Pyrometallurgical partitioning of minor actinides and lanthanides in LiCl-KCl eutectic molten salt / liquid metal system

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Abstract

Distribution coefficient of actinides and rare earth elements were measured in LiCl-KCl eutectic molten salt / liquid cadmium system and in LiCl-KCl eutectic molten salt / liquid bismuth system. According to separation factor experimentally determined, the LiCl-KCl / bismuth system is also preferable to separate the actinides and the rare earth elements, nevertheless cadmium can be a candidate solvent if electrorefining has a excellent capability of separation of these elements.

1. Introduction

High level radioactive waste (HLW) from reprocessing of spent fuels of light water reactors contains a small amount of long-lived nuclides, mainly minor actinides (MA), which remain radioactive toxicity for more than one million years. If the MA could be separated from the HLW and transmuted to short-lived nuclides, it is expected that this technology could substantially reduce the isolation period of the HLW from biosphere and could simplify the disposal of the HLW, and thus, that would have a potential to provide an ideal nuclear fuel cycle strategy, by which the long-lived toxic elements could be imprisoned in the nuclear fuel cycle. Pyrometallurgical partitioning of the MA, which is expected to produce a lower amount of secondary radioactive wastes and to favor compact facilities although the products have lower purity as compared with the conventional aqueous processes, is being developed by Central Research Institute of Electric Power Industry (CRIEPI) [1]. The pyrometallurgical partitioning can be combined with the transmutation of the MA in the U-Pu-Zr metallic fuel by the addition of the extracted MA.

Fig. 1 represents the flow diagram of the pyrometallurgical process for the partitioning of the MA from the HLW proposed by CRIEPI. This process mainly consists of (1) denitration of the HLW to oxides by heating, (2) chlorination of the oxides, (3) reductive extraction of noble metals from the molten chlorides using Cd, (4) reductive extraction to separate the MA from molten chlorides using Li and (5) electrorefining to increase purity of the recovered MA. Both the denitration and chlorination steps are pre-processing for partitioning. The main separation of the MA is performed both in the reductive extraction and in the electrorefining, in which the most important parameter is the separation factor between the MA and the rare earth elements (RE) which are existed 10 times large amount of the actinides in the HLW. The calculated composition of the HLW after chlorination step is represented in table 1. According to the preliminary estimation [1], the comparable weight of the lanthanides can be accompanied with the MA in the U-Pu-Zr alloy based metallic fuel.

The separation factor of the actinides and the RE are largely affected by (1) temperature, (2) composition of the molten chloride, (3) the sort of liquid metal solvent. In the reductive extraction process, relatively low temperature, around 500 ℃, is preferable because the difference of the formation of Gibbs energy of chloride of actinides and lanthanides becomes large along with decrease in temperature. The chlorides from the chlorination step are dissolved in LiCl-KCl eutectic salt to maintain the liquidus temperature of the mixed chlorides less than 500 ℃. Cd, Zn, Pb, Bi or others is available as liquid metal solvent from the point of the melting temperature. However, the solubility of actinides and lanthanides in Zn and Pb is very low, then Cd or Bi can be selected as the candidate solvent. The difference of the separation behavior of some actinides and lanthanides using LiCl-KCl/Cd or -/Bi system is studied and material balances of both systems are also investigated.

In this study, the separation factors between neodymium and four actinides (U, Np, Pu, Am) and seven lanthanides (Y, La, Ce, Pr, Sm, Eu, Gd) and those between neodymium and two actinides (U, Np) and seven lanthanides are experimentally determined in the LiCl-KCl/Cd system and in the LiCl-KCl/Bi system, respectively.

2. Experimental

2.1 Reagents

Polarographic grade LiCl-KCl eutectic salt (59:41mol%) and unhydrated lanthanide trichlorides obtained from the Anderson Physics Laboratories, U.S.A., were used for the experiment. The actinide trichlorides were made by the oxidation of the actinide metals dissolved in liquid Cd or Bi by the addition of $CdCl_2$ or $BiCl_3$. The Cd and Bi metal with a purity of 99.9999 % obtained from the Rare Earth Products, U.S.A., were melted at 500 ℃ along with LiCl-KCl eutectic salt in the argon atmosphere glove box for thorough removal of oxygen in the metals and then the surface of the metals were mechanically polished after cooling. Li-Cd and Li-Bi alloy were used as the reductant and $CdCl_2$ or $BiCl_3$ as the oxidant in this experiment.

2.2 Apparatus

The measurement was carried out by setting the apparatus shown in Fig. 2 in the furnace well of an argon atmosphere glove box. The oxygen content and dew point in the glove box were maintained less than 0.5 ppm and -80 ℃, respectively.

