

EFFECTS OF PROCESS CONDITIONS ON RARE EARTH ELEMENT SEPARATION BY COUNTERCURRENT MULTISTAGE EXTRACTION

Student Number: 19M51697 Name: Junki KURIHARA Supervisor: Ryuichi EGASHIRA, Hiroaki HABAKI

1. Introduction

Rare earth elements (REEs) have been widely used for various high technology products, such as neodymium magnets and secondary batteries, and the techniques for the selective recovery of REEs from the resources are important.

Solvent extraction is known as a commercial method which is effective to separate the metal elements contained in acidic leaching solution, using the difference in selectivity to the extracting agents (extractants) between elements. In the solvent extraction for separation and purification of REEs, organophosphorus acids such as D2EHPA and PC-88A are mainly selected as extractants and diluted with organic solvent which is not mixed with aqueous phase^[1]. REEs which have close atomic numbers are difficult to separate due to the similarity in chemical properties, and separation process of solvent extraction requires a number of stages to obtain individual REE products with high quality.

Countercurrent multistage extraction is one of the solvent extraction process with a series of stages, where organic and aqueous phases flow in opposite directions. The qualities of products depend on the process configurations and their operating conditions, therefore, for the effective separation, it is important to set the conditions appropriately to the configurations. However, there are few calculation studies of the process configurations and their operating conditions.

In this study, several process configurations of countercurrent multistage extraction for separation of dysprosium (Dy) and terbium (Tb), as the examples of REEs, were considered and they were simulated by calculation, and the effects of process conditions on the yield and purity of products and the process profile were investigated.

2. Process Configurations

Process configurations of this study are shown in Figure 1. Process (1) is the simple process with only the extraction section, Process (2) is the process with the substitution and extraction sections, Process (3) is the process with extraction and scrubbing sections, and Process (4) is the process with substitution, extraction and scrubbing sections.

Processes (2) and (4) have the substitution section, where the hydrogen ions in extractant are substituted for other metal ions such as sodium (Na) before the solvent is supplied to the extraction section, in order to prevent the release of hydrogen ions from extractant to aqueous phase, which will promote the back reaction of extraction.

Process (3) and (4) have the scrubbing section, where lighter rare earth elements (LREEs) contained in organic

phase are recovered by the aqueous solution with lower pH supplied into scrubbing section^[2]. The feed is supplied to the extraction section and the organic phase containing REEs goes to the scrubbing section.

LREE product was assumed to be obtained in aqueous phase from extraction section outlet in every process, and heavier rare earth element (HREE) product was assumed to be obtained in organic phase from extraction section outlet in Processes (1) and (2), and from scrubbing section outlet in Processes (3) and (4).

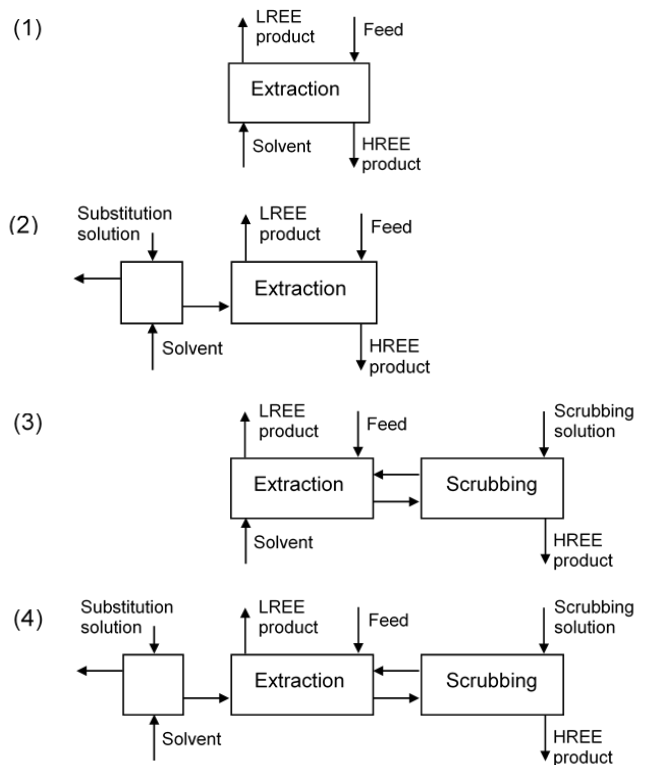
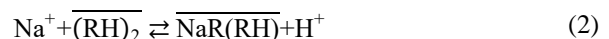
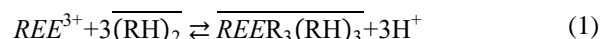


