

PREDICTION OF A MUTUAL SEPARATION OF ACTINIDE AND RARE EARTH GROUPS IN A MULTISTAGE REDUCTIVE EXTRACTION SYSTEM

JAЕ-HYUNG YOO*, HAN-SOO LEE and EUNG-HO KIM

Korea Atomic Energy Research Institute

150 Duckjin-dong, Yuseong, Daejeon 305-353, Korea

*Corresponding author. E-mail : njhyou@kaeri.re.kr

Received April 30, 2007

Accepted for Publication July 25, 2007

The mutual separation behavior of actinides and rare earths in a countercurrent multistage reductive extraction system was predicted by computer calculation. The distribution information for actinides and rare earths in the reductive extraction systems of LiCl-KCl/Cd and LiCl-KCl/Bi was collected from literature and then it was used for the calculation of a multistage extraction. The results of the concentration profiles throughout the extraction cascade, recovery yields of various metal solutes, and separation factors between the actinides and rare earths were calculated. The effects of the major process parameters, such as reducing agent content in the metal phase, number of stages, and salt/metal flow ratio, etc., on the extraction behavior were also examined.

KEYWORDS : Reductive Extraction, Pyrometallurgical Process, Equilibrium Stage Operation

1. INTRODUCTION

A solute's equilibrium relationship between the extraction and raffinate phases is one of the most important factors in extraction systems because it determines the distribution of the solute between the two phases. Furthermore, when an extraction system involves a chemical reduction between the two phases, the content of the reducing agent also affects the equilibrium relationship and, thus, influences the distribution of the solutes. Therefore, once we know the equilibrium relationship for a certain solute in an extraction system accompanied by chemical reactions, we can predict the recovery yield as well as the separation efficiency for a given solute from other unwanted solutes.

In this study, an equilibrium stage model [1] was employed for the prediction of a countercurrent multistage reductive extraction with the purpose of a mutual separation of actinides and rare earths in the reductive extraction systems of LiCl-KCl/Cd and LiCl-KCl/Bi. In these systems, LiCl-KCl eutectic salt (58 mol % LiCl) is used as the raffinate phase, while liquid Bi or liquid Cd containing liquid Li is used for the extraction phase. In this case, the liquid Li works as a chemical reducing agent [2-5]. Accordingly, this type of extraction takes place via a heterogeneous chemical reaction; in other words, metallic salts dissolved

in the molten salt phase react with the reducing agent, Li, at the interface of the salt and metal phases. Then, the metallic forms created from the metallic salts transfer into the liquid Bi or liquid Cd phase.

Since the equilibrium relationships for various actinides and rare earths with the Li content in the metal phase have already been reported in the literature [2,3], this distribution data was quoted in this study in order to calculate the recovery yields as well as the separation efficiencies between actinides and rare earths in a multistage countercurrent extraction system.

Since most transuraniums (TRU) contained in high-level waste are composed of long-lived radionuclides, their transmutation would be beneficial from the viewpoint of environmental safety when they are disposed of in an underground repository. However, since the TRU product is chemically analogous to the rare earth group, it tends to accompany rare earths as impurities in a partitioning process, and this requires the elimination of the rare earths from the TRU product up to a certain level in order to meet the requirements to make TRU a nuclear fuel in a transmutation reactor. For example, future TRU burners may be suitable reactors to transmute long-lived radionuclides. As a result, the approach in this study would provide a robust basis for the design of a satisfactory pyroprocessing system related to a future transmutation.

2. REDUCTIVE EXTRACTION

Reductive extraction can be applied to the purification of a certain metal element mixed with other metallic impurities. For example, a metallic chloride dissolved in a salt phase can be reduced by lithium dissolved in a liquid metal phase in the following reaction:



where M denotes the m-valence metal element and the overhead bar denotes the species in a metal phase during a heterogeneous chemical reaction. Since the metal(M) and lithium(Li) are distributed between the salt phase and the metal phase in this system, Kurata and his coworkers [2] expressed the distribution relationship of D_M and D_{Li} as follows:

$$\text{Log}(1/D_M) = a + b \log (1/D_{Li}) \quad (2)$$

where the distribution coefficients D_M and D_{Li} are defined as

$$D_M = \frac{C_M}{C_{MCl_m}} \quad (3)$$

$$D_{Li} = \frac{C_{Li}}{C_{LiCl}} \quad (4)$$

They plotted $\text{Log}(1/D_M)$ against $\log (1/D_{Li})$ for each

metal solute and found both the parameters have a linear relationship each other, indicating that the activity coefficients of the solutes varied in neither the salt nor metal phases in their experiments where the condition $C_{Li} \gg C_{MCl_m}$ also held. Then, in their experimental results, they determined the constant values of a and b by least-square calculations for various actinides and rare earths in the LiCl-KCl/Cd and LiCl-KCl/Bi systems.

