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Separation of Rare Earth Elements Using Flotation and Emulsion Separation based on Differences of Surface Properties

이멀젼 선별과 부유 선별을 이용한 표면 특성 차이에 따른 희토류 광물의 분리

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에너지시스템공학부

정 찬 기

Abstract

Separation of Rare Earth Elements Using Flotation and Emulsion Separation based on Differences of Surface Properties

Chan Ki Jeong

Department of Energy Systems Engineering

The Graduate School

Seoul National University

Rare earth elements (REEs) are important resources for many cutting-edge industries. To separate REEs from ore, flotation has commonly been used. However, flotation of REE minerals is very challenging because of low selectivity and efficiency. Therefore, in this study, an emulsion process is developed to separate REE minerals.

The major REE mineral of the studied ore samples is monazite. However, the content of iron oxide (goethite) of the ore was over the 50%. The value of d10, d50 and d90 of ore sample are 1.31 μm, 11.105 μm and 51.285 μm respectively.

Emulsion separation is a procees similar to flotation whereby surface properties are used to separate minerals. The only difference is that for the hydrophobic phase, oil is used instead of air. Since emulsion separation is the process for separating minerals according to their surface properties, collectors, depressants and activator are used, as they are in flotation.

Various factors are examined: the volume ratio of slurry to oil, pH, particle size, type of oil, type and dosage of collectors, and type and dosage of depressants. The optimum volume ratio of slurry to oil is 2:1, and the pH is adjusted to 9.5. Ore samples are separated with a micro sieve with a mesh of 10 μm to evaluate the effect of particle size. Fine particles are important to stabilize the emulsion and help coarse particles to become stabilized in the emulsion. However, there is no difference in grade between over and under products, which indicates that only surface properties affect the performance of emulsion separation. Kerosene is the best oil phase, and sodium oleate is selected as the collector. The dosage of the collector is determined based on the number of molecules of REEs in ore sample. Sodium silicate is the best depressant for the REE emulsion separation test.

To determine the optimum conditions for the emulsion separation process, the dosages of depressant (sodium silicate) and activator (calcium chloride) are varied. The original feed and deslimed feed are used for emulsion separation for comparison. The optimum condition for emulsion separation is 0.875x calcium chloride and 2.625x sodium silicate for the original feed. 75% of recovery is achieved. The value of TREE (emulsion)/TREE (water) was 1.465, and the value of TREE (emulsion)/TREE (feed) is 1.114. The performance of emulsion separation with the deslimed feed is poor compared with the original feed. This finding is attributed to the size effect and the low degree of liberation in the deslimed feed.

Keywords: Emulsion, Mineral separation, Flotation, Surface chemistry, Rare Earth Element
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Chapter 1. Introduction

1.1 Research Background

The rare earth elements (REEs), which include the 15 lanthanide elements (Z = 57 through 71) and yttrium (Z = 39), are so called because most of the elements were originally isolated in the 18th and 19th centuries as oxides from rare minerals. Because of their reactivity, the REEs were found to be difficult to be refined to pure metals. Furthermore, efficient separation processes did not developed until the 20th century because of the chemical similarity of REEs. Most REEs are not as uncommon in nature as the name implies. Cerium, the most abundant REE (Table 1), comprises a larger proportion of the earth’s crust than does copper or lead. Many REEs are more common than tin and molybdenum, and all but promethium are more common than silver or mercury (Castor et al., 2006). REEs are divided into two groups based on atomic weight: the light REEs are lanthanum through gadolinium (atomic numbers 57 through 64), and the heavy REEs comprise terbium through lutetium (atomic numbers 65 through 71). Yttrium, although light (atomic number 39), is included in the heavy REE group because of its similar chemical and physical properties (Van Gosen et al., 2014).

Table 1 REEs, atomic numbers, and abundances

Element	**Symbol**	**Atomic number**	**Upper Crust Abundance, ppm**	**Chondrite Abundance, ppm**
Yttrium	Y	39	22	
Lanthanum	La	57	30	0.34
Cerium	Ce	58	64	0.91
Praseodymium	Pr	59	7.1	0.121
Neodymium	Nd	60	26	0.64
Promethium	Pm	61		
Samarium	Sm	62	4.5	0.195
Europium	Eu	63	0.88	0.073
Gadolinium	Gd	64	3.8	0.26
Terbium	Tb	65	0.64	0.047
Dysprosium	Dy	66	3.5	0.30
Holmium	Ho	67	0.80	0.078
Erbium	Er	68	2.3	0.20
Thulium	Ym	69	0.33	0.032
Ytterbium	Yb	70	2.2	0.22
Lutetium	Lu	71	0.32	0.034

Currently, the dominant end uses for rare earth elements are for automobile catalysts, petroleum refining catalysts, phosphors in color television and flat-panel displays (e.g., cell phones, portable DVD players, and laptop computers), permanent magnets, rechargeable batteries for hybrid and electric vehicles, and numerous medical devices (see Table 2). There are important defense applications such as in jet fighter engines, missile guidance systems, antimissile defense, and satellite and communication systems. Permanent magnets containing neodymium, gadolinium, dysprosium, and terbium are used in numerous electrical and electronic components and new-generation generators for wind turbines. About 75% of permanent magnet production occurs in China. See Table 1 for selected end uses of rare earth elements (Humphries, 2013).

REEs are acquired from natural reserves in several countries. As shown in Table 3, about 37% of the REE reserves are concentrated in China. Also China produces more than 80% of REEs (USGS, 2017). Because the reserves were concentrated in China, the supply of REEs has been quite limited. In 2010, the price of REEs has risen dramatically due to both increased demand for rare earths products and a limited supply chain. There are several reasons for the skyrocketing rare earths prices from 2007 to 2011, and they all stem from policy decisions within China. These policy decisions resulted in a decrease in supply of rare earths to the outside world (Butler, 2014). Although the prices of REEs are not high, there is a risk from China. In Korea, there is no commercialized REE ore manufacturing process or plant. Therefore, the technologies of treating REEs are needed.

Table 2 Rare earth elements (lanthanides): selected end uses

LREE	Major Use	HREE	Major Use
Lanthanum	Hybrid engines, metal alloys	**Terbium**	Phosphors, permanent magnets
Cerium	Auto catalyst, petroleum refining, metal alloys	**Dysprosium**	Permanent magnets, hybrid engines
Praseodymium	magents	**Erbium**	Phosphors
Neodymium	Auto catalyst, petroleum refining, hard drives in laptops, headphones, hybrid engines	**Yttrium**	Red color, fluorescent lamps, ceramics, metal alloy agent
Samarium	Magnets	**Holmium**	Glass coloring, lasers
Europium	Red color for television and computer screens	**Thulium**	Medical x-ray units
		Lutetium	Catalysts in petroleum
		Ytterbium	Lasers, steel alloys
		Gadolinium	Magnets

Table 3 World mine production and reserves (Unit : Metric ton) (USGS, 2017)

	Mine production		**reserves**
	2015	**2016**	
United states	5,900	-	1,400,000
Australia	12,000	14,000	3,400,000
Brazil	880	1,100	22,000,000
Canada	-	-	830,000
China	105,000	105,000	44,000,000
Greenland	-	-	1,500,000
India	1,700	1,700	6,900,000
Malaysia	500	300	30,000
Malawi	-	-	136,000
Russia	2,800	3,000	18,000,000
South Africa	-	-	860,000
Thailand	760	800	NA
Vietnam	250	300	22,000,000
world total	130,000	126,000	120,000,000

REEs are found, usually several together, in a variety of accessory minerals, such as phosphates, carbonates, fluorides and silicates, and are especially common in pegmatites, granites and related metamorphic and igneous rocks. They rarely form more continuous ore bodies. Some phosphate minerals may be rich in REEs. In xenotime, Y ions are often replaced by lanthanides with an emphasis on HREEs. Locally, monazite even forms bodies of economic importance (Forster, 1998), and apatites (fluoro-phosphates) may also contain REEs (Bauluz et al., 2000; Braun et al., 1993).

Other REE-containing minerals are fluorites and fluoro-carbonates, which often contain Ba or Ca (Hong et al., 1999b). Of commercial importance is bastnaesite. The carbonatite pyrochlore may be enriched in LREEs (Tyler G, 2004).

The principal commercial sources of Rare earth element oxides (REOs) are monazite (a phosphate mineral of Ce and other LREEs; general formula: $(REE)PO_3$), bastnaesite (carbonate-fluoride minerals, e.g., $LaCO_3F$), xenotime (major components are YPO_4 and other HREEs) and loparite. Because it contains considerable amounts of radioactive thorium, loparite is no longer an attractive source of REEs. Most REEs are found in only a few minerals (bastnaesite, monazite and xenotime), and flotation methods are used to produce REOs from these ores; other REOs (50%) are produced from heavy mineral sands and gangue with physical concentration methods or using a cationic collector, such as fatty acids or alkyl sulfate and phosphate esters (Massari and Ruberti, 2013).

The principle separation processes employed in the beneficiation of rare earth minerals include gravity separation, magnetic separation, electrostatic separation and froth flotation. Rare earth minerals are good candidates for gravity separation because they have relatively high specific gravities (4–7) and are typically associated with gangue material that is significantly less dense. The most commonly utilized application of gravity separation is in monazite beneficiation from heavy mineral sands. Magnetic separation techniques are also commonly used separation step in rare earth mineral beneficiation to eliminate highly magnetic gangue, or to concentrate the desired paramagnetic REE-bearing minerals, such as monazite or xenotime. Electrostatic separation techniques are typically only used when alternative processing techniques will not suffice, because the comminution steps in mineral processing flowsheets are generally wet processes, and the energy requirements to drive off all moisture prior to electrostatic separation can be significant. Froth flotation is commonly applied in the beneficiation of rare earth ores because it can be used to process a wide range of fine particle sizes, and because the process can be tailored to the unique mineralogy of a given deposit (Jordens et al., 2013).

1.2 Recent Studies

Nonetheless, flotation of REE minerals is not exempt from challenges, which are reflected in discrepancies in REE minerals compositions or in high similarity for REE minerals associated with gangue minerals, from the standpoint of surface chemistry. Therefore, research on REE mineral froth flotation has received greater attention than other beneficiation techniques. One focus of these investigations is discovering collectors that can improve REE minerals flotation. Thus, the effectiveness of various collectors bearing carboxylic, hydroxamic and phosphorous acid functional groups for bastnaesite and monazite REE minerals have been studied in recent years (Azizi et al., 2016).

In general, oxhydryl collectors (e.g., carboxylates, phosphoric acid esters and hydroxamates) have been the focus of rare earth mineral flotation studies (Zhang, X et al., 2013). These oxhydryl collectors have two oxygen atoms, which are responsible for bonding with metal cations. Carboxylates (e.g., fatty acids, oleates and tall oils) are the most widely used industrial collectors; however, they have poor selectivity toward rare earth elements minerals (Espiritu, 2017). Hydroxamates have attracted the interest of many researchers because of their selectivity and efficiency. Various flotation studies have demonstrated that this collector is more selective than carboxylates (Fuerstenau, 2013; Zhang, X et al., 2013), which is attributed to its formation of more stable chelates with rare earth cations than with alkaline earth cations (Fuerstenau, 2005).

