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공학석사학위논문

**Selective Stripping of
Light Rare Earth Elements using
Acidic Organophosphorus Reagents**

산성 유기인계 시약을 이용한

경희토류의 선택적 탈거

2016 년 8 월

서울대학교 공과대학원

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Abstract

Selective Stripping of Light Rare Earth Elements using Acidic Organophosphorus Reagents

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Light rare earth elements (LREEs) are essential resources widely used in modern industries. Due to their similar chemical and physical properties, a design of the streamlined separation process is important for operational efficiency and cost-effectiveness. Although solvent extraction is the most common separation method for LREEs, many stages and a high concentration of acid are needed. Therefore, in this study, a novel separation process for LREEs is developed using selective stripping.

Prior to applying selective stripping to the four-LREE- component system, the optimization for stripping was carried out in the two-adjacent-LREE system. The effects of extractant type and concentration, REE concentration ratio in the feed solution, organic-phase-to-aqueous-phase (OA) volumetric ratio and the concentration of acid on the stripping behavior of two LREEs were investigated, and the optimum conditions of these factors were determined in the two-LREE-component system. 0.5M PC88A was selected as a suitable extractant, and three stages of stripping at an OA ratio of 7:4 with 0.10M HCl was needed for the selective stripping of La and Ce. In the Ce and Pr system, it was found that selective stripping could be achieved in six stages of stripping at an OA ratio of

5:3 with 0.14M HCl, while seven stages of stripping at an OA ratio of 3:2 with 0.15M HCl was required for the separation of Pr and Nd.

Furthermore, the slope analysis method was adopted to determine the LREE-extractant complex structure and stoichiometry of stripping reaction. The results show that LREEs make a complex with PC88A extractant including chloride ion, and more chloride ions tend to be included in the lighter LREE-extractant complex in the organic phase.

Optimization experiments with the same factors were carried out in the four-LREE-component system and compared with the results in the two-component system. In addition, a McCabe-Thiele diagram was drawn for the determination of the number of stages and OA ratio.

Based on the optimization results and McCabe-Thiele diagram, a semi-continuous counter-current process using selective stripping was introduced in the four-LREE system. The process consists of three steps: four extraction stages to separate La in the aqueous phase, three stages of the first stripping to strip the extracted La to the aqueous phase, and seven stages of the second stripping to strip Ce and Pr to the aqueous phase while Nd remains in the organic phase. After this process, a 89.8% purity of La was obtained in the aqueous phase and a 90.3% purity of Nd could be achieved in the organic phase.

In this research, the optimization of stripping conditions in the LREE system was studied and a novel semi-continuous counter-current process using selective stripping was designed. The experimental results suggest that LREEs can be selectively separated in the stripping step, as well as in the extraction step. Because this is the first study about the selective stripping of four LREEs, it has a significance in verifying the possibility of selective stripping of LREEs and designing the new process using selective stripping.

Keywords: stripping, LREE, solvent extraction, counter-current process, stripping optimization

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Chapter 1. Introduction

1.1 Research background

Rare earth elements (REEs) consist of 17 elements in the periodic table, including scandium (atomic number $Z=21$), yttrium ($Z=39$), and lanthanides ($Z=57$ to 71), as shown in Figure 1. They are generally classified into two groups: the light REE (LREE) group, also called the cerium group, including lanthanum to europium ($Z=57$ to 63), and the heavy REE (HREE) including gadolinium to lutetium ($Z=64$ to 71). REEs can also be categorized into three groups: LREEs including lanthanum to neodymium ($Z=57$ to 60), medium REEs (MREEs) including samarium to gadolinium ($Z=62$ to 64), and HREEs including terbium to lutetium and yttrium ($Z=65$ to 71, 39). Yttrium is classified into the HREE group because it has similar physical and chemical properties to HREEs and co-exists with them in minerals, and scandium does not belong to any groups due to its unique properties (Gosen et al., 2014). In this study, the term LREE indicates four elements from La to Nd, as categorized in the second criterion.

Although it is not easy to categorize REEs into constant groups due to the various standards of different authors, a logical explanation about the grouping of REEs is based on the difference of electronic configuration between two groups (Zepf, 2013). Table 1 shows the electronic configuration and valance state of the REEs. When elements have electronic configurations of f^0 , f^7 or f^{14} , they tend to remain stable in nature. The LREE group elements have zero to six unpaired electrons in the $4f$ shell. Since exactly half of the f -instances of gadolinium are occupied, this element behaves as the boundary of LREEs and HREEs (Röhr, 2016).

IUPAC Periodic Table of the Elements

Key																																																																									
atomic number		Symbol		name		element atomic weight																																																																			
1	H	hydrogen	[1.007 94]	2	He	helium	[4.002 602]	3	Li	lithium	[6.941 69]	4	Be	beryllium	[9.012 182]	5	B	boron	[10.811 70]	6	C	carbon	[12.010 74]	7	N	nitrogen	[14.006 44]	8	O	oxygen	[15.999 4]	9	F	fluorine	[18.998 403]	10	Ne	neon	[20.179 7]																																		
11	Na	sodium	[22.989 769 28]	12	Mg	magnesium	[24.304 08]	13	Al	aluminum	[26.981 538 6]	14	Si	silicon	[28.085 528 6]	15	P	phosphorus	[30.973 762 2]	16	S	sulfur	[32.06 5]	17	Cl	chlorine	[35.45 3]	18	Ar	argon	[39.948 41]																																										
19	K	potassium	[39.098 31]	20	Ca	calcium	[40.078 4]	21	Sc	scandium	[44.955 912 3]	22	Ti	titanium	[47.88 7]	23	V	vanadium	[50.941 5]	24	Cr	chromium	[51.996 1]	25	Mn	manganese	[54.938 044]	26	Fe	iron	[55.845 2]	27	Co	cobalt	[58.933 154]	28	Ni	nickel	[58.69 34]	29	Cu	copper	[63.546 8]	30	Zn	zinc	[65.38 2]	31	Ga	gallium	[69.723 17]	32	Ge	germanium	[72.63 0]	33	As	arsenic	[74.921 6]	34	Se	selenium	[78.971 8]	35	Br	bromine	[79.904 7]	36	Kr	krypton	[83.80 1]		
37	Rb	rubidium	[85.467 8]	38	Sr	strontium	[87.62]	39	Y	yttrium	[88.905 84]	40	Zr	zirconium	[91.224]	41	Nb	niobium	[92.906 38]	42	Mo	molybdenum	[95.94]	43	Tc	technetium	[98]	44	Ru	ruthenium	[101.07]	45	Rh	rhodium	[102.905 5]	46	Pd	palladium	[106.42]	47	Ag	silver	[107.868 2]	48	Cd	cadmium	[112.411]	49	In	indium	[114.818]	50	Sn	tin	[118.710]	51	Sb	antimony	[121.757]	52	Te	tellurium	[127.6]	53	I	iodine	[126.905 4]	54	Xe	xenon	[131.29]		
55	Cs	caesium	[132.905 4]	56	Ba	barium	[137.327]	57-71	lanthanoids					72	Hf	hafnium	[178.49]	73	Ta	tantalum	[180.948]	74	W	tungsten	[183.84]	75	Re	rhenium	[186.207]	76	Os	osmium	[190.23]	77	Ir	iridium	[192.222]	78	Pt	platinum	[195.084]	79	Au	gold	[196.967]	80	Hg	mercury	[200.59]	81	Tl	thallium	[204.38]	82	Pb	lead	[207.2]	83	Bi	bismuth	[208.98]	84	Po	polonium	[209]	85	At	astatine	[210]	86	Rn	radon	[222]
87	Fr	francium	[223]	88	Ra	radium	[226]	89-103	actinoids					104	Rf	rutherfordium	[261]	105	Db	dubnium	[262]	106	Sg	seaborgium	[263]	107	Bh	bohrium	[264]	108	Hs	hassium	[265]	109	Mt	meitnerium	[266]	110	Ds	darmstadtium	[267]	111	Rg	roentgenium	[268]	112	Cn	copernicium	[269]	113	Uut	ununtrium	[270]	114	Fl	flerovium	[271]	115	Uup	ununpentium	[272]	116	Lv	livermorium	[273]	117	Uus	ununseptium	[274]	118	Uuo	ununoctium	[276]
57	La	lanthanum	[138.905 47]	58	Ce	cerium	[140.12]	59	Pr	praseodymium	[140.907 6]	60	Nd	neodymium	[144.242]	61	Pm	promethium	[145]	62	Sm	samarium	[150.4]	63	Eu	europtium	[151.964]	64	Gd	gadolinium	[157.25]	65	Tb	terbium	[158.925 3]	66	Dy	dysprosium	[162.5]	67	Ho	holmium	[164.930 3]	68	Er	erbium	[167.259]	69	Tm	thulium	[168.934]	70	Yb	ytterbium	[173.054]	71	Lu	lutetium	[174.967]														
89	Ac	actinium	[227]	90	Th	thorium	[232.037 7]	91	Pa	protactinium	[231.036 888]	92	U	uranium	[238.028 91]	93	Np	neptunium	[237]	94	Pu	plutonium	[244]	95	Am	americium	[243]	96	Cm	curium	[247]	97	Bk	berkelium	[247]	98	Cf	californium	[251]	99	Es	einsteinium	[252]	100	Fm	fermium	[257]	101	Md	meitnerium	[258]	102	No	nobelium	[259]	103	Lr	lawrencium	[260]														

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Figure 1. Periodic table

Table 1. The electronic configuration and valance state of the REEs(Zhang et al., 2016)

	Atomic number	Atomic electronic configuration					REE ³⁺ electronic configuration	Valance state	
		<i>K, L, M, N</i>		<i>O</i>					<i>P</i>
		Inner	<i>4f</i>	<i>5s</i>	<i>5p</i>	<i>5d</i>			<i>6s</i>
La	57	Full 46	0	2	6	1	2	[Xe]4f ⁰	+3
Ce	58		1	2	6	1	2	[Xe]4f ¹	+3, +4
Pr	59		3	2	6		2	[Xe]4f ²	+3, +4
Nd	60		4	2	6		2	[Xe]4f ³	+3
Pm	61		5	2	6		2	[Xe]4f ⁴	+3
Sm	62		6	2	6		2	[Xe]4f ⁵	+2, +3
Eu	63		7	2	6		2	[Xe]4f ⁶	+2, +3
Gd	64		7	2	6	1	2	[Xe]4f ⁷	+3
Tb	65		9	2	6		2	[Xe]4f ⁸	+3, +4
Dy	66		10	2	6		2	[Xe]4f ⁹	+3
Ho	67		11	2	6		2	[Xe]4f ¹⁰	+3
Er	68		12	2	6		2	[Xe]4f ¹¹	+3
Tm	69		13	2	6		2	[Xe]4f ¹²	+3
Yb	70		14	2	6		2	[Xe]4f ¹³	+2, +3
Lu	71	14	2	6	1	2	[Xe]4f ¹⁴	+3	
			<i>3d</i>	<i>4s</i>	<i>4p</i>	<i>4d</i>	<i>5s</i>		
Sc	21	Full 18	1	2				[Ar]	+3
Y	39		10	2	6	1	2	[Kr]	+3

The atomic electronic configurations of lanthanum, cerium, and gadolinium can be described as $[\text{Xe}]4f^{n-1}5d^16s^2$ and those of scandium and yttrium can be described as $(n-1)d^1ns^2$. The other REEs have the atomic electronic configuration of $[\text{Xe}]4f^n6s^2$. This similarity of electronic configurations leads to the similar chemical behavior of all the REEs (Zhang et al., 2016).

REEs are strong reducing agents with high melting and boiling points. Their high density and electrical conductivity lead to an infinite variety of uses in broad fields. They are mainly used for auto catalysts and petroleum-refining catalysts in the United States. REEs also contribute to high technology, such as permanent magnets, generators for wind turbines, hybrid vehicles, and fluorescent light bulbs. REEs also play a vital role in medicine and health fields, contributing to the development of X-ray imaging, medical tracers, display phosphors, and magnetic resonance imaging (MRI) machines (Humphries, 2010). In Table 2, common uses of REEs are shown.

Because REEs are used for a wide range of fields, the importance of REE separation has rapidly increased. Several traditional separation methods have been adopted, including solvent extraction, ion exchange, fractional precipitation, fractional crystallization, selective oxidation, selective reduction, gravity separation, and magnetic separation (Voncken, 2016; Jordens et al., 2014; Lucas et al., 2015).

Table 2. Common uses of REEs

Element	Uses
Scandium	Lightweight aerospace components, armor alloys
Yttrium	Lasers, high-strength materials, high-temperature superconductors, high-temperature ceramics, radar
Lanthanum	Hydrogen storage, nickel-lanthanum hydride battery electrodes, optical lenses, phosphors, fluid-cracking catalyst
Cerium	Polishing powder, phosphors, fluid-cracking catalyst
Praseodymium	Magnets, lasers, x-ray scintillators
Neodymium	Magnets, lasers, glass pigments
Promethium	Batteries
Samarium	Magnets, lasers, phosphors
Europium	Phosphors, lasers, lighting, nuclear physics studies
Gadolinium	Magnets, lasers, computer memory, pharmaceutical tracers for MRI, neutron capture, optics
Terbium	Phosphors, lasers, lighting, sonar, x-ray detectors
Dysprosium	Magnets, lasers, halide lamps
Holmium	Magnets, lasers, materials & nuclear research
Erbium	Lasers, fiber optics, synthetic gems
Thulium	X-ray machines, lasers, nuclear physics
Ytterbium	Lasers, nuclear medicine, high-strength alloys, optics, pressure sensors
Lutetium	PET scan detectors, scintillometers

However, most of these methods are not suitable for REEs separation because of their low separation efficiency and long reaction time. Many researchers are trying to develop a more efficient REEs separation method(Uda, 2000), but solvent extraction is still generally used in industrial plants due to its fast reaction speed, simple operation, reusability, and capability of attaining high purity(Krishnamurthy and Gupta, 2004).

Solvent extraction, typically known as liquid–liquid extraction, is a process that selectively dissolves desirable compounds of a solution into a solvent through the distribution of metal species between two immiscible phases. These compounds transfer from one liquid solvent to another, generally from the aqueous phase to the organic phase. Meanwhile, undesirable impurities or compounds remain in the aqueous phase due to their low affinity with the organic phase. By using this simple principle, solvent extraction has long been used in the separation and purification of compounds for over one hundred years(Pierce, 1939). Scrubbing is the subsequent process of solvent extraction that removes impurities or unwanted compounds from the organic phase with a second immiscible solvent. The final process is stripping, which brings desirable compounds back to the aqueous phase by using a strip solution(Figure 2). This technique can be applied to petroleum refining, the remediation of soil, and especially hydrometallurgy for the separation of REEs.