3. PREDICTION OF THE EXTRACTION BEHAVIOR FOR A MULTISTAGE COUNTERCURRENT CASCADE

The multistage countercurrent extraction system with N stages is shown in Fig.1, where X and Y denote a solute's concentration in the salt phase and the metal phase, respectively. Since a reducing agent is contained in the metal phase, the chemical reaction expressed by Equation (1) occurs in each stage and, thus, certain concentration profiles for X and Y are created throughout the extraction stages.

3.1 Equilibrium Stage Model

The equilibrium stage model [1] was employed in this study. The extraction cascade is assumed to be a series of perfectly mixed equilibrium stages of a constant volume. For general stage n, the mass balance for a metal solute at the steady state is expressed by

$$f X_{n-1} + g Y_{n+1} - (f X_n + g Y_n) = 0 \quad (5)$$

where f and g are the flow rates of the salt phase and the metal phase, respectively, and X_n and Y_n are the concentrations of an objective solute in the salt and metal phases,

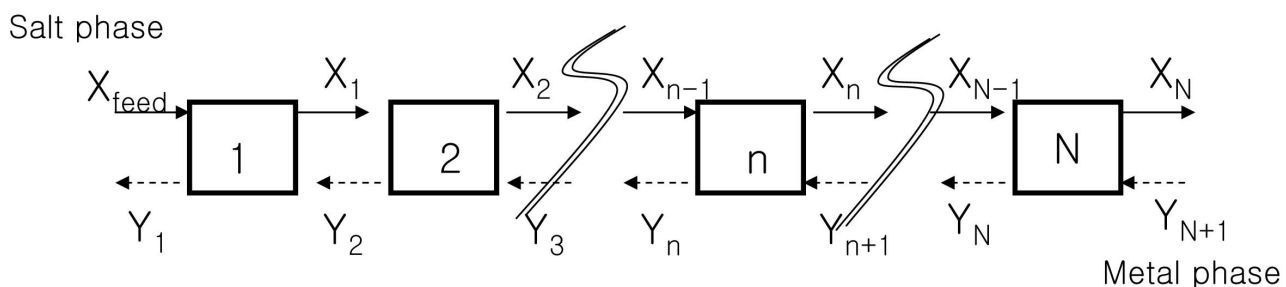


Fig.1. Diagram of a Multistage Countercurrent Extraction Cascade

respectively, leaving stage n . However, for the first stage, Equation (5) is expressed as

$$f X_{\text{feed}} + g Y_2 - (f X_1 + g Y_1) = 0 \quad (6)$$

and for the last stage ($n = N$), Equation (5) is specified as

$$f X_{N-1} + g Y_{\text{feed}} - (f X_N + g Y_N) = 0 \quad (7)$$

Since $Y_{\text{feed}} = 0$ in general extraction systems, Equation (7) can be rearranged as

$$f X_{N-1} - (f X_N + g Y_N) = 0 \quad (8)$$

The equilibrium stage condition is satisfied by

$$Y_n = D X_n \quad (9)$$

for a linear equilibrium relationship, where D is the distribution coefficient. When the Li content in the metal phase is much higher than that of the metallic solutes which are reduced and transferred into the metal phase, the Li content can be assumed as constant from stage to stage. This assumption means that the distribution coefficients of various metal solutes are constant throughout the cascade.

