# MOLTEN SALT ELECTROREFINING TO SEPARATE TRANSURANIUM ELEMENTS FROM RARE EARTH ELEMENTS

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ABSTRACT

CRIEPI has proposed a pyrometallurgical process to separate actinides from high level radioactive waste (HLW) and solvent scrubbing waste. In the concept, HLW is converted to chlorides, and the molten chlorides are reduced into liquid cadmium and/or bismuth by the addition of lithium metal as reductant. Then, the actinides are purified by electrorefining. Since rare earth elements (RE), which are chemically similar to actinides, are existing an order of magnitude more than actinides in the HLW, a key issue in the pyrometallurgical process is the efficient separation of the actinides from RE.

This study shows the separation between actinides and RE by the electrorefining with two stages. The first stage was carried out to transport actinides to the molten salt electrolyte and the Ta cathode from Cd anode. After removing the actinides was removed from Cd, the anode was changed to $Li_2Sb$ for the following electrorefining, in which actinides were reduced on the Ta cathode from molten salt. The chemical composition in the system was adjusted according to the ratio of actinides to RE (Y, La, Ce, Nd and Gd) with HLW, except U and Pr. In the result, U and Np were easy to separate from RE, and Pu and Am showed small separation factor from RE, because the concentration of Pu in molten salt and Cd is quite low ( log $X_{Pu} < -4$ ) and the redox potential was similar to RE. The current efficiency in this experiment was less than 30 %, since the deposition of actinides, especially U, dropped from the cathode. In the second stage, as the concentration of actinides in the salt, the separation of actinides from RE became more difficult. The final ratio of actinides to RE on the cathode was more than unity through this experiment.

# INTRODUCTION

Central Research Institute of Electric Power Industry (CRIEPI) in Japan has proposed a concept to separate actinides from HLW by a pyrometallurgical process and then to transmute them to short-lived nuclides in a metallic fuel FBR [1]. The pyrometallurgical process has been predicted to reduce the total amount of radioactive waste and has been suggested to favor compact facilities as compared with the aqueous processes such as solvent extraction, ion exchange etc., in spite of a relatively low purity of actinides elements in a final product. The pyrometallurgical partitioning process of HLW from PUREX process is shown in Fig. 1. The pyrometallurgical process consists of (1) denitration to form oxides, (2) chlorination of oxides to form chlorides, (3) reductive extraction of actinides from molten chlorides into liquid cadmium (Cd) or bismuth [2-6] and (4) electrorefining of actinides from fission product [7,8].

Since the amount of rare earth elements (RE) are in order of magnitude more than that of actinides in HLW, a key issue in the pyrometallurgical process is the efficient separation of actinides ( U, Np, Pu, Am and Cm) from RE. In this study, separation of actinides from RE was carried out by the electrorefining in following two stages. In the first stage was transported actinides from Cd anode to the Ta cathode through the molten salt electrolyte. In the second stage, the anode was replaced by $Li_2Sb$, and actinides in the molten salt were reduced on the Ta cathode.

# EXPERIMENT

The electrorefining apparatus was equipped in the furnace well of glove box where circulating argon gas was purified by DRYTRAIN and NITRAIN. During the experiments, oxygen and water content were both maintained at < 1ppm and nitrogen content was at < 500ppm. The electrorefining cell is shown in Fig. 2. The cell which contained molten salt and liquid Cd was made of Ta tube with a half inch size in an outside diameter. A Ta wire of 1 mm diameter was used as a cathode in the cell. As shown in Fig. 2 (A) and (B), actinides-Cd alloy was used as an anode for the electrorefining of first stage and the anode was replaced by $Li_2Sb$ for the second stage. All experiment was controlled by galvanometry in the range of 2 mA to 5 mA in the first stage and 2 mA to 3 mA in the second stage.

The initial amount of the elements in liquid Cd and molten salt were determined as Table 1. According to the ratio of actinides (U, Np, Pu and Am) to RE (Y, La, Ce, Nd and Gd) in HLW, excepting U, Cd alloy was prepared by mixing Cd with U-Cd, Np-Cd, Pu-Cd and Am-Cd alloy at about 773 K. The resulting concentration of each element in the alloy was determined by Inductively Coupled Plasma atomic emission spectrometry( ICP). The salt was prepared by mixing the weighted amount of LiCl-KCl eutectic salt with $YCl_3$, $LaCl_3$, $CeCl_3$, $NdCl_3$ and $GdCl_3$ according Table 1. The alloy and the salt were put into Ta tube and then, heated to 723 K.

