtain the separation factor denoted by 'Electrorefining' in Table 4. The separation factors of RE elements were a little larger than the values denoted by 'Annealed'. According to the 'diffusion layer model' [17], electrorefining develops gradients in the concentration of An and RE elements in the molten salt due to the ion transfer. Consequently, the ratios of RE elements to Pu in the salt on the cathode surface

are different from those in the bulk salt analyzed. The change in the ratios might give a little difference between the separation factors of 'Annealed' and 'Electrorefining'. In this study, the liquid Cd cathode was not agitated. Stirring of the liquid Cd cathode could decrease the discrepancy in the separation factors of the electrorefining and equilibrium experiments.

The separation factors for the cathodes with 3 wt% An elements were close to those for the equilibrium unsaturated liquid Cd [12]. For the unsaturated cathode of RUN La-3a, the separation factors of La and Nd against Pu were obtained to be 0.012 and 0.041, respectively. The unsaturated cathodes, in which no solid phase precipitate is formed, might nearly reach equilibrium with the molten salt during the cooling in the furnace. The electrorefining experiments were performed with a low current density of 47 mA/cm^2. For quantitative analysis of the effect of the concentration gradient on the separation factors, electrorefining experiments need be carried out with higher current densities, which would cause larger concentration gradient in the molten salt during electrorefining.

The electrorefining experiments were conducted at the various concentrations of the RE elements in the molten salt. In Fig. 8(a) and (b), the Nd/Pu and La/Pu weight ratios in the saturated Cd cathodes were plotted with respect to those in the salt, respectively. The plots show essentially linear increase, which are reproduced by the dotted lines in the figures. The slopes of the dotted lines indicate the separation factors shown in the 'Electrorefining' column in Table 4. The straight lines show that each separation factor is constant to be unaffected by the concentrations of the RE elements over the studied composition ranges of the molten salt.

The separation factors of U against Pu scattered in a range from 1.3 to 1.8, which are consistent with those obtained in the authors' previous electrorefining data without RE elements [5]. The separation factor of U for the 'Annealed' Cd alloy was 1.5, which is smaller than 1.9 for unsaturated liquid Cd. This difference suggests that the U/Pu ratio in MCd$_{11}$ formed in the saturated Cd alloy is smaller than that in liquid Cd phase. Fig. 9 shows the separation factors of Am against Pu, $SF_{Am/Pu}$, for the saturated Cd cathode. The horizontal axis is the concentration of RE elements in the molten salt to examine the influence of the coexisting RE elements on the separation factor. The separation factors scattered between 0.7 and 0.8, which were compared

Table 4
Separation factor against Pu in the molten LiCl–KCl eutectic/Cd alloy system

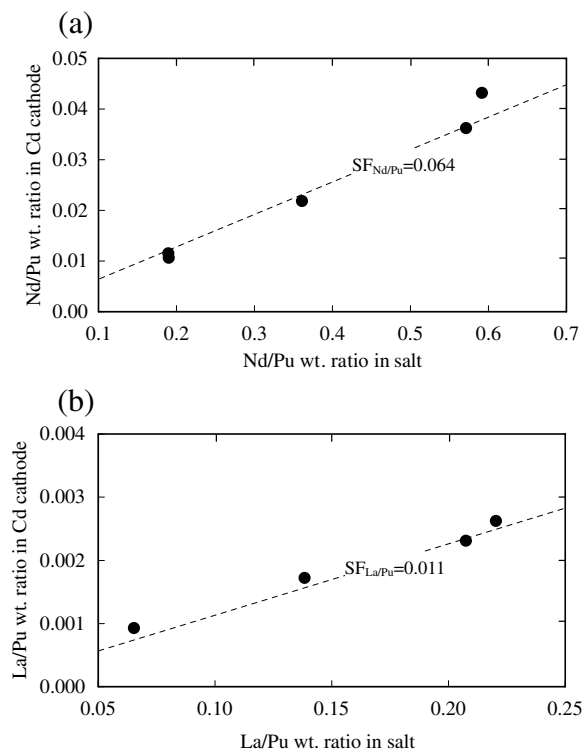| Element	Equilibrium unsaturated liquid Cd [12]	Saturated Cd alloy with 10 wt% An elements (RUN Ce-1b)	
		Annealed	Electrorefining
Pu	1 (basis)	←	←
La	0.014	0.009	0.011
Ce	0.038	0.030	0.044
Pr	0.044	0.040	0.064
Nd	0.043	0.043	0.064
Am	0.65	NA	0.77
U	1.9	1.5	1.3

NA: Not analyzed.

Fig. 8. Weight ratios of RE elements to Pu in Cd cathode plotted against those in molten salt: (a) Nd/Pu and (b): La/Pu.
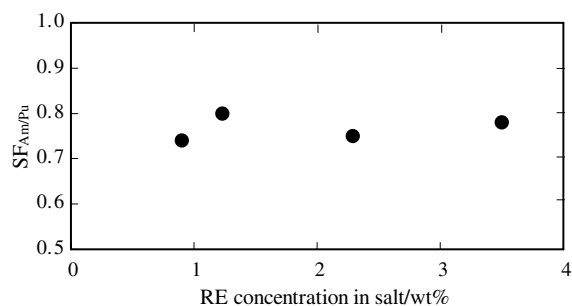

Fig. 9. Separation factors of Am against Pu obtained for saturated Cd cathodes including RE elements.

with 0.65 for the equilibrium unsaturated liquid Cd [12]. The dependence of $SF_{Am/Pu}$ on the concentration of RE elements was small if any.

4. Conclusions

In order to examine the deposition of An and RE elements in the liquid Cd cathode, electrorefining experiments were conducted in the molten LiCl–KCl eutectic salt containing An and RE elements at the various ratios of RE to An elements. The actinide elements were recovered up to 10 wt% in

the cathode. This value is much higher than the solubility, i.e. 4 wt% An elements in liquid Cd at the experimental temperature of 773 K. The amounts of the respective elements in the Cd cathode increased with increasing passed charge. The observation of the cathode Cd ingots using EPMA and XRD showed that U and Pu were recovered forming a compound of the $PuCd_{11}$ type, i.e. MCd_{11}, in the saturated Cd cathode. Since the characteristic X-ray of Nd was also detected from the compound, it was considered that the RE elements form MCd_{11} solid solutions together with An elements.

The separation factors of element M against Pu defined as [M/Pu in Cd alloy]/[M/Pu in molten salt] were obtained for the Cd alloy containing 10 wt% An elements. For the annealed alloy, where the saturated liquid Cd phase and MCd_{11} exist in equilibrium with the molten salt, the separation factors of La, Ce, Pr, and Nd, were 0.009, 0.030, 0.040, and 0.043, respectively. These values were compared with 0.014, 0.038, 0.044, and 0.043 in the equilibrium unsaturated liquid Cd. The small difference in the above separation factors was caused by the solid phase formation in the saturated Cd cathode. For the saturated Cd cathodes of the electrorefining experiments, the separation factors were 0.011, 0.044, 0.064, and 0.064 for RE = La, Ce, Pr, and Nd, respectively. The discrepancy in the separation factors of the equilibrium and electrorefining experiments might mean that the composition of the molten salt on the cathode surface would vary a little from those in the bulk salt because of the concentration gradients of An and RE elements migrating in the molten salt during electrorefining.

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