2.3 Procedure

The weighed salt was loaded in an alumina crucible (SSA-S) which was placed at the bottom of the reaction cell. The cell was then heated to melt the salt and then the Cd or Bi was added in the crucible. After melting the metal, an agitator was, then, lowered into the liquid metal phase and the melt was stirred continuously at 60 rpm. The distribution of the lanthanides and actinides was controlled by the incremental addition of the Li-Cd or Li-Bi alloy or the addition of $CdCl_2$ or $BiCl_3$ to the system. Preliminary experiments indicated that the equilibrium was attained in less than 4 hours after the addition of reductant or oxidant when the liquid metal phase was not saturated with the rare earth elements [4].

After the attainment of equilibrium, the samples of the salt and metal were taken by inserting a Pyrex glass tube into the salt or metal phase and then by withdrawing into the tube with a glass syringe. The salt samples were dissolved in 1 N HNO_3 , while the metal samples were washed with water for removal of salt contamination, and then were dissolved in 1 N HNO_3 by heating at about 100 ℃. The lanthanides and actinides in these solutions were analyzed by ICP, and Li and K by atomic absorption spectroscopy.

3. Results and discussion

3.1 Determination of distribution coefficients for lanthanides and actinides

The distribution of a trivalent element, such as the lanthanides and actinides, between molten LiCl-KCl eutectic salt and liquid metal can be expressed by the following reaction:

$$M^A(\text{in metal}) + M^BCl_3(\text{in salt}) \Leftrightarrow M^ACl_3(\text{in salt}) + M^B(\text{in metal}).$$

The suffix A and B represent two different heavy metals with same valence. The equilibrium constant K can be written as

$$K = \frac{a_{M^BCl_3} a_{M^A}}{a_{M^B} a_{M^ACl_3}} = \frac{\gamma_{M^BCl_3} \gamma_{M^A}}{\gamma_{M^B} \gamma_{M^ACl_3}} \cdot \frac{X_{M^BCl_3} X_{M^A}}{X_{M^B} X_{M^ACl_3}}, \qquad (1)$$

in which a, X and γ denote activity, mole fraction and activity coefficient, respectively. If the activity coefficients are constant in the system followed by Henry's law, an apparent equilibrium constant K' is given by

$$K' = K \cdot \frac{\gamma_{M^B} \gamma_{M^ACl_3}}{\gamma_{M^BCl_3} \gamma_{M^A}} = \frac{X_{M^BCl_3} X_{M^A}}{X_{M^B} X_{M^ACl_3}}. \qquad (2)$$

When the distribution coefficients are defined as

$$D_M = \frac{X_M}{X_{MCl_3}} , \tag{3}$$

eq. (2) can be written in logarithmic form as

$$\log\left(D_{M^A}\right) = \log\left(D_{M^B}\right) + \log\left(K'\right) . \tag{4}$$

Thus, a relationship of logarithm of distribution coefficient of two trivalent heavy metals should give a straight line having a slope of unity. The separation factor of element B to element A is defined as

$$SF = \frac{D_{M^B}}{D_{M^A}} . \tag{5}$$

Fig. 3 shows the relationship of the distribution coefficient of the various heavy metals and that of Nd in LiCl-KCl/Cd system. The slope of each line is almost unity with the exception of Sm, Eu and Am which behave as a divalent element in LiCl-KCl molten salt [2]. It suggests that the actinides and the rare earth elements behave as trivalent and that activity coefficient of each element is nearly constant both in the LiCl-KCl molten salt and in the liquid Cd in the concentration measured. From the results, the reductivity of the elements into the liquid Cd is an order of

$$U > Np > Pu > Am > Pr, Nd > Ce > La > Gd > Y.$$

Fig. 4 shows the relationship of the distribution coefficients in the LiCl-KCl/Bi system. The slopes are almost unity with the exception of Sm and Eu and the order of the reduction in the LiCl-KCl/Bi is the same as that in the LiCl/KCl/Cd system, however, the SF between the elements becomes larger in -/Bi than in -/Cd.

3.2 Separation factor of actinides and lanthanides

The separation factors of various elements versus Nd both in the LiCl-KCl/Cd and in the LiCl-KCl/Bi system are summarized in table 2. The separation factor of U and Np versus Nd is rather smaller in the LiCl-KCl/Bi than in the LiCl-KCl/Cd and that of the heavy lanthanides (Y, Gd) is larger, nevertheless, that of light lanthanides (La, Ce, Pr) is similar in the both systems.