Ta wire with 1 mm $\phi$ was immersed in the molten salt and was connected to the cathode. A liquid Cd alloy was then connected to the anode through Ta tube. The cathode of the first stage was covered on the alumina tube of a quarter inch in an outside diameter with a small window and a small amount of Cd was placed in the tube, in order to catch the dropped deposits. The molten salt and liquid Cd were stirred by Ta stirrer. After passing about 10 to 20 coulomb, the cathode deposit and /or a trace amount of Cd alloy and salt were taken

out for the analysis by ICP, and then the new cathode was inserted. The amount of metal deposit were derived by subtracting the amount of salt entrained in the deposit. The amount of entrained salt was estimated from the concentration of potassium in the deposits.

After removing actinides from Cd alloy, Cd was taken out from the cell and then, the anode was changed to $Li_2Sb$ in order to remove actinides from the salt, as shown in Fig. 2 (B). After passing about 20 to 50 coulomb, the cathode deposit and the salt were analyzed.

## RESULTS AND DISCUSSION

Figure 3 shows the concentration change in the salt with the total charge passed. It was observed that the U concentration decreased faster than Np with passing charge. While, the final deposit was consisted of ca.42 % - U, ca. 42% - Np, 0.7% - Pu, 1% - Am and 15% - RE. The total charge needed for removal of all actinides from Cd alloy three times as much as the calculated value of 77 coulomb. This was due to the drop of actinides deposited from Ta, because the content of U and Np in a catch Cd and a catch tube were higher concentrated than the other part. These results suggest that some portion of U deposits dropped into the salt. On the other hand, the concentration of Am in the salt was increased with increasing charge passed, and suggesting that Am was hard to deposit on the cathode. The content of RE in the salt didn't change with passing charge, which means to no deposition on the cathode at this electrolysis condition.

Figure 4 shows that the relationship between the current efficiencies and the total passed charge. The current efficiencies of cathode and anode were defined as the equations of ( 1 ) and ( 2 ),respectively.

$$\text{The cathode current efficiency} = \frac{\Sigma \text{ amount of deposit observed}}{\Sigma \text{ amount of deposit calculated from the coulomb passed}} \qquad (1)$$

$$\text{The anode current efficiency} = \frac{\Sigma \text{ amount of elements removed from Cd phase}}{\Sigma \text{ amount of removed elements calculated from the coulomb passed}} \qquad (2)$$

This figure indicates that the current efficiencies of the cathode and anode were ca. 20% and ca. 30%, respectively. If the dropped deposits were recovered by a catch tube, the anode current efficiency was still far less than 100%. Hence, most of the dropped deposit was returned to Cd anode through a window in a catch tube as a form metal fog [9]. The existence of the floating particles like metal fog was supported by salt entrained in the cathode deposit showed gray color with small black particles.

Figure 5 shows that the relationship between the separation ratio of actinides from RE at an use of Cd anode and total charge. This separation ratio was defined as the equation of ( 3 ).

$$\text{Separation ratio} = \frac{\dfrac{\Sigma \text{ amount of M deposit}}{\Sigma \text{ amount of RE depsoit}}}{\dfrac{\text{amount of M before the electrolysis}}{\text{amount of RE before the electrolysis}}} \qquad (3)$$

(M : U, Np, Pu or Am)

The amount of M and RE were shown in Table 1. Figure 5 shows the separation ratios as ca. 20 for U, ca. 40 for Np, ca. 8 for Pu, ca. 1 for Am. Assuming that thermodynamic equilibrium are established, the separation ratio of actinides from RE can be derived from the standard redox potential in molten salt [7], The derived values of separation ratio of U was larger than that of Np, although the measured value of U was smaller than that of Np. This difference could be attributed to drop of U from the deposit as mentioned above. Figure 5 shows that the tendency of separation ratio among actinides was in order of Np > U > Pu > Am, which agreed with the prediction from the standard redox potential [7], except U. In this stage, only small amount of Pu and Am were deposited on the cathode, resulting in the small separation ratio of Pu and Am. It means that Am were still remained in the salt after most of actinides were removed from Cd anode in this stage. The averaged separation ratio of actinides kept ca. 20 during the electrolysis using Cd anode. This value was dominantly affected by U and Np, because the deposits consisted mainly of U and Np in the first stage.