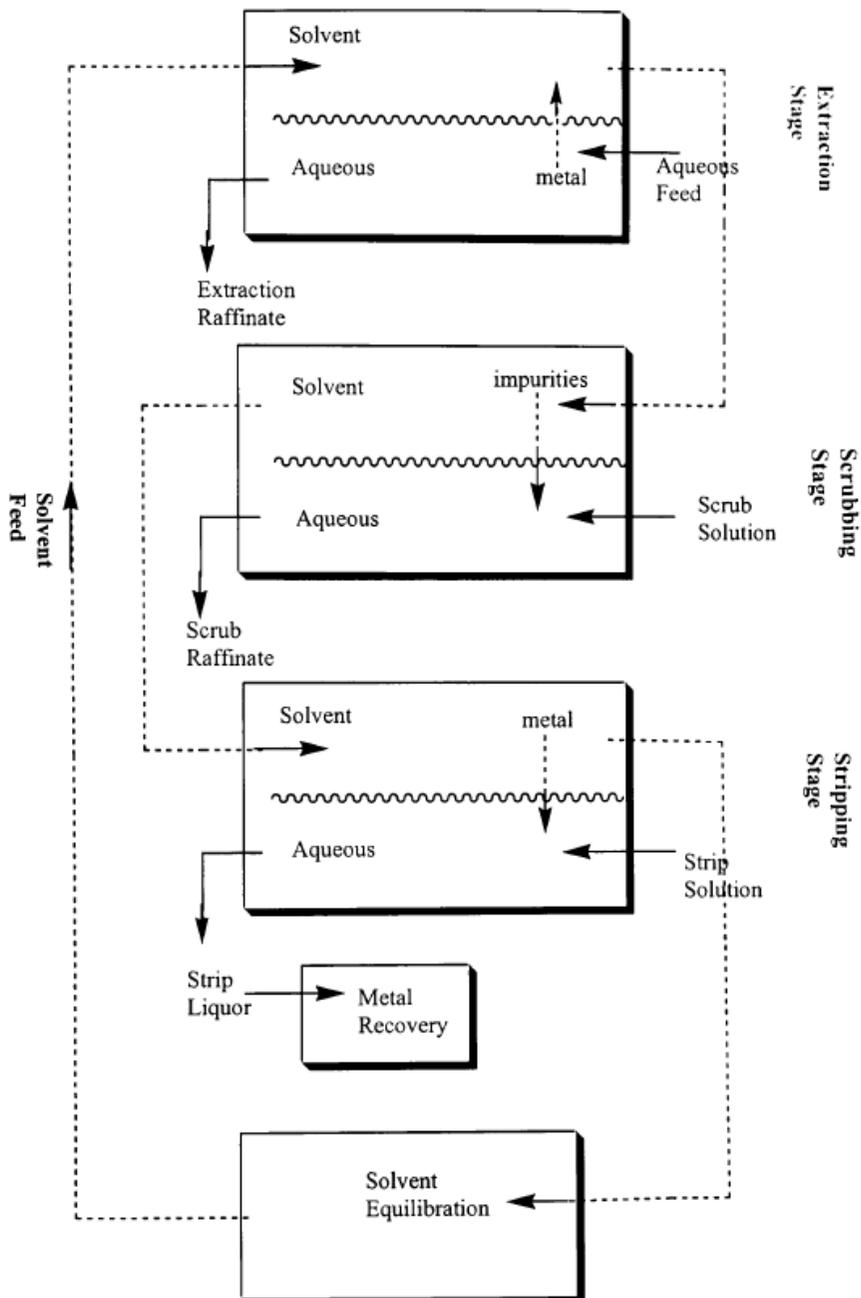


Figure 2. General process of solvent extraction (Desouky, 2006)

In the solvent extraction process, various factors affect the extraction

behavior of metal elements. Extractant concentration, pH, metal ion concentration in the feed solution, type of diluents, loading capacity, and the organic-phase-to-aqueous-phase (OA) volumetric ratio can serve as examples. Therefore, it is important to optimize these factors before starting the continuous process. Furthermore, the specification of the final product has one of the biggest impacts on the decision regarding the solvent extraction process method(Rane et al., 2006).

1.2 Recent studies

In the last several decades, numerous studies have investigated solvent extraction for the separation and purification of REEs. Several extractants, including cation exchangers, chelating exchangers, solvating extractants, and anion exchangers, have been applied to the leachate of rare earth ores or concentrates (Xie et al., 2014). In particular, a family of acidic organophosphorus extractants (e.g. di-[2-ethylhexyl] phosphoric acid [D2EHPA], 2-Ethylhexyl phosphoric acid mono-[2-ethylhexyl] ester [PC88A, EHEHPA, HEHEHP, P507], bis[2,4,4-trimethylpentyl] phosphinic acid [Cyanex 272], bis[2,4,4-trimethylpentyl] dithiophosphinic acid [Cyanex 301], and bis[2,4,4-trimethylpentyl] monothiophosphinic acid [Cyanex 302]) were extensively used to separate LREEs (Basualto et al., 2013; Banda et al., 2012; Sato and Sato, 1993; Sato, 1989).

Since a single extractant has low separation factors between each LREE, countless stages of extraction are needed in continuous processes (Xie et al., 2014). Therefore, many researchers have carried out synergistic solvent extraction experiments with mixtures of extractants to enhance the separation efficiency (Jia et al., 2009; Wang et al., 2011). Jia et al. (2009) investigated the extraction behavior of REEs with nitrate media through a mixture of D2EHPA and sec-octylphenoxyacetic acid (CA 12) and found the synergistic enhancement for La, Ce, Nd, and Y. Sun et al. (2006) studied the synergistic extraction of trivalent REEs from hydrochloride medium with a mixture of Cyanex 272 and sec-nonylphenoxy acetic acid. In this research, the extraction

mechanisms and thermodynamics of the extraction process were determined. Tian et al. (2013) investigated REE extraction with nitrate medium through mixtures of 8-hydroxyquinoline with Cyanex 301 or Cyanex 302 and concluded that there was a possibility of separating yttrium from other REEs easily by using these mixtures.

Although there are a number of studies about the solvent extraction of REEs, only a few papers deal with the following process, stripping (Wang et al., 2011; Tian et al., 2013; Chen et al., In press; Nasab et al., 2011). Rabie (2007) developed a process that can separate MREE from Egyptian monazite. This process consisted of the repetition of solvent extraction and stripping twice with D2EHPA diluted with kerosene. In the first stripping stage, MREE and LREE transferred to the strip liquor, while HREE remained in the organic phase. As a result, a concentrate with 98% of MREE (Sm, Eu, Gd) was obtained with 78% recovery. Preston (1996) devised a way to recover 95% of neodymium oxide from LREE nitrate liquor by using a 0.5M solution of Aliquat 336 nitrate in Shellsol AB. In this study, McCabe-Thiele diagrams for the stripping of La and Nd were drawn and it was concluded that a high OA ratio for the removal of co-extracted Nd is needed after stripping La at a lower OA ratio. Banda et al. (2015) studied the co-extraction and selective scrubbing method for the separation of Pr and Nd with 50% saponified 0.15M PC88A as an extractant and pure Nd solution as scrub liquor. Five-stage counter-current scrubbing was attempted at an OA ratio of 0.5, and the results indicated that more than 99% Nd solution purity could be achieved by selective scrubbing.

However, an approach to separate all LREEs in the stripping process has

not been attempted yet. In consideration of the fact that many researchers are conducting experiments about the separation of other metals by selective stripping and the results are widely used in real industrial processes for better separation efficiency, it is necessary to investigate the selective stripping behavior of LREEs(Parija and Sarma, 2000; Sastre and Alguacil, 2001; Taghizadeh et al., 2007; Sridhar et al., 2010; Li et al., 2012).

1.3 Research purpose

In general, processes for solvent extraction separation of REEs are made up of many stages of selective extraction. Rhône-Poulenc process, considered as the standard process in all industries, can produce over 99.999% purity of all REEs by conducting at least fifty stages of counter-current experiments in each circuit (Xie et al., 2014). This process is used in a wide variety of application, because high purity of REEs can be achieved. However, a number of stages are needed to separate each REE. Moreover, large amount of acid and base are required, since extracted REEs should be stripped with a high concentration of acid after one circuit and the stripped solution should be neutralized with a high concentration of base.

In this research, a novel process with selective stripping is developed to address the deficiency of the existing process. To decrease the number of stages and the amount of required acid and base, optimization of the stripping and semi-continuous counter-current experiments were conducted.

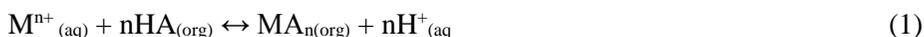
The optimum stripping conditions of LREEs in the two-component system were investigated for the effective separation of LREEs through selective stripping. The factors studied in this research were extractant type, extractant concentration, REE concentration ratio, OA ratio, and the concentration of acid. In addition, the slope analysis method was used to investigate the stoichiometry and structure of LREE-extractant complexes, and a McCabe–Thiele diagram was drawn for the determination of the optimum counter-current process.

To compare against the stripping behavior of LREEs in the two-component

system, the optimization experiments were also carried out in the four-LREE system. Based on the optimization results, a semi-continuous counter-current process was established for the separation of La, Ce/Pr, and Nd by using selective stripping. The process consists of three steps. In the first step, four stages of extraction was tried to separate La, by extracting Ce, Pr and Nd selectively. Three stages of selective stripping were followed to sweep extracted La away. Finally, seven stages of selective stripping were conducted to maintain Nd with high purity in the organic phase, while stripping Ce and Pr to the aqueous phase. Finally, a high concentration of acid was used to strip Nd.

Chapter 2. Background theory

When metal ions in an aqueous phase react with the extractant in an organic phase, some of them transfer to the organic phase due to the affinity with the organic phase. The simplest equation that depicts the solvent extraction process is shown below.



M^{n+} is a metal ion that needs to be separated, and HA is an acidic extractant.

To describe the selectivity of a desired metal ion with two immiscible phases, the distribution coefficient (D) is generally used. The definition of D is the ratio of the total concentration of the a metal ion in the organic phase to its total concentration in the aqueous phase at equilibrium state(Freiser, 1987). Therefore, in the solvent extraction process, D can be illustrated as

$$D = \frac{\text{Concentration of a metal ion in the organic phase}}{\text{Concentration of a metal ion in the aqueous phase}} = \frac{[M]_{org}}{[M]_{aq}} \quad (2)$$

The extraction percentage (% E) is another key factor that shows the extraction efficiency of a desired metal ion, which is related to D, as

$$\% \text{ Extraction (\% E)} = \frac{[M]_{org}V_{org}}{[M]_{org}V_{org} + [M]_{aq}V_{aq}} \times 100 = \frac{D}{D + V_{aq}/V_{org}} \times 100 \quad (3)$$

where V_{or} and V_{aq} represent the volumes of the organic and aqueous phases, respectively.

D and % E describe the selectivity of one desired metal ion; however, in the industrial process, the separation of different metals from each other is important. The separation factor, SF or β , is a term defined as the ratio of D

of one metal to D of another metal and is expressed as follows

$$SF = \frac{[M_1]_{org}/[M_1]_{aq}}{[M_2]_{org}/[M_2]_{aq}} = \frac{D_{M_1}}{D_{M_2}} \quad (4)$$

where M_1 and M_2 represent two different metals.

If the SF is high, this means that two metals can be separated easily. If the SF is close to 1, separation is extremely difficult and other techniques, such as a large number of stages or synergism, are indispensable.

To increase the extraction efficiency and enhance the SF of two metals, mixtures of two extractants are used in the solvent extraction process. To determine the synergistic extent of these extractants, the synergistic enhancement factor, R, is defined as

$$R = \frac{D_{HA+HB}}{D_{HA}+D_{HB}} \quad (5)$$

where HA and HB represent two different acidic extractants.

Batch tests are generally carried out using a separating funnel in laboratory experiments. However, it is difficult to separate two elements with a low SF with batch tests. Therefore, continuous process is employed to increase the separation efficiency. Three types of continuous processes are generally used in industry: co-current, cross-current, and counter-current(Figure 3).

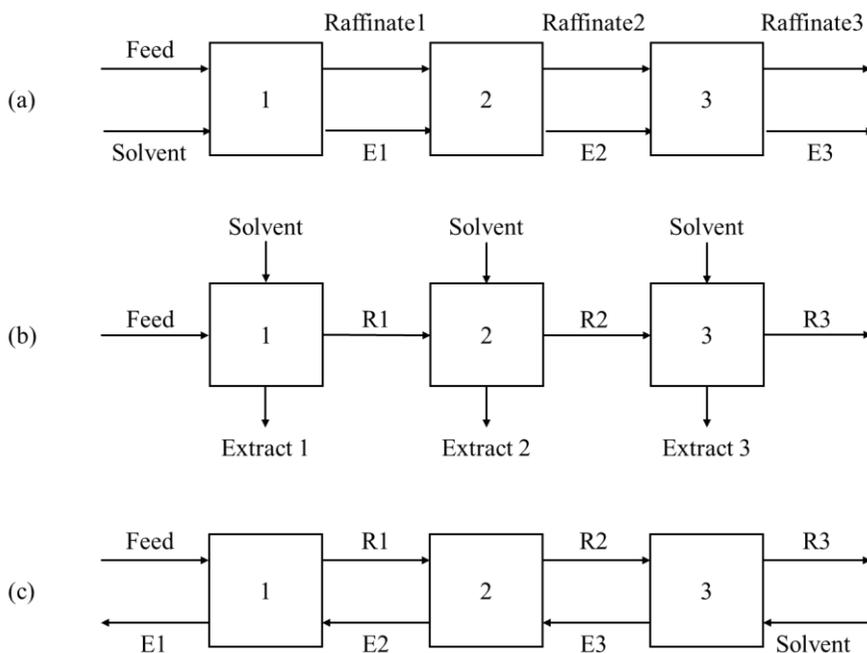


Figure 3. Flowsheet of three types of continuous extraction processes: (a) co-current; (b) cross-current; and (c) counter-current (Rydberg, 2004)

In co-current extraction, the organic phase and the aqueous phase move in the same direction. Co-current extraction is not an efficient process because the two phases make contact several times in different contactors, though they reach equilibrium in the first contactor.

In cross-current extraction of two phases, raffinate transfers to the second contactor and is shaken with fresh solvent after the first extraction. As this process repeats numerous times, the recovery of a desired metal can be enhanced. However, this method is not suitable for the industrial process because the product phases contain a lower concentration of the metal (Rydberg,

2004).

Counter-current extraction is the most commonly used method in the industry. In this process, the two phases flow in opposite directions in many contactors. Due to the difference of D of several metal ions in the aqueous phase, each metal ion is collected in different contactors (David, 2001).