Figure 1 Configurations of Processes (1) to (4)

3. Equations and Calculation

3.1. Equations

Extraction reactions of REEs and sodium with dimeric extractant are generally expressed as Equation 1 and 2.



A stage and its related streams in the process were generalized and shown as Figure 2. F_k and S_k are the flow rates of aqueous and organic phases supplied to stage k from external system, R_k and E_k are the flow rates of aqueous and organic phases from stage k to the next stage, and P_k and Q_k are the flow rates of aqueous and organic phases from stage k to external system, respectively.

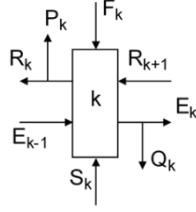


Figure 2 A generalized stage and related streams

Flow rate balances (Eq. 3,4), material balances (Eq. 5~7), equalities of concentrations in the sidecut (Eq. 8,9) equilibrium relations (Eq. 10,11), ion product of water (Eq. 12) and electrical neutrality in aqueous phase (Eq. 13) were considered in the process calculation based on Equations 1, 2, and Figure 2, under the following assumptions: stages in the process are equilibrium stages, volumes of aqueous and organic phases do not change before and after equilibrium, extractant in organic phase does not move to aqueous phase, REE ions are prepared from chloride salts and pH are adjusted by HCl and NaOH, These equations were solved by the program written in VBA.

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

$$F_k + R_{k+1} = P_k + R_k \quad (4)$$

$$S_k C_{S,k,i} + E_{k-1} C_{E,k-1,i} + F_k C_{F,k,i} + R_{k+1} C_{R,k+1,i} = Q_k C_{Q,k,i} + E_k C_{E,k,i} + P_k C_{P,k,i} + R_k C_{R,k,i} \quad (5)$$

$(i = Dy, Tb, Na)$

$$S_k (C_{S,k,RH2} + 3 \sum C_{S,k,REE} + C_{S,k,Na}) + E_{k-1} (C_{E,k-1,RH2} + 3 \sum C_{E,k-1,REE} + C_{E,k-1,Na}) = Q_k (C_{Q,k,RH2} + 3 \sum C_{Q,k,REE} + C_{Q,k,Na}) + E_k (C_{E,k,RH2} + 3 \sum C_{E,k,REE} + C_{E,k,Na}) = S_1 C_{S,1,RH2,total} \quad (6)$$

$$F_k C_{F,k,Cl} + R_{k+1} C_{R,k+1,Cl} = P_k C_{P,k,Cl} + R_k C_{R,k,Cl} \quad (7)$$

$$C_{Q,k,i} = C_{E,k,i} \quad (i = Dy, Tb, Na, RH2) \quad (8)$$

$$C_{P,k,i} = C_{R,k,i} \quad (i = Dy, Tb, Na, Cl, H, OH) \quad (9)$$

$$(C_{E,k,i} C_{R,k,H}) / (C_{R,k,i} C_{E,k,RH2}) = K_i \quad (i = Dy, Tb) \quad (10)$$

$$(C_{E,k,Na} C_{R,k,H}) / (C_{R,k,Na} C_{E,k,RH2}) = K_{Na} \quad (11)$$

$$C_{s,k,H} C_{s,k,OH} = K_w \quad (s = F, R) \quad (12)$$

$$C_{s,k,H} + 3 \sum C_{s,k,REE} + C_{s,k,Na} - C_{s,k,OH} - C_{s,k,Cl} = 0 \quad (s = F, R) \quad (13)$$