Substituting Equation (9) for Y_n in Equations (5), (6), and (8), then the following Equations are obtained for all the stages in the cascade.

$$-(f + g D) X_n + g D X_{n+1} = -f X_{\text{feed}} \quad \text{for } n = 1 \quad (10)$$

$$f X_{n-1} - (f D + g) X_n + g D X_{n+1} = 0 \quad \text{for } n = 2 \sim N-1 \quad (11)$$

$$f X_{N-1} - (f + g D) X_N = 0 \quad \text{for } n = N \quad (12)$$

This rearrangement results in a set of N simultaneous tri-diagonal equations with the process parameters of f , g , D , and X_{feed} . These equations can be solved by using the Thomas algorithm [7] to give the following solution:

$$X_n = \Psi_n - \frac{g D X_{n+1}}{\beta_n} \quad \text{with } X_N = \Psi_N \quad (13)$$

where

$$\beta_n = -(f + g D) - \frac{f g D}{\beta_{n-1}} \quad \text{with } \beta_1 = -(f + g D) \quad (14)$$

$$\Psi_n = -\frac{f \Psi_{n-1}}{\beta_n} \quad \text{with } \Psi_1 = \frac{f X_{\text{feed}}}{f + g D} \quad (15)$$

From Equations (13)-(15), both β_n and Ψ_n can be calculated consecutively from $n=1$ to $n=N$, while X_n can only be calculated in reverse from $n=N$ to $n=1$.

3.2 Separation Factor and Recovery yield

When the separation of solute i against another solute j is implemented in a multistage system, the separation factor between i and j is defined as

$$\Phi_{ij} = \frac{(Y_i / Y_j)_{\text{product}}}{(X_i / X_j)_{\text{feed}}} \quad (16)$$

The recovery yield for each solute can be expressed by

$$\xi (\%) = \frac{X_{\text{feed}} - X_N}{X_{\text{feed}}} \times 100 \quad (17)$$

and the dimensionless concentration of each solute in the metal phase output is defined as

$$Y^* = \frac{g Y_{\text{product}}}{f X_{\text{feed}}} \quad (18)$$

4. RESULTS AND DISCUSSION

4.1 Distribution Coefficients

The most important parameter in an extraction process is the distribution coefficients of the objective solute and other solutes to be excluded from the product because the recovery yield is completely dependent on its distribution coefficient, while its separation from other unwanted solutes is determined by the differences in their distribution coefficients. In general, the objective group, which is to be a product, should be recovered as much as possible while, on the contrary, the latter group should be excluded from the product as much as possible. In this study, the

actinides correspond to the objective solutes group, whereas the rare earths correspond to the unwanted solutes group. The information on the distribution coefficients of actinides and rare earths in the systems of LiCl-KCl/Cd and LiCl-KCl/Bi were collected from the literature, as listed in Table 1. The distribution coefficients of actinides in Table 1 were obtained by a calculation of Equation (2) using the values of a and b presented by Kurata et al. [2].

In addition, the distribution coefficients of Pu and Am in the LiCl-KCl/Bi system were estimated from the relationship between $\log D_M$ and $\log D_{Np}$, which was obtained by Kinoshita et al. [3].

According to Table 1, the distribution coefficients of both actinides and rare earths are significantly affected by the Li distribution coefficient, which means that the Li content in the metal phase dominates the distributions,

Table 1. Distribution Coefficients of the Actinides and Rare Earths with the Distribution of Li at 773°K in the Systems of LiCl-KCl/Bi and LiCl-KCl/Cd

D_{Li}	Element	Distribution coefficient(D_M)	
		LiCl-KCl/Bi	LiCl-KCl/Cd
$10^{-3.0}$	U	2238	1862
	Np	363	631
	Pu	345	-
	Am	126	-
	Y	9.3E-03	0.15
	La	0.76	8.32
	Ce	2.45	24.5
	Nd	2.19	23.4
	Gd	0.18	5.62
$10^{-3.5}$	U	79.4	42.7
	Np	10.2	18.4
	Pu	8.11	-
	Am	3.23	-
	Y	7.8E-04	7.4E-03
	La	3.1E-02	0.29
	Ce	9.9E-02	0.78
	Nd	7.9E-02	0.79
	Gd	6.5E-03	0.21
$10^{-4.0}$	U	2.82	0.98
	Np	0.29	0.54
	Pu	0.19	-
	Am	0.08	-
	Y	6.6E-05	3.7E-04
	La	1.2E-03	1.0E-02
	Ce	4.0E-03	2.5E-02
	Nd	2.9E-03	2.6E-02
	Gd	2.3E-04	7.9E-03

especially those of the actinides, due to the higher rates of the chemical reduction of the actinide chlorides contained in the salt phase.

