EFFECTS OF OPERATING CONDITIONS ON SEPARATION OF RARE EARTH ELEMENTS BY COUNTERCURRENT MULTISTAGE EXTRACTION

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1. Introduction

Rare earth elements (REEs) are a series of seventeen elements and widely applied to high technology products in many fields. Since REEs have similarities of chemical property, they are coexisting in the natural resources and it is difficult to separate and purify them. Therefore the improvement of separation technique of REEs is very important.

One of the commercialized techniques for separation of REEs is solvent extraction. Many researchers have been studied on separation of REEs by solvent extraction [1]. The objective metals are selectively extracted from the aqueous phase to the organic phase containing extractant, such as 2-ethylhexyl 2-ethylhexyl phosphate (PC-88A). This extraction is generally described as,

$$REE^{3+} + 3\overline{(RH)_2} \rightleftarrows \overline{REE\,R_3(RH)_3} + 3H^+ \qquad (1)$$

where the overbar refers to the organic phase [1]. When the atomic number of target metal is larger, this reaction is generally progress more.

The problem in this reaction is that due to exchange of target metal with the hydrogen in extractant, the concentration of hydrogen ion in aqueous phase increases and the back reaction progresses. In order to overcome this problem, another external cation, such as sodium is conventionally substituted for the hydrogen in extractant before extraction reaction. Therefore the investigation for the liquid-liquid equilibrium of external cation and target metal is important. In the previous study, the liquid-liquid equilibrium of neodymium and sodium in the binary elements system was experimentally investigated by solvent extraction [2].

For the commercial process, the countercurrent multistage extraction is utilized as the methods to separate REEs. Akira Hino *et al.* studied on the REEs separation extractant by countercurrent multistage extraction [3]. However there are a few calculation studies about the process with substituted extractant.

In this study, the REEs separation by countercurrent multistage extraction were calculated based on the mass balance of metal, equilibrium equations and electrical neutrality in aqueous phase. The extraction processes without substitution, with substitution by external sodium and substitution by raffinate product were compared in order to study the effects of substitution and operating conditions.

2. Process outline and calculation
2.1. Process outline

Figure 1 shows the process flow diagram of general countercurrent multistage extraction. It mainly consisted of extraction and scrubbing sections. The aqueous phase containing mixed REEs was supplied into extraction section and contacted countercurrently with the organic phase containing extractant. In this process, a heavier rare earth element (HRE), whose atomic number was larger, was selectively extracted into organic phase. It was extracted in the extraction section and concentrated in the scrubbing section. As a result, a lighter rare earth element (LRE) was concentrated in the aqueous phase and taken as product. In this study, the separation in the extraction section was studied. Figure 2 shows the extraction sections studied here in detail: without hydrogen ion substitution of extractant (A); with the substitution by external sodium ion (B); and with that by the LRE product (C). In the process (B), sodium hydroxide is used for substitution of extractant at stage 0 and the extractant is supplied into extraction stage. In the case of process (C), the product stream from stage 1 (P_1) was rich in LRE, and some part of this product (R_1) was used for substitution at stage 0. This was expected to have effects of reflux to concentrate LRE more.