Figure 6 shows the concentration of each element in the salt with passing charge at the use of $Li_2Sb$ anode. It was seen in this figure that the concentration of all elements decreased with charge. In contrast at the case of Fig.3 with use of Cd anode, we observed the decrease of Am content, which indicated the deposition of Am on the cathode. Hence, the important factor in order to deposit Am could be that the concentration of Am in the salt increased an order of magnitude over the concentration of U and Np in this electrolysis. On the other hand, it was seen in Fig.6 that the concentration of RE was also decreasing with passing charge. Ce and Nd showed remarkable decrease among RE, especially, because the standard redox potential of Ce and Nd was close to Am [7], and then Ce and Nd were higher content in the salt than another RE as shown in Table 1. Consequently, the electrolysis accelerated to deposit RE in particular Ce and Nd as well as Am on the cathode. It might be predicted that much amount of RE was accompanied on the cathode when Am was further removed ( > 99%) from the salt. As shown in Fig.6, the concentration of Ce and Nd in the salt decreased remarkably after 220 coulomb passed. In this last deposit, the content of Ce and Nd became higher than all actinides. It should be ascribed the extremely low concentration of Am in the salt after 220 coulomb passed.

The cathode current efficiency in the second stage was lower than that of first stage. This may be come from the minimized current for getting better separation and from increase of the drop of the deposit with decreasing the concentration of actinides in the salt.

Figure 7 shows the relationship between the separation ratio and the total charge passed at an use of $Li_2Sb$ anode. This separation ratio was replaced the denominator in the equation of (3) with the amount of actinides and RE before using of $Li_2Sb$ anode. It was seen in Fig. 7 that the separation ratio became ca. 8 for U, ca. 60 for Np, ca. 20 for Pu and ca. 2 for Am, except the last deposition. As compared with Fig.5, the separation ratio of Np, Pu and Am from RE increased. It was due to low the concentration of U in the salt and high the content of Np, Pu and Am in the deposit. The order of the separation ratio was Np > Pu > U > Am. This behavior of U does not agree with the prediction from the standard redox potential[7]. It may be due to the low concentration of U in the salt and the fall of U deposit. The separation ratio of all actinides from RE became 10 in the second stage and was a half value of the case using Cd anode. This is because the main deposit of actinides was changed from U and Np to Am. It means that U and Np were easy to be separated from RE, but Am was difficult.

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The recovered ratio of TRU (Np, Pu and Am) to RE was defined as the total amount of deposited TRU in divided by that of RE, and was derived to be 1.2 for this experiment. Since the ratio of TRU to RE before the electrolysis was 0.14, the molten salt electrorefining can be multiply the TRU ratio to RE about 8.6 times in this experiment.

## CONCLUSION

1. The separation ratio of actinides to RE became 22 by using Cd anode.

2. The separation ratio became 10 by using $Li_2Sb$ anode and was a low compared with the case of Cd anode. It was due to the change of the main deposit of actinides from U and Np to Am.

3. The molten salt electrorefining could be separated 8.6 times TRU from RE in this experiment.

## ACKNOWLEDGMENTS

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Table 1    The initial composition of the experiment*

| | Total    (mg) | Cd Phase (mg) | Salt Phase (mg) |
|---|---|---|---|
| LiCl-KCl | | | 4.4962    (g) |
| Cd | | 7.4214(g) | |
| U** | 37.0 | 30.0 | 7.0 |
| Np | 15.0 | 9.0 | 6.0 |
| Pu | 1.6 | 0.8 | 0.8 |
| Am | 16.9 | 9.2 | 7.7 |
| Y | 11.7 | D.L. | 11.7 |
| La | 36.4 | 0.5 | 35.9 |
| Ce | 69.0 | 2.9 | 66.1 |
| Nd | 110.0 | 5.2 | 104.8 |
| Gd | 7.3 | 0.3 | 7.0 |

*:The chemical composition in the system was adjusted to the ratio of actinides to RE (Y, La, Ce, Nd and Gd) with HLW.