Before starting counter-current extraction, the calculation of a number of stages for the desired separation should be conducted. The McCabe–Thiele diagram is a graphic construction of a counter-current cascade, which is composed of an equilibrium isotherm and an operating line (Figure 4). The equilibrium isotherm can be plotted by mixing two phases at different OA volumetric ratios. Because the equilibrium isotherm varies with extractant concentration, the metal ion concentration, equilibrium pH, acidity, temperature, and loading capacity, factors should be fixed during the experiments (Sadanandam et al., n.d.). After plotting the equilibrium isotherm, the operating line can be drawn. The slope of the operating line describes the flow ratio of the organic phase to that of the aqueous phase, which is needed to achieve a desired separation (Mular et al., 2002). By changing the slope of the operating line, selective extraction of a metal ion can be achieved (Rousseau, 1987)

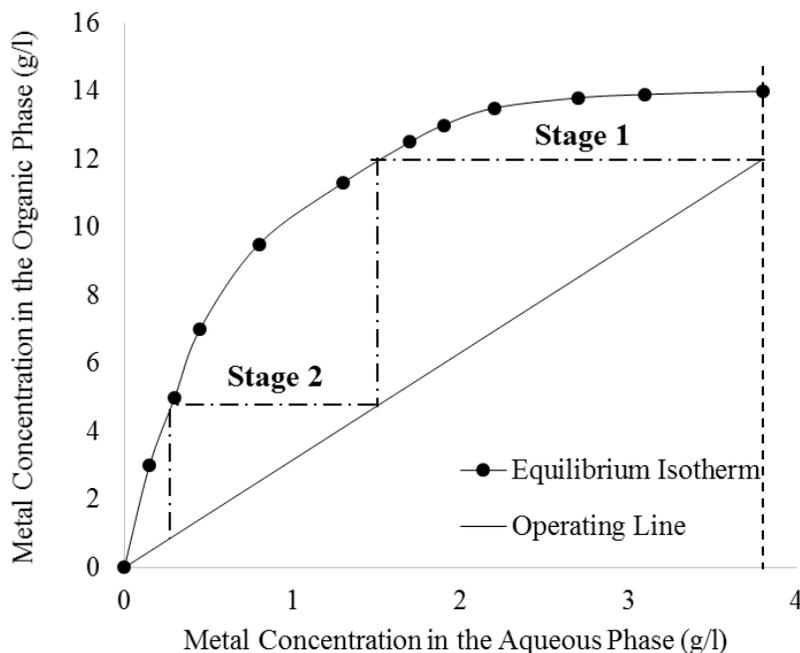


Figure 4. McCabe–Thiele diagram for counter-current extraction

Because the equilibrium constant can be used for determining the spontaneity of a specific reaction and maximizing the yield of the product, it is important to determine the stoichiometry and the equilibrium constant of the extraction reaction. The slope analysis method is the most conventional method for studying the stoichiometry and structure of metal–organic complexes. In the general extraction reaction, the equilibrium constant can be represented as follows:

$$K = \frac{[MA_n]_{org}[H^+]_{aq}^n}{[M^{n+}]_{aq}[HA]_{org}^n} = D \times \frac{[H^+]_{aq}^n}{[HA]_{org}^n} \quad (6)$$

By taking the logarithm of both sides,

$$\log D = \log K + n pH + n \log [HA]_{org} \quad (7)$$

This equation indicates a straight line, plotting log D versus pH at a constant extractant concentration. Additionally, a linear line can be made when log D is plotted versus extractant concentration at a constant pH. The slopes of these equations are equivalent to the total stoichiometric number of hydrogen ions and extractants involved in this reaction, respectively.

Chapter 3. Experimental set-up and procedures

3.1 Reagents and apparatus

D2EHPA and n-heptane were purchased from Sigma-Aldrich, USA. PC88A was obtained from Daihachi Chemical Industry, Japan. Cyanex272, Cyanex301, and Cyanex572 were supplied by CYTEC Canada Inc. All extractants were used without further purification and diluted with n-heptane to the required concentrations.

$\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (99.999%), $\text{PrCl}_3 \cdot x\text{H}_2\text{O}$ (99.9%), and $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) were purchased from Sigma-Aldrich, USA. The stock solutions of REEs (III) were prepared by dissolving these chlorides in deionized water. To make constant ionic strengths ($\mu = 0.5 \text{ mol/L}$), NaCl (Dae Jung Chemicals, Korea) was also dissolved in the stock solutions. The concentration of LREEs in the initial solutions was 1000 mg/L, respectively. All other reagents were of analytical reagent grade.

The pH of the aqueous phase was measured by a pH meter (Thermo Orion Star A211). An inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8300 spectrometer) was used to determine the concentrations of REEs (Figure 5).

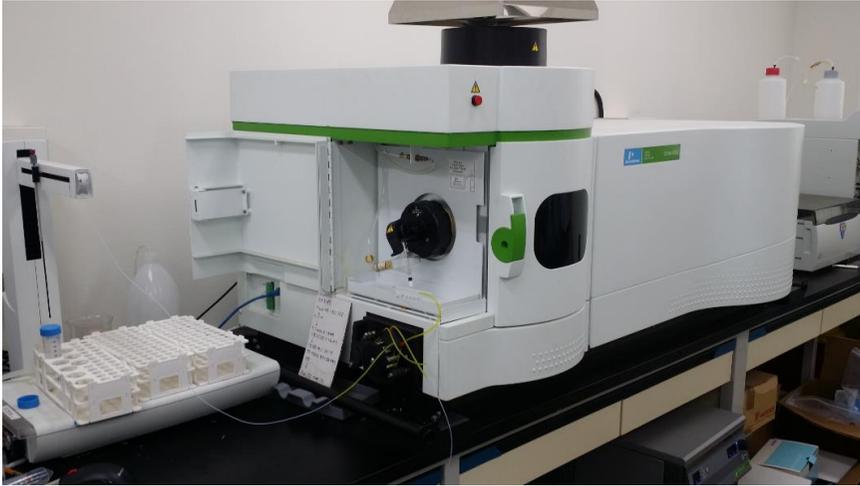


Figure 5. Inductively coupled plasma optical emission spectrometer

3.2 Solvent extraction and stripping process

A funnel shaker (Duksan Jonghap Science, Korea) was used for the solvent extraction and stripping experiments(Figure 6). Equal volumes (10 mL each) of aqueous and organic solutions were shaken for 20 minutes at 293 ± 1 K unless otherwise stated. In preliminary experiments for the kinetics of extraction, it was confirmed that 20 minutes was enough time to reach the equilibrium state.

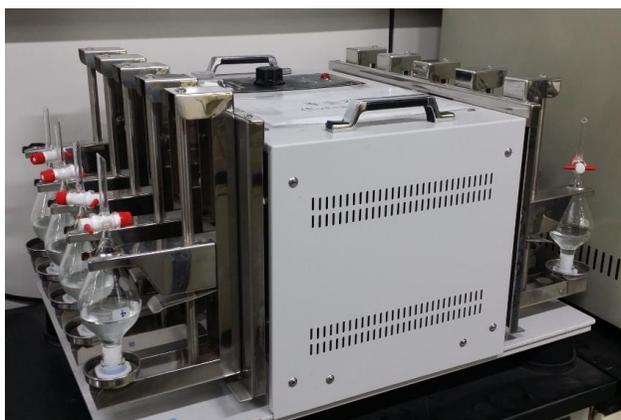


Figure 6. Funnel shaker

After phase separation, equilibrium pH was measured by using a pH meter, and the concentrations of REEs in the aqueous phase were determined by ICP-OES. The concentrations of REEs in the organic phase were obtained by mass balance. Because all the experiments were conducted more than three times, the experimental data were proven to be reliable. D of each element and SF between two elements were calculated.

3.3 Batch counter-current extraction and stripping

The multistage counter-current extraction and stripping experiments were simulated on the batch laboratory scale. Figure 7 shows the batch simulation of the three-stage counter-current system. In this flowsheet, each circle indicates the separating funnel and the symbols F, S, L, and A represent the feed solution, fresh organic solution of extractant/n-heptane, loaded organic solution, and acidic strip liquor. The number of circles means the number of funnels used in this system. This system resembles a real counter-current process after numerous cycles. Further counter-current extraction and stripping experiments were carried out by these batch-type cycles.

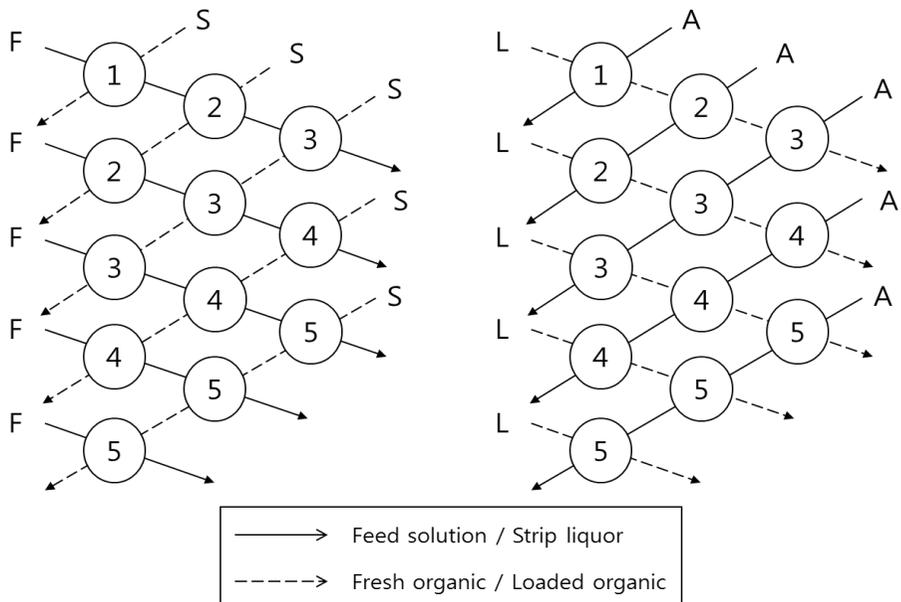


Figure 7. Flowsheet of batch simulation of three-stage counter-current system

Chapter 4. Results and discussion

4.1 Optimization of stripping in the two-LREE-component systems

The optimization experiments were conducted to examine the stripping behavior of LREEs in the two-component systems. Three combinations of two adjacent LREEs – La/Ce, Ce/Pr, and Pr/Nd – became the subjects of the experiments, and divergent factors, such as extractant type and concentration, REE concentration ratio in the feed solution, OA ratio, and HCl concentration, were changed.

4.1.1 La and Ce system

4.1.1.1 Effect of extractant type and concentration

The experiments regarding the effect of extractant type and concentration on the separation of La and Ce were carried out using various concentrations of acidic organophosphorus extractants in n-heptane diluent. Five types of extractants (D2EHPA, PC88A, Cyanex 272, Cyanex 301, Cyanex 572) were used at a 0.1M to 1M concentration. The experimental results are shown in Figure 8. As the extractant concentration increased, the extraction percentage of La and Ce also increased regardless of the extractant type. However, the extraction behavior of the two LREEs changed depending on the extractant type.

While using D2EHPA, the selectivity was low, but showed high extraction efficiency for La and Ce. Since the extraction percentage reached the maximum level at 0.5M D2EHPA, a higher concentration is not required for better extraction. 0.5M PC88A extracted more than 77% of Ce and 43.4% of La, which denotes that PC88A has high selectivity with high recovery. Cyanex 301 was not an adequate extractant for the separation of La and Ce because it had low extraction ability and low selectivity. Cyanex 272 and Cyanex 572 showed high selectivity between La and Ce; however, Cyanex 272 had low extraction ability for LREEs. Consequently, PC88A and Cyanex 572 were appropriate extractants due to their high recovery and selectivity.

Because this research is about the selective stripping of LREEs, it is necessary to transfer at least half of both LREEs to the organic phase before

studying the stripping behavior of LREEs. To this end, PC88A was selected as an extractant and the concentration of PC88A was decided to 0.5M. Furthermore, PC88A has high economic efficiency and is widely used in industry. Therefore, 0.5M PC88A was used for extraction for further stripping experiments.

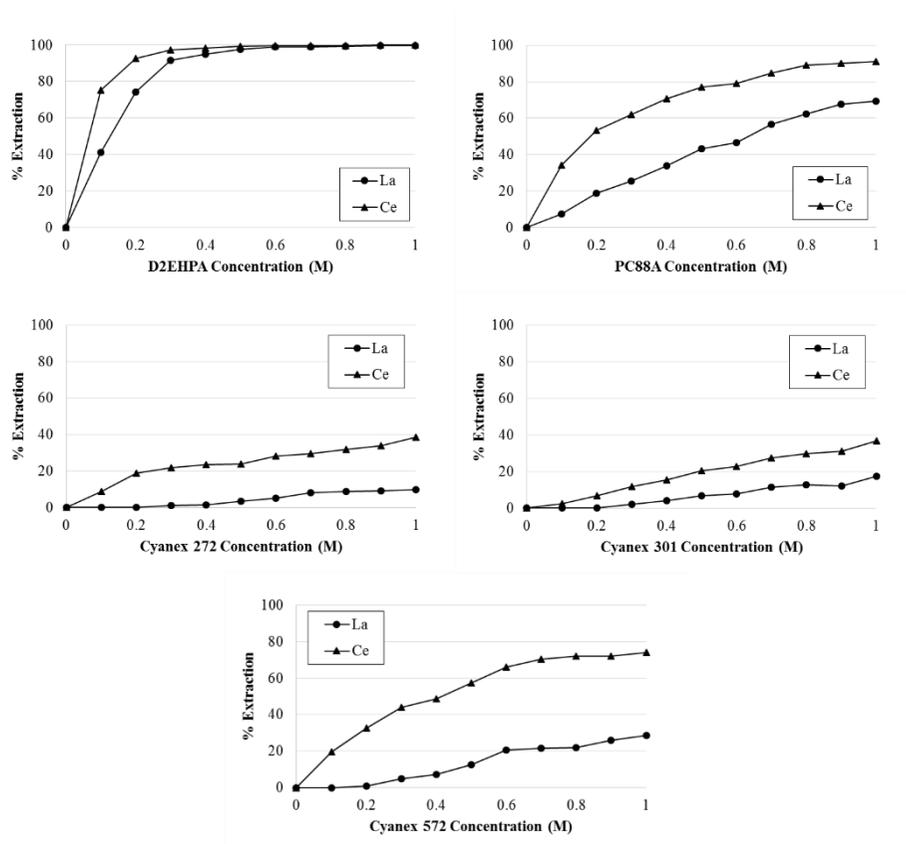


Figure 8. The extraction percentage of La and Ce using: (a) D2EHPA; (b) PC88A; (c) Cyanex 272; (d) Cyanex 301; and (e) Cyanex 572 (1000ppm of La and Ce respectively, extraction OA ratio = 1)

4.1.1.2 Effect of La/Ce concentration ratio in the feed solution

To determine the impact of the concentration ratio of two REEs on the stripping behavior, several experiments were conducted with varying concentration ratios of La and Ce in the feed solution (Figures 9, 10). The total concentration of REEs was kept constant at 2000 ppm and the concentration of La compared with that of Ce changed to 1, 2, 3, and 4. As shown in Figure 9, the stripping percentages were almost constant as the concentration ratio changed. Because D and SF also showed only slight variation, there were no meaningful results. This is because the concentration of H^+ ions in the aqueous phase was large enough to react with REE-extractant complexes thoroughly. If La and Ce had to react with H^+ ions competitively, La would hinder Ce from stripping and SF may be enhanced. Since the concentration ratio of LREEs could not affect the stripping behavior, the optimum concentration ratio was determined to be 1 considering the general existing ratio of REEs in the leach liquors.