2.2. Basic equations

Figure 3 shows a quite-general extraction stage k in the multistage extractor.
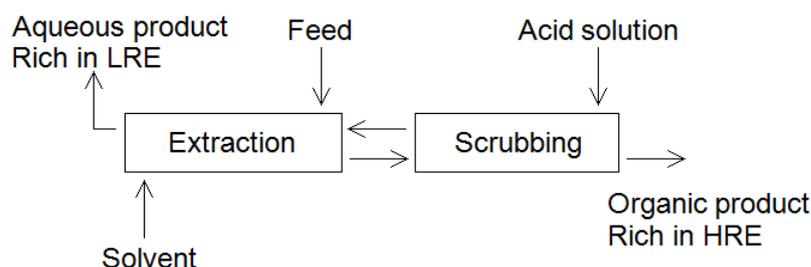
Fig. 1 Process flow diagram for countercurrent multistage extraction
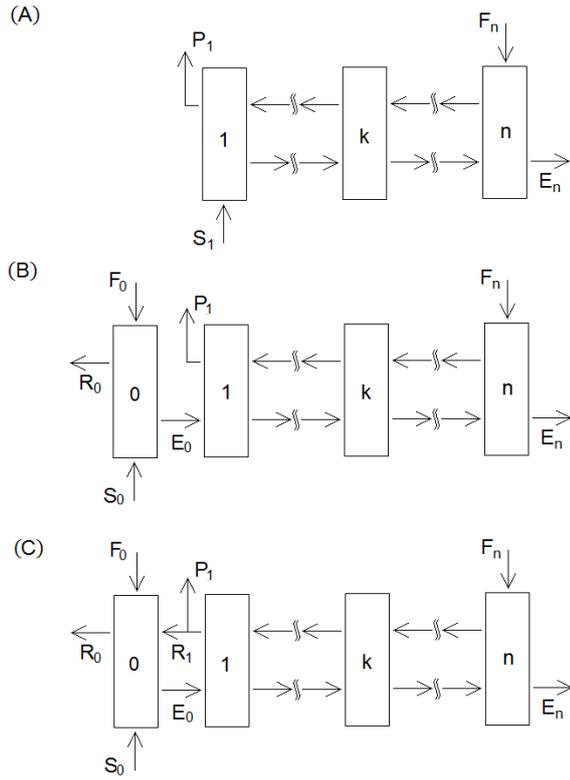
Fig. 2 (A) Counter current multistage extraction, (B) With sodium substitution, (C) With LRE substitution

For an extraction stage k, the material balances, the equilibrium relations, the constraints of extractant in organic phase and that of electrical neutrality in aqueous phase were established as,

$$F_k + R_{k+1} = R_k + P_k \qquad (2)$$

$$S_k + E_{k-1} = E_k + Q_k \qquad (3)$$

$$F_k C_{F,k,i} + R_{k+1} C_{R,k+1,i} + S_k C_{S,k,i} + E_{k-1} C_{E,k-1,i}$$
$$= R_k C_{R,k,i} + P_k C_{P,k,i} + E_k C_{E,k,i} + Q_k C_{Q,k,i} \qquad (4)$$

$$K_{REE} = (C_{E,k,REE} C_{R,k,H}^3)/(C_{R,k,REE}(C_{E,k,RH}/2)^3) \qquad (5)$$

$$K_{Na} = (C_{E,k,Na} C_{R,k,H})/(C_{R,k,Na} C_{E,k,RH}/2) \qquad (6)$$

$$C_{R,k,H} C_{R,k,OH} = 10^{-14} \qquad (7)$$

$$C_{E,k,Rtotal} = 6\sum C_{E,k,REE} + 2C_{E,k,Na} + C_{E,k,RH} \qquad (8)$$

$$3\sum C_{R,k,REE} + C_{R,k,Na} + C_{R,k,H} - C_{R,k,OH} - C_{R,k,Cl} = 0 \qquad (9)$$

The purities of LRE and HRE, yields of LRE and HRE, hydrogen ion substitution fraction, reflux ratio and the separation factor were defined as follows:

$$\rho_{LRE} = C_{P,1,LRE}/(C_{P,1,LRE} + C_{P,1,HRE}) \qquad (10)$$

$$\rho_{HRE} = C_{E,n,HRE}/(C_{E,n,LRE} + C_{E,n,HRE}) \qquad (11)$$

$$Y_{LRE} = P_1 C_{P,1,LRE}/F_n C_{F,n,LRE} \qquad (12)$$

$$Y_{HRE} = E_n C_{E,n,HRE}/F_n C_{F,n,HRE} \qquad (13)$$

$$\alpha = 1 - C_{E,0,RH}/C_{E,0,Rtotal} \qquad (14)$$

$$\gamma_R = R_1/P_1 \qquad (15)$$

$$\beta = K_{LRE}/K_{HRE} \qquad (16)$$

These basic equations were solved simultaneously using a program written in MATLAB.
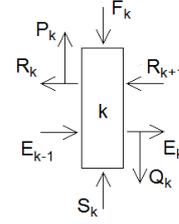
Fig. 3 A quite-general extraction stage k in the multistage extractor

2.3. Operating conditions and specification

Table 1 shows the operating conditions and specifications of product for process calculation. In this study the separation of binary REE was calculated. The feed containing binary REE was supplied into stage 1 to 4. The pH in the feed was varied from 0.5 to 3.0. In some cases, dysprosium and neodymium were selected as HRE and LRE respectively and sodium was selected as external metal. The equilibrium constant of dysprosium with PC-88A was cited from Yazaki et al. [4] and that of neodymium and sodium with PC-88A were cited in previous study [2]. The equilibrium constant of HRE was set to be constant and that of LRE was varied. The purity of LRE was set to 0.97 or 0.90 as specification of product.