Substitution ratio (Eq. 14), the yield of dysprosium (Eq. 15), molar fraction of dysprosium in organic phase in stage k (Eq. 16), and the purity of dysprosium (Eq. 17) were defined as follows:

$$\alpha = C_{S,1,Na} / C_{S,1,RH2,total} \quad (14)$$

$$Y_{Dy} = Q_N C_{Q,N,Dy} / F_{Nf} C_{F,Nf,Dy} \quad (15)$$

$$y_{k,Dy} = C_{E,k,Dy} / (C_{E,k,Dy} + C_{E,k,Tb}) \quad (16)$$

$$y_{N,Dy} = C_{Q,N,Dy} / (C_{Q,N,Dy} + C_{Q,N,Tb}) \quad (17)$$

3.2. Calculation

Table 1 shows the conditions for this calculation. PC-88A in kerosene was selected as extractant. The equilibrium constants of dysprosium and terbium with PC-88A were cited from previous research^[3], and that of sodium was cited from Mori^[4]. Stages in the substitution section was omitted and hydrogen ions of extractant were assumed to be substituted for sodium as appropriate in advance.

Concentration of extractant, concentration of REEs and every equilibrium constant were constant and the effects of hydrogen ion concentration, substitution ratio, the number of stages and the feed entry stage were investigated based on these conditions.

Table 1 Conditions for calculation

Table 1 Conditions for calculation	
The number of stages, N [-]	10
Feed entry stage number, N_f [-]	7
Feed	
Flow rate, F_{Nf} [$m^3 h^{-1}$]	1
REE	Dy, Tb
REE conc., $C_{F,Nf,REE}$ [$kmol m^{-3}$]	0.07
H+ conc., $C_{F,Nf,H}$ [$kmol m^{-3}$]	0.05
Solvent	
Flow rate, S_1 [$m^3 h^{-1}$]	10
Extractant,	PC-88A
Extractant conc., $C_{S,1,RH2,total}$ [$kmol m^{-3}$]	0.25
Substitution ratio, α [-]	0.5
Scrubbing solution	
Flow rate, F_N [$m^3 h^{-1}$]	1
H+ conc., $C_{F,N,H}$ [$kmol m^{-3}$]	1.35
Equilibrium constant	
Dysprosium, K_{Dy} [-]	3.0
Terbium, K_{Tb} [-]	1.3
Sodium, K_{Na} [-]	3.1×10^{-6}
Ion product of water, K_w [$kmol^2 m^{-6}$]	1.0×10^{-14}

4. Result and discussion

4.1. Process comparison

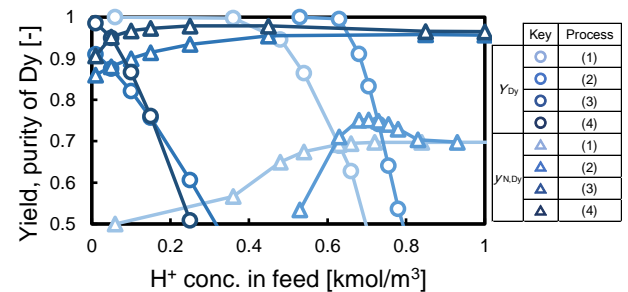


Figure 3 Effect of feed hydrogen ion concentration in Processes (1) to (4)

- (1) $N_f = 10, F_{Nf} = 2, \alpha = 0$
- (2) $N_f = 10, F_{Nf} = 2, \alpha = 0.5$
- (3) $N_f = 7, C_{F,N,H} = 1.0, F_{Nf} = 1, \alpha = 0$
- (4) $N_f = 7, C_{F,N,H} = 1.35, F_{Nf} = 1, \alpha = 0.5$

Figure 3 shows the effect of feed hydrogen ion concentration on Processes (1) to (4). In every process, the yield of dysprosium decreased and the purity increased according to the increase of feed hydrogen ion concentration. In Processes (1) and (2), which didn't have scrubbing section, the highest purities of dysprosium were about 0.7 and 0.75, respectively, and it is considered that the scrubbing section is necessary for the purification of the product in organic phase.