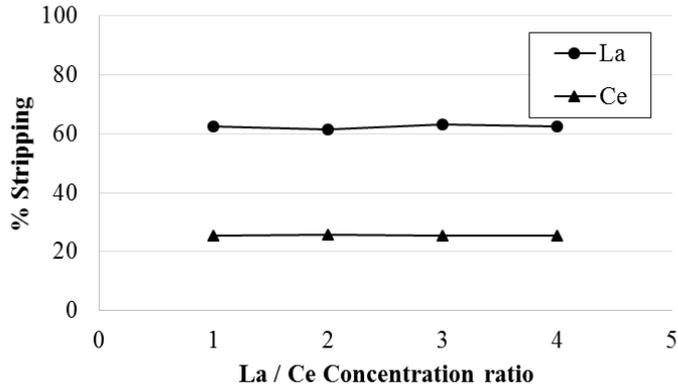


Figure 9. The stripping percentage of La and Ce with change of REE concentration ratio (0.05M HCl, stripping OA ratio = 1)

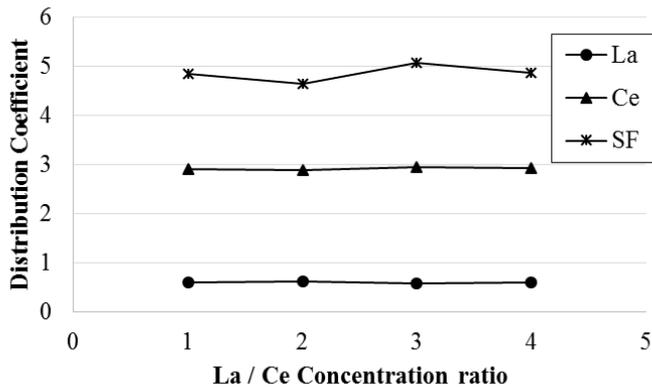


Figure 10. The distribution coefficient of La and Ce with change of REE concentration ratio (0.05M HCl, stripping OA ratio = 1)

4.1.1.3 Effect of hydrochloric acid concentration of strip liquors

In Figures 11 and 12, the stripping behavior of La and Ce depending on the concentration of HCl is represented. It was found that a higher concentration of HCl leads to strip more LREEs to the aqueous phase. The biggest distinction between the stripping percentages of the two LREEs of about 39% was obtained when using 0.06M HCl, and the SF between La and Ce reached the maximum point with 0.1M HCl. Since SF is the most important factor for the determination of purity, 0.1M HCl was used to separate La from other LREEs in the first stripping stage of a novel semi-continuous process.

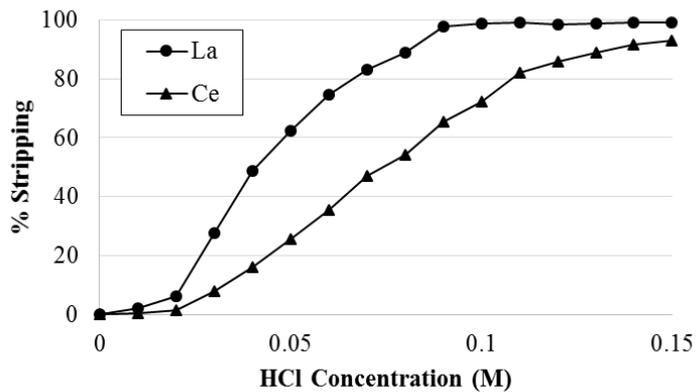


Figure 11. The stripping percentage of La and Ce with change of HCl concentration (La/Ce concentration ratio = 1, stripping OA ratio = 1)

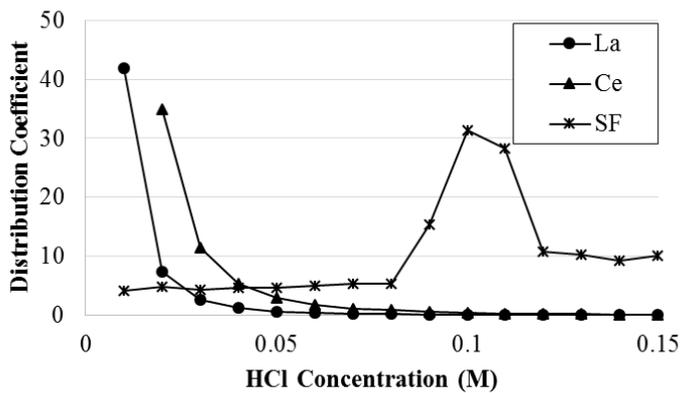


Figure 12. The distribution coefficients of La and Ce with change of HCl concentration (La/Ce concentration ratio = 1, stripping OA ratio = 1)

4.1.1.4 Effect of organic-phase-to-strip-liquor volumetric ratio and McCabe-Thiele method

According to the literature, the OA ratio is a key factor for the separation of two metal ions. Hence, the experiments were performed under the condition of different volumetric ratios of the organic phase to strip liquor while using 0.5M PC88A, 1000 ppm of La and Ce solutions, respectively, and 0.10M HCl(Figure 13). As the volumetric ratio of the organic phase to strip liquor increased, the stripping percentage of two LREEs decreased significantly due to the small amount of hydrogen ions in the strip liquor. When the OA ratio was 1, the stripping percentages of La and Ce were 98.8% and 72.1%, respectively; however they decreased to 34.2% and 11.8% at the OA ratio of 9. SF is shown in Figure 14. SF diminished sharply from 31.4 to 3.90 within this experimental range, and the maximum SF was obtained at the OA ratio of 1.

Although SF between the two LREEs maximized at the OA ratio of 1, this does not prove that selective stripping would be achieved in this condition. To determine the optimum OA ratio and number of stages for the selective stripping, a McCabe–Thiele method was introduced in the next section.

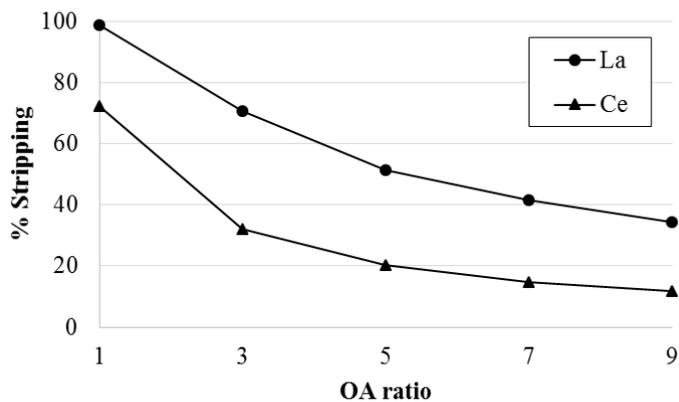


Figure 13. The stripping percentage of La and Ce with change of OA ratio
(La/Ce concentration ratio = 1, 0.10M HCl)

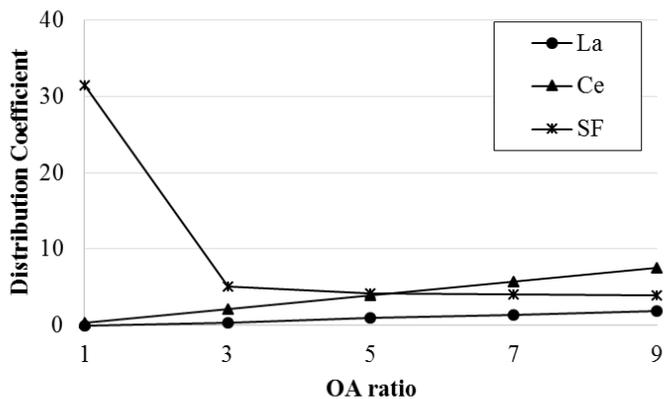


Figure 14. The distribution coefficient of La and Ce with change of OA ratio
(La/Ce concentration ratio = 1, 0.10M HCl)

The McCabe–Thiele method is a way of determining a suitable OA ratio and number of stages to separate two or more metal ions by determining the concentration of ions in the aqueous phase and organic phase. The diagram was drawn based on the experimental data of OA ratio.

In Figure 15, the operating line of stripping was drawn between the equilibrium line of La and Ce because Ce should remain in the organic phase while La strips with HCl. In this condition, the applicable OA ratio was 7:4; thus, at least three stages of stripping at the OA ratio of 7:4 were envisioned. The semi-continuous counter-current experiments were carried out based on this McCabe–Thiele diagram.

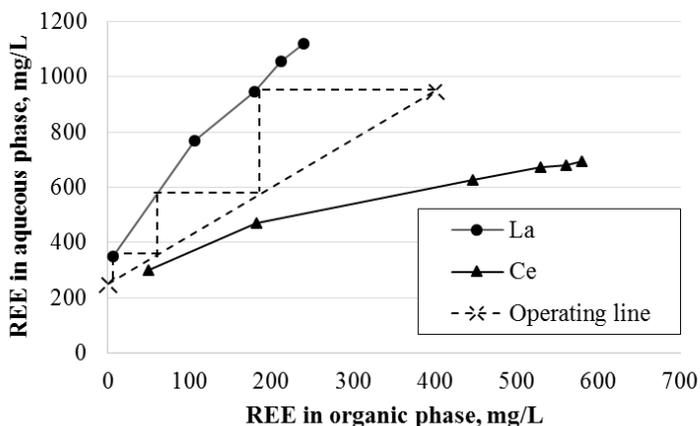
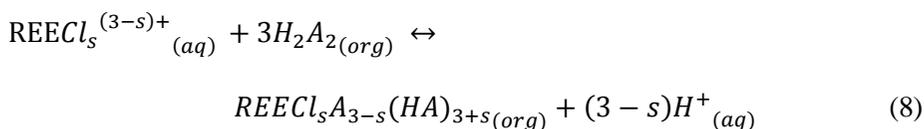


Figure 15. McCabe–Thiele diagram of the stripping of La and Ce (La/Ce concentration ratio = 1, 0.10M HCl)

4.1.1.5 Slope analysis method

The slope analysis method was used to determine the stoichiometry of the La and Ce complex containing an extractant and anion. In Figure 16, the relationship between pH and D of La and Ce in the stripping stage is shown. When the trend lines were drawn, the slopes of those lines came close to 2.7 for both LREEs and were slightly lower than 3. From these results, it could be predicted that two or three moles of H⁺ ions reacted with one mole of the LREE-extractant complex in the stripping reaction. This implies that there is a possibility of LREE-chloride-extractant complexes formation in the La/Ce system. This can be expressed as follows (Mohammadi et al., 2015):



According to the equation 8, it is suggested that the decomplexation of REEs and PC88A extractant in the stripping stage does not involve three hydrogen ions exactly, but around two to three hydrogen ions. In other words, some REE ions form complexes with extractant and chloride ions in the form of REECl_sA₂(HA)₄ in the organic phase.

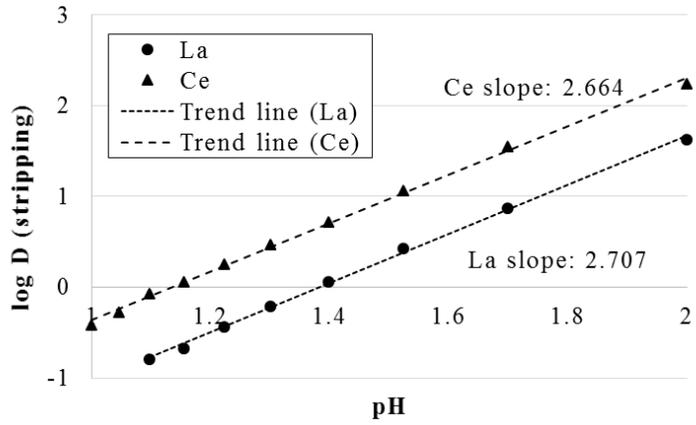


Figure 16. Relationship of distribution coefficients of La and Ce and the equilibrium pH of the strip liquor (La/Ce concentration ratio = 1, stripping OA ratio = 1)

4.1.2 Ce and Pr system

4.1.2.1 Effect of extractant type and concentration

The extraction percentages using five types of acidic extractants with concentrations of 0.1M to 1M are shown in Figure 17. It was found that D2EHPA and Cyanex 301 were not suitable for selective stripping, since they have relatively low selectivity with LREEs. Among the three extractants except them, selectivity increased in the order of Cyanex 272, PC88A, and Cyanex 572, and the recovery increased in the order of Cyanex 272, PC88A, and Cyanex 572. The maximum SF was 1.96 when using 0.6M Cyanex 272.

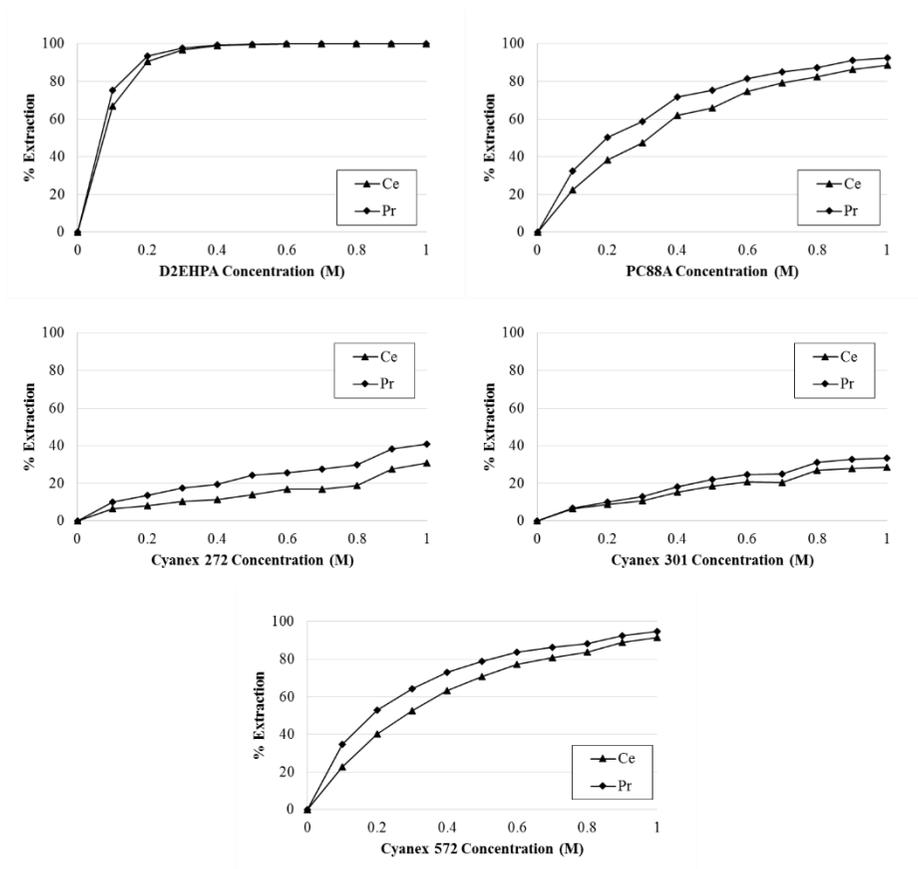


Figure 17. The extraction percentage of Ce and Pr using: (a) D2EHPA; (b) PC88A; (c) Cyanex 272; (d) Cyanex 301; and (e) Cyanex 572 (1000ppm of Ce and Pr, respectively, extraction OA ratio = 1)

4.1.2.2 Effect of Ce/Pr concentration ratio in the feed solution

The concentration ratio of Ce to Pr was varied from 1 to 4 at a fixed total concentration of Ce and Pr to investigate the relationship between the concentration ratio of two LREEs in the feed solution and stripping percentage. As shown in Figures 18 and 19, there was little difference in the stripping behavior of two LREEs. The stripping percentage of Ce varied from 27.0% to 28.8%, while that of Pr changed from 19.8% to 22.9%. SF fluctuated between 1.33 and 1.53 and had a maximum value at an REE concentration ratio of 1. Therefore, the concentration ratio of Ce and Pr was determined to be 1 from the consideration of two factors – the existing ratio in the leach liquor and the highest SF in the stripping stage.