4.2 Predicted Results for the Separation of Actinides from Rare Earths

By using Equations (13)-(15), we calculated the concentration profiles of the actinides and rare earths throughout the extraction cascade. Then we also calculated the recovery yields and separation factors between the actinides and rare earths by using Equations (16) and (17). When calculating the separation factor of each actinide relative to rare earth, Nd was chosen as a reference element because it is the element of largest amount among the rare earths in spent PWR fuels.

Fig.2 shows the concentration profiles of various actinides and rare earths throughout a five-stage cascade. In this case, the metal phase enters stage 5 and flows towards stage 1, whereas the salt phase enters stage 1 and flows towards stage 5 so that they should flow and contact each other countercurrently in the cascade. As shown in Fig. 2, the U concentration in the metal phase increases

rapidly from stage to stage since its distribution coefficient is higher than that of the TRU. The concentration profiles of the rare earths, however, are so flat all throughout the cascade as shown in Fig. 2(b), meaning that their low distribution coefficients create pinching points in the McCabe-Thiele diagram [8,9]. The formation of the pinching results in slight changes in the concentrations (X and Y) along the stages near the salt feeding stage(#1).

Table 2 shows the effect of the Li distribution coefficient on the distribution of various metal solutes and, thus, on their recovery yields as well as on their separation factors. Since a higher distribution of Li (Li in metal/ Li in salt) represents a higher content of Li in the metal phase, it brings about a higher reduction of the metal salts and, therefore, a higher distribution. As a result, the recovery yields of various metals increase with the D_{Li} ; however, the separation factors of the actinides relative to Nd decrease due to the differences in their recovery yields. As the Li content becomes higher in the metal phase, the actinide recovery yields also increase, but the rate is so small, whereas the Nd recovery yield rises with a higher rate, thus decreasing the separation