The representative results for Processes (1) to (4), where the hydrogen ion concentration in feed were 0.63, 0.73, 0.05 and 0.05, respectively, were compared. Figure 4 shows the profile of REE concentration and molar fraction of dysprosium in organic phase of the 4 processes.

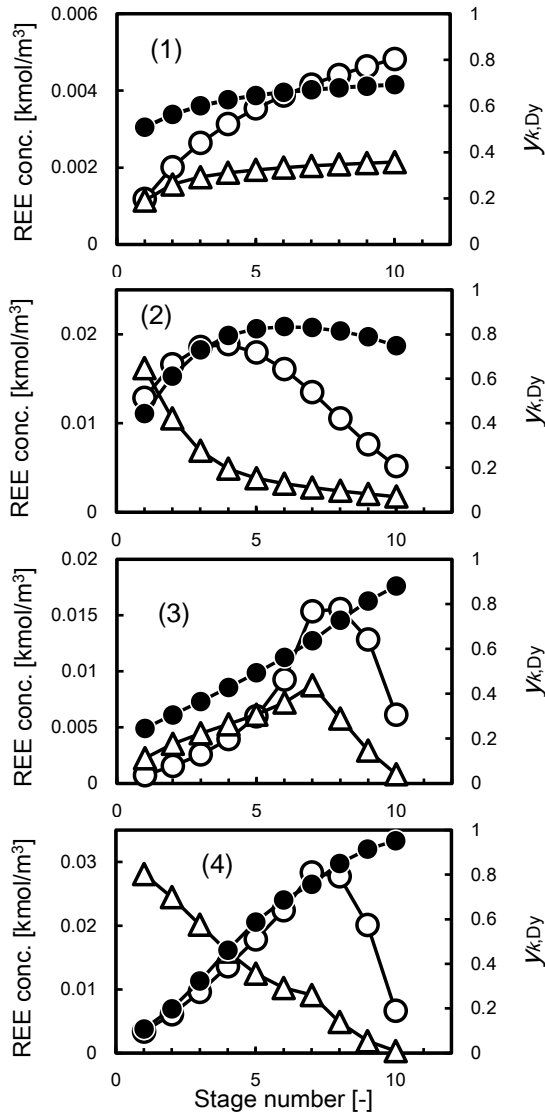


Figure 4 REE concentration and dysprosium molar fraction in organic phase in Processes (1) to (4)

- : Dy conc. △: Tb conc. ●: $y_{k,Dy}$
- (1) $N_f = 10$, $C_{F,Nf,H} = 0.63$, $F_{Nf} = 2$, $\alpha = 0$
 - (2) $N_f = 10$, $C_{F,Nf,H} = 0.73$, $F_{Nf} = 2$, $\alpha = 0.5$
 - (3) $N_f = 7$, $C_{F,Nf,H} = 0.05$, $C_{F,N,H} = 1.0$, $F_{Nf} = 1$, $\alpha = 0$
 - (4) $N_f = 7$, $C_{F,Nf,H} = 0.05$, $C_{F,N,H} = 1.35$, $F_{Nf} = 1$, $\alpha = 0.5$

In Process (1), obtained yield and purity of dysprosium were about 0.69. REE concentration in organic phase was increased in the higher stage, but the molar fraction of dysprosium was gradually saturated from around stage 5.

In Process (2), obtained yield and purity of dysprosium were about 0.74 and 0.75 respectively and the separation was improved from the simple extraction process. Concentration of terbium was decreased in the higher stage, and the concentration of dysprosium was highest at stage 4. Molar fraction of dysprosium reached 0.83 at stage 6, but slightly decreased towards stage 10.

In Process (3), obtained yield and purity of dysprosium were about 0.88. The separation was improved from the case of the simple extraction process and was greater than in the processes with substitution. Concentrations of dysprosium and terbium were highest at the stage 7 and 8 respectively, and the molar fraction of dysprosium increased in higher stage.