3.3 Material flow in LiCl-KCl/Cd system and -/Bi system

Material flow of the lanthanides and actinides during the Li reduction step in the LiCl-KCl/Cd and LiCl-KCl/Bi system is calculated for the HLW concentration shown in table 1, using the separation factor of the elements under the condition that 99 % of Am and Np are extracted from molten salt into liquid metal. The relatively poor capability of the separation between the actinides and the rare earth elements in the LiCl-KCl/Cd system requires the multistep reductions and extractions to obtain improved purity of the actinides. Fig. 5 (a) shows the extracted ratio of the elements as a function of the number of Li reduction step in the LiCl-KCl/Cd system. After the first reduction step, ca. 90 % for Ce, Pr and Nd, ca. 70 % for La and Gd and 7 % for Y are accompanied with actinides and then, after the second step, ca. 60 % for Ce, Pr and Nd and ca. 25 % for La and Gd are accompanied. The amount of the lanthanides accompanied gradually decreases along with increase in the number of the step, however, even after the eighth step, ca 40 % for Ce, Pr and Nd and about 10 % for La and Gd still come along with the actinides. The composition of the rare earth elements and the actinides between before the Li reduction and after the eight times Li reduction step is compared in table 3. About 5 times larger amount of the rare earth elements is still accompanied with the minor actinides after the eight times Li reduction and it suggests that further separation step, e. g. the electrorefining, should be required to improve the purity of the final products.

On the other hand, when the LiCl-KCl/Bi is employed for the separation between the rare earth elements and the actinides, the relatively high capability was attained. Fig. 5 (b) shows the extracted ratio of the elements as s function of the number of the reduction steps in the LiCl-KCl/Bi system. After only two steps of the reduction the accompanied amount of the rare earth elements is rather low when the actinides were reduced more than 99 %. The composition of the final products using the LiCl-KCl/Bi system is compared with using the LiCl-KCl/Cd system in table 3.

3.4 Designing of pyrometallurgical partitioning process

Several options for pyrometallurgical partitioning process can be designed, because of the large flexibility of the system. Two types of typical block diagram of the process using the LiCl-KCl / Cd system or the - / Bi system are represented in figures 6 and 7. The number of the Li reduction steps would be smaller in the LiCl-KCl / Bi system than in the - / Cd system.

4. Conclusions

The separation factor between the actinides and the rare earth elements is experimentally measured in the LiCl-KCl / Cd and in the LiCl-KCl / Bi system. The multistep Li reduction and further separation after Li reduction would be required when Cd was used as the solvent. On the other hand, Bi has the high capability for separating the actinides from the rare earth elements and the composition of the final products after two steps could be provided for the transmutation. Two types of the process flow are proposed.

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Table 1 Composition of fission products after chlorination step (based on the calculation by ORIGEN-II) .

group	composition(wt%)
U	10.3
MA	3.2
alkali	9.0
alkaline	7.6
lanthanide	32.3
Zr	10.9
Mo	10.5
noble metal	16.3

Table 2. Separation factor of various elements to Nd at 500 C.

element	LiCl-KCl/Cd	LiCl-KCl/Bi
U	0.022	0.00091
Np	0.043	0.0095
Pu	0.056**	0.012***
Am *	0.067**	0.014***
Pr	0.91	0.77
Nd	1.0	1.0
Ce	1.1	0.91
La	2.8	2.8
Gd	3.8	11
Y	110	710
Sm *	1400	3700
Eu *	2600	7700
Li*	2800	1300

* where log D(Nd) = 0
** measured at 450 C
*** estimated value

Table 3 Comparison of calculated composition after Li reduction step by using LiCl-KCl/Cd or LiCl-KCl/Bi system .

element	starting composition (at%)	after 8th step using LiCl-KCl/Cd (at%)	after 2nd step using LiCl-KCl/Bi (at%)	CRIEPI target (at%)
U	15.0	37.7	71.0	62.1
Np	2.3	5.7	10.8	as total of MA
Pu	0.2	0.4	0.8	18.9
Am	2.1	5.4	10.1	
actinide;total	19.6	49.2	92.7	81.1
Y	5.3	0.1	0.0	
La	9.5	3.1	0.7	
Ce	18.3	14.2	3.9	
Pr	8.5	7.5	2.0	
Nd	30.5	25.5	5.9	
Sm	5.9	0.0	0.0	
Eu	1.1	0.0	0.0	
Gd	1.2	0.3	0.0	
lanthanide;total	80.4	50.8	7.3	18.9