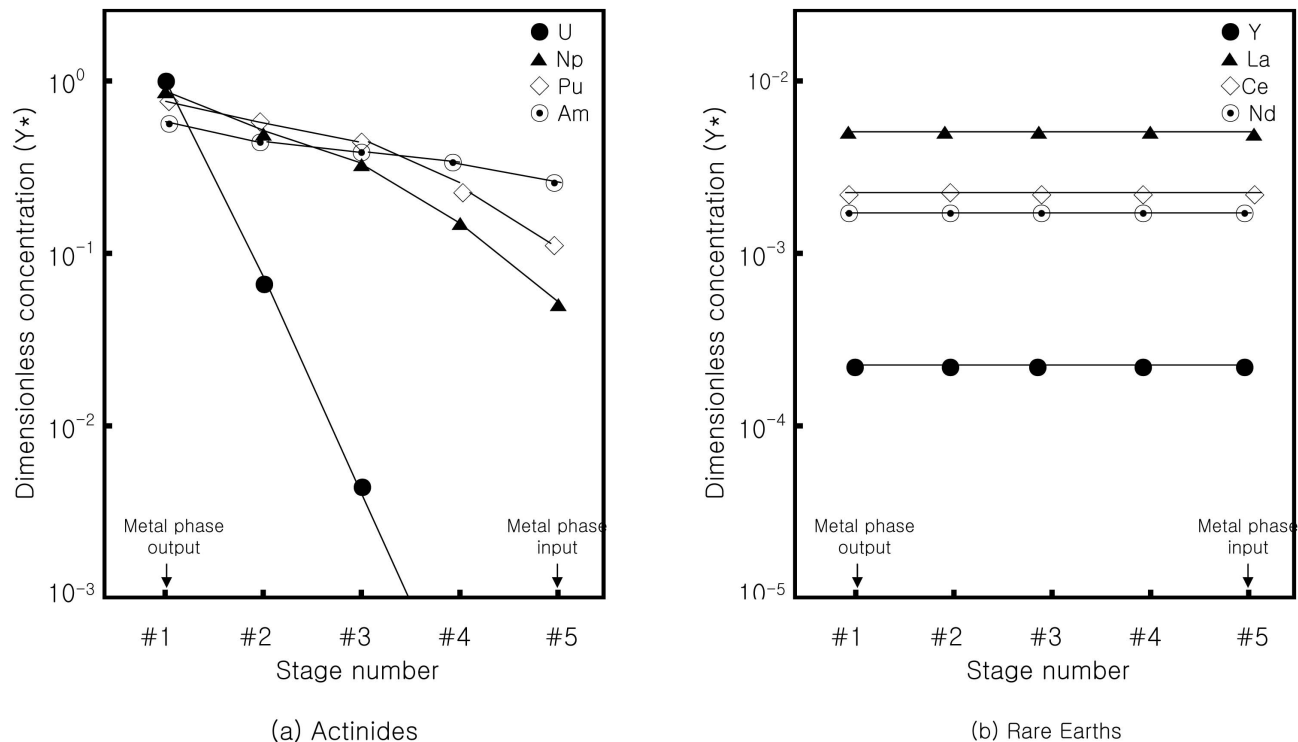


Fig.2. Concentration profiles of actinides and rare earths in the metal phase throughout the cascade ($\log D_{Li} = -3.75$, flow ratio = 1.0, number of stage = 5, LiCl-KCl/Bi system)

Table 2. Effect of the D_{Li} on the Separation Behavior of Actinides Relative to Nd (LiCl-KCl/Bi System)

D_{Li}	1.0×10^{-4}	1.8×10^{-4}	3.2×10^{-4}	5.6×10^{-4}	10.0×10^{-4}
Distribution coefficient					
D_U	2.82	15.0	79.4	422	2238
D_{Np}	0.288	1.72	10.2	61.0	363
D_{Pu}	0.19	1.25	8.11	53.0	345
D_{Am}	0.08	0.52	3.23	20.2	126
D_{Nd}	0.0029	0.015	0.079	0.42	2.18
Recovery yield					
ξ_U	97.1	>99.9	>99.9	>99.9	>99.9
ξ_{Np}	28.3	90.7	99.9	>99.9	>99.9
ξ_{Pu}	18.9	82.7	99.8	>99.9	>99.9
ξ_{Am}	8.0	48.2	97.9	>99.9	>99.9
ξ_{Nd}	0.3	1.5	7.9	40.1	94.6
Separation factor					
$\phi_{U/Nd}$	335	66.6	12.6	2.5	1.1
$\phi_{Np/Nd}$	97.6	60.4	12.6	2.5	1.1
$\phi_{Pu/Nd}$	65.2	55.1	12.6	2.5	1.1
$\phi_{Am/Nd}$	27.6	32.1	12.4	2.5	1.1

* Extraction condition : Flow ratio = 1.0
Number of stages(N) = 3
Temperature = 773 °K

factor. Consequently, the optimum condition of the mutual separation of actinides/rare earths should be determined on the basis of the recovery yields, as well as the separation factors of the objective group. In fact, both parameters should be fulfilled in the design of a reductive extraction process. For example, a higher recovery of TRU would be required in the process, but it should also meet the purity requirements of the actinides so that the actinides could be used as a fuel source in a future reactor such as a TRU burner.

The effect of the flow ratio(f/g) on the recovery yields and separation factors of the actinides relative to Nd was estimated as shown in Table 3. The recovery yields of the actinides tend to decrease as the flow ratio increases. This phenomenon is attributed to the increase in the slope of the operating line in the McCabe-Thiele diagram(see Fig. 3). Operating line ② (flow ratio = 1.0) results in a higher value of $X_3(X_{out})$ when compared to operating line ① (flow ratio = 0.5). Though the recovery yields decrease with the flow ratio, the separation rate

increases with the flow ratio. This result is due to the difference in the recovery yields between the actinides and Nd continuing to increase with the flow ratio. As a result, the optimum condition of the flow ratio should be determined by considering both the recovery and separation levels in order that process conditions can meet the requirements of product quality.

The number of stages of the extraction cascade also affects the recovery and separation rates as shown in Table 4. Since the distribution coefficient of uranium is much larger than those of the other solutes, it requires only three stages to recover nearly the entire amount of uranium that is fed into the cascade, whereas, the other solutes need more stages to elevate their recovery yields. As for the separation of other actinides relative to Nd, the separation factor grows with the same trend of its recovery yield, which is due to the quite low distribution of Nd and thus a nearly constant extraction of Nd without regard to the number of stages. As shown in Fig. 2(b), the Nd concentration is nearly constant throughout the