**:Uranium was one fourth of the simulated composition, and praseodymium was none in the composition.
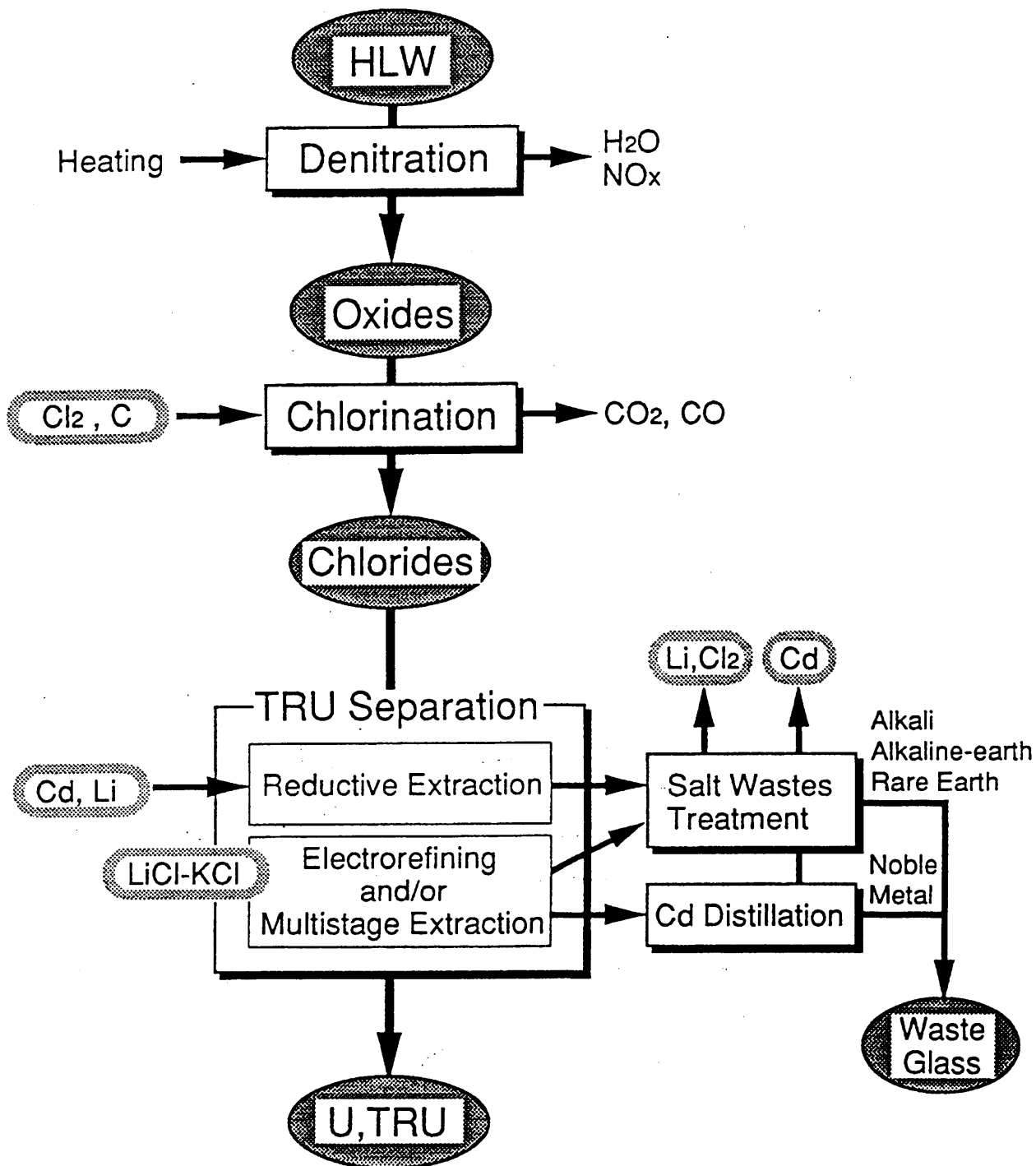
Fig. 1 Schematic flow diagram for TRU pyrometallurgical partitioning from high level wastes.
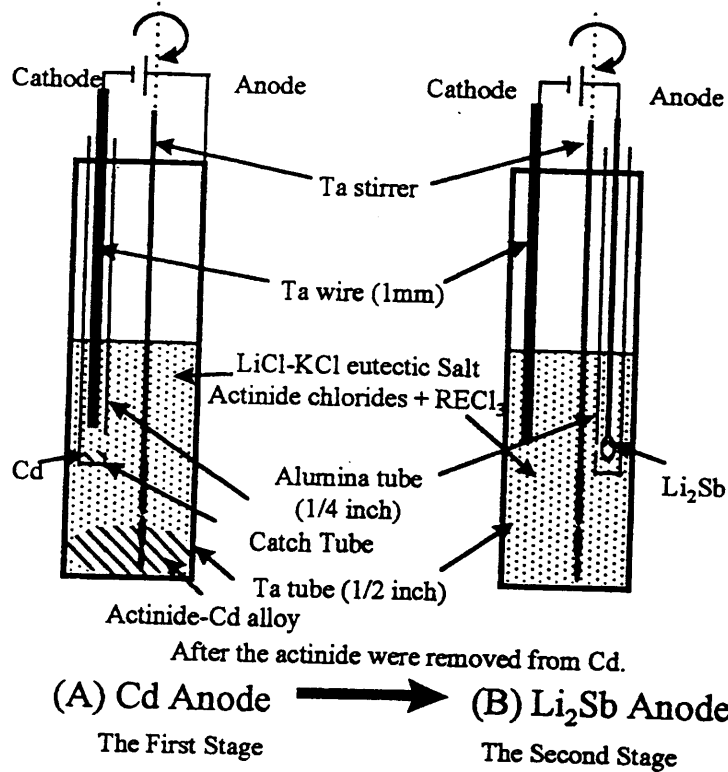
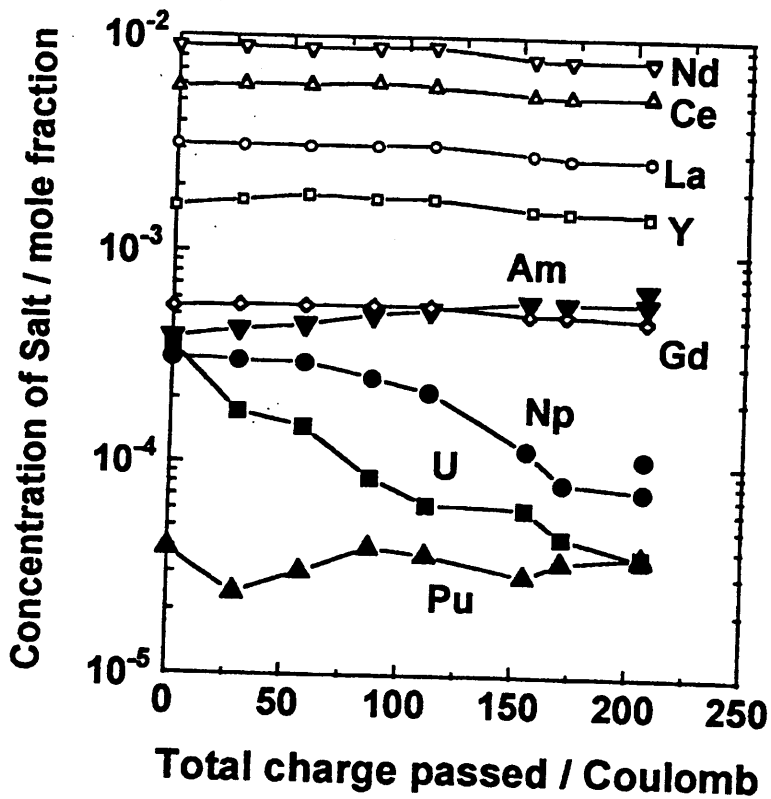Fig.2 Schematic diagram of the experimental cell.
(A) Cd anode (B) Li₂Sb anode