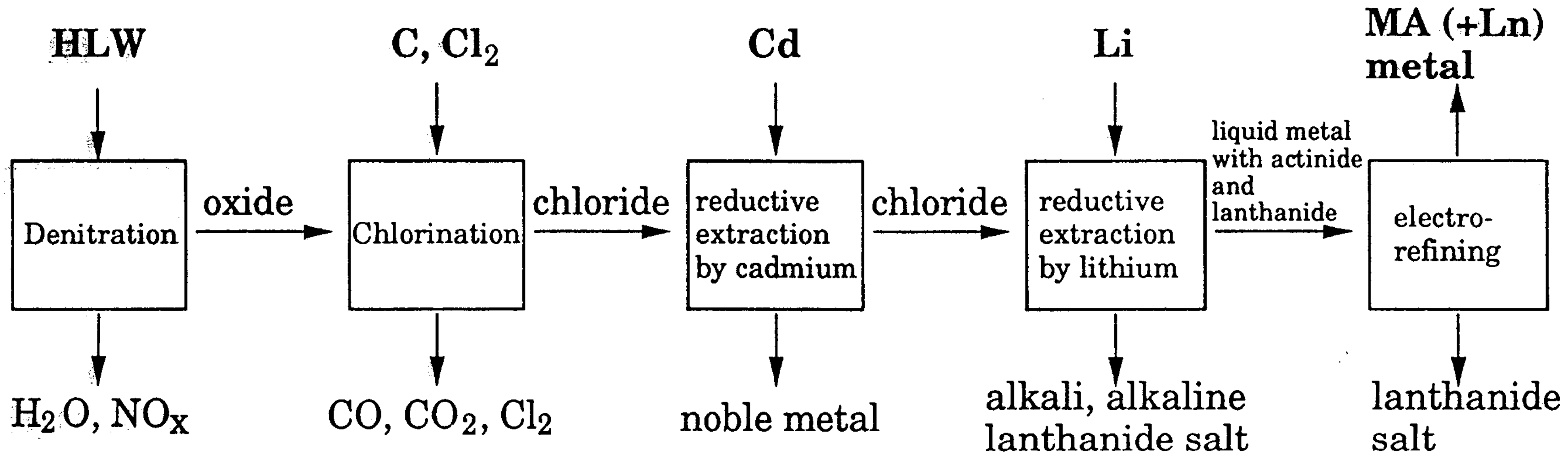

Fig. 1 Flow diagram of pyrometallurgical process for partitioning of MA from HLW.