Table 1 Operating conditions and specification

Feed	
Stage number, n	$1-4$
Flow rate, F_n [m³/h]	20
REEs conc., $C_{F,n,M}$ [kmol/m³]	0.07, 0.02
pH, pH$_n$	$0.5 - 3.0$
Stream for substitution	
Stage number	0
Flow rate, F_1 [m³/h]	$5 - 100$
Na conc., $C_{F,1,Na}$ [kmol/m³]	1.0
pH, pH$_1$	13
Solvent	
Stage number	0, 1
Flow rate, S [m³/h]	20 - 170
Extractant in solvent	PC-88A
Extractant conc., $C_{S,1,RH}$ [kmol/m³]	0.5
Product	
Purity of LRE, ρ_{LRE}[-]	0.97, 0.90
Equilibrium constant	
Dysprosium(Dy), K_{Dy} [-]	1.9
Neodymium(Nd), K_{Nd} [-]	1.36×10^{-2}
Sodium(Na), K_{Na} [-]	3.12×10^{-6}
HRE, K_{HRE} [-]	1.9
LRE, K_{LRE} [-]	$10^{-4} - 10^{-1}$

3. Result and Discussion
3.1. Effects of stages and substitution fraction

Figure 4 shows the effects of number of stage and substitution fraction on the flow ratio of solvent to feed
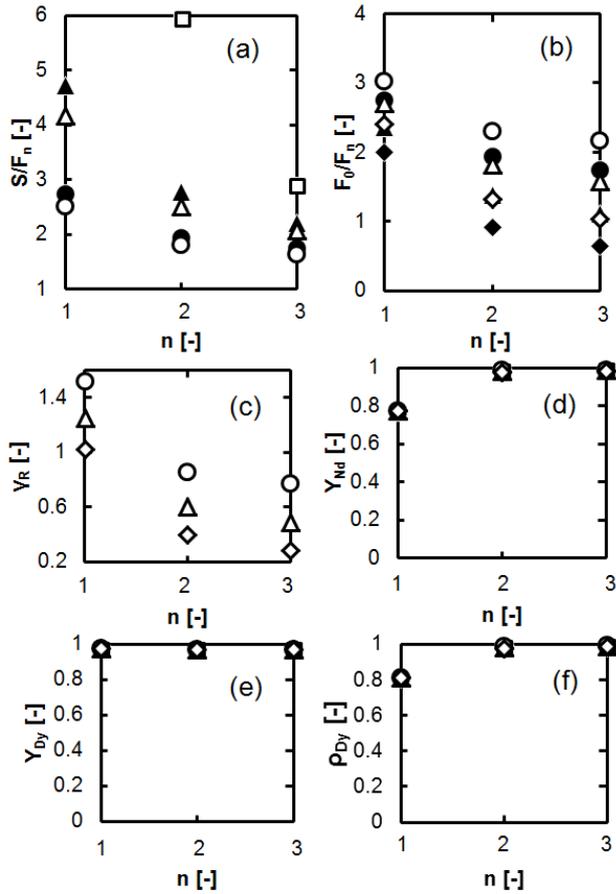
Fig. 4 Effects of number of stage and substitution fraction on (a) S/F_n, (b) F_0/F_n, (c)γ_R, (d) Y_{Nd}, (e) Y_{Dy} and (f) ρ_{Dy} of Nd/Dy separation

□: $\alpha=0$, ◆: $\alpha=0.1$ (B), ◇: $\alpha=0.1$ (C), ▲: $\alpha=0.2$ (B),
△: $\alpha=0.2$ (C), ●: $\alpha=0.4$ (B), ○: $\alpha=0.4$ (C),
$pH_n=1.0$, $C_{F,n,M}=0.07$, $\rho_{Nd}=0.97$

Fig. 5 Effects of feed pH on (a) S/F_n, (b) F_1/F_n and (c) γ_R of Nd/Dy separation