In addition, the role of the depressant is very important for the flotation test because of the efficiency of flotation, conducted only with collector is very low. The type of depressant differs depending on the gangue minerals to be depressed. For the flotation tests to extract rare earth elements minerals, the major gangue minerals are carbonates, silicates (e.g., quartz, feldspar and clay minerals), and iron-bearing minerals (e.g., magnetite, hematite). Sulfuric acid (H_2SO_4) is effective for depressing carbonate minerals, and helps to separate calcium and magnesium carbonates from the ore (Liu et al., 2017). The application of sodium silicate as a depressant and dispersant agent in the flotation of apatite from iron-bearing minerals has been studied (Tohry and Ali, 2016). In addition, sodium silicate is frequently used as depressant in phosphate flotation to depress siliceous gangue and carbonates (Arantes and Lima, 2013). The starch molecules depress both the iron oxide and silica particles, but the amines, because of their large radical size and high electronegativity, ionize in water and react with the silica particles preferably at slightly alkaline pH (Kar et al., 2013).

An emulsion is a mixture of two normally immiscible phases (e.g., oil and water) that consists of small droplets of one liquid dispersed throughout the second, continuous liquid. The contact between the dispersed phase and the continuous phase is thermodynamically unfavorable, and common emulsions are inherently unstable. Emulsions can be kinetically stabilized by the absorption of an emulsifier (surfactant) at the oil/water (O/W) contact surfaces, which lowers interfacial tension, and thus reduces the extent of coalescence caused by the effects of repulsion and viscosity (Ye et al., 2017). In recent decades, numerous studies have investigated methods and surfactants for stabilizing emulsions. Pickering emulsions are emulsions stabilized by solid particles in place of surfactants. Unlike surfactants, once solid particles become attached to the surfaces of dispersed droplets in Pickering emulsions, they are irreversibly anchored therein under quiescent conditions (Zeng et al., 2017). However, no studies have been conducted on the application of Pickering emulsions to separate minerals based on different surface property, as in flotation.

1.3 Research Purpose

In general, the particle size of an ore is one of the dominant factor that influence efficiency of separation. For flotation, even when the minerals in an ore are fully liberated, the maximum size depends the requirements of selectivity. If the selectivity is high, the region for high recoveries may extend to very coarse sizes (300 μm or more), but if the selectivity is low, particles above 40–50 μm in size may become difficult to recover (Trahar, 1981). As the maximum size of feed samples is about to 50 μm, it is difficult to increase recovery even if selectivity is high, and fine minerals separation should be focused on instead.

In this study, flotation and emulsion separation processes are conducted to concentrate REEs. As the separation efficiency and selectivity of REE ores with traditional separation processes, including flotation, was very low, a new process (emulsion separation) was developed. To increase the selectivity and determine the optimum condition, emulsion separation tests is conducted.

The optimum conditions of emulsion separation testing for REE ores are investigated based on several factors: the volume ratio of slurry to oil, pH, dosage and type of collectors, dosage and type of depressant, and the type of oil. For the comparison tests, flotation tests are conducted for several conditions.

To compare the efficiency and selectivity of REEs in the products, the ratios of REE grade between products, tail and feed are calculated: the ratios of total REE (TREE) grades of product and tail (TREE(product)/TREE(tail), distribution coefficient) and ratios of total REE grade of product and feed (TREE(product)/TREE (feed)). To determine the optimum conditions for emulsion separation, recovery and ratio of REE grade are analyzed.

Chapter 2. Theoretical background

2.1 Flotation

Flotation is a physico-chemical separation process that utilizes the difference in surface properties of valuable minerals and the unwanted gangue minerals. The theory of froth flotation is complex, involving three phases (solids, water, and froth) with many sub-processes and interactions, and is not fully understood (Napier-Munn and Wills, 2006).

The attachment of valuable minerals to air bubbles is the most important mechanism and accounts for the majority of particles that are recovered in the concentrate. Although true flotation is the dominant mechanism for the recovery of valuable minerals, the separation efficiency between valuable minerals and gangue also depends on the degree of entrainment and physical entrapment. Unlike true flotation, which is chemically selective based on mineral surface properties, both gangue and valuable minerals alike can be recovered through entrainment and entrapment. In industrial flotation plant practice, entrainment of unwanted gangue can be common, and a single flotation stage is therefore uncommon (Napier-Munn and Wills, 2006).

Most minerals are not water-repellent in their natural state, and flotation reagents must be added to the pulp. The most important reagents are the collectors, which adsorb onto mineral surfaces, which renders them hydrophobic (or aerophilic) and facilitates bubble attachment. The frothers help maintain a reasonably stable froth. Regulators are used to control the flotation process; these reagents either activate or depress mineral attachment to air bubbles and are used to control the pH of the system (Napier-Munn and Wills, 2006).

Figure 1 shows the apparatus of the flotation. Flotation experiments were carried out using a 500 mL laboratory Denver Flotation Machine with 20% solids concentration. The pH of flotation was adjusted to about 9.5 with sodium hydroxide and hydrochloric acid. The oleic acid, sodium oleate, MIBC, sodium silicate and starch were added for flotation. Based on previous research on flotation tests of REE minerals with an anionic collector, pH 9–10 is optimal (Abaka-Wood et al., 2017; Zhang, W et al., 2017, Tranvik et al., 2017). An inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8300) was used to determine the concentrations of REEs (Figure 2).

2.2 Emulsion Separation

Emulsion separation is a separation process based on a principle similar to that of flotation that utilizes differences in surface properties. The difference between flotation and emulsion separation is simply based on the type of hydrophobic medium. In the case of flotation, bubbles (air) are the hydrophobic medium; however, oil is used as the hydrophobic medium in emulsion separation. When the emulsion is formed, hydrophilic minerals remain in the water layer, whereas hydrophobic minerals move to the emulsion layer. Because the density of the emulsion is smaller than that of the water layer, after the emulsion is formed, the two layers are separated by gravity.

As in flotation, when reagents are not added, the separation efficiency of valuable minerals from unwanted gangue is low. To increase the efficiency of emulsion separation, reagents such as collectors, depressants, activators and pH regulators must be added. The collectors help minerals move to the emulsion layers by rendering surfaces hydrophobic. The regulators (e.g., depressants, activators, and pH regulators) make collector action more selective toward certain minerals by intensifying or reducing the water repellent effect on the mineral surface.

Apparatus of emulsion separation is shown in Figure 1. To form an emulsion, slurry and oil were treated by stirring and sonication. Collectors, depressant, activator and pH regulators were added to the slurry. The solid concentration of the slurry was 10% of the mass, and the volume ratio of slurry to oil was varied. Mixtures of oil and slurry were stirred for 15 min at a rotor speed of 1,000 rpm. After the mixture of oil and slurry was stirred, it was then sonicated (Sonics & Materials, Inc., USA, VC 505) at 30% amplitude for 5 min (10,000 J). After sonication, the mixture was given 1 hour of treat time to make easier to separate the emulsion layer and water layer. The two layers could be separated using separatory funnel because of the difference in density. The water layer stays in the lower part of the mixture, and emulsion layer moves to the upper part. The concentrations of

REEs were then determined via ICP-OES.