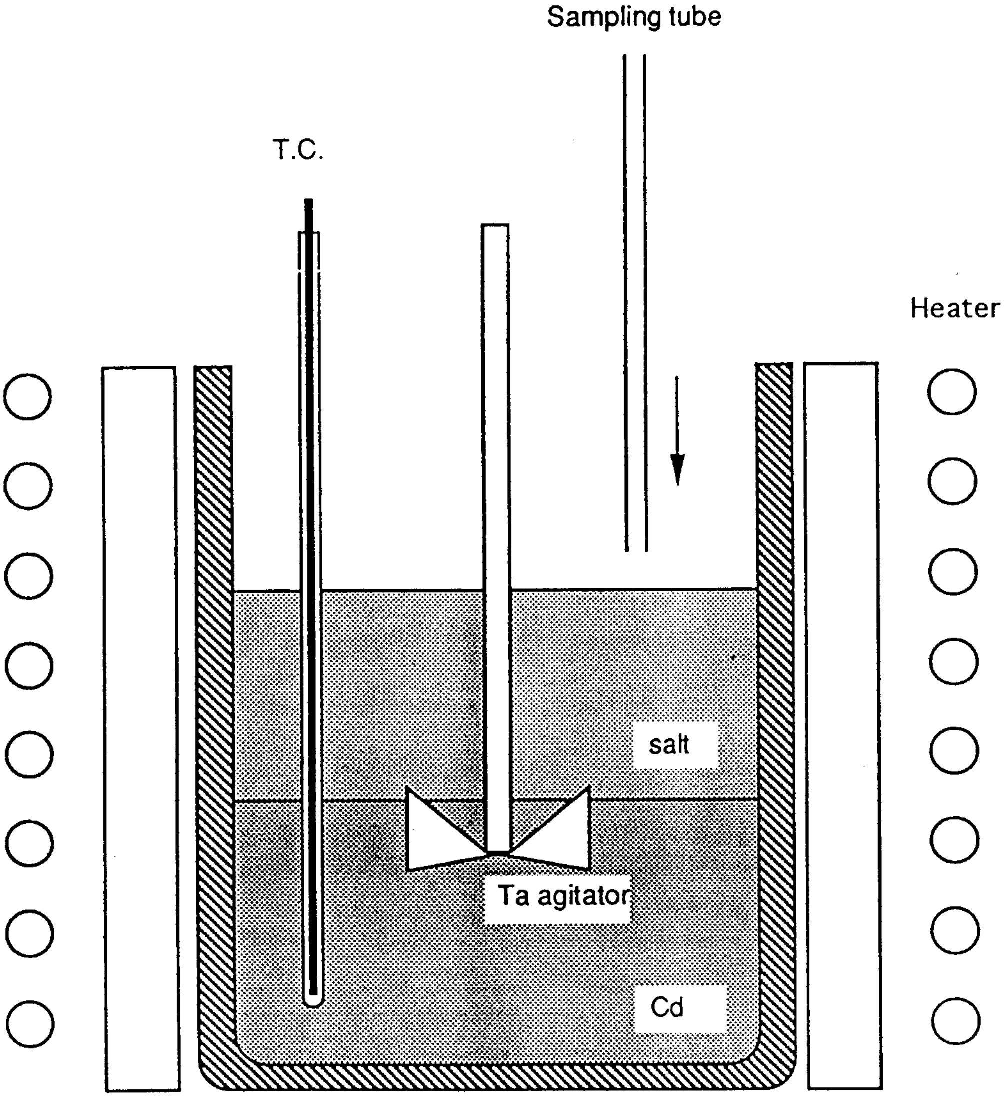

Fig. 2 Reaction cell

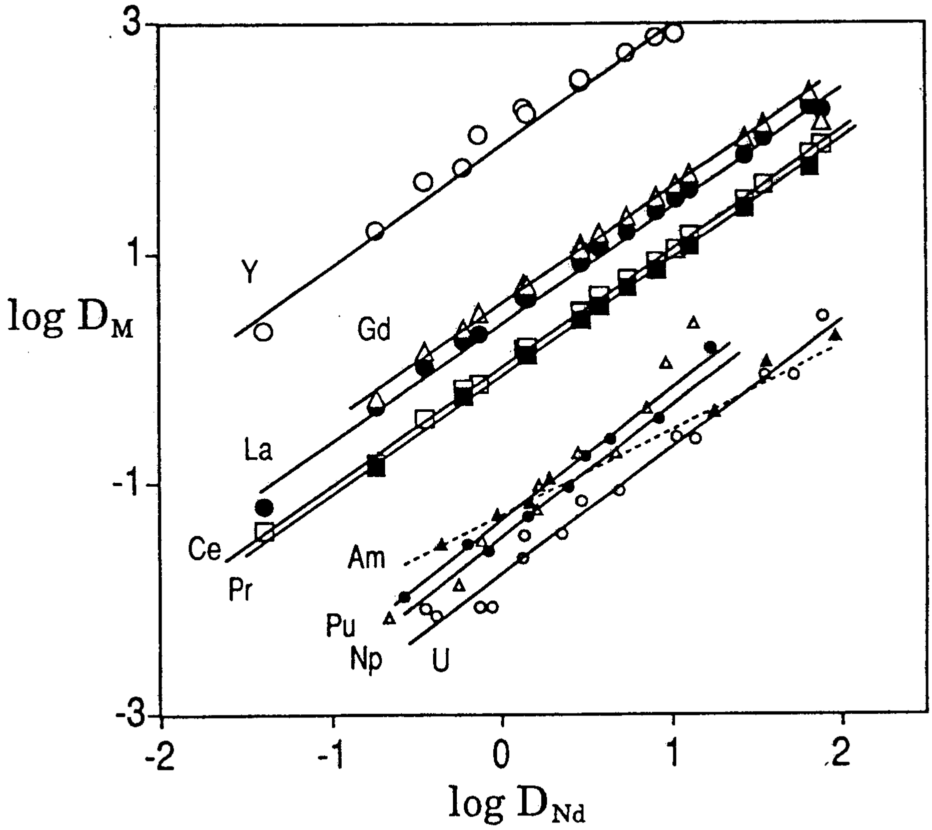

Fig. 3 Distribution coefficient of various elements vs. distribution coefficient of neodymium between LiCl-KCl eutectic molten salt and liquid cadmium at 500 ℃. (The coefficients of Np, Pu and Am were measured at 450 ℃)