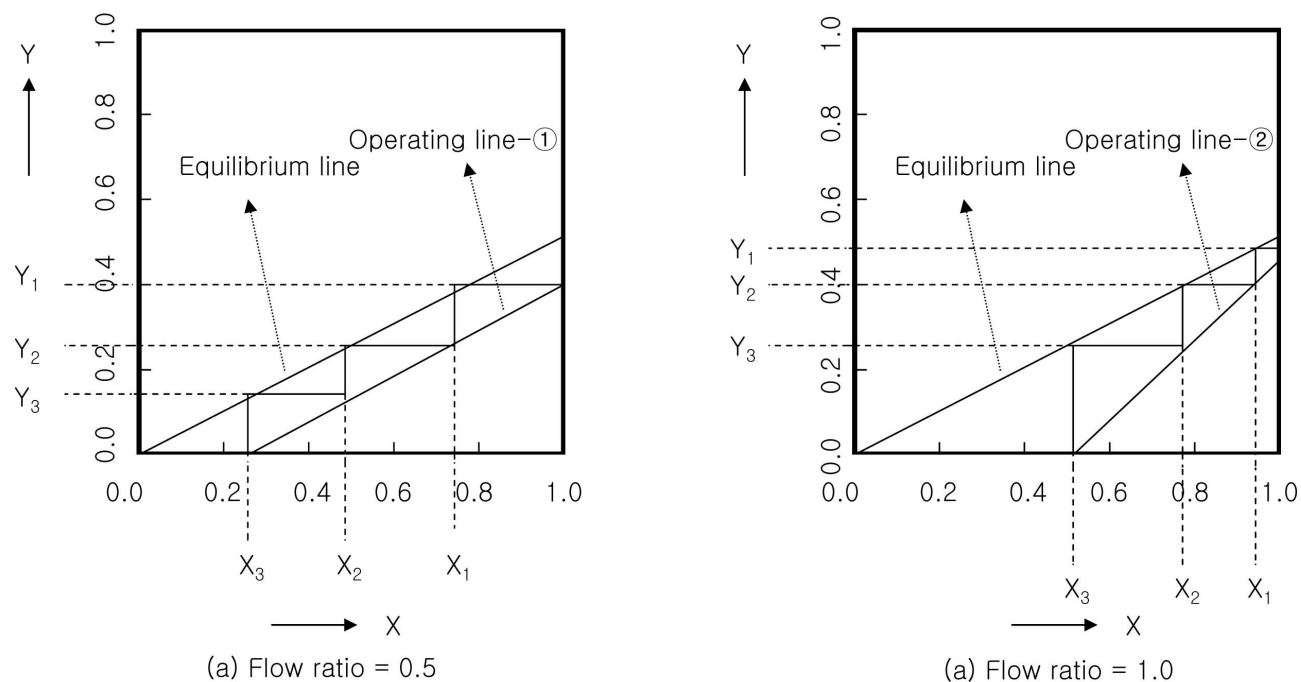


Fig.3. McCabe-Thiele Diagram for Am Extraction(N=3) ; Effect of Flow Ratio

Table 3. Effect of the Flow Ratio on the Separation Behavior of Actinides Relative to Nd (LiCl-KCl/Bi System)

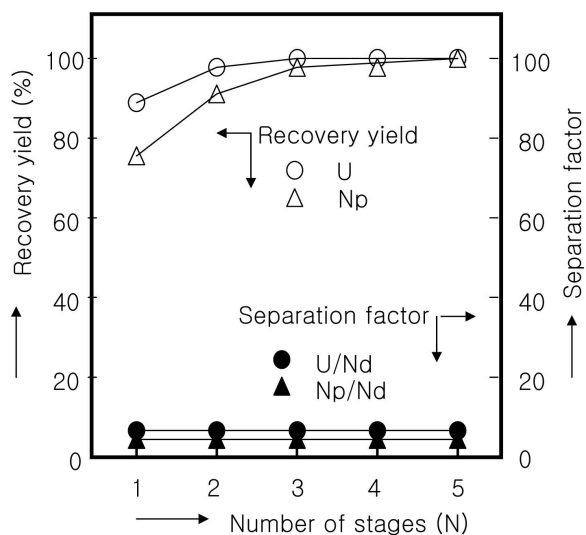
Flow ratio (f/g)	0.1	0.5	1.0	2.0
Recovery yield (%)				
ξ_U	>99.9	>99.9	>99.9	99.8
ξ_{Np}	>99.9	98.3	90.7	69.1
ξ_{Pu}	>99.9	96.1	82.7	55.8
ξ_{Am}	99.4	76.5	48.2	25.7
Separation factor				
$\phi_{U/Nd}$	6.7	33.3	66.7	133.1
$\phi_{Np/Nd}$	6.7	32.8	60.5	92.1
$\phi_{Pu/Nd}$	6.7	32.0	55.1	74.3
$\phi_{Am/Nd}$	6.7	25.5	32.1	34.2
Distribution coefficient (D_M)	$D_U = 15.0$ $D_{Np} = 1.72$ $D_{Pu} = 1.25$ $D_{Am} = 0.52$ $D_{Nd} = 1.5E-02$			