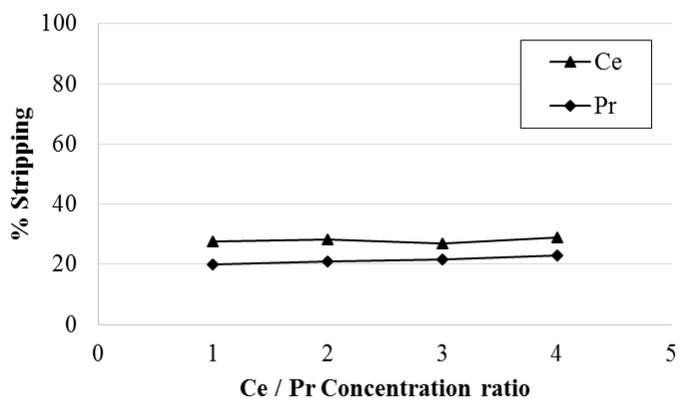


Figure 18. The stripping percentage of Ce and Pr with change of REE concentration ratio (0.05M HCl, stripping OA ratio = 1)

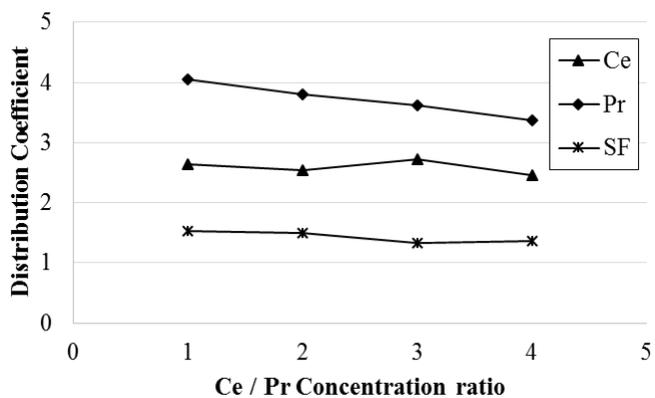


Figure 19. The distribution coefficient of Ce and Pr with change of REE concentration ratio (0.05M HCl, stripping OA ratio = 1)

4.1.2.3 Effect of hydrochloric acid concentration of strip liquors

The stripping percentages over the HCl concentration are represented in Figure 20. It was confirmed that Ce and Pr are much more difficult to separate from each other than La and Ce, since the percentage difference between Ce and Pr was minor. 0.14M HCl stripped two LREEs with the maximum SF(Figure 21). Consequently, the optimum HCl concentration for the selective stripping of Ce and Pr was determined to be 0.14M.

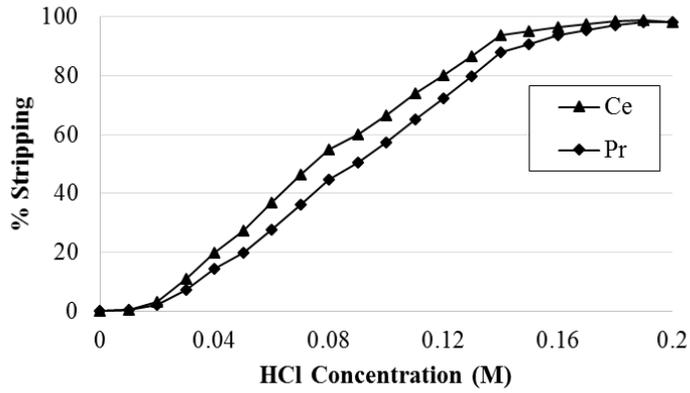


Figure 20. The stripping percentage of Ce and Pr with change of HCl concentration (Ce/Pr concentration ratio = 1, stripping OA ratio = 1)

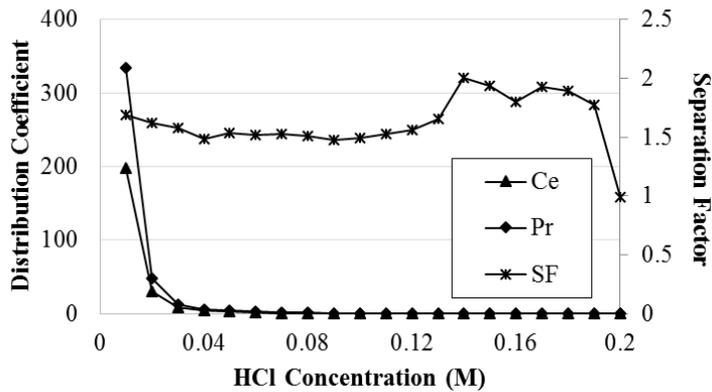


Figure 21. The distribution coefficient of Ce and Pr with change of HCl concentration (Ce/Pr concentration ratio = 1, stripping OA ratio = 1)

4.1.2.4. Effect of organic-phase-to-strip-liquor volumetric ratio and McCabe-Thiele method

In Figures 22 and 23, the relationship between OA ratio and the stripping percentage of Ce and Pr are represented. The OA ratio varied from 1 to 9, while the total volume of the aqueous phase and organic phase was fixed, and the optimum concentration of HCl of 0.14M was used.

In this system, selective stripping was difficult due to the similar stripping behavior of Ce and Pr. The stripping percentage of the two LREEs diminished smoothly, and D increased in line with an increase of OA ratio. The McCabe–Thiele method was adopted in sequence for deciding the OA ratio and number of stages.

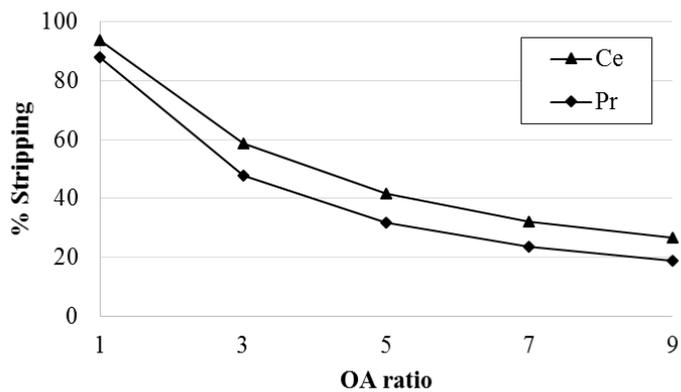


Figure 22. The stripping percentage of Ce and Pr with change of OA ratio
(Ce/Pr concentration ratio = 1, 0.10M HCl)

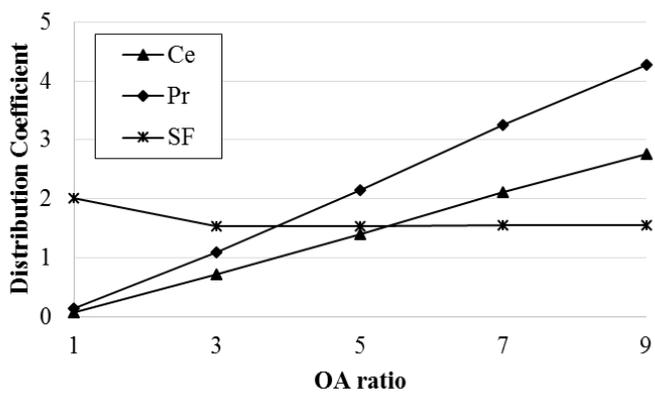


Figure 23. The distribution coefficient of Ce and Pr with change of OA ratio
(Ce/Pr concentration ratio = 1, 0.10M HCl)

By analyzing the experimental data, a McCabe–Thiele diagram was drawn. Figure 24 shows the distribution isotherms for the stripping of Ce and Pr with 0.14M HCl. Since Ce and Pr have similar stripping behaviors, a number of stages were required for the selective stripping. As shown in the diagram, the separation of Ce and Pr could be achieved by at least six counter-current stages of stripping at an OA ratio of 5:3.

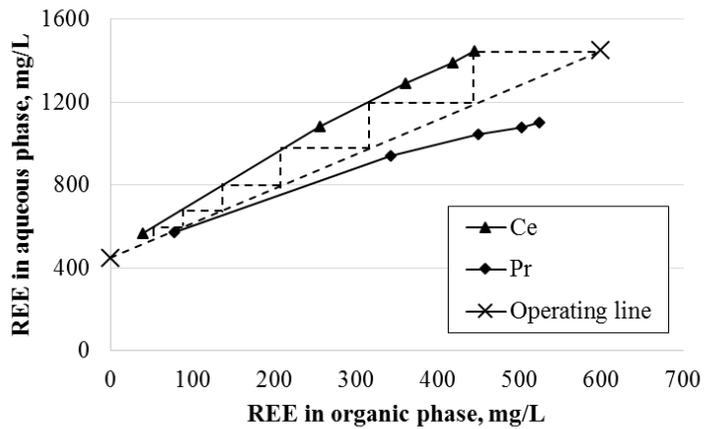


Figure 24. McCabe–Thiele diagram of the stripping of Ce and Pr (Ce/Pr concentration ratio = 1, 0.10M HCl)

4.1.2.5 Slope analysis method

The slope analysis method was also adopted in the Ce and Pr system to understand the complex structure in the organic phase. As shown in Figure 25, the slopes of the straight lines of two LREEs were approximately 2.6 for the 0.5M PC88A in n-heptane. This suggests that about 60% of Ce and Pr ions form mixed complexes, including three dimers of PC88A and one chloride ion, while the others form complexes without chloride ions.

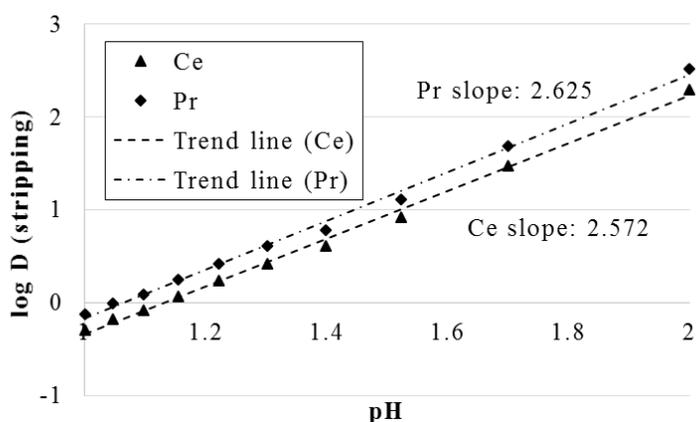


Figure 25. Relationship of distribution coefficients of Ce and Pr and the equilibrium pH of the strip liquor (Ce/Pr concentration ratio = 1, stripping OA ratio = 1)

4.1.3 Pr and Nd system

4.1.3.1. Effect of extractant type and concentration

The extraction behavior of Pr and Nd was investigated using five different types of cationic extractants(Figure 26). The experimental conditions were the same as those of the previous two-LREE-component systems. D2EHPA and Cyanex 301 were unsuitable extractants due to their low selectivity. Among the other three extractants, PC88A had the highest recovery while Cyanex 572 had the highest selectivity. The maximum SF was 2.2 using 0.1M Cyanex 572.

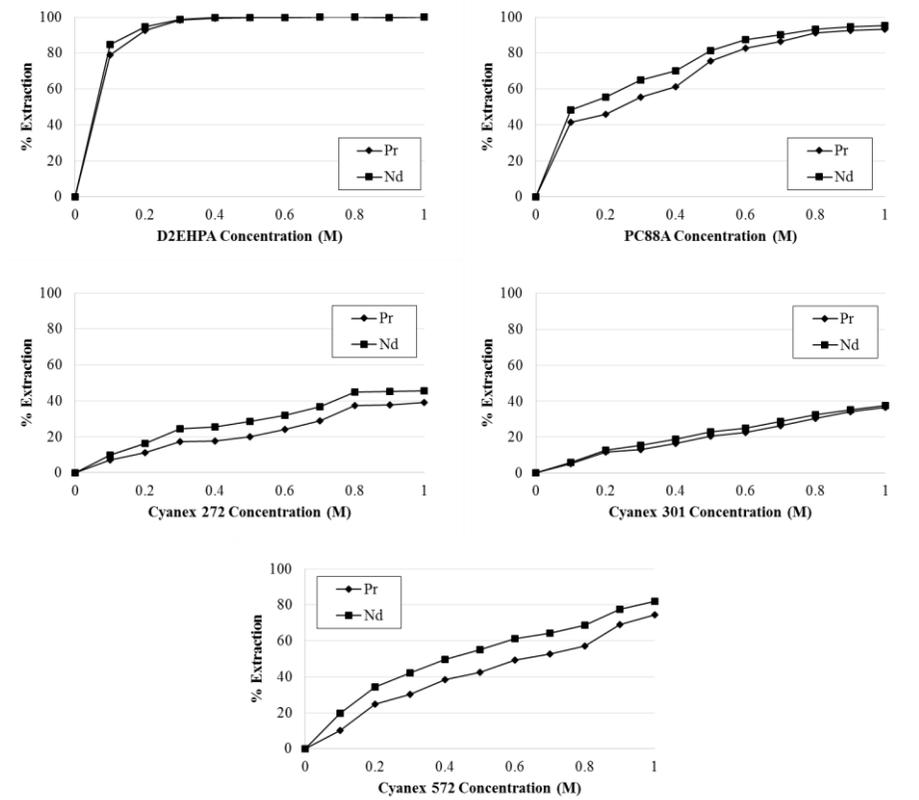


Figure 26. The extraction percentage of Pr and Nd by using: (a) D2EHPA; (b) PC88A; (c) Cyanex 272; (d) Cyanex 301; and (e) Cyanex 572 (1000ppm of Pr and Nd respectively, extraction OA ratio = 1)

4.1.3.2. Effect of Pr/Nd concentration ratio in the feed solution

Figures 27 and 28 show the effect of the Pr/Nd concentration ratio in the feed solution on the stripping behavior of two LREEs with 0.5M PC88A and 0.05M HCl at an OA ratio of 1. Although the LREE concentration ratio varied from 1 to 4, the stripping percentage did not fluctuate. D of Pr and Nd slightly decreased as the concentration ratio increased, but SF remained almost constant regardless of the ratio. The maximum SF was obtained at a concentration ratio of 1. Therefore, Pr and Nd solutions of 1000ppm, respectively, were used as the feed solutions in the following experiments.