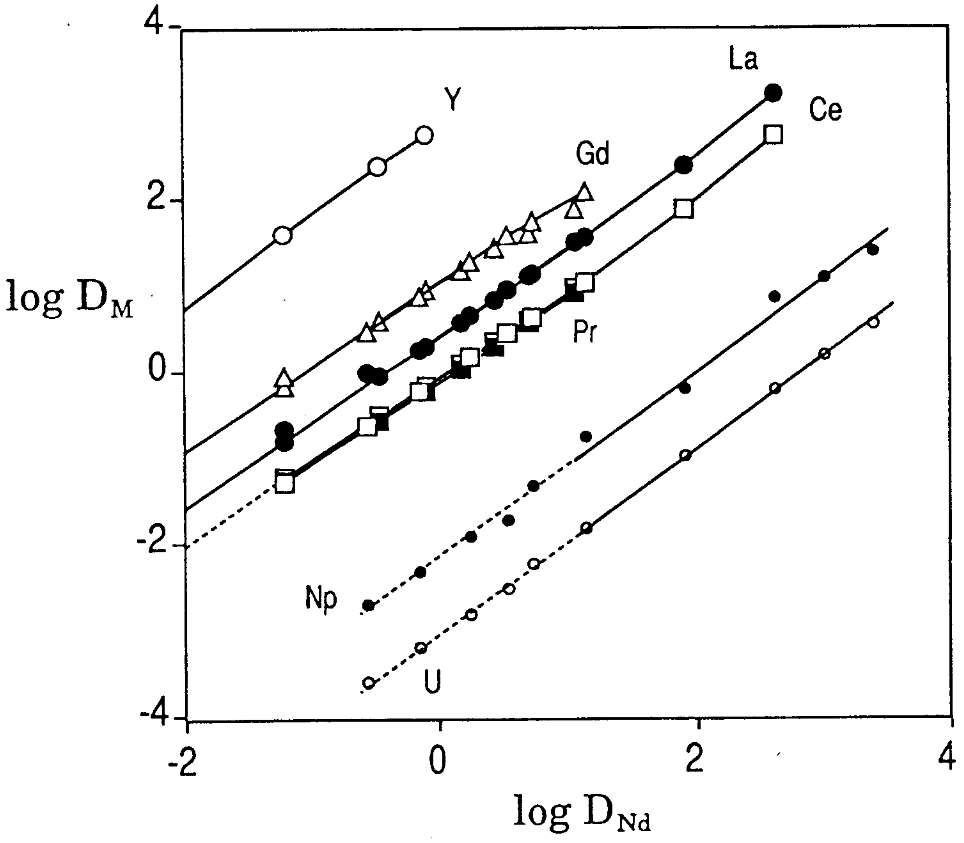

Fig. 4 Distribution coefficient of various elements vs. distribution coefficient of neodymium between LiCl-KCl eutectic molten salt and liquid bismuth at 500 ℃.