In process (4), obtained yield and purity of dysprosium were about 0.95, which was highest of the 4 processes. Concentration of terbium decreased in higher stage and that of dysprosium was highest at stage 7. The molar fraction of dysprosium increased in higher stage.

Figure 5 shows the profile of hydrogen ion concentration in aqueous phase. Separation was performed within the range of hydrogen ion concentration of 0.1 to 1 in every process. While the hydrogen ion concentration decreased from stage 1 to stage 7 in Processes (1) and (3), the hydrogen ion concentration in stage 1 was lowest in Processes (2) and (4), where the substituted extractant was used and it is considered that the ion exchange of the sodium ions of substituted extractant and hydrogen ions in stage 1 decreased the hydrogen ion concentration in every stage and promoted the extraction of REEs.

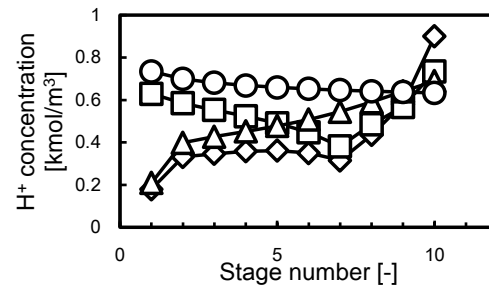


Figure 5 Hydrogen ion concentration in aqueous phase in Processes (1) to (4)

- : (1) $N_f = 10$, $C_{F,Nf,H} = 0.63$, $F_{Nf} = 2$, $\alpha = 0$
 △: (2) $N_f = 10$, $C_{F,Nf,H} = 0.73$, $F_{Nf} = 2$, $\alpha = 0.5$
 □: (3) $N_f = 7$, $C_{F,Nf,H} = 0.05$, $C_{F,N,H} = 1.0$, $F_{Nf} = 1$, $\alpha = 0$
 ◇: (4) $N_f = 7$, $C_{F,Nf,H} = 0.05$, $C_{F,N,H} = 1.35$, $F_{Nf} = 1$, $\alpha = 0.5$

4.2. Effect of hydrogen ion concentration

Figure 6 shows the effect of hydrogen ion of feed and scrubbing solution. Hydrogen ion concentration of scrubbing solution suitable for separation was decreased according to the increase of feed hydrogen ion

concentration. When the hydrogen ion concentration of feed was 0.05, yield and purity of dysprosium were 0.95 with the hydrogen ion concentration in scrubbing solution of 1.35. But when the hydrogen ion concentration of feed was 1.2, yield and purity were about 0.75 with the hydrogen concentration of scrubbing solution of 0.28. It can be considered that the scrubbing section didn't work effectively because the hydrogen ion concentration of feed was higher than that of scrubbing solution.

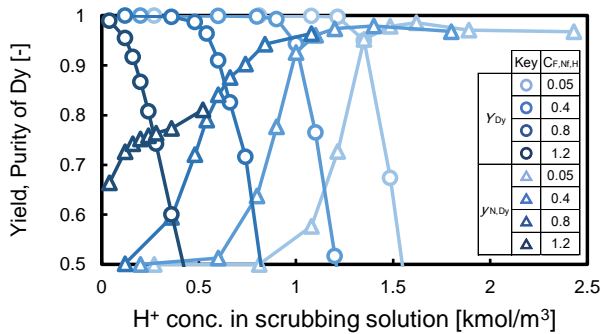


Figure 6 Effect of hydrogen ion concentration of feed and scrubbing solution

4.3. Effect of substitution

Figure 7 shows the effect of substitution ratio on S_1/F_{Nf} and yield and purity of dysprosium. According to the increase of substitution ratio, S_1/F_{Nf} required for the separation was decreased, and compared at the points where the yield and purity have close values, yield and purity were increased.