* Extraction condition : $\log D_{Li} = -3.75$
 Number of stages(N) = 3
 Temperature = 773 °K

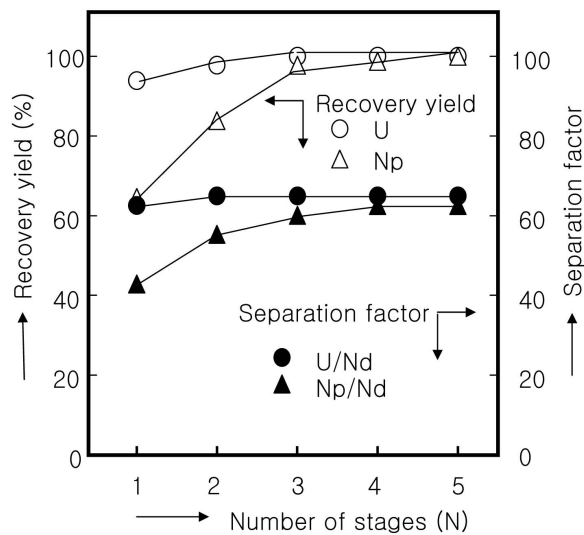
Table 4. Effect of the Number of Stage on the Separation Behavior of Actinides Relative to Nd (LiCl-KCl/Bi System)

Number of stage	1	3	5	7
Recovery yield (%)				
ξ_U	93.8	>99.9	>99.9	>99.9
ξ_{Np}	63.2	90.7	97.1	99.1
ξ_{Pu}	55.6	82.7	91.1	95.0
ξ_{Am}	14.8	48.2	51.0	51.7
Separation factor				
$\phi_{U/Nd}$	63.4	66.7	66.7	66.7
$\phi_{Np/Nd}$	42.8	60.5	64.7	66.0
$\phi_{Pu/Nd}$	37.6	55.1	60.8	63.3
$\phi_{Am/Nd}$	23.2	32.1	34.0	34.5
Distribution coefficient (D_M)	$D_U = 15.0$ $D_{Np} = 1.72$ $D_{Pu} = 1.25$ $D_{Am} = 0.52$ $D_{Nd} = 1.5E-02$			

* Extraction condition : $\log D_{Li} = -3.75$
Flow ratio $f/g = 1.0$
Temperature = 773 °K



(a) LiCl-KCl/Cd system



(b) LiCl-KCl/Bi system

Fig.4. Comparison of the U/Nd and Np/Nd Separation Behaviors for the LiCl-KCl/Cd and LiCl-KCl/Bi Systems

cascade. This low distribution of Nd, as described above, forms a pinching point in the McCabe-Thiele diagram [8,9], and, thus, it brings about a slight increase in the separation rate between the actinides and Nd as the actinide recovery rate gradually increases with the number of stages, whereas the Nd recovery rate is not changed.

4.3 Comparison of the LiCl-KCl/Cd and LiCl-KCl/Bi Systems

Kurata and his coworkers [2] have already compared both extraction systems of LiCl-KCl/Cd and LiCl-KCl/Bi in terms of their separation efficiency between actinides and rare earths. They found that a better separation can be achieved in the latter system because the difference in the distribution coefficients of the actinides and rare earths is larger than that in the former system. With this background, a multistage extraction was predicted for both systems and their separation behaviors were compared. When the value of D_{Li} is set by $\log D_{Li} = -3.75$ and the flow ratio = 1.0, the distribution coefficients, recovery yields, and separation factors of U and Np against Nd were estimated, as shown in Fig. 4. This result also shows a higher separation of U and Np against Nd in the Bi system rather than that in the Cd system. The dominating factor here is the higher distribution of Nd in the Cd system compared with that in the Bi system. Meanwhile, the number of stages affected the separation of U/Nd and Np/Nd very slightly in both systems because the recovery yield of each solute is nearly constant even though more stages are employed.