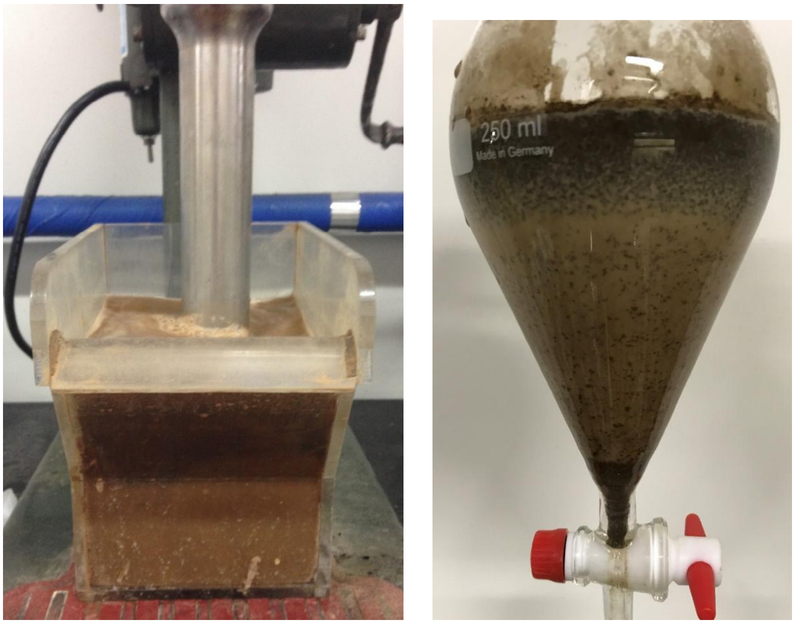


Figure 1 Apparatus of (a) flotation and (b) emulsion separation

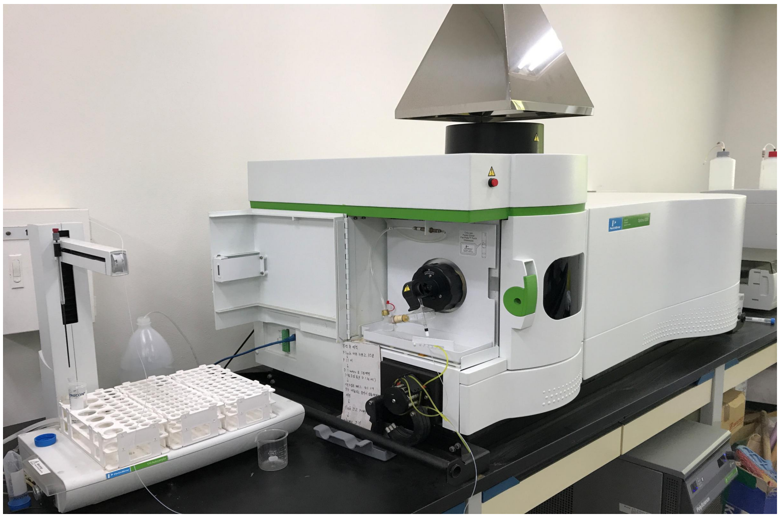


Figure 2 Inductively coupled plasma optical emission spectrometer

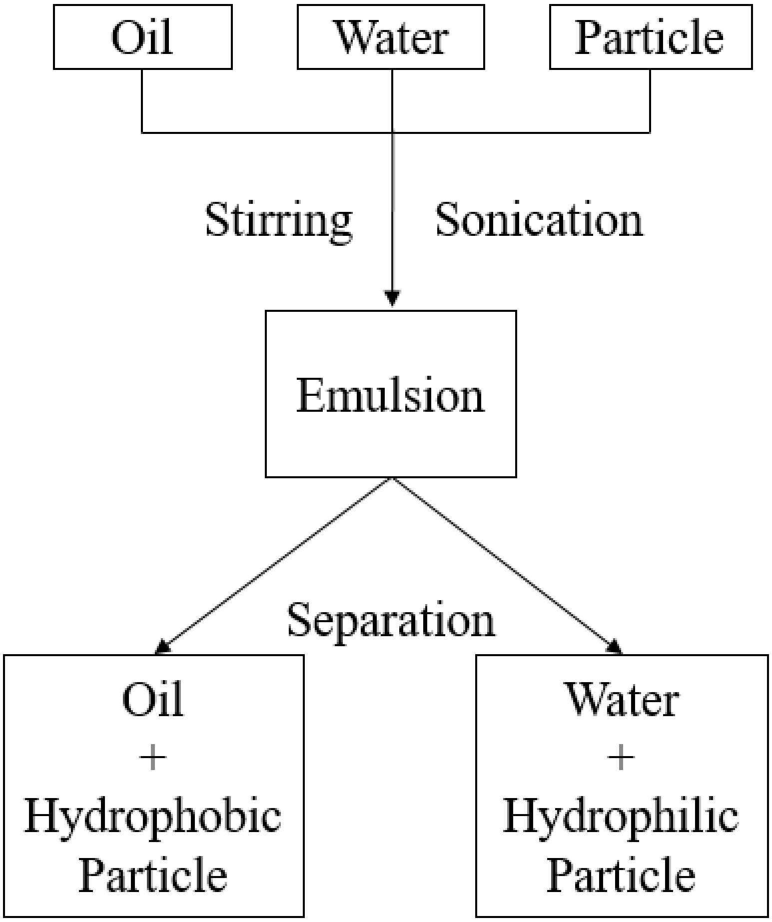


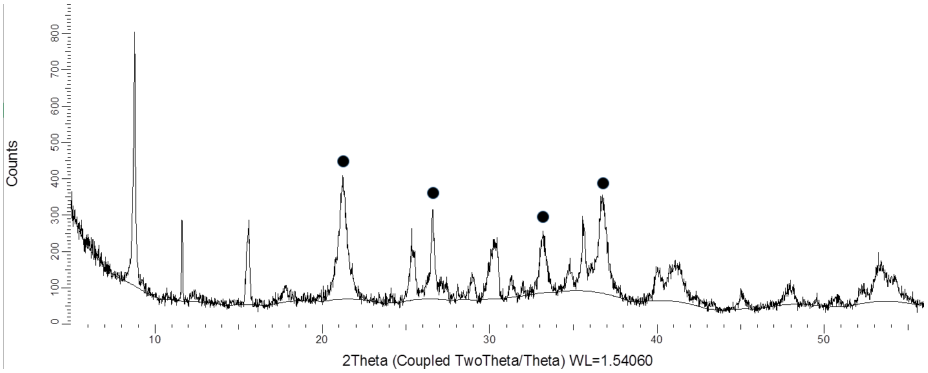
Figure 3 Schematic diagram of emulsion separation

Chapter 3. Materials and methods

3.1 Ore sample

Minerals were analyzed with XRD and XRF. The XRD patterns were detected using a conventional instrument (Bruker, D8 Advance with Davinci) with a 2 theta range from 5° to 90°. Figure 4 shows the XRD results for the ore sample. It shows that iron is present in the form of goethite. Because the amount of REE minerals is low, the XRD data were reanalyzed focusing on REE phosphate. Figure 5 shows the results of XRD for REE phosphate. Most of the REEs exist as monazite, and some are substituted for Ca in apatite. Table 4 shows the XRF results. The XRF results were collected using a S8 Tiger spectrometer by Bruker. Iron content was very high, more than 50%, and the total REE oxide grade was about 4%. Ce was the most abundant REE, followed in order by La, Nd and Y.

The sizes of samples were analyzed using a Mastersizer 2000 device (Malvern). The cumulative size distribution of the feed sample is shown in Figure 6. The values of d10, d50 and d90 were 1.31 μm, 11.105 μm and 51.285 μm, respectively.



Pattern #	Compound Name	Formula	System
PDF 00-055-0539	Barium Strontium Titanium Oxide	(Ba0.70 Sr1.30) Ti O4	Orthorhombic
PDF 01-080-4889	Waylandite	(Bi0.49 Sr0.28 Ca0.23) H0.31 Al3 ((P0.90 Si0.10) O4)2 (O H)6	Rhombo.H.axes
PDF 01-080-8465	Chlor cesium holmium selenide	(Cl Cs6) (Ho21 Se34)	Monoclinic
PDF 00-059-0344	Al-substituted goethite	(Fe0.93 Al0.07) O (O H)	Orthorhombic
PDF 00-055-0176	Silver Manganese Hafnium Molybdenum Oxide	Ag4 Mn2 Hf (Mo O4)6	Orthorhombic
PDF 00-051-0060	lithium iodoethanoate, lithium iodoacetate	C2 H2 I Li O2	Monoclinic
PDF 00-060-1516	Muscovite-2M1	K Al2 (Al Si3 O10) (O H)2	Monoclinic
PDF 01-084-1550	Sodium Zirconium Carbide Chloride	Na.5 Zr6 C Cl15	Cubic

Figure 4 XRD data of ore sample (● : Goethite)

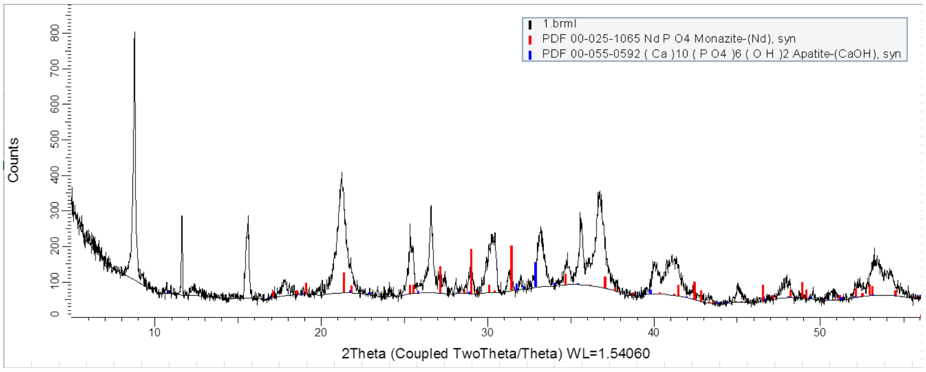


Figure 5 XRD data of ore sample focusing REE phosphate

Table 4 XRF results of ore sample

Formula	Concentration(%)	Formula	Concentration(%)
Fe_2O_3	53.30	Nd_2O_3	0.61
MnO	9.43	SrO	0.60
SiO_2	7.77	Cl	0.59
Al_2O_3	6.19	Nb_2O_5	0.39
P_2O_5	5.09	ZnO	0.29
TiO_2	4.26	V_2O_5	0.14
CaO	2.20	Y_2O_3	0.14
CeO_2	2.19	ZrO_2	0.14
BaO	2.00	MoO_3	0.07
MgO	1.43	ThO_2	0.03
La_2O_3	0.93	PbO	0.03
Na_2O	0.80	NiO	0.01
K_2O	0.73	CuO	0.01
SO_3	0.65		

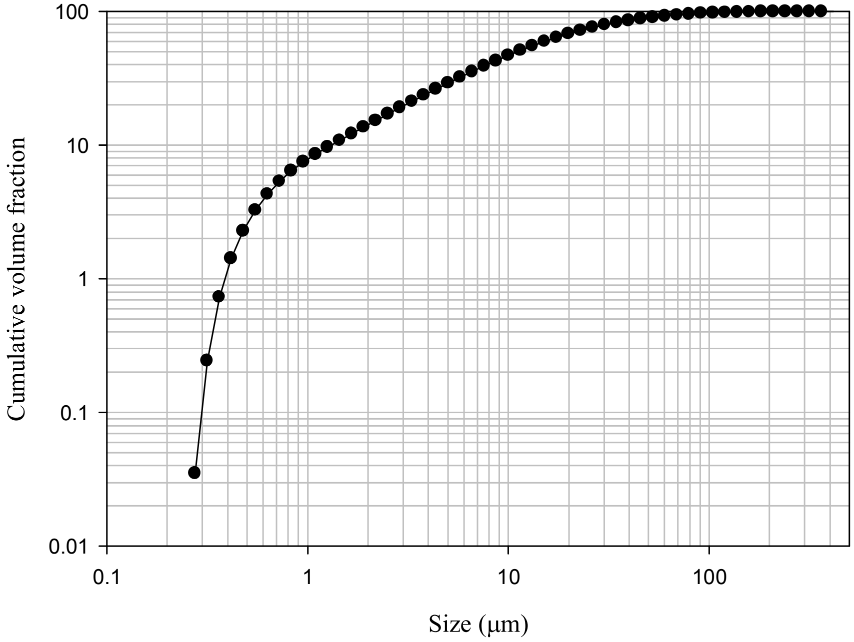


Figure 6 Cumulative size distribution of REE ore sample

3.2 Reagents and chemicals

Oleic acid (extra pure) was purchased from Samchun Pure Chemical Co. Ltd. Anhydrous calcium chloride, sodium silicate (9–10% Na_2O, 28–30% SiO_2), starch (corn, chemical pure), and kerosene (chemical pure) were purchased from Daejung Chemicals & Metals Co. Ltd. Salicylhydroxamic acid (99%), MIBC (98%), and sodium oleate ($\geq$ 82%) were purchased from Sigma-Aldrich. Oleic acid, sodium oleate and salicylhydroxamic acid were used as collectors, and MIBC was used as a frother. Sodium silicate and starch were used as depressants. Calcium chloride was used as the activator. Hydrochloric acid and sodium hydroxide were used to regulate pH. Kerosene was the hydrophobic medium of emulsion separation.

Chapter 4. Results and discussion

4.1 Flotation test

Flotation tests were conducted for specific conditions to compare with the results of emulsion separations. Tables 5 and 6 show the concentrations and recoveries of important elements of the froth product and tail respectively when 2 ml of oleic acid, 1 ml of MIBC and 2,700 g/ton of starch. The concentrations of elemental oxides were analyzed via XRF. The yield of froth was 50.1%, and the mean recovery of REEs was about to 53%. The value of TREE (froth)/TREE (tail) was 1.124, and the value of TREE (froth)/TREE (feed) was 1.071, which indicates that there are no differences in the grade of REEs and recovery of REEs between froth and tail. The selectivity of the flotation test was so low that separation could be considered negligible.

Table 7 and 8 shows the concentrations and recoveries of important elements for the flotation product when 2 ml of oleic acid, 1 ml of MIBC and 2,000 g/ton of sodium silicate. The yield of forth was 39.5% and mean recovery of REEs was about to 43%. The value of TREE (froth)/TREE (tail) was 1.129, and the value of TREE (froth)/TREE (feed) was 1.073. The ratio value was similar with the value of flotation test of starch used. The selectivity of the flotation test was low that separation could be considered negligible.