Fig.3 The concentration change in the salt with the charge passed at an use of Cd anode.
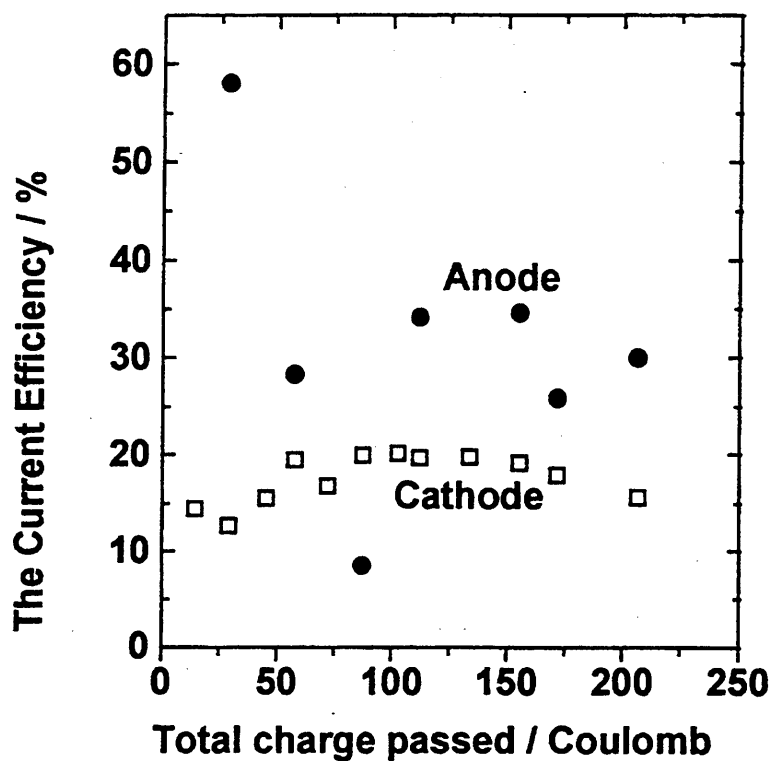
Fig.4 The relationship between the current efficiencies and the charge passed at an use of Cd anode.
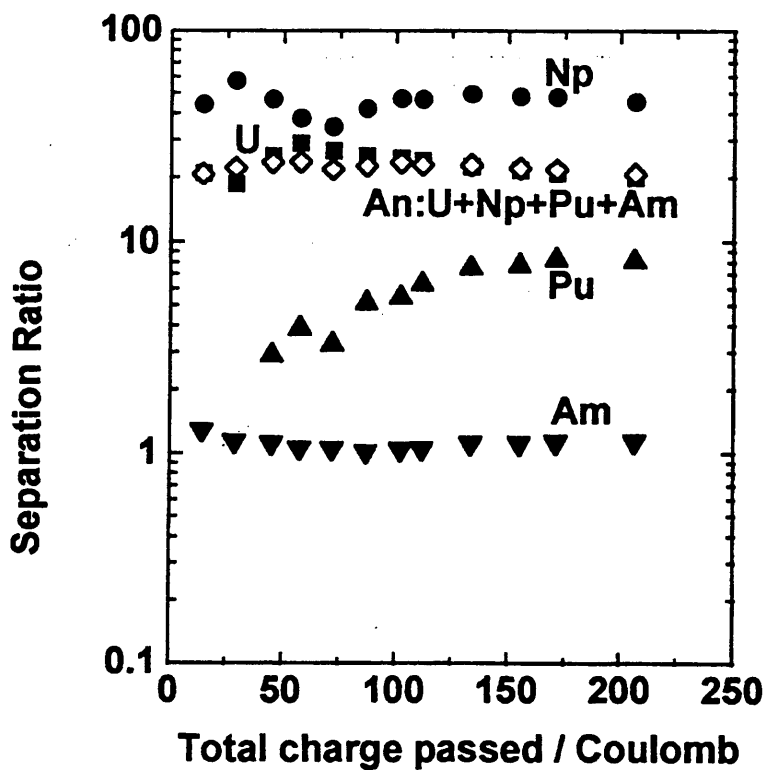