5. CONCLUSIONS

The behavior of a mutual separation of actinides and rare earths in a countercurrent reductive extraction cascade was predicted by a computer calculation approach. Such parameters as reducing agent content, flow ratio, and number of stages, etc. were examined to see how much they affect the separation efficiency between actinides and rare earths in the reductive extraction systems of LiCl-KCl/Bi and LiCl-KCl/Cd. The Li content in the metal phase was found to be the most significant factor affecting the distribution of both actinides and rare earths, and, thus, it dominated the recovery yields as well as the separation factors between the actinides and rare earths. Since the recovery yields and separation factors are easily obtained with a variation of the parameters, an optimum combination of system parameters can be elucidated by this approach once the requirements for the process or for the product are given. Consequently, this approach is expected to provide a great benefit to the design of actinides/rare earths separation processes by means of a countercurrent

multistage reductive extraction system.

NOMENCLATURE

- a, b : Constants in equation (2)
- C : Concentration of solute (mol)
- D : Distribution coefficient (metal phase/salt phase)
- f, g : Flow rate of salt and metal phase, respectively (ml/min)
- M : Metallic solute
- N : Number of stages of a cascade
- n : Stage number in a cascade
- X, Y : Concentration of solute in salt and metal phase, respectively (mol)
- X_{feed} : Concentration of solute in the salt phase fed into the 1st stage (mol)
- Y^* : Dimensionless concentration for Y defined by equation (18)

Geek Letters

- β : Function defined by equation (14)
- ξ : Recovery yield (%)
- i/j : Separation factor for component i against component j
- γ : Function defined by equation (15)

REFERENCES

- [1] M.Benedict, Thomas H.Pigford, Hans W. Levi, Nuclear Chemical Engineering, 2nd ed., p.176, McGraw-Hill Book Co.(1981).
- [2] M.Kurata, Y.Sakamura, T.Hijikata, K.Kinoshita, "Distribution behavior of uranium, neptunium, rare-earth elements and alkaline-earth metals between molten LiCl-KCl eutectic salt and liquid cadmium or bismuth", *J. Nuclear Materials*, **227**, 110 (1995).
- [3] K.Kinoshita, T.Inoue, S.P.Fusselman, D.L.Grimmett, J.J.Roy, R.L.Gay, C.L.Krueger, C.R.Nabelek and T.S.Storvick, "Separation of uranium and transuranic elements from rare-earth elements by means of multistage extraction in LiCl-KCl/Bi system", *J.Nuclear Sci. and Tech.*, **36**, 2, 189 (1999).
- [4] M.Sakata, M.Kurata, T.Hijikata, and T.Inoue, "Equilibrium distribution of rare earth elements between molten KCl-LiCl eutectic salt and liquid cadmium", *J.Nuclear Materials*, **185**, 56 (1991).
- [5] J.J.Roy, L.F.Grantham, D.I.Grimmett, S.P.Fusselman, C.L.Krueger and T.S.Storvick, T.Inoue, Y.Sakamura, N.Takahashi, "Thermodynamic properties of U, Np, Pu and Am in molten LiCl-KCl eutectic and liquid cadmium", *J.Electrochem. Soc.*, **143**, 8, 2487 (1996).
- [6] K.Uozumi, K.Kinoshita, T.Inoue, S.P.Fusselman, D.L.Grimmett, J.J.Roy, T.S.Storvick, C.L.Krueger, C.R.Nabelek, "Pyrometallurgical partitioning of uranium and transuranic elements from rare earth elements by electrorefining and reductive extraction", *J.Nuclear Sci. and Tech.*, **38**, 1, 36 (2001).
- [7] D.U.von Rosenberg, *Methods for the Numerical Solution of Partial Differential Equations*, p.113, American Elsevier Pub. Co. Inc., New York (1969).
- [8] J.T.Long, *Engineering for Nuclear Fuel Reprocessing*,

p.177, Gordon and Breach Science Publishers, New York (1967).

[9] C.Judson King, *Separation Processes*, pp.230, McGraw-Hill Book Co., New York (1980).