Table 5 XRF results of the flotation test (2ml oleic acid, 1ml MIBC, 2700g/ton starch)

Concentration	**Froth**	**Tail**	**Reconstituted**
Mass (%)	50.1	49.9	
Fe_2O_3 (%)	53.9	54.4	54.15
CaO (%)	2.3	2.15	2.23
CeO_2 (%)	2.27	2.07	2.17
La_2O_3 (%)	1.01	0.85	0.93
Nd_2O_3 (%)	0.64	0.572	0.61
Y_2O_3 (%)	0.15	0.13	0.14

Table 6 Recovery of the flotation test (2ml oleic acid, 1ml MIBC, 2700g/ton starch)

Recovery	**Froth**	**Tail**
Mass (%)	50.1	49.9
Fe_2O_3 (%)	49.9	50.1
CaO (%)	51.8	48.2
CeO_2 (%)	53.1	46.9
La_2O_3 (%)	54.6	45.4
Nd_2O_3 (%)	52.9	47.1
Y_2O_3 (%)	54.6	45.4

Table 7 XRF results of the flotation test (2ml oleic acid, 1ml MIBC, 2000g/ton sodium silicate)

Concentration	**Froth**	**Tail**	**Reconstituted**
Mass (%)	39.5	60.5	
Fe_2O_3 (%)	49.5	56.5	53.74
CaO (%)	2.43	2.05	2.20
CeO_2 (%)	2.25	2.09	2.15
La_2O_3 (%)	1.03	0.86	0.93
Nd_2O_3 (%)	0.68	0.56	0.61
Y_2O_3 (%)	0.15	0.13	0.14

Table 8 Recovery of the flotation test (2ml oleic acid, 1ml MIBC, 2000g/ton sodium silicate)

Recovery	**Froth**	**Tail**
Mass (%)	39.5	60.5
Fe_2O_3 (%)	36.4	63.6
CaO (%)	43.6	56.4
CeO_2 (%)	41.3	58.7
La_2O_3 (%)	43.9	56.1
Nd_2O_3 (%)	44.2	55.8
Y_2O_3 (%)	43.0	57.0

4.2 Emulsion Separation

4.2.1 Volume ratio of slurry and oil

The volume ratio of slurry and oil was varied to find the most appropriate conditions for emulsion separation. No reagents were added to the slurry. Tables 9 and 10 show the results of the emulsion separation test when the volume ratio of slurry to oil was 1:2. Tables 11 and 12 show the results of the emulsion separation test when the volume ratio of slurry to oil was 1:1. The results of the emulsion separation test of the volume ratio of slurry to oil of 2:1 is presented in Tables 13 and 14. Figure 7 shows the concentration of important elements and recovery of REEs and other elements.

When the volume ratio was 1:2, the yield of emulsion layer products was 48.4%, and the grade of REEs was lower than that of the water layer products and that of the feed. The value of TREE (emulsion)/TREE (water) was 1.157, and the value of TREE (emulsion)/TREE (water) was 1.075, which indicates that REEs were concentrated in the emulsion layer. However, when the volume ratio was 1:1, the yield of emulsion layer products was 48.4%, which is similar to the results for the 1:2 ratio; REEs were moved to the water layer. The value of TREE (emulsion)/TREE (water) was 0.876, and the value of TREE (emulsion)/TREE (feed) was 0.9. The results of the emulsion separation test when the volume ratio was 2:1 indicates that the most appropriate volume ratio is 2:1. The value of TREE (emulsion)/TREE (water) was 1.189, and the value of TREE (emulsion)/TREE (feed) was 1.107. For further emulsion separation tests, the volume ratio was fixed at 2:1.

Table 9 Concentrations of important elements in the water and emulsion layer products (volume ratio of slurry:oil = 1:2, pH 9.5)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	51.6	48.4	
Ca (ppm)	14173	14084	14129
Fe (ppm)	277882	280152	278980
Ce (ppm)	9743	11294	10493
La (ppm)	5722	6524	6110
Pr (ppm)	1727	2240	1975
Nd (ppm)	3211	3532	3366
Y (ppm)	1009	1177	1090

Table 10 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 1:2, pH 9.5)

	Water	**Emulsion**
Mass (%)	51.6	48.4
Ca (%)	51.8	48.2
Fe (%)	51.4	48.6
Ce (%)	47.9	52.1
La (%)	48.3	51.7
Pr (%)	45.1	54.9
Nd (%)	49.2	50.8
Y (%)	47.8	52.2

Table 11 Concentrations of important elements in the water and emulsion layer products (volume ratio of slurry:oil = 1:1, pH 9.5)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	51.2	48.8	
Ca (ppm)	14125	14841	14474
Fe (ppm)	263914	290788	277029
Ce (ppm)	11052	10215	10644
La (ppm)	6414	5735	6083
Pr (ppm)	2273	1626	1957
Nd (ppm)	3740	3115	3435
Y (ppm)	1252	979	1119

Table 12 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 1:1, pH 9.5)

	Water	**Emulsion**
Mass (%)	51.2	48.8
Ca (%)	50.0	50.0
Fe (%)	48.8	51.2
Ce (%)	53.2	46.8
La (%)	54.0	46.0
Pr (%)	59.5	40.5
Nd (%)	55.7	44.3
Y (%)	57.3	42.7

Table 13 Concentrations of important elements in the water and emulsion layer products (volume ratio of slurry:oil = 2:1, pH 9.5)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	60.9	39.1	
Ca (ppm)	14335	14090	14239
Fe (ppm)	284550	271550	279467
Ce (ppm)	9735	12035	10634
La (ppm)	5914	6550	6163
Pr (ppm)	1850	2290	2022
Nd (ppm)	3289	3805	3491
Y (ppm)	1008	1250	1103

Table 14 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5)

	Water	**Emulsion**
Mass (%)	60.9	39.1
Ca (%)	61.3	38.7
Fe (%)	62.0	38.0
Ce (%)	55.7	44.3
La (%)	58.4	41.6
Pr (%)	55.7	44.3
Nd (%)	57.4	42.6
Y (%)	55.7	44.3

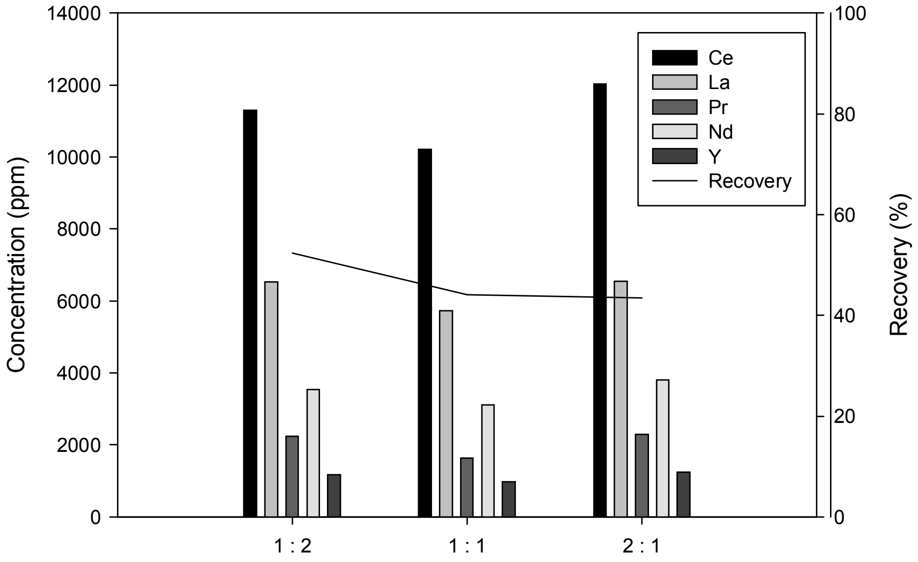


Figure 7 Concentrations and recovery of REEs for various volume ratio (pH 9.5)

4.2.2 Slurry pH

Emulsion Separation tests were conducted with various pH levels (4, 7, 9.5, 11) with a volume ratio of slurry to oil of 2:1. Emulsion was not generated when the pH was 4 or 7. Tables 13 and 14 show the results of emulsion separation when the pH was 9.5. The results of the emulsion separation test of pH 11 are presented in Tables 15 and 16.

When the pH was 11, the yield of emulsion layer products was 39.8%, and the grade of REEs was higher than that of the feed and water layer products. The value of TREE (emulsion)/TREE (water) was 1.132, and the value of TREE (emulsion)/TREE (feed) was 1.10, which were lower than the results for pH 9.5. Based on these results, when the pH was 9.5, the highest value of separation efficiency and selectivity was achieved. This finding is comparable to those of flotation research, where pH 9.5 has been found to be optimal.

Table 15 Concentrations of important elements in the water and emulsion layer products (volume ratio of slurry:oil = 2:1, pH 11)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	60.2	39.8	
Ca (ppm)	14285	13690	14048
Fe (ppm)	287200	271850	281091
Ce (ppm)	9960	11335	10507
La (ppm)	5760	6460	6039
Pr (ppm)	1820	2085	1925
Nd (ppm)	3240	3690	3419
Y (ppm)	1030	1135	1072

Table 16 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 11)

	Water	**Emulsion**
Mass (%)	60.2	39.8
Ca (%)	61.2	38.8
Fe (%)	61.5	38.5
Ce (%)	57.1	42.9
La (%)	57.4	42.6
Pr (%)	56.9	43.1
Nd (%)	57.0	43.0
Y (%)	57.9	42.1

4.2.3 Effect of particle size

As shown in Figure 6, about half of all particles are less than 11 μm in size. To evaluate the effect of size on emulsion separation, feed was separated with a micro sieve with a mesh size of 10 μm using a micro sieve shaker (ANALYSETTE 3 PRO Vibratory Sieve Shaker, FRITSCH). The size distributions of the over products, under products and feed are shown in Figure 8. The values of d10, d50 and d90 of the over products were 2.282 μm, 15.99 μm and 58.04 μm, respectively. The values of d10, d50 and d90 of the under products were 0.849 μm, 5.041 μm and 14.594 μm, respectively. Although separation by size was not perfectly achieved, differences in size were observed. Table 17 shows the concentration of elements of the under products and over products. The differences in concentration between the under products and over products were about 4%, and could be considered negligible. This finding indicates that there are no differences in concentration with changes in size.

As a result of emulsion separation of the under products, most of the particles moved to the emulsion layer. However, most particles moved to water layer for the emulsion separation test of the over products. It seems likely that coarse particles have a lower tendency to stabilize the emulsion compared with finer particles. For bitumen, particles from nanometers to microns in size are ideal for stabilizing emulsions. Particles of 1–10 mm in diameter could stabilize water-in-hydrocarbon emulsions (Chen et al., 2017). Yan et al. (1999) observed that solids larger than 8 mm in size do not affect emulsion stability, but that fine solids are capable of stabilizing emulsions.

Although the particles used in emulsion are not all the same size, the size effect could be similar if they have same size distribution. Large particles may be not reasonable for stabilizing emulsion, but with fine particles, the emulsion could be stabilized (emulsion separation test of feed). For those reasons, the feed sample could be separated based on surface properties with emulsion separation, and the size effect could be considered negligible.