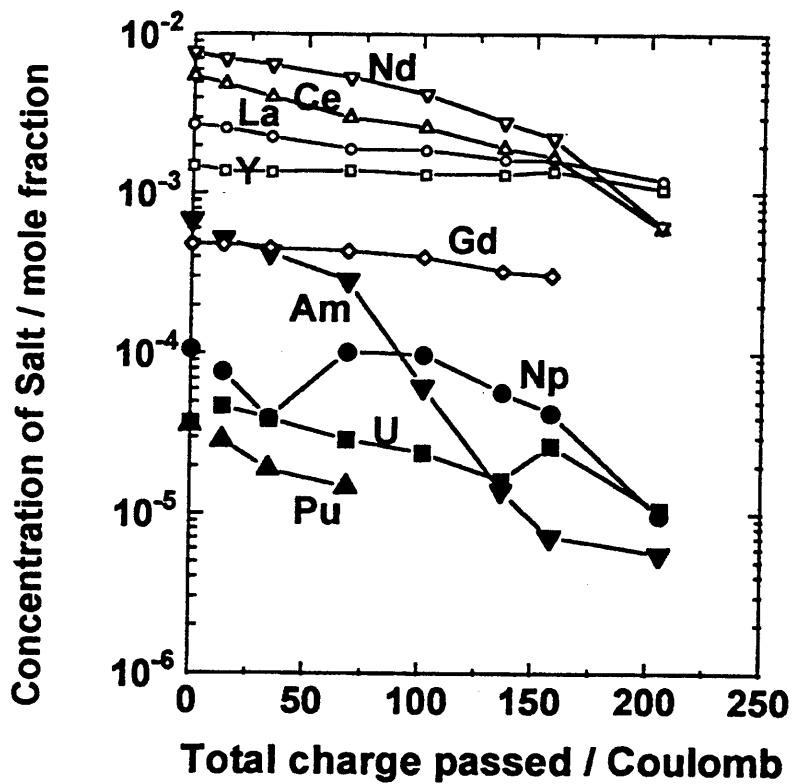Fig.5 The relationship between the separation ratio at an use of Cd anode and the total charge.