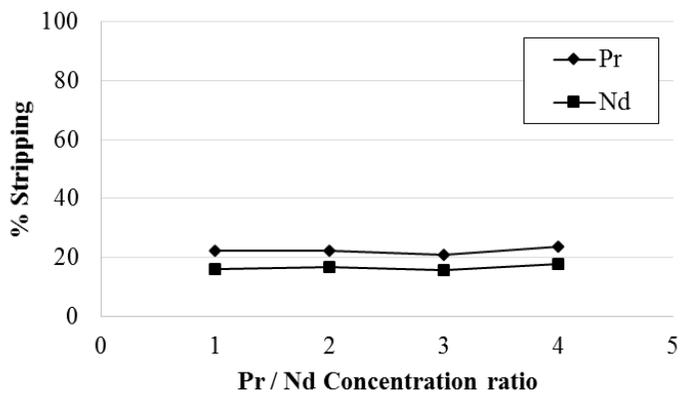


Figure 27. The stripping percentage of Pr and Nd with change of REE concentration ratio (0.05M HCl, stripping OA ratio = 1)

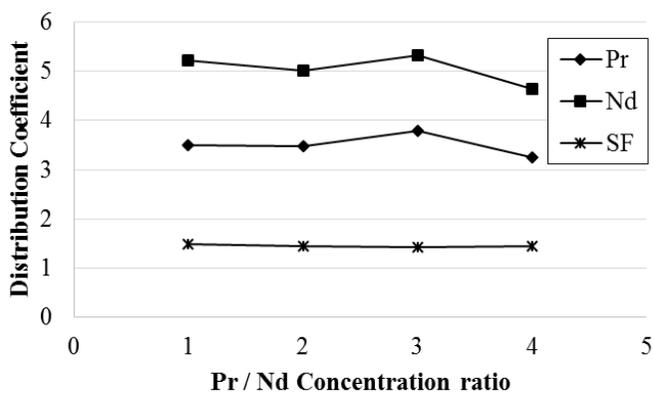


Figure 28. The distribution coefficient of Pr and Nd with change of REE concentration ratio (0.05M HCl, stripping OA ratio = 1)

4.1.3.3. Effect of hydrochloric acid concentration of strip liquors

The concentration of the strip liquor as changed from 0.01M to 0.2M to determine the optimum concentration(Figures 29, 30). It is generally known that Pr and Nd are challenging to separate completely from each other. The graph demonstrates this fact, since the difference of stripping percentage is less than 10% for all intervals.

D of both LREEs diminished sharply with an increase of HCl concentration, and SF fluctuated in the narrow range of 1.02 to 1.79. The maximum SF between Pr and Nd was 1.79 at 0.15M HCl. Accordingly, the optimum concentration of HCl in the Pr and Nd system was determined to be 0.15M.

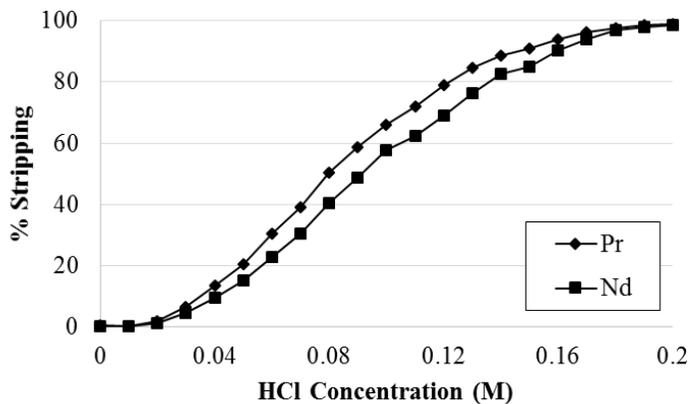


Figure 29. The stripping percentage of Pr and Nd with change of HCl concentration (Pr/Nd concentration ratio = 1, stripping OA ratio = 1)

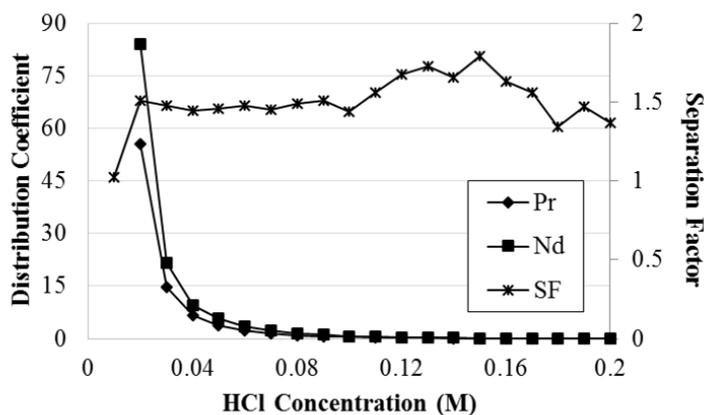


Figure 30. The distribution coefficient of Pr and Nd with change of HCl concentration (Pr/Nd concentration ratio = 1, stripping OA ratio = 1)

4.1.3.4. Effect of organic-phase-to-strip-liquor volumetric ratio and McCabe-Thiele method

The variation of stripping percentage with OA ratios of 1, 3, 5, 7, and 9 is shown in Figure 31. The experiments were carried out under the conditions of 0.5M PC88A, 1000ppm of Pr and Nd, respectively, and 0.15M HCl.

The stripping percentages of Pr and Nd were 91.1% and 85.1% at an OA ratio of 1, and then decreased steadily to 23.0% and 17.1% at an OA ratio of 9. Moreover, there was a linear relationship between OA ratio and D of two LREEs in this section(Figure 32). The maximum SF was gained at an OA ratio of 1, and a McCabe–Thiele diagram is drawn in the next section based on these experimental data.

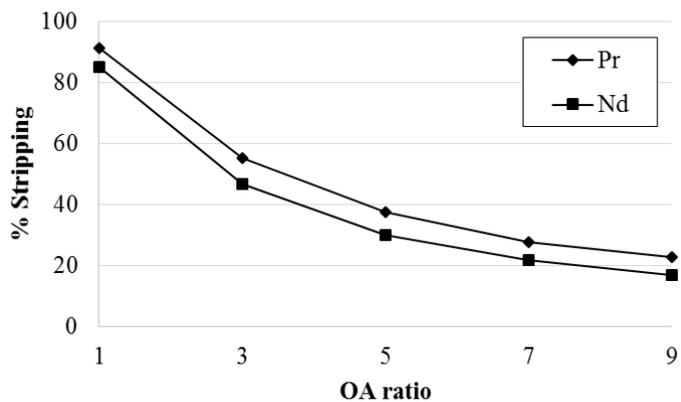


Figure 31. The stripping percentage of Pr and Nd with change of OA ratio
(Pr/Nd concentration ratio = 1, 0.10M HCl)

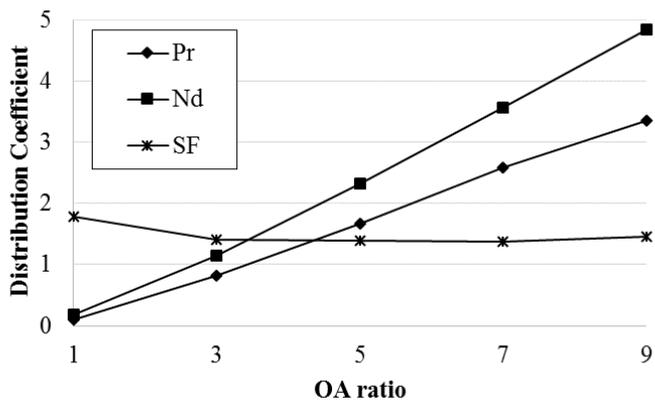


Figure 32. The distribution coefficient of Pr and Nd with change of OA ratio
(Pr/Nd concentration ratio = 1, 0.10M HCl)

In Figure 33, a McCabe–Thiele diagram plots the concentration of Pr or Nd in the aqueous phase versus that in the organic phase. In this investigation, it was concluded that the selective stripping of Pr could be achieved in at least seven stages of stripping at an OA ratio of 3:2. This result was used to design the semi-continuous counter-current experiments in Part 4.3.

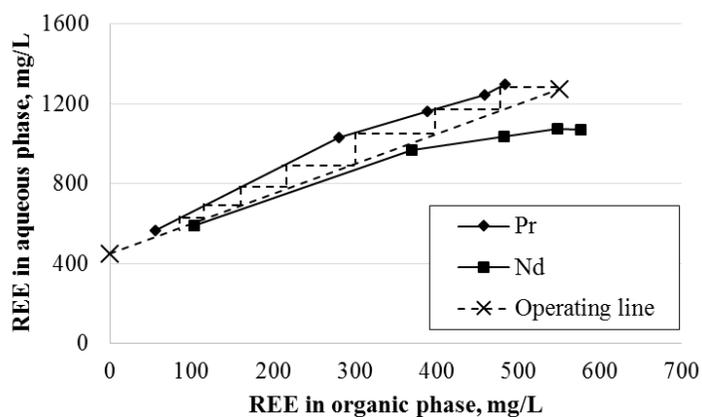


Figure 33. McCabe–Thiele diagram of the stripping of Pr and Nd (Pr/Nd concentration ratio = 1, 0.10M HCl)

4.1.3.5 Slope analysis method

The stoichiometric number of H⁺ ions participated in the reaction could be investigated with the slope analysis method(Figure 34). The slope of the trend line reveals that exactly three moles of H⁺ ions are needed to decompose one mole of Pr and Nd complexes with extractant in the stripping stage. This can be simply represented as follows:

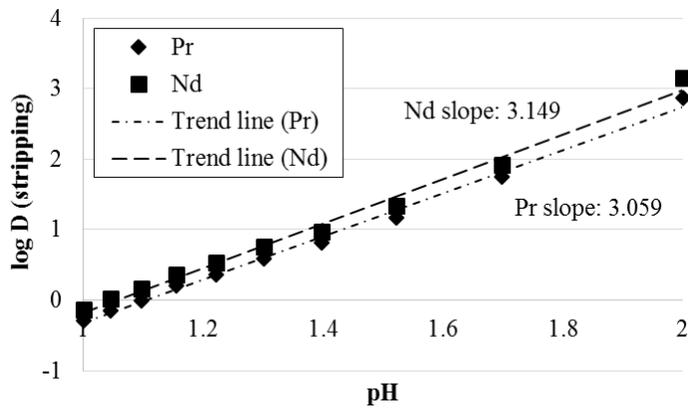


Figure 34. Relationship of distribution coefficients of Pr and Nd and the equilibrium pH of the strip liquor (Pr/Nd concentration ratio = 1, stripping OA ratio = 1)

4.2 Semi-continuous process using selective stripping of four LREEs

A new separation process including selective stripping was contrived for four LREEs based on the previous experimental results. The process consisted of three steps: the extraction of Ce, Pr, and Nd; the selective stripping of the extracted La; and the selective stripping of Ce and Pr.

The main objective of Part 4.2.1. was the comparison of the stripping behavior of each LREEs in the two-component systems and that in the four-component system. Furthermore, the OA ratio and number of stages for extraction were determined to extract only Ce, Pr, and Nd while La remained in the aqueous phase.

In Part 4.2.2., a semi-continuous process adapted from the existing counter-current process was introduced. The optimum conditions of selective stripping in the two-component systems were utilized for the design of a new process.

4.2.1 Optimization

4.2.1.1. Effect of extractant type and concentration

Four LREEs were extracted with five different types of acidic organophosphorus extractants. The feed solution consisted of 1000 ppm of La, Ce, Pr, and Nd, respectively, and the concentration of each extractant varied from 0.1M to 1M, as in the preceding two-component systems. The extraction percentages are presented in Figure 35.

The extraction percentages of all LREEs in the four-component system were lower than those in the two-component systems. This is because the total concentration of LREEs in the four-component system was twice that in the two-component systems, and many kinds of LREEs can create competitive conditions in the extraction reaction.

Because only La had to be left in the aqueous phase in the extraction stage of the final semi-continuous process, it was important to select an appropriate extractant type and concentration that can extract Ce, Pr and Nd selectively. Based on the findings in Figure 35, the most suitable extractant with high recovery and selectivity was PC88A. Moreover, PC88A is an economic efficient extractant and is widely used in the industries. Therefore, further experiments were conducted using 0.5M PC88A to identify the impact of various stripping factors on the stripping behavior of LREEs in the four-component system.

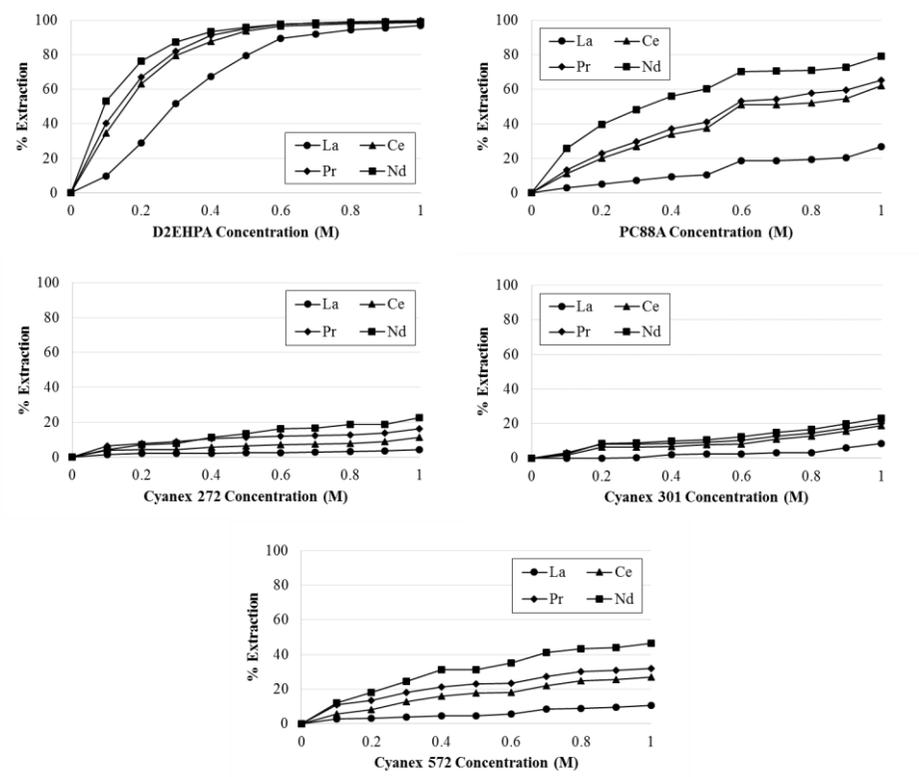


Figure 35. The extraction percentage of four LREEs using: (a) D2EHPA; (b) PC88A; (c) Cyanex 272; (d) Cyanex 301; and (e) Cyanex 572 (1000ppm of LREEs, respectively, extraction OA ratio = 1)

4.2.1.2. Effect of organic-phase-to-feed-solution volumetric ratio and McCabe-Thiele method for extraction

To comprehend the relationship between the OA ratio of the extraction stage and the extraction percentage, the organic-phase-to-feed-solution volumetric ratio was changed from 1/5 to 5 (Figures 36, 37). The extraction percentage of all LREEs increased as the OA ratio increased. This is because a larger portion of LREEs in the aqueous phase can make a complex with extractant if the OA ratio is higher.