Table 17 ICP results of products of micro sieve (10 under and 10 over)

	10 Under	**10 Over**	**Reconstituted**
Ca (ppm)	15950	13990	14170
Fe (ppm)	265150	280250	282940
Ce (ppm)	11160	10595	10651
La (ppm)	6285	6045	6069
Pr (ppm)	2090	1975	1986
Nd (ppm)	3540	3425	3436
Y (ppm)	1140	1100	1104

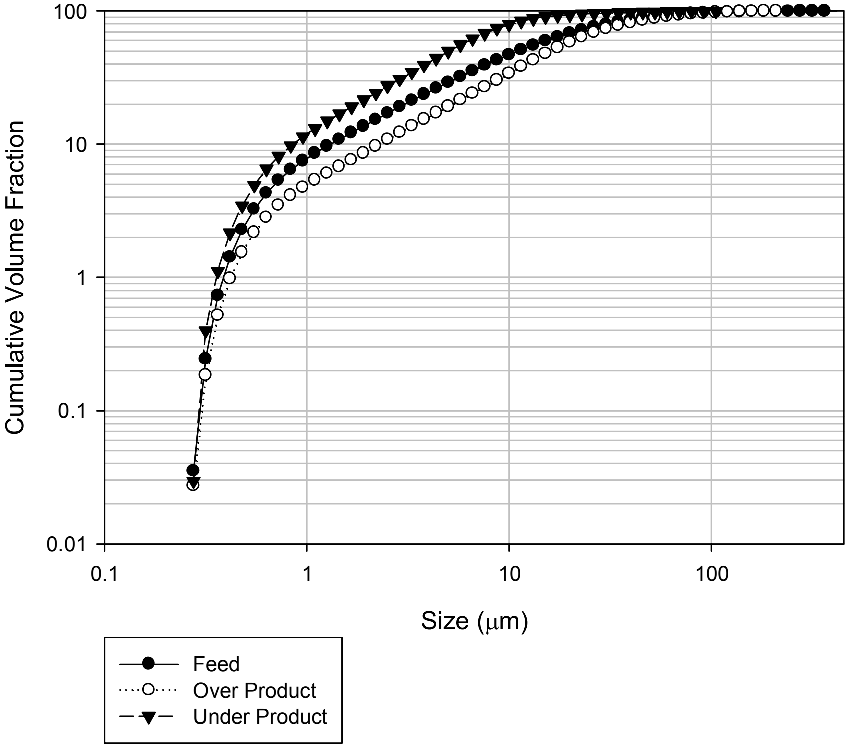


Figure 8 Cumulative size distribution of feed, over product and under product of the micro sieve

4.2.4 Effect of collectors

Two type of cationic collectors were used for emulsion separation tests: fatty acid (sodium oleate) and hydroxamic acid (salicylhydroxamic acid). The pH was adjusted to about 9.5, and the volume ratio of slurry to oil was 2:1.

4.2.4.1 Sodium Oleate

The dosage of sodium oleate was determined based on the number of moles of REEs; for each mole of REEs, one molecule of sodium oleate was added, or a multiple of that number. Tables 18 and 19 show the results of the emulsion separation test when the number of moles of REEs was equal to the number of molecules of oleic acid. Tables 20 and 21 show the results when the amount of oleic acid was doubled. Figure 9 shows the concentration and recovery of REEs.

When the 1x amount of sodium oleate was added, there was little separation; the value of TREE (emulsion)/TREE (water) was 1.221, and the value of TREE (emulsion)/TREE (feed) was 1.161. Greater efficiency was achieved when the 2x amount of oleic acid was added. The yield of water layer products was 72.2 %, and the recovery of REEs was almost 80%. The value of TREE (emulsion)/TREE (water) was 1.770, and the value of TREE (emulsion)/TREE (feed) was 1.137. As the mean recovery of REEs and the value of TREE (emulsion)/TREE (water) were higer when 2x dosage of sodium oleate, 2x sodium oleate is the more appropriate condition.

Table 18 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry:oil = 2:1, pH 9.5, 1x sodium oleate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	76.6	23.4	
Ca (ppm)	13327	16622	14098
Fe (ppm)	264147	331612	279934
Ce (ppm)	10589	11455	10792
La (ppm)	5821	7352	6179
Pr (ppm)	1781	2728	2003
Nd (ppm)	3163	4478	3471
Y (ppm)	1046	1340	1115

Table 19 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, 1x sodium oleate)

	Water	**Emulsion**
Mass (%)	76.6	23.4
Ca (%)	72.4	27.6
Fe (%)	72.3	27.7
Ce (%)	75.2	24.8
La (%)	72.2	27.8
Pr (%)	68.1	31.9
Nd (%)	69.8	30.2
Y (%)	71.9	28.1

Table 20 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry : oil = 2 : 1, pH 9.5, 2x sodium oleate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	27.8	72.2	
Ca (ppm)	13014	14936	14401
Fe (ppm)	259798	292867	283673
Ce (ppm)	6162	12157	10490
La (ppm)	4366	6910	6202
Pr (ppm)	1267	2248	1975
Nd (ppm)	2270	3966	3494
Y (ppm)	882	1182	1098

Table 21 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, 2x sodium oleate)

	Water	**Emulsion**
Mass (%)	27.8	72.2
Ca (%)	25.1	74.9
Fe (%)	25.5	74.5
Ce (%)	16.3	83.7
La (%)	19.6	80.4
Pr (%)	17.8	82.2
Nd (%)	18.1	81.9
Y (%)	22.3	77.7

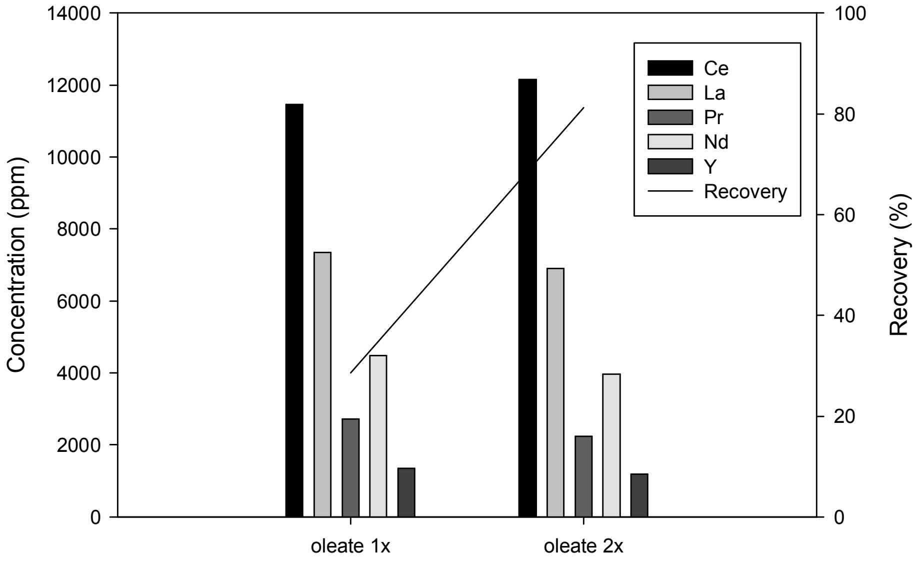


Figure 9 Concentrations and recovery of REEs for various dosage of sodium oleate (volume ratio of slurry:oil = 2:1, pH 9.5)

4.2.4.2 Salicylhydroxamic acid

The dosage of salicylhydroxamic acid was determined based on the number of moles of REEs; for each mole of REEs, one molecule of salicylhydroxamic acid was added, or a multiple of that number. Tables 22 and 23 show the results of the emulsion separation test when the number of moles of REEs was equal to the number of molecules of salicylhydroxamic acid. Tables 24 and 25 show the results when the amount of salicylhydroxamic acid was doubled. Figure 10 shows the concentration and recovery of REEs for various dosage of salicylhydroxamic acid.

Separation efficiency was low for the emulsion separation tests in both these conditions. When 1x salicylhydroxamic acid was added, the value of TREE (emulsion)/TREE (water) was 1.035, and the value of TREE (emulsion)/TREE (feed) was 1.022. The value of TREE (emulsion)/TREE (water) was 0.996, and the value of TREE (emulsion)/TREE (feed) was 0.997, when 2x salicylhydroxamic acid was added. Because separation did not occur with salicylhydroxamic acid, sodium oleate was fixed as the collector for subsequent emulsion separation tests.

Table 22 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry:oil = 2:1, pH 9.5, 1x salicylhydroxamic acid)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	64.0	36.0	
Ca (ppm)	15286	14514	15008
Fe (ppm)	279740	273049	277331
Ce (ppm)	10805	11185	10941
La (ppm)	6141	6349	6215
Pr (ppm)	1991	2072	2020
Nd (ppm)	3549	3682	3596
Y (ppm)	1084	1111	1093

Table 23 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, 1x salicylhydroxamic acid)

	Water	**Emulsion**
Mass (%)	**64.0**	**36.0**
Ca (%)	65.2	34.8
Fe (%)	64.6	35.4
Ce (%)	63.2	36.8
La (%)	63.2	36.8
Pr (%)	63.1	36.9
Nd (%)	63.1	36.9
Y (%)	63.4	36.6

Table 24 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry:oil = 2:1, pH 9.5, salicylhydroxamic acid 2x)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	65.5	34.5	
Ca (ppm)	13441	13735	13542
Fe (ppm)	260074	274614	265090
Ce (ppm)	10159	10108	10141
La (ppm)	6011	6000	6007
Pr (ppm)	1918	1903	1913
Nd (ppm)	3512	3487	3503
Y (ppm)	1145	1158	1149

Table 25 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, salicylhydroxamic acid 2x)

	Water	**Emulsion**
Mass (%)	65.5	34.5
Ca (%)	65.0	35.0
Fe (%)	64.3	35.7
Ce (%)	65.6	34.4
La (%)	65.5	34.5
Pr (%)	65.7	34.3
Nd (%)	65.7	34.3
Y (%)	65.2	34.8

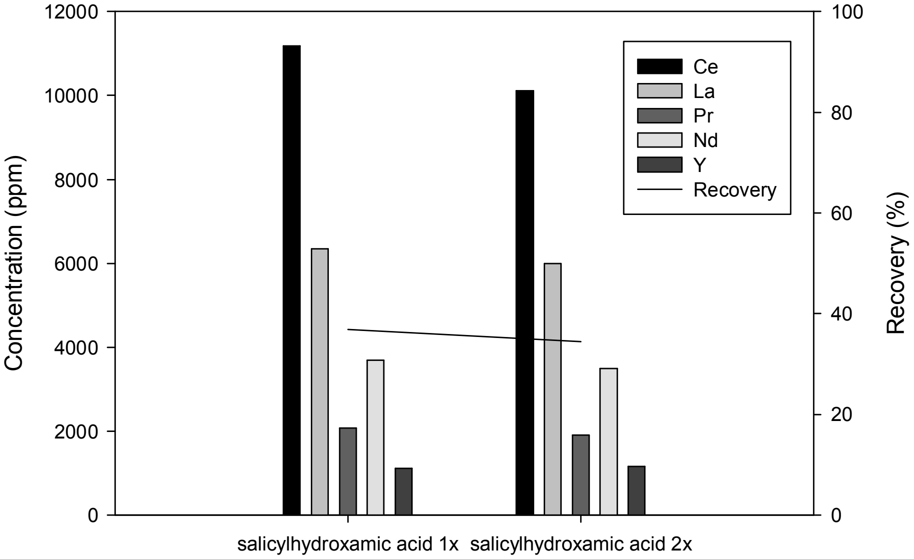


Figure 10 Concentrations and recovery of REEs for various dosage of salicylhdroxamic acid (volume ratio of slurry:oil = 2:1, pH 9.5)

4.2.5 Effect of oil type

To compare the effect of the type of oil in emulsion separation, decane was used as the oil. The volume ratio of slurry to oil was 2:1, and the pH was adjusted to 9.5; sodium oleate was added as a collector. Tables 26 and 27 show the results when the oil was decane and no sodium oleate was added. Tables 28 and 29 show the results when the dosage of the collector was 1x and the oil was decane. Tables 30 and 31 show the results of the emulsion separation when 2x sodium oleate was added and the oil was decane. Figure 11 shows the concentration and recovery of REEs.