■: $pH_n=1.0$ (B), □: $pH_n=1.0$ (C), ◆: $pH_n=0.5$ (B),
◇: $pH_n=0.5$ (C), ▲: $pH_n=2.0$ (B), △: $pH_n=2.0$ (C),
●: $pH_n=3.0$ (B), ○: $pH_n=3.0$ (C),
$C_{F,n,M}=0.07$, $\rho_{Nd}=0.97$, $\alpha=0.2$

(S/F_n), flow ratio of stream for substitution to feed (F_0/F_n), γ_R, Y_{Nd}, Y_{Dy} and ρ_{Dy} of Nd/Dy separation. The S/F_n and F_0/F_n decreased as the number of stage increased, and Y_{Nd} attained more than 0.96 when $n = 2$ and 3. The S/F_n of (B) was smaller than that of (A) and the S/F_n of (C) was smaller than that of (B). There were no differences of Y_{Nd} and ρ_{Dy} among (A) to (C). In other words, (C) needed less amount of solvent in order to obtain same specification of product as (A) and (B). However F_0/F_n of (C) was larger than that of (B). This was because the concentration of hydrogen in aqueous phase, which flowed into stage 1 (R_1), was so high that a large amount of alkaline solution at stage 0 was needed.

From Fig. 4 (a), S/F_n decreased as substitution fraction increased. The reflux ratio increased with increasing substitution fraction. It is necessary to turn much product back to stage 0 in order to increase substitution fraction. Due to substitution of extractant, the hydrogen concentration at stage 1 was inhibited from increasing and therefore Dy was extracted more into organic phase at stage 1 compared with (A). On the other hand, the purities and yields of Nd and Dy were almost same values regardless of substitution fraction. There

was no possibility to form the precipitate of REEs in aqueous outflow from substitution stage because the pH in it was below 2.5.

3.2. Effects of feed pH and concentration

Figure 5 shows the effects of feed pH, pH_n, on S/F_n, F_1/F_n and γ_R of Nd/Dy separation. From Fig. 5 (a) and (c), S/F_n and γ_R deceased as pH_n increased. In the case of $pH_n = 2.0$, the hydrogen concentration in the aqueous stream from stage 1 was lower than that in the case of $pH_n = 0.5$. In other words, when $pH_n = 2.0$, more Dy was concentrated and less amount of stream for substitution was required compared with $pH_n = 0.5$. From Fig. 5 (b), the larger pH_n was, the smaller the difference of F_1/F_n between (B) and (C) was. And there were no difference of the purity and yield of Nd and Dy by changing pH_n.

Figure 6 shows effects of feed concentration and LRE purity on S/F_n and γ_R of Nd/Dy separation. From Fig.6 (a), S/F_n and F_1/F_n in the case of $C_{F,n,M} = 0.02$ was smaller than that in the case of $C_{F,n,M} = 0.07$. The reflux ratio was smaller than that of $C_{F,n,M} = 0.07$.

3.3. Effects of LRE purity

From Fig.6, when the purity of Nd was set to 0.90 the less amount of solvent and stream for substitution were needed compared with 0.97 of Nd purity. When $n = 1$, the difference of S/F_n of $\rho_{Nd} = 0.90$ was smaller than that of $\rho_{Nd} = 0.97$. In other words, (C) is more effective than (B) when the specification of product is better.
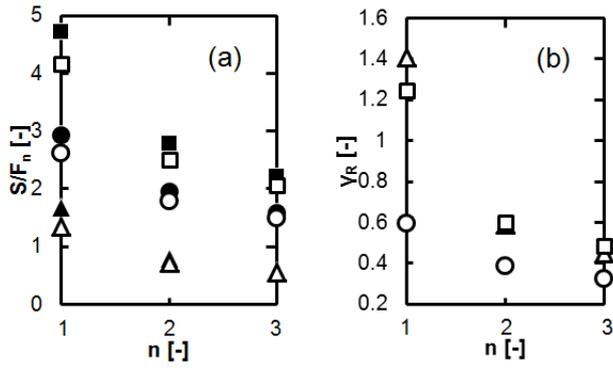
Fig. 6 The effect of feed concentration and LRE purity on (a) S/F_n and (b) γ_R of Nd/Dy separation

■:$C_{F,n,M}$=0.07 ρ_{Nd}=0.97 (B),□:$C_{F,n,M}$=0.07 ρ_{Nd}=0.97 (C),
▲:$C_{F,n,M}$=0.02 ρ_{Nd}=0.97 (B),△:$C_{F,n,M}$=0.02 ρ_{Nd}=0.97 (C),
●:$C_{F,n,M}$=0.07 ρ_{Nd}=0.90 (B),○:$C_{F,n,M}$=0.07 ρ_{Nd}=0.90 (C),
pH_n=1.0, α=0.2