Fig.6 The concentration change in the salt with the charge passed at an use of Li$_2$Sb anode.
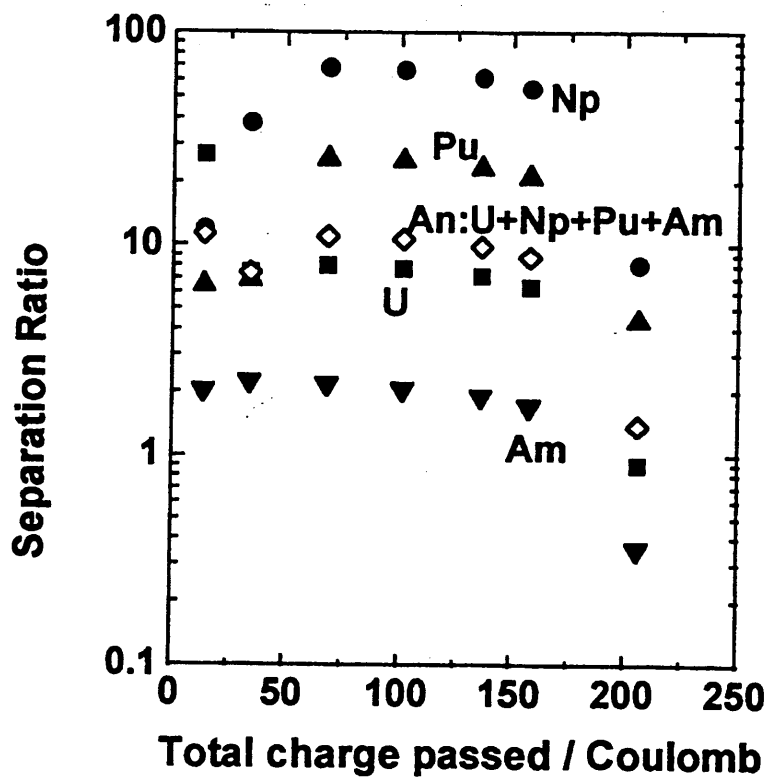


Fig.7 The relationship between the separation ratio at an use of Li$_2$Sb anode and the total charge.