For no sodium oleate, the value of TREE (emulsion)/TREE (water) was 1.219, and the value of TREE (emulsion)/TREE (feed) was 1.201. The recovery of REEs was low (about 8%), and the concentration of REEs was not so high. When 1x sodium oleate was added, the value of TREE (emulsion)/TREE (water) was 1.054, and the value of TREE (emulsion)/TREE (feed) was 1.044. The results indicate that no separation occurred. In the case of a collector dosage of 2x, the value of TREE (emulsion)/TREE (water) was 1.885, and the value of TREE (emulsion)/TREE (feed) was 1.027. The concentrations of REEs in the water layers were very low; however, the yield of water layer products was low, and therefore there was no difference between the feed and emulsion layer products. Based on comparing these results with those obtained using kerosene, the oil phase of kerosene is more suitable for emulsion separation.

Long-chain hydrocarbons seem to be more appropriate for emulsion separation of REE minerals (e.g., oleic acid, kerosene).

Table 26 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry:oil = 2:1, pH 9.5, no sodium oleate, decane)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	93.0	7.0	
Ca (ppm)	14066	14314	14083
Fe (ppm)	272564	237944	270141
Ce (ppm)	10205	12141	10341
La (ppm)	5985	7469	6089
Pr (ppm)	1965	2433	1998
Nd (ppm)	3340	4184	3399
Y (ppm)	1104	1327	1120

Table 27 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, no sodium oleate, decane)

	Water	**Emulsion**
Mass (%)	93.0	7.0
Ca (%)	92.9	7.1
Fe (%)	93.8	6.2
Ce (%)	91.8	8.2
La (%)	91.4	8.6
Pr (%)	91.5	8.5
Nd (%)	91.4	8.6
Y (%)	91.7	8.3

Table 28 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry : oil = 2 : 1, pH 9.5, 1x sodium oleate, decane)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	82.8	17.2	
Ca (ppm)	13276	15500	13659
Fe (ppm)	269138	253198	266396
Ce (ppm)	10044	10865	10185
La (ppm)	5964	6167	5999
Pr (ppm)	1876	1994	1896
Nd (ppm)	3380	3494	3400
Y (ppm)	1113	1082	1108

Table 29 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, sodium oleate 1x, decane)

	Water	**Emulsion**
Mass (%)	82.8	17.2
Ca (%)	80.5	19.5
Fe (%)	83.7	16.3
Ce (%)	81.7	18.3
La (%)	82.3	17.7
Pr (%)	81.9	18.1
Nd (%)	82.3	17.7
Y (%)	83.2	16.8

Table 30 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry : oil = 2 : 1, pH 9.5, 2x sodium oleate, decane)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	5.8	94.2	
Ca (ppm)	11729	14172	14030
Fe (ppm)	249880	268197	267135
Ce (ppm)	5881	10625	10350
La (ppm)	3361	6420	6243
Pr (ppm)	953	2097	2031
Nd (ppm)	1779	3604	3498
Y (ppm)	666	1079	1055

Table 31 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, sodium oleate 2x, decane)

	Water	**Emulsion**
Mass (%)	5.8	94.2
Ca (%)	4.8	95.2
Fe (%)	5.4	94.6
Ce (%)	3.3	96.7
La (%)	3.1	96.9
Pr (%)	2.7	97.3
Nd (%)	2.9	97.1
Y (%)	3.7	96.3

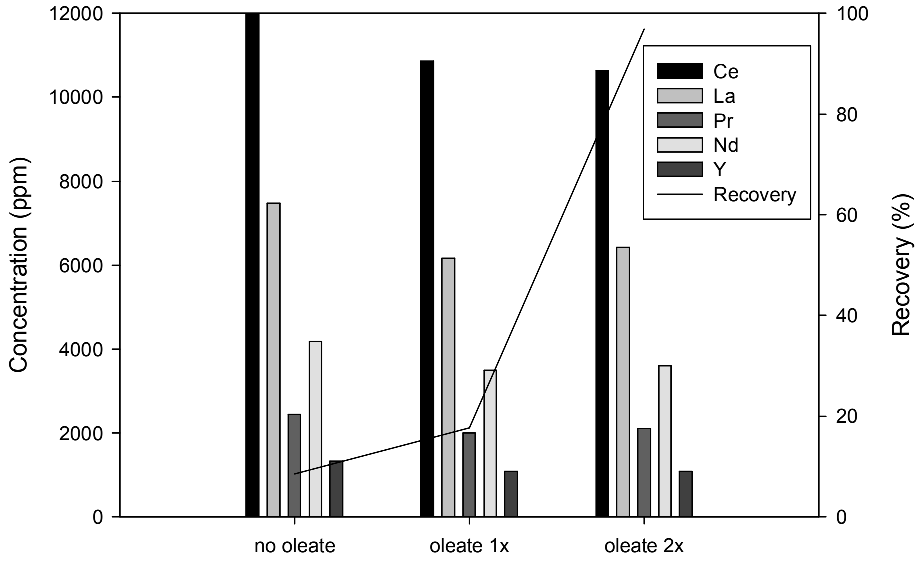


Figure 11 Concentrations and recovery of REEs for various dosage of sodium oleate (volume ratio of slurry:oil = 2:1, pH 9.5, decane)

4.2.6 Transform of iron oxide

Transforming process of iron oxide was conducted. By heating the ore sample with bituminous coal (carbon > 70%), as the role of oxidant, goethite could be changed to the another form of iron oxide such as hematite or magnetite. Mixture of coal and ore sample was heated at 650℃ for 4hrs and products was analyzed by XRD. Figure 12 shows the result of XRD. Goethite was transformed to the form of hematite. As the zeta potential of hematite was more negative than that of goethite at pH range of 9.5 ~ 10 (Hou et al., 2007), performance of emulsion separation is expected to upgrade.

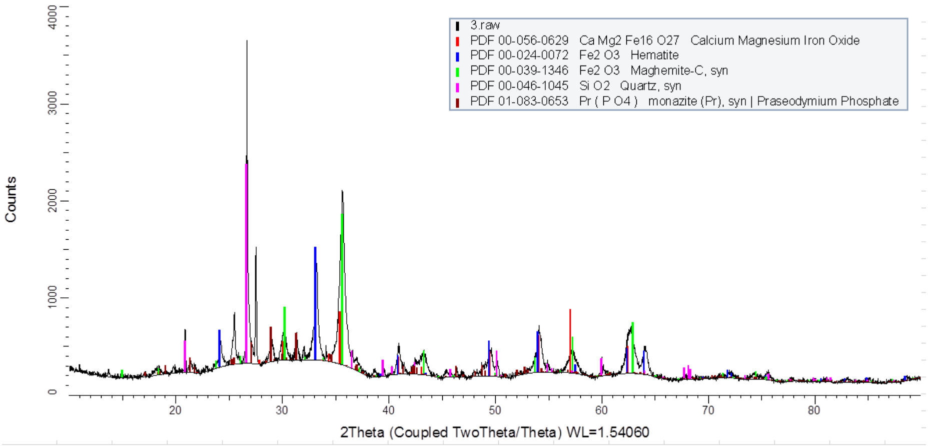


Figure 12 XRD data of the heat treated sample

With transformed ore sample, emulsion separation test was conducted with 2x sodium oleate. Table 32 and 33 shows the results of emulsion separation with transformed ore sample. However, no separation was occurred; the value of TREE (emulsion) / TREE (water) was 1.013 and the value of TREE (emulsion) / TREE (feed) was 1.012. Also more than 85% of particles were move to water layer. Based on the concentrations and recovery, transformation of iron oxide by heating with coal is not appropriate pretreatment.

Table 32 Concentrations of important elements of the water and emulsion layer products (volume ratio of slurry:oil = 2:1, pH 9.5, 2x sodium oleate, transformed sample)

	Water	Emulsion	Reconstituted
Mass (%)	87.1	12.9	
Ca (ppm)	13622	13524	13609
Fe (ppm)	290703	284323	289880
Ce (ppm)	10206	10193	10204
La (ppm)	5939	6200	5973
Pr (ppm)	1941	1941	1941
Nd (ppm)	3375	3455	3385
Y (ppm)	1056	1029	1053

Table 33 Recovery of elements from emulsion separation (volume ratio of slurry:oil = 2:1, pH 9.5, 2x sodium oleate, transformed sample)

	Water	Emulsion
Mass (%)	87.1	12.9
Ca (%)	87.2	12.8
Fe (%)	87.3	12.7
Ce (%)	87.1	12.9
La (%)	86.6	13.4
Pr (%)	87.1	12.9
Nd (%)	86.8	13.2
Y (%)	87.4	12.6

4.2.7 Effect of depressants

Two depressants were used to determine which was more appropriate for emulsion separation tests: sodium silicate and starch (corn). The pH was adjusted to 9.5, and the volume ratio of slurry to oil was 2:1. The dosage of the collector (sodium oleate) was twice the number of moles of REEs.

4.2.7.1 Sodium silicate

The amount of sodium silicate was determined based on the amount of sodium oleate; 0.25, 0.5 and 1 times the mass of sodium oleate were added to the slurry. Tables 34 and 35 show the results when the dosage of sodium silicate was 0.25x. Tables 36 and 37 show the results when 0.5x sodium silicate was added to the slurry. The results of the emulsion separation test when 1x sodium silicate was added are presented in Tables 38 and 39. Figure 13 shows the concentration and recovery of REEs for various dosage of sodium oleate.

As sodium silicate was added, most of the particles moved to the water layer (yields of water layer product were over 65%). For 0.25x sodium silicate, the value of TREE (emulsion)/TREE (water) was 1.165, and the value of TREE (emulsion)/TREE (feed) was 1.103. When 0.5x sodium silicate was added, the value of TREE (emulsion)/TREE (water) was 1.075, and the value of TREE (emulsion)/TREE (feed) was 1.058. When 1x sodium silicate was added, values of 1.071 and 1.053 were achieved, respectively. Sodium silicate was a strong depressant, and depressed a large proportion of the particles. The best performance was achieved when 0.25x sodium silicate was added.