Unlike two-component systems, many SF values were obtained from a four-component system. Because these SF values undergo different changes from each other, they are not a good criterion of optimum OA ratio in the four-component system. Therefore, the optimum OA ratio for the semi-continuous process is determined by a McCabe–Thiele diagram in the next section.

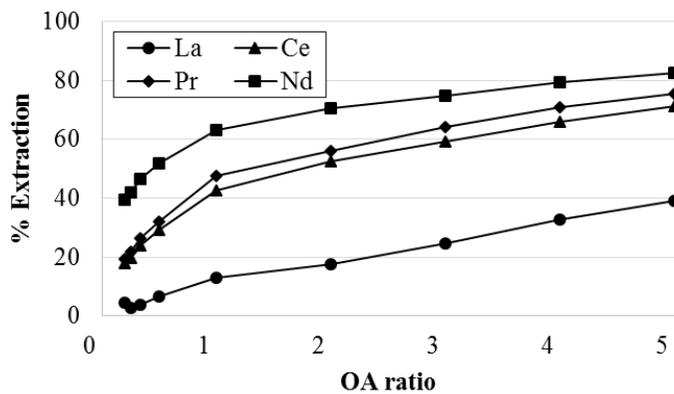


Figure 36. The extraction percentage of four LREEs with change of OA ratio (0.5M PC88A)

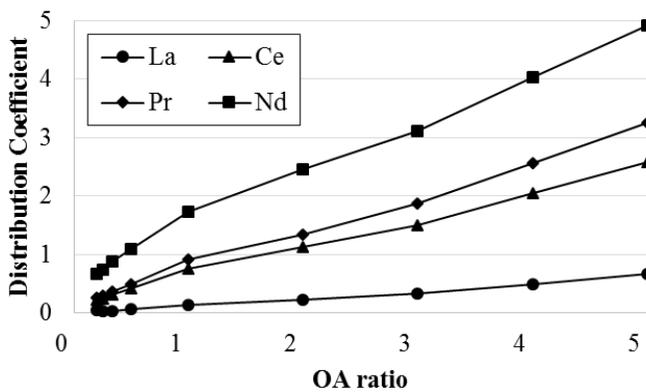


Figure 37. The distribution coefficient of four LREEs with change of OA ratio (0.5M PC88A)

The OA ratio is the most important factor that affects the recovery and purity of target elements in the continuous process. By analyzing the data on the OA ratio, a McCabe–Thiele diagram could be drawn to determine the OA ratio and number of stages of extraction(Figure 38).

The objective of the extraction stage is to keep La in the aqueous phase and only extract other LREEs. Therefore, the operating line should be located between the equilibrium line of La and that of Ce, Pr and Nd. By calculating the slope of the equilibrium line of La and Ce, the appropriate OA ratio range was 2.5 to 5. Consequently, it was expected that a solution containing a high purity of La would be obtained after four stages of extraction with an OA ratio of 4.

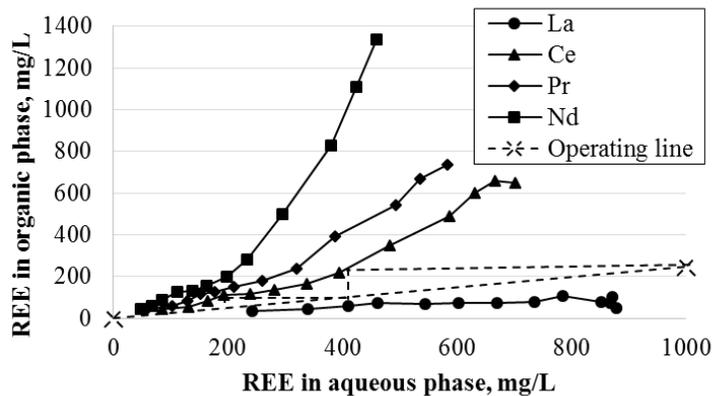


Figure 38. McCabe–Thiele diagram of the extraction of four LREEs (0.5M PC88A)

4.2.1.3. Effect of hydrochloric acid concentration of strip liquors

The selective stripping fell under the influence of the concentration of HCl. 0.01M to 0.1M of HCl was used for the stripping of four LREEs, and the results are illustrated in Figures 39 and 40. If a too-high concentration of HCl was used, the stripping percentages of all LREEs were too high to strip each element selectively. In contrast, if the concentration of HCl was too low, many stages were required, since the stripping percentages were insufficient. The stripping behavior of each LREE was almost the same in the two-component system and the four-component system.

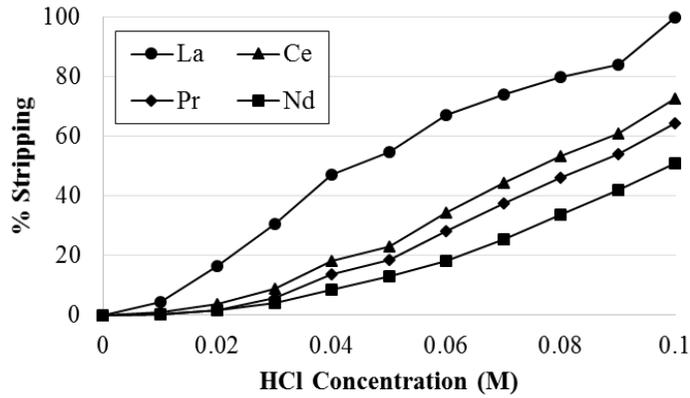


Figure 39. The stripping percentage of four LREEs with change of HCl concentration (stripping OA ratio = 1)

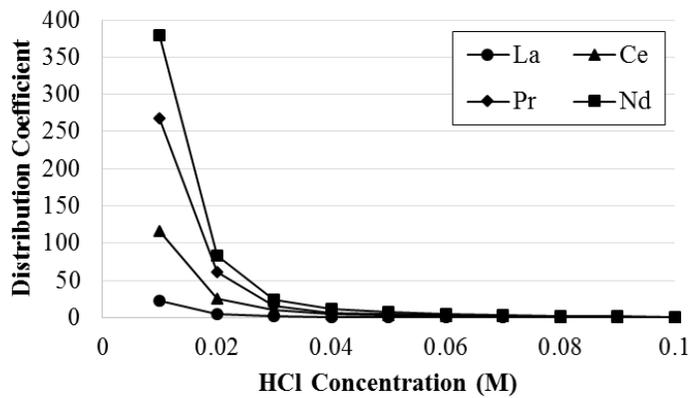


Figure 40. The distribution coefficient of four LREEs with change of HCl concentration (stripping OA ratio = 1)

4.2.1.4. Slope analysis method

The slope analysis method was adopted based on the experimental results of the effect of HCl concentration on the stripping. The graphs and trend lines are shown in Figure 41. As shown in this figure, the slopes were changed from 2 to 3 depending on the types of REEs, which means that the stoichiometric numbers of H^+ ions involved in the decomplexation of REEs and extractant were affected by the REEs types.

These phenomena can be explained by the hard and soft acids and bases (HSAB) theory developed by Pearson. The main point of this theory is that hard acids prefer to coordinate the hard bases, while soft acids prefer to bind to the soft bases. Atoms or ions that are less polarizable and have high charge are classes as “high” and a more polarizable atoms or ions as “soft”. This criteria for classification is relative, hence the degree of hardness and softness can be varied with systems. Since the chloride ion belongs to the borderline or soft base in the LREE and chloride system, the interaction of chloride ions with a softer acid makes them more stable. REEs are basically classified as a hard acid, though a lighter REE can have relatively softer properties. Therefore, chloride ions tend to make a complex with a lighter REE to make the system stable. This is why one mole of La needs two moles of H^+ ions and that of Nd needs 2.6 moles of H^+ ions for the decomplexation reaction.

In comparison with the two-REE component system, the slopes of the trend lines of all LREEs decreased. This means that the percentage of REEs making chloride complexes in the aqueous phase increased in this system. A

possible explanation is that the intercationic repulsion became greater in the four-component system. Therefore, more LREEs tried to produce a complex with Cl^- ions for electrical stability.

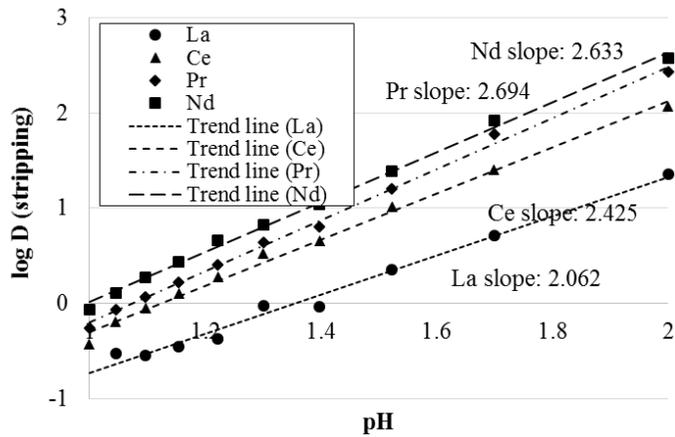


Figure 41. Relationship of distribution coefficients of four LREEs and the equilibrium pH of the strip liquor (stripping OA ratio = 1)

4.2.2 Semi-continuous counter-current process

4.2.2.1. The optimum conditions for extraction and selective stripping

Prior to the semi counter-current experiments, the optimum conditions for the extraction and selective stripping were tabulated in Table 3. The results of the extraction were obtained from Part 4.2.1., and the results of the stripping were gained from Part 4.1.

Table 3. The optimum conditions for extraction and selective stripping of four LREEs

	Extraction	Stripping of La, Ce	Stripping of Ce, Pr	Stripping of Pr, Nd
Extractant / Acid	0.5M PC88A	0.10M HCl	0.14M HCl	0.15M HCl
OA ratio	4	7:4	5:3	3:2
No. of stages	4	3	6	7

In the extraction, it was predicted that the high purity and recovery of La would remain in the aqueous phase through four stages extraction at an OA ratio of 4. The selective stripping of La and Ce could be achieved with three stages at an OA ratio of 7:4 with 0.10M HCl. Additionally, Ce and Pr could be stripped selectively in six stages at an OA ratio of 5:3 with 0.14M HCl. Finally, seven stages of stripping were needed to separate Pr and Nd at an OA ratio of

3:2 with 0.15M HCl.

Based on the optimum conditions, a process for the separation of La, Ce/Pr, and Nd was devised. At first, La remained in the aqueous phase after the extraction stage. After that, the extracted La strips with 0.10M HCl while Ce, Pr, and Nd remain in the organic phase with high purity. Finally, Ce and Pr strips with 0.15M HCl, and high purity of Nd remains in the organic phase.

4.2.2.2. The experimental results of a semi-continuous counter-current process

A semi-continuous counter-current process was designed in consideration of the optimum conditions of extraction and selective stripping. It is composed of three steps – extraction, the first selective stripping, and the second selective stripping.

The main objective of the extraction step is to keep La in the aqueous phase with high purity while most of the other three LREEs are extracted. For 0.5M PC88A, four stages of extraction were conducted at OA ratio of 4. The change of purity and remaining percentage of LREEs in the aqueous phase with the number of stages are represented in Figure 42 and 43. The initial purity of La was 25.9%, and it increased gradually with an increase of the number of stages. After four stages, La was left in the aqueous phase with 42.2% remaining and 89.8% purity. Although the extraction was carried out under the optimum conditions, about 57.8% of La was extracted with other LREEs. To this end, the selective stripping of La followed.

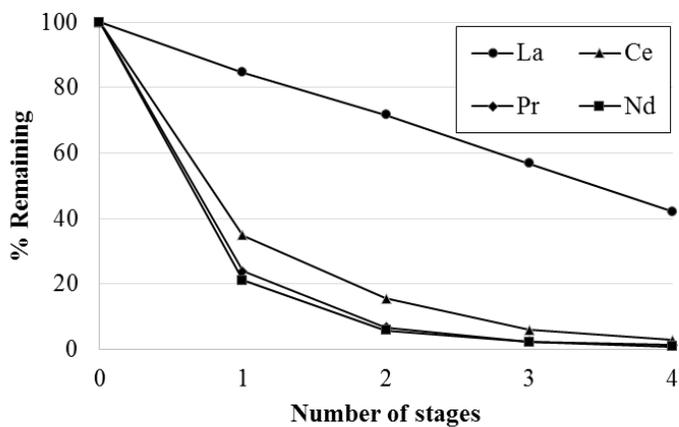


Figure 42. The remaining percentage of four LREEs in the aqueous phase with change of number of stages of extraction (0.5M PC88A, extraction OA ratio = 4, four stages)

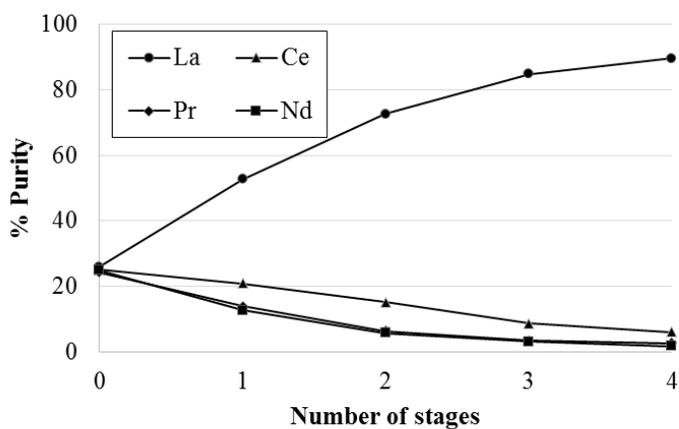


Figure 43. The purity of four LREEs in the aqueous phase with change of number of stages of extraction (0.5M PC88A, extraction OA ratio = 4, four stages)

The experimental conditions of the first stripping step were three stages at an OA ratio of 7:4 while using 0.10M HCl. Figures 44 and 45 plot the variation of remaining percentage and purity of LREEs in the aqueous phase versus the number of stages. Almost all of the extracted La stripped with HCl after three stages. The purity of La in the organic phase was less than 1%. Therefore, it could be concluded that only three LREEs except La were remained in the organic phase after the first selective stripping.