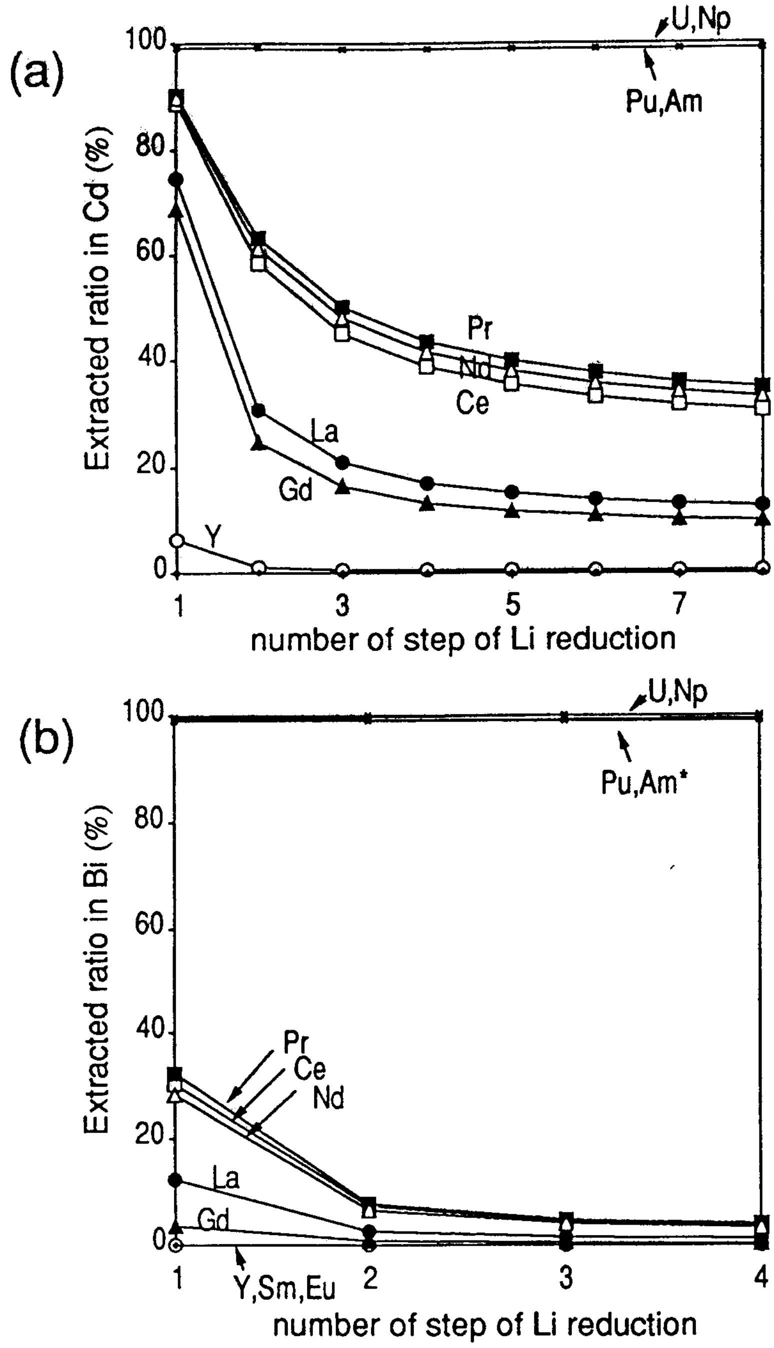

Fig. 5 Extracted ratio of actinides and lanthanides in multistep Li reduction at 500 ℃ under the condition of 99% of Am and Np is extracted. (*using estimated value)
(a) in LiCl-KCl / liquid Cd system
(b) in LiCl-KCl / liquid Bi system

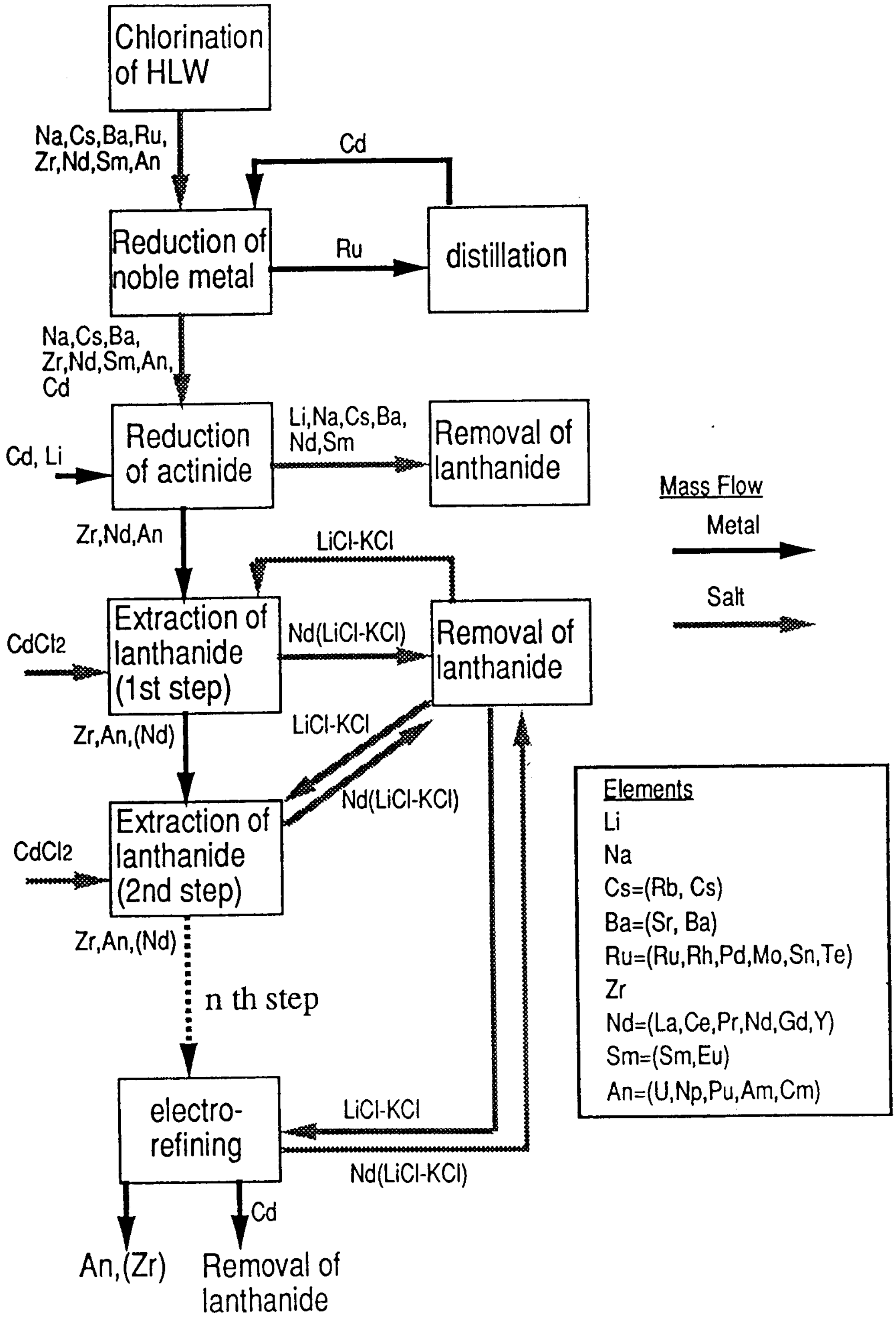

Fig. 6 Process flow of pyrometallurgical partitioning using liquid cadmium as a solvent.