Table 34 Concentrations of important elements of the water and emulsion layer products (0.25x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	65.7	34.3	
Ca (ppm)	13657	14624	13989
Fe (ppm)	254800	295795	268861
Ce (ppm)	9667	11300	10227
La (ppm)	5507	6320	5786
Pr (ppm)	1846	2059	1919
Nd (ppm)	3064	3681	3276
Y (ppm)	995	1200	1065

Table 35 Recovery of elements from emulsion separation (0.25x sodium silicate)

	Water	**Emulsion**
Mass (%)	65.7	34.3
Ca (%)	64.1	35.9
Fe (%)	62.3	37.7
Ce (%)	62.1	37.9
La (%)	62.5	37.5
Pr (%)	63.2	36.8
Nd (%)	61.5	38.5
Y (%)	61.4	38.6

Table 36 Concentrations of important elements of the water and emulsion layer products (0.5x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	78.9	21.1	
Ca (ppm)	13695	16924	14376
Fe (ppm)	276289	286619	278469
Ce (ppm)	10284	10595	10350
La (ppm)	5802	6751	6002
Pr (ppm)	1891	1981	1910
Nd (ppm)	3405	3692	3466
Y (ppm)	1123	1185	1136

Table 37 Recovery of elements from emulsion separation (0.5x sodium silicate)

	Water	**Emulsion**
Mass (%)	78.9	21.1
Ca (%)	75.2	24.8
Fe (%)	78.3	21.7
Ce (%)	78.4	21.6
La (%)	76.3	23.7
Pr (%)	78.1	21.9
Nd (%)	77.5	22.5
Y (%)	78.0	22.0

Table 38 Concentrations of important elements of the water and emulsion layer products (1x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	76.0	24.0	
Ca (ppm)	14197	15417	14490
Fe (ppm)	281198	279937	280895
Ce (ppm)	10397	10957	10531
La (ppm)	5749	6430	5912
Pr (ppm)	1924	2050	1954
Nd (ppm)	3456	3681	3510
Y (ppm)	1117	1144	1123

Table 39 Recovery of elements from emulsion separation (1x sodium silicate)

	Water	**Emulsion**
Mass (%)	76.0	24.0
Ca (%)	74.5	25.5
Fe (%)	76.1	23.9
Ce (%)	75.0	25.0
La (%)	73.9	26.1
Pr (%)	74.8	25.2
Nd (%)	74.8	25.2
Y (%)	75.6	24.4

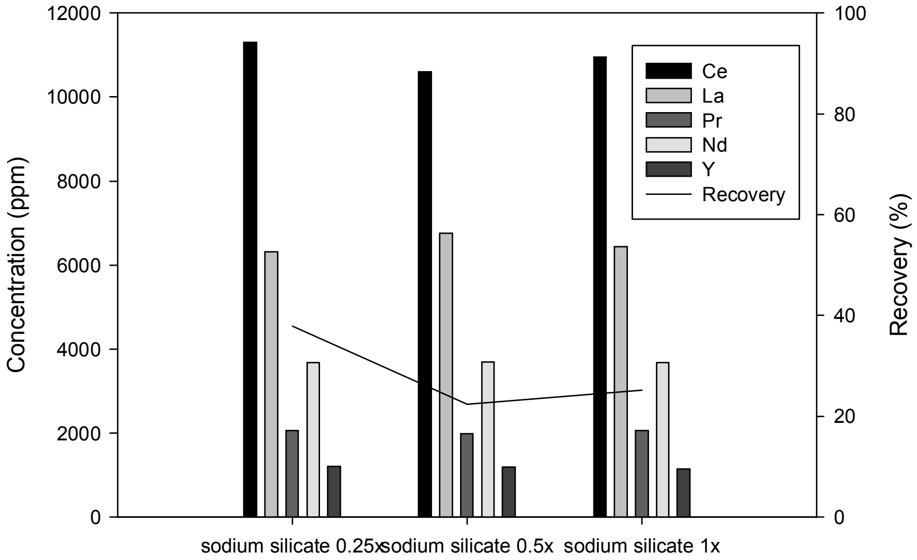


Figure 13 Concentrations and recovery of REEs for various dosage of sodium silicate (volume ratio of slurry:oil = 2:1, pH 9.5, 2x sodium oleate)

4.2.7.2 Starch (corn)

The dosage of starch was determined based on the mass of sodium oleate: 1x, 2x and 3x mass. Dosage was differ from the case of sodium silicate because starch is weaker depressant. Tables 40 and 41 show the results for 1x starch. Tables 42 and 43 show the results of emulsion separation test when 2x starch was added. The results of emulsion separation when 3x of starch was added are presented in Tables 44 and 45. Figure 14 shows the concentration and recovery of REEs.

Compared with sodium silicate, starch was a weaker and poorer depressant. The yield of water layer products was lower, even when 3x starch was added. When 1x starch was added, the value of TREE (emulsion)/TREE (water) was 0.887, and the value of TREE (emulsion)/TREE (feed) was 0.946. For 2x starch, the value of TREE (emulsion)/TREE (water) was 1.096, and the value of TREE (emulsion)/TREE (feed) was 1.041. When the dosage of starch was 3x, the value of TREE (emulsion)/TREE (water) was 0.963, and the value of TREE (emulsion)/TREE (feed) was 0.971.

The performance of emulsion separation when starch was used as the depressant was poor. Only for 2x dosage, some REEs were concentrated in the emulsion layer, but efficiency and selectivity were poor. These results indicate that sodium silicate is more appropriate for emulsion separation than starch.

Table 40 Concentration of important elements of water and emulsion layer products (1x starch)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	45.1	54.9	
Ca (ppm)	15315	13055	14074
Fe (ppm)	300950	235800	265183
Ce (ppm)	11075	9755	10350
La (ppm)	6260	5640	5920
Pr (ppm)	2040	1805	1911
Nd (ppm)	3555	3145	3330
Y (ppm)	1210	1070	1133

Table 41 Recovery of elements from emulsion separation (1x starch)

	Water	**Emulsion**
Mass (%)	45.1	54.9
Ca (%)	49.1	50.9
Fe (%)	51.2	48.8
Ce (%)	48.3	51.7
La (%)	47.7	52.3
Pr (%)	48.1	51.9
Nd (%)	48.1	51.9
Y (%)	48.2	51.8

Table 42 Concentration of important elements of water and emulsion layer products (2x starch)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	45.2	54.8	
Ca (ppm)	13247	15324	14385
Fe (ppm)	253004	279925	267757
Ce (ppm)	9808	10568	10224
La (ppm)	5769	6510	6175
Pr (ppm)	1869	2052	1969
Nd (ppm)	3118	3420	3283
Y (ppm)	1084	1169	1131

Table 43 Recovery of elements from emulsion separation (2x starch)

	Water	**Emulsion**
Mass (%)	45.2	54.8
Ca (%)	41.6	58.4
Fe (%)	42.7	57.3
Ce (%)	43.4	56.6
La (%)	42.2	57.8
Pr (%)	42.9	57.1
Nd (%)	42.9	57.1
Y (%)	43.3	56.7

Table 44 Concentrations of important elements of the water and emulsion layer products (3x starch)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	77.7	22.3	
Ca (ppm)	13525	15940	14064
Fe (ppm)	277800	276493	277509
Ce (ppm)	10700	10537	10664
La (ppm)	6170	5834	6095
Pr (ppm)	1955	1936	1951
Nd (ppm)	3470	3246	3420
Y (ppm)	1125	1015	1100

Table 45 Recovery of elements from emulsion separation (3x starch)

	Water	**Emulsion**
Mass (%)	77.7	22.3
Ca (%)	74.7	25.3
Fe (%)	77.8	22.2
Ce (%)	78.0	22.0
La (%)	78.7	21.3
Pr (%)	77.9	22.1
Nd (%)	78.8	21.2
Y (%)	79.4	20.6

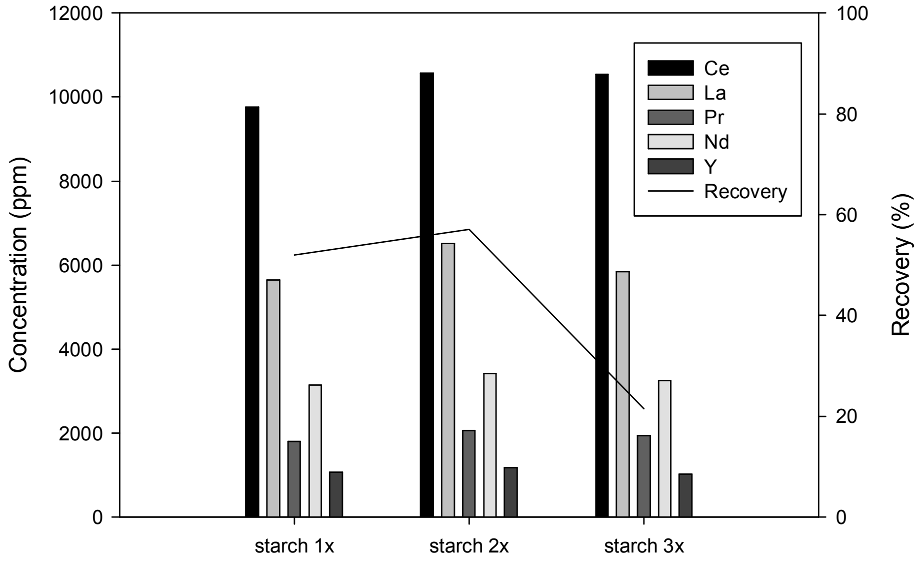


Figure 14 Concentrations and recovery of REEs for various dosage of starch (volume ratio of slurry:oil = 2:1, pH 9.5, 2x sodium oleate)

4.3 Optimum condition for emulsion separation

To determine the optimum conditions for emulsion separation, dosages of the depressant and activator were varied. The pH was adjusted to 9.5, and the volume ratio of slurry to oil was 2:1. Sodium oleate was used as a collector, and the dosage was 2x the number of moles of REEs in the feed. The oil phase was fixed to kerosene. Sodium silicate was used as the depressant, and calcium chloride was used as the activator. In addition, the original feed and deslimed feed were used for comparison.

4.3.1 Original feed

For the first step, the dosages of sodium silicate and calcium chloride were varied roughly: 0.5x, 1x and 2x for calcium chloride, and 1x, 2x and 3x for sodium silicate. However, emulsion separation tests were available to analyze for only two conditions (0.5x calcium chloride and 2x sodium silicate; 1x calcium chloride and 3x sodium silicate) because of the yield of products. Tables 46 and 47 show the results of emulsion separation for the conditions of 0.5x calcium chloride and 2x sodium silicate. Tables 48 and 49 show the results when the conditions were 1x calcium chloride and 3x sodium silicate.

With the combination of 0.5x C.C (calcium chloride) and 2x S.S (sodium silicate), the value of TREE (emulsion)/TREE (water) was 0.989 and the value of TREE (emulsion)/TREE (feed) was 0.990, which indicates that there was no separation. With 1x C.C and 3x S.S, the value of TREE (emulsion)/TREE (water) was 1.277 and the value of TREE (emulsion)/TREE (feed) was 1.220, which indicates that separation efficiency and selectivity were not bad, but that more improvements were needed.

Table 46 Concentrations of important elements of the water and emulsion layer products (0.5x calcium chloride, 2x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	89.4	10.6	
Ca (ppm)	13815	17985	14257
Fe (ppm)	279200	227500	273720
Ce (ppm)	10720	10380	10684
La (ppm)	5970	6210	5995
Pr (ppm)	2055	1990	2048
Nd (ppm)	3515	3455	3509
Y (ppm)	1140	1105	1136

Table 47 Recovery of elements from emulsion separation (0.5x calcium chloride, 2x sodium silicate)

	Water	**Emulsion**
Mass (%)	89.4	10.6
Ca (%)	86.6	13.4
Fe (%)	91.2	8.8
Ce (%)	89.7	10.3
La (%)	89.0	11.0
Pr (%)	89.7	10.3
Nd (%)	89.6	10.4
Y (%)	89.7	10.3

Table 48 Concentrations of important elements of the water and emulsion layer products (1x calcium chloride, 3x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	83.0	17.0	
Ca (ppm)	13310	16263	13812
Fe (ppm)	261650	299607	268103
Ce (ppm)	9660	12281	10106
La (ppm)	5710	7444	6005
Pr (ppm)	1815	2309	1899
Nd (ppm)	3115	3938	3255
Y (ppm)	1055	1312	1099

Table 49 Recovery of elements from emulsion separation (1x calcium chloride, 3x sodium silicate)

	Water	**Emulsion**
Mass (%)	83.0	17.0
Ca (%)	80.0	20.0
Fe (%)	81.0	19.0
Ce (%)	79.3	20.7
La (%)	78.9	21.1
Pr (%)	79.3	20.7
Nd (%)	79.4	20.6
Y (%)	79.7	20.3

To improve these results, conditions were narrowed around the combination of 1x of C.C and 3x of S.S. Tables 50 and 51 show the results for 1x C.C and 2.75x S.S. The results of emulsion separation with 0.75x C.C and 2.75x S.S are presented in Tables 52 and 53. Tables 54 and 55 show the results with the condition of 0.875x C.C and 0.2625x S.S.