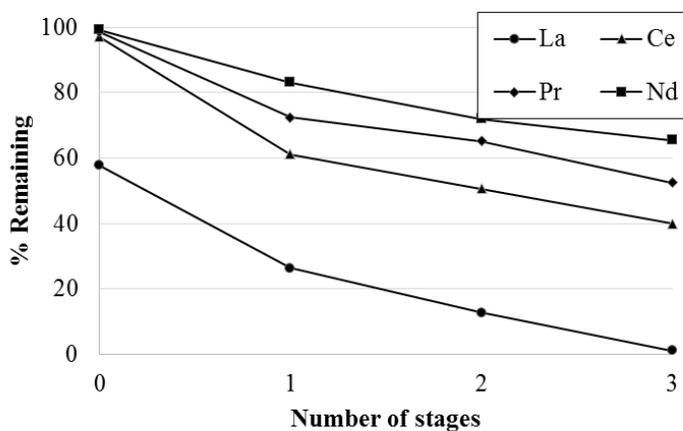


Figure 44. The remaining percentage of four LREEs in the organic phase with change of number of stages in the first stripping (0.10M HCl, stripping OA ratio = 7/4, three stages)

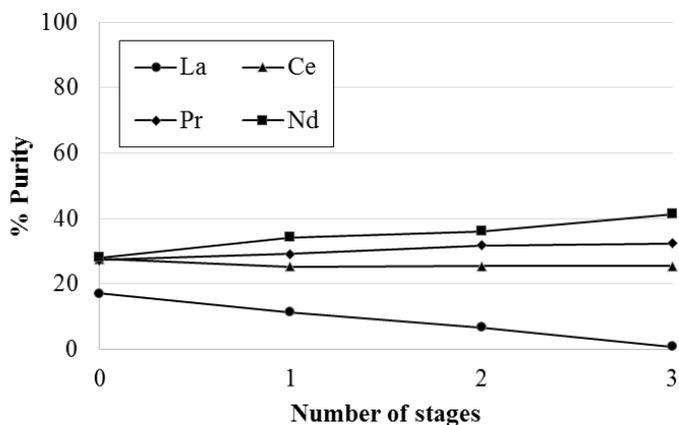


Figure 45. The purity of four LREEs in the organic phase with change of number of stages in the first stripping (0.10M HCl, stripping OA ratio = 7/4, three stages)

Finally, the second stripping was conducted to separate Nd from Ce and Pr. Seven stages of stripping at OA ratio of 3:2 with 0.15M HCl was needed to keep only Nd in the organic phase. In Figures 46 and 47, the remaining percentage and purity of Nd in the organic phase are shown. The remaining percentage decreased about 30% to 34.9% after seven stages, while the purity increased about 48% to 90.3%. At the end, 0.5M of HCl was used to strip extracted Nd in the organic phase.

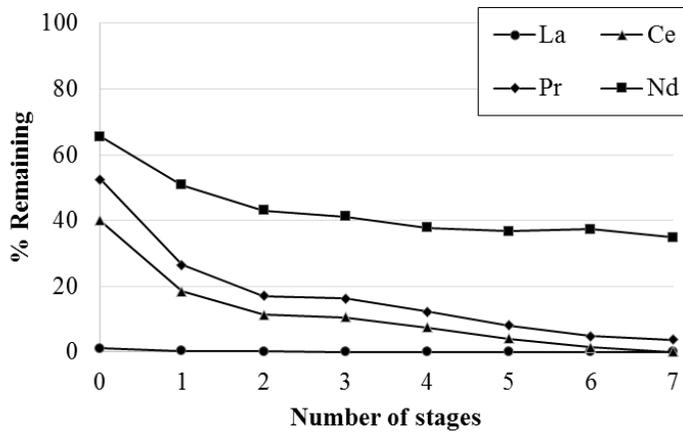


Figure 46. The remaining percentage of four LREEs in the organic phase with change of number of stages of in the second stripping (0.15M HCl, stripping OA ratio = 3/2, seven stages)

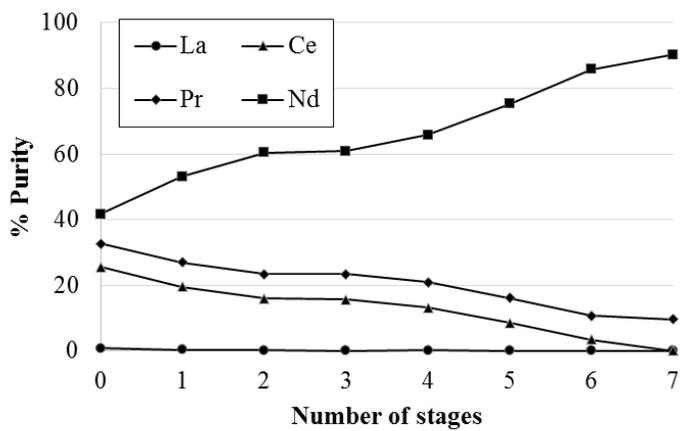


Figure 47. The purity of four LREEs in the organic phase with change of number of stages of in the second stripping (0.15M HCl, stripping OA ratio = 3/2, seven stages)

A flowsheet of overall process is represented in Figure 48. Consequently, La purity of 89.8% was obtained in the aqueous phase and Nd purity of 90.3% was obtained in the organic phase.

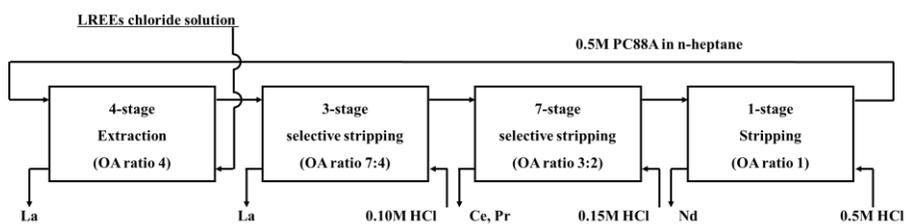


Figure 48. A flowsheet of novel semi-continuous counter-current process

Chapter 5. Conclusion

The selective stripping of light rare earth elements (LREEs) was studied for the design of a novel semi-continuous counter-current process. The optimization of stripping was carried out in the La/Ce, Ce/Pr, Pr/Nd, and a total of four LREE systems. Five types of acidic organophosphorus reagents were used as extractants for investigating the effects of extractant type, extractant concentration, LREE concentration ratio in the feed solution, acid concentration, and organic-phase-to-aqueous-phase (OA) volumetric ratio. Based on these optimization results, a new separation process including the selective stripping of LREEs was conducted.

The change of extraction percentage was studied using five acidic extractants (D2EHPA, PC88A, Cyanex 272, Cyanex 301, and Cyanex 572) at concentrations of 0.1M to 1M. The suitable extractants with high selectivity were PC88A, Cyanex 272, and Cyanex 572. PC88A was selected as an extractant for further stripping experiments due to its high recovery and selectivity, cost efficiency, and the degree of its use in industry.

The LREE concentration ratio in the feed solution did not have any impact on the stripping behavior of LREEs. The stripping percentage and SF remained constant at different LREE concentration ratios regardless of the LREE system.

Hydrochloric acid was used as the strip liquor. The increase of HCl concentration led to the increase of the stripping percentage of four LREEs. Since the separation efficiency can be decided by SF, the optimum HCl

concentration was determined where the maximum SF was obtained. The optimum HCl concentrations were 0.10M, 0.14M, and 0.15M in the La/Ce, Ce/Pr, and Pr/Nd systems, respectively.

The stripping percentage of LREEs changed significantly, affected by the OA volumetric ratio. The stripping percentage decreased with an increase of the OA ratio, since the amount of H^+ ions reacting with the LREE-extractant complex diminished. These experimental data were used to draw a McCabe–Thiele diagram of stripping. By plotting the LREE concentrations in the aqueous phase versus those in the organic phase, it was possible to determine the optimum OA ratio and the number of stages in the counter-current process.

The structure of the LREE-extractant complex and the chemical reaction equation of stripping were examined using the slope analysis method. Approximately three moles of H^+ ions participated in the stripping reaction with one mole of the LREE-extractant complex in the Pr/Nd systems, while 2.7 moles of H^+ ions reacted in the La/Ce and Ce/Pr systems. The difference of the stoichiometric number of H^+ ions participating in the stripping reaction can be explained by HSAB theory.

The optimization was also conducted in the four LREE-component system, and the results were compared with the data obtained in the two LREE-component systems. Through the McCabe–Thiele diagram of extraction, the conditions of extraction in the novel process were established.

A new semi-continuous counter-current process using selective stripping was designed based on the optimization results and McCabe-Thiele diagram. To separate LREEs effectively, the extraction and two steps of selective

stripping were applied to the counter-current process. In the extraction step, four stages of extraction were conducted at an OA ratio of 4 with 0.5M PC88A, maintaining 89.8% purity and 42.2% remaining of La in the aqueous phase while other LREEs were extracted. To remove the extracted La completely in the organic phase, the first selective stripping stage was adopted, three stages at an OA ratio 7:4 with 0.10M HCl. Seven stages of stripping at an OA ratio of 3:2 with 0.15M HCl was followed to strip extracted Ce and Pr, maintaining the high purity of Nd in the organic phase. After the process, 34.9% of Nd was left in the organic phase with 90.3% purity. Finally, 0.5M of HCl was used to strip Nd to the aqueous phase.

Although solvent extraction of LREEs are actively discussed and studied, sufficient research about stripping has not been performed. Since this is the first study about the selective stripping of four LREEs, it has significant implications. Because stripping is a requisite process after extraction, the efficiency of the overall process can be enhanced if the LREEs are separated not only in the extraction step, but also in the stripping step. Before a design of a process, the optimization of stripping conditions should be preceded, considering five factors including extractant type, extractant concentration, LREE concentration ratio in the feed solution, acid concentration, and OA volumetric ratio. After the optimization experiments, the possibility of the selective stripping of LREEs was verified and a process including selective stripping was designed in this research. In the future, the selective stripping of other REEs and the mechanism of the stripping reaction should be investigated.

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초 록

경희토류 원소는 현대 사회의 산업에서 널리 사용되고 있는 중요한 자원이다. 이 원소들은 유사한 화학적, 물리적 성질을 가지고 있기 때문에, 운영적 효율성과 경제성을 고려한 능률적인 분리 공정을 설계하는 것이 중요하다. 용매 추출법은 경희토류의 분리에 가장 많이 사용되는 방법이나, 수 십 단에서 수 백 단에 이르는 많은 추출 단수 및 탈거 과정에서 높은 농도의 산과 염기가 필요하다는 단점을 가지고 있다. 따라서 이 연구에서는 선택적 탈거를 통한 새로운 경희토류 분리 공정을 개발하였다.

네 종류의 경희토류 원소 계에 선택적 탈거를 도입하기에 앞서, 주기율표 상에서 인접하게 위치한 두 개의 경희토류 조합들에 대하여 탈거 과정에서의 최적화를 실시하였다. 추출제 종류, 추출제의 농도, 유입 용액에서 경희토류의 농도 비, 유기상과 수용액상의 부피 비, 그리고 산의 농도가 경희토류의 탈거에 미치는 영향을 조사하였으며, 이러한 변수들의 최적 조건을 각각의 두 경희토류 조합에 대하여 결정하였다. 추출제로는 0.5M PC88A가 선택되었으며, La 및 Ce 용액에 대하여 0.10M HCl을 사용해 유기상과 수용액상의 부피 비를 7:4로 고정한 상태에서 3단의 탈거를 실시하였을 때 탈거 과정을 통해 두 원소를 선택적으로 분리해 낼 수 있음을 확인하였다. 또한 Ce와 Pr 용액은 0.14M HCl로 유기상과 수용액상의 부피 비를 5:3으로 고정한 뒤 6단의 탈거를 진행하였을 때 가장 효율적으로 선택적 탈거가 진행되었으며, Pr과

Nd 용액에서는 0.15M HCl로 유기상과 수용액상의 부피 비를 3:2로 둔 상태에서 7단의 탈거를 실시하는 것이 최적의 조건임을 확인하였다.

경희토류와 추출제 간의 복합체 구조를 알아내고 추출 및 탈거 과정에서의 화학량론을 조사하기 위하여 기울기 해석 방법이 적용되었다. 그 결과, 경희토류는 유기상에서 염화 이온을 포함하며 PC88A 추출제와 복합체를 이루며, 원자번호가 작아 가벼운 희토류 원소일수록 추출제와의 복합체를 이룰 때 염화 이온을 더 많이 포함한다는 것을 알 수 있었다.

동일한 변수들에 대하여 네 개의 경희토류 계에서 탈거 과정의 최적화 조건을 알아보기 위한 실험을 진행하였으며, 그 결과를 두 개의 경희토류 계에서 얻은 값과 비교하였다. 또한, McCabe-Thiele 법을 사용하여 선택적 탈거를 위한 역류형 탈거 과정의 단수 및 유기상과 수용액상의 부피 비를 결정하였다.

최적화 실험 결과와 McCabe-Thiele 도표를 바탕으로, 선택적 탈거를 이용한 반연속성 역류 과정을 네 개의 경희토류 계에 도입하였다. 이 과정은 세 개의 단계로 구성되어 있으며, La를 수용액상에서 분리하기 위한 4단 추출, 추출된 La를 유기상으로 탈거시키기 위한 3단 탈거, 그리고 추출된 Ce와 Pr 을 탈거시키고 Nd만 수용액 상에 남기기 위한 7단 탈거가 그것이었다. 이 과정을 통해, 수용액 상에는 89.8% 순도의 La를 얻을 수 있었으며, 유기상에서는 90.3% 순도의 Nd를 획득할 수 있었다.

본 연구에서는 경희토류 계에서 탈거의 최적 조건을 찾아내었으며 선택적 탈거를 이용한 새로운 반연속성 역류 공정을

고안하였다. 실험 결과 경희토류는 추출 과정뿐만 아니라 탈거 과정에서도 선택적으로 분리가 됨을 확인할 수 있었다. 이 논문은 네 개의 경희토류 원소의 선택적 탈거에 관한 최초의 연구이므로, 이를 통해 경희토류의 선택적 탈거의 가능성을 확인하고 이를 이용한 공정을 고안하였다는 데에 큰 의의가 있다.

주요어: 탈거, 경희토류, 용매 추출, 역류 과정, 탈거 최적화

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