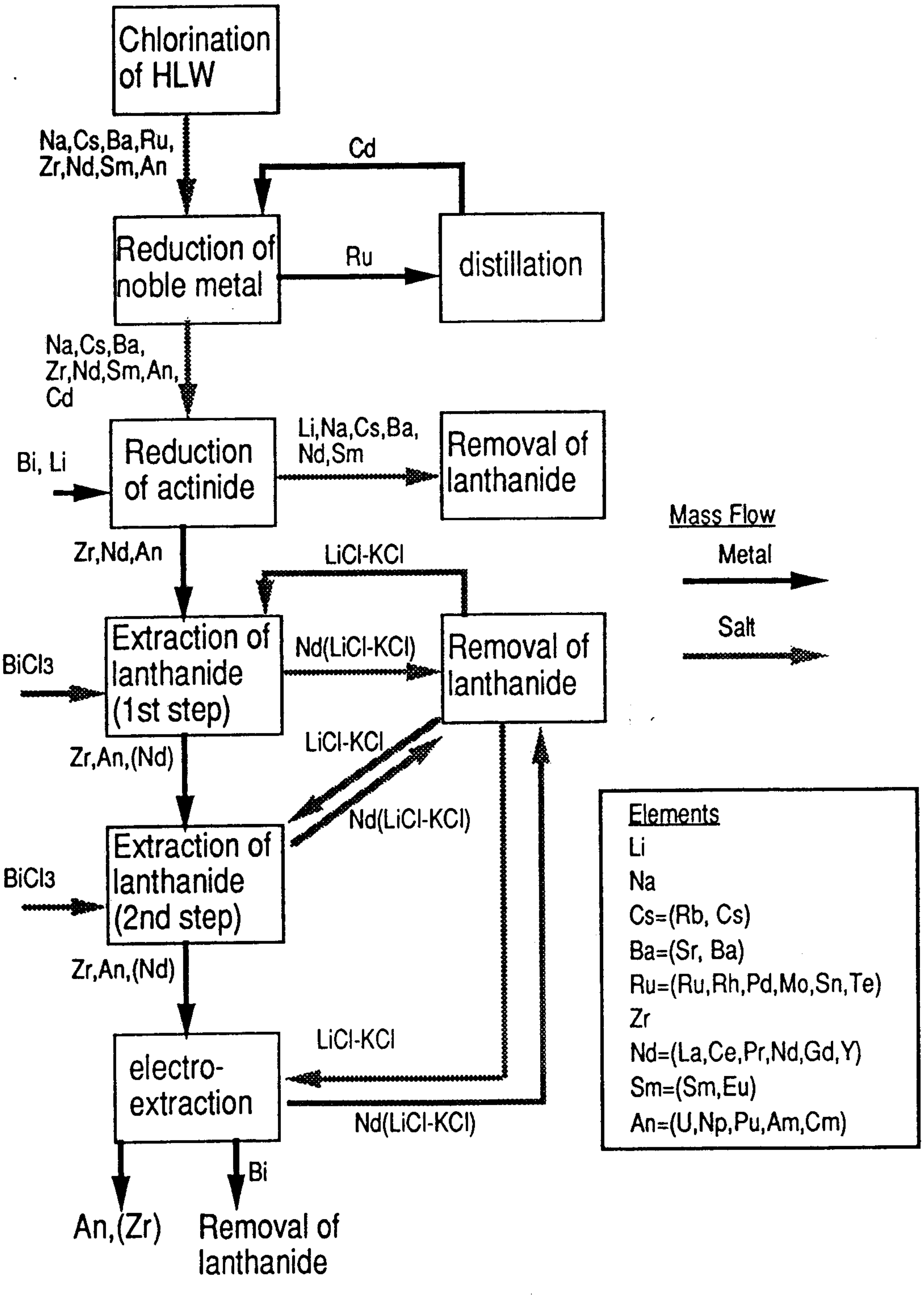

Fig. 7 Process flow of pyrometallurgical partitioning using liquid bismuth as a solvent.