3.4. Effects of feed rare earth elements

Figure 7 shows the effects of feed REEs on the solvent ratio of process (C) to (B), the ratio of stream for substitution of process (C) to (B), Y_{LRE} and ρ_{HRE}. In the range of $10^{-4.0} < \beta < 10^{-2.5}$, the solvent ratio of process (C) to (B) was almost constant at any number of stage. In the rage of $K_{L/H} > 10^{-2.5}$, it decreased with approaching $\beta = 0$. In other words, the (C) is much more effective than (B) when the separation of HRE and LRE becomes more difficult. On the other hand, the ratio of stream for substitution of process (C) to (B) was over 1.0 and deceased with approaching $\beta = 0$. From Fig. 7 (c) and (d), although there were no differences of the purity of HRE and the yield of LRE between (B) and (C), they
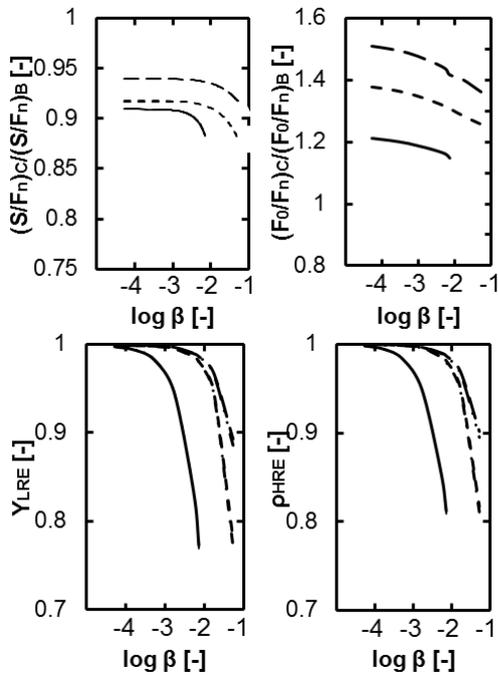
decreased with approaching $\beta = 0$. When the number of stage is 2, the purity of HRE was around 0.7 and the yield of LRE was around 0.5. This can be improved by combining the scrubbing section with the extraction section calculated in this study.

4. Conclusion

The countercurrent multistage extraction with substitution by the LRE product was the effective process for separation of REEs. S/F_n decreased in the process although F_0/F_n in the countercurrent multistage extraction with substitution by sodium was smaller. Furthermore the larger the number of stages was, the less amounts of solvent and stream for substitution required. And due to substitution of extractant, the hydrogen concentration in aqueous phase was inhibited from increasing. In the case of separation of Nd and Dy, yield of Nd attained more than 0.96 regardless of operating conditions when $n = 3$ and 4. With increasing the difficulties of separation, the difference of S/F_n between two processes became larger and the countercurrent multistage extraction with substitution by the LRE product is much more effective for separation. However the yield of LRE decreased to around 0.5 when $n = 2$ and $\beta = 0.1$. This can be improved by combining the scrubbing section with the process.

Nomenclature and Subscript

F	[m³/h]	; Flow rate of feed
S	[m³/h]	; Flow rate of solvent
R	[m³/h]	; Flow rate of aqueous phase
E	[m³/h]	; Flow rate of organic phase
P	[m³/h]	; Flow rate of product
Q	[m³/h]	; Flow rate of product
C	[kmol/m³]	; Concentration
K	[-]	; Equilibrium constant
γ_R	[-]	; Reflux ratio
ρ	[-]	; Purity
Y	[-]	; Yield
α	[-]	; Substitution fraction
n		; Number of stage
i		; Metal (REEs, Na)
RH		; Monomer free extractant
Rtotal		; Total extractant
H		; Hydrogen
OH		; Hydroxide
Cl		; Chloride

References

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Fig. 7 The effect of feed REE on (a) $S_{C/B}$ (b) $F_{0C/B}$ (c) Y_{LRE}, (d) ρ_{HRE}
－: n=1, ⋯: n=2, --: n=3
pH_n=1.0, $C_{F,n,M}$=0.07, ρ_{Nd}=0.97, α=0.2