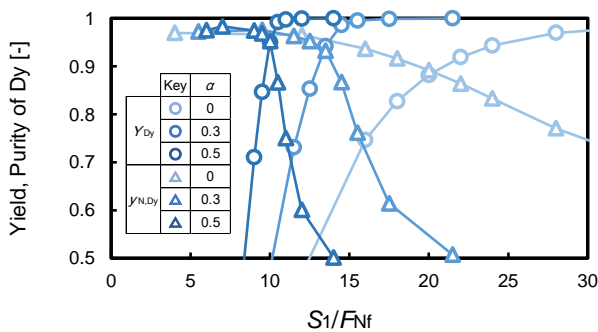


Figure 7 Effect of substitution ratio on the relation of S_1/F_{Nf} and yield and purity of dysprosium

4.4. Effect of the number of stages and feed entry stage

Figure 8 shows the effect of the number of stage on the relation of S_1/F_{Nf} and yield and purity of dysprosium. As the number of stage increased, yield and purity were both increased in the wide range of S_1/F_{Nf} . No significant change was found in the range of S_1/F_{Nf} suitable for separation and it is suggested that the increase of the total stage number can increase both yield and purity without changing other operating conditions.

Figure 9 shows the effect of feed entry stage on the relation of S_1/F_{Nf} and yield and purity of dysprosium. Feed entry stage was changed from 1 to 9. When the feed entry stage was 1 to 5, purity of dysprosium was not

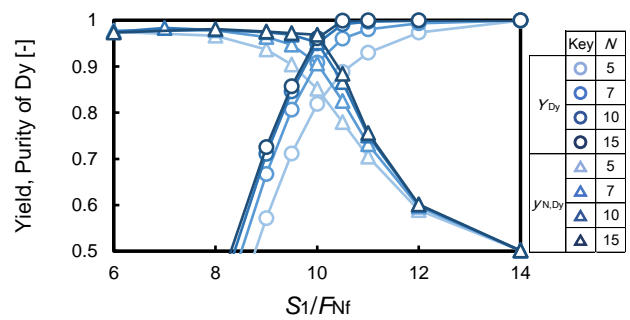


Figure 8 Effect of the number of stages on the relation of S_1/F_{Nf} and yield and purity of dysprosium

changed significantly in the wide range of S_1/F_{Nf} . On the other hand, the yield of dysprosium was increased with the higher entry stage. When the feed entry stage was 5 to 9, while there was no significant effects on the yield, the purity was decreased in the range of $S_1/F_{Nf} < 11$, with the higher entry stage. For this condition, better separation can be obtained by setting the feed entry stage to 5, and it is suggested that the entry stage suitable for separation can be decided by the molar fraction of target elements in the feed.

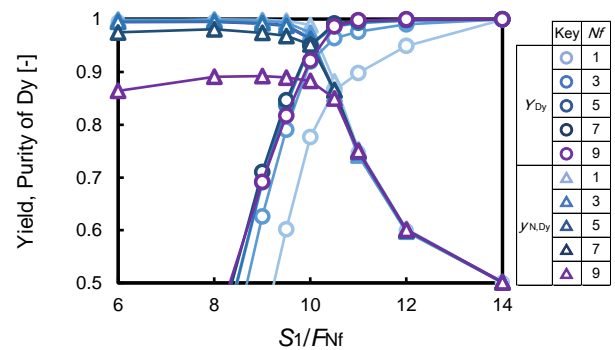


Figure 9 Effect of feed entry stage on the relation of F_N/F_{Nf} and yield and purity of dysprosium

5. Conclusion

In this study, the effects of process conditions were investigated and clarified. Introducing the scrubbing section could improve the separation of REEs. Substitution of hydrogen ion in extractant could improve the separation and decrease the required solvent flow rate. Increase of the number of stages could improve the separation and there was no significant change in the range of S_1/F_{Nf} suitable for separation.

References

- [1] F. Xie *et al.*, Minerals Engineering, 56 (2014) 10–28
- [2] 芝田隼次, 表面技術, 53 (2002) 641-646
- [3] 栗原淳希, 東京工業大学平成 30 年度卒業論文
- [4] 森信義, 東京工業大学平成 27 年度卒業論文