With 1x C.C and 2.75x S.S, the value of the value of TREE (emulsion)/TREE (water) was 1.612, and the value of TREE (emulsion)/TREE (feed) was 1.043. The differences in concentrations of REEs between the emulsion layer products and water layer product were considerable; however, concentration from the feed did not occur. With 0.75x C.C and 2.75x S.S, the value of TREE (emulsion)/TREE (water) was 1.215, and the value of TREE (emulsion)/TREE (feed) was 1.121. When the conditions of the emulsion separation test were 0.875x C.C and 0.2625 S.S, the value of TREE (emulsion)/TREE (water) was 1.465, and the value of TREE (emulsion)/TREE (feed) was 1.114. Recovery of REEs was high, at almost 75%, which indicates that the conditions of 0.875x C.C and 0.2625 S.S yielded good results. The concentration and recovery of REEs with various dosage of calcium chloride and sodium silicate is shown at figure 15.

Table 50 Concentrations of important elements of the water and emulsion layer products (1x calcium chloride, 2.75x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	10.9	89.1	
Ca (ppm)	11748	14482	14184
Fe (ppm)	271209	268038	268384
Ce (ppm)	5795	10695	10161
La (ppm)	4522	6073	5904
Pr (ppm)	1185	2066	1970
Nd (ppm)	2215	3477	3339
Y (ppm)	808	1097	1065

Table 51 Recovery of elements from emulsion separation (1x calcium chloride, 2.75x sodium silicate)

	Water	**Emulsion**
Mass (%)	10.9	89.1
Ca (%)	9.0	91.0
Fe (%)	11.0	89.0
Ce (%)	6.2	93.8
La (%)	8.3	91.7
Pr (%)	6.6	93.4
Nd (%)	7.2	92.8
Y (%)	8.3	91.7

Table 52 Concentrations of important elements of the water and emulsion layer products (0.75x calcium chloride, 2.75x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	60.8	39.2	
Ca (%)	13838	14087	13936
Fe (%)	278488	245577	265587
Ce (%)	9335	11425	10154
La (%)	5614	6745	6057
Pr (%)	1740	2134	1894
Nd (%)	3037	3746	3315
Y (%)	1061	1206	1118

Table 53 Recovery of elements from emulsion separation (0.75x calcium chloride, 2.75x sodium silicate)

	Water	**Emulsion**
Mass (%)	60.8	39.2
Ca (%)	60.4	39.6
Fe (%)	63.8	36.2
Ce (%)	55.9	44.1
La (%)	56.3	43.7
Pr (%)	55.8	44.2
Nd (%)	55.7	44.3
Y (%)	57.7	42.3

Table 54 Concentrations of important elements of the water and emulsion layer products (0.875x calcium chloride, 2.625x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	32.4	67.6	
Ca (ppm)	11330	14970	13791
Fe (ppm)	286150	262500	270163
Ce (ppm)	7710	11685	10397
La (ppm)	4650	6750	6070
Pr (ppm)	1490	2175	1953
Nd (ppm)	2660	3715	3373
Y (ppm)	905	1190	1098

Table 55 Recovery of elements from emulsion separation (0.875x calcium chloride, 2.625x sodium silicate)

	Water	**Emulsion**
Mass (%)	32.4	67.6
Ca (%)	26.6	73.4
Fe (%)	34.3	65.7
Ce (%)	24.0	76.0
La (%)	24.8	75.2
Pr (%)	24.7	75.3
Nd (%)	25.5	74.5
Y (%)	26.7	73.3

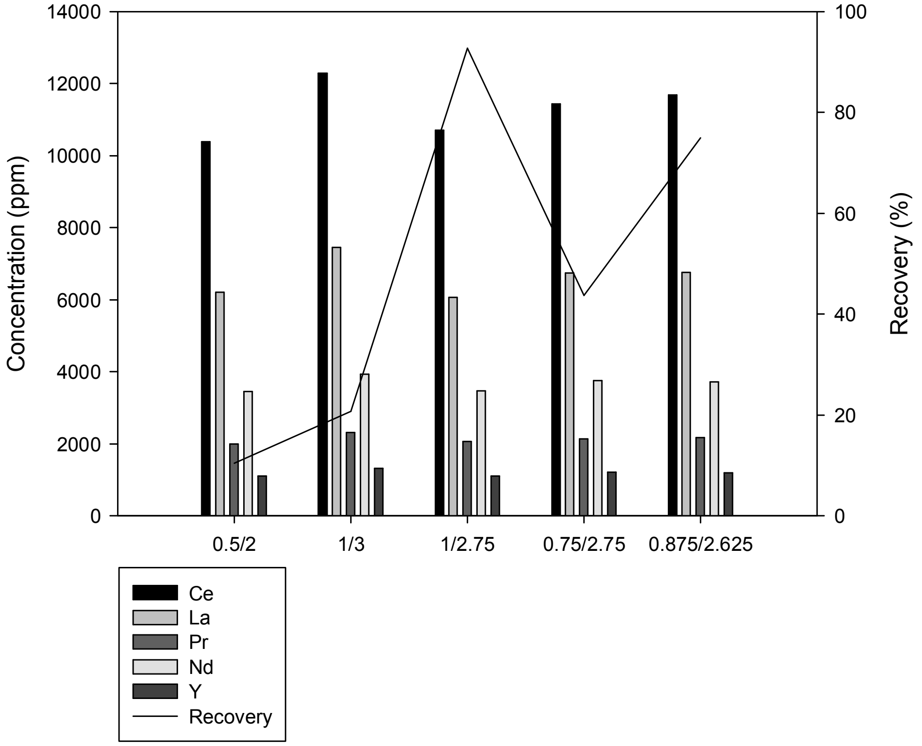


Figure 15 Concentrations and recovery of REEs for various dosage of calcium chloride and sodium silicate (volume ratio of slurry:oil = 2:1, pH 9.5, 2x sodium oleate, original feed)

4.3.2 Deslimed feed

Figure 16 shows the size distribution of the original feed and deslimed feed. By desliming, some fine particles are removed. A similar procedure that was used to find the appropriate conditions for emulsion separation of the original feed was done for the deslimed feed with same conditions, except that the dosages of depressant and activator differed.

Tables 56 and 57 show the results of emulsion separation with 1x C.C and 1.75x S.S. Because there was no separation (the value of TREE (emulsion)/TREE (water) was 1.048, and the value of TREE (emulsion)/TREE (feed) was 1.025), another condition was needed to determine the optimum conditions. Lower dosages of C.C and S.S were insufficient to achieve separation; therefore, higher dosages of C.C and S.S were examined.

Tables 58 and 59 show the results of emulsion separation with the conditions of 1.125x C.C and 2x S.S. The yield of emulsion layer products was about 66%, and the recovery of REEs was almost 70%. The value of TREE (emulsion)/TREE (water) was 1.259, and the value of TREE (emulsion)/TREE (feed) was 1.075, which indicates that the feed and emulsion layer products differed little, and that little separation occurred.

The emulsion test results with 1.125x C.C and 2.25x S.S are presented in Tables 60 and 61. The yield of emulsion layer products was 83.7%, and the recovery of REEs was about 86%. The value of TREE (emulsion)/TREE (water) was 1.217, and the value of TREE (emulsion)/TREE (feed) was 1.030.

The recovery was high, but there was no difference between the feed and emulsion layer products, and little difference between the emulsion layer products and water layer products. Figure 17 shows the concentration and recovery of REEs with various dosage of calcium chloride and sodium silicate.

The results of the emulsion separation of the deslimed feed indicates that desliming is not an appropriate treatment for emulsion separation. Fine particles could be considered a stabilizer for emulsion, and could increase the efficiency of the emulsion separation test. The degree of liberation could affect the performance of emulsion separation; fine particles tends to be more liberated and could be more effectively separated.

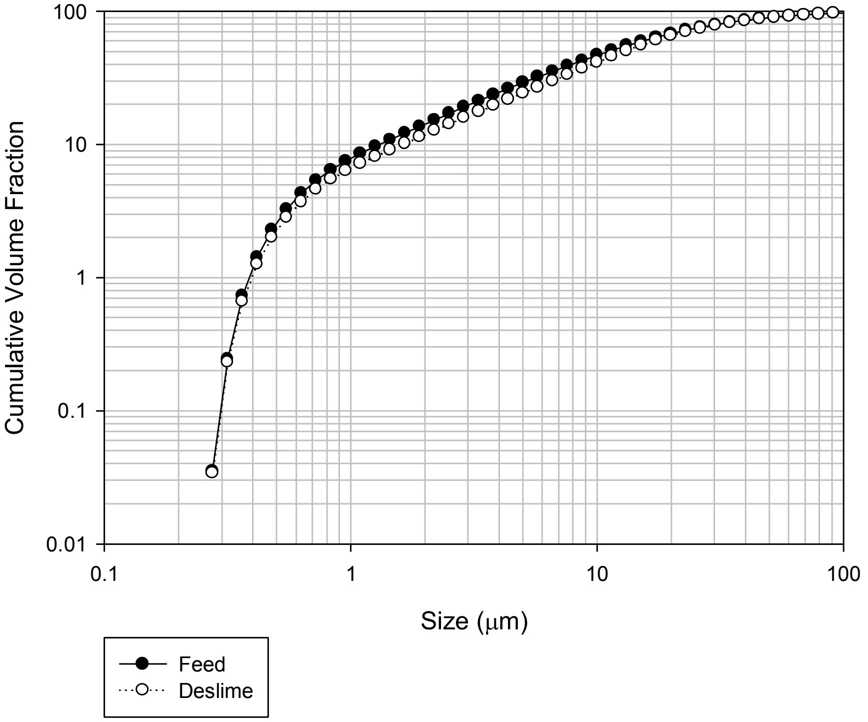


Figure 16 Cumulative size distribution of the feed and deslimed feed

Table 56 Concentrations of important elements of the water and emulsion layer products (1x calcium chloride, 1.75x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	53.2	46.8	
Ca (ppm)	13500	13860	13668
Fe (ppm)	283950	248100	267172
Ce (ppm)	10205	10675	10425
La (ppm)	6190	6520	6344
Pr (ppm)	1960	2050	2002
Nd (ppm)	3310	3485	3392
Y (ppm)	1070	1110	1089

Table 57 Recovery of elements from emulsion separation (1x calcium chloride, 1.75x sodium silicate)

	Water	**Emulsion**
Mass (%)	53.2	46.8
Ca (%)	52.5	47.5
Fe (%)	56.5	43.5
Ce (%)	52.1	47.9
La (%)	51.9	48.1
Pr (%)	52.1	47.9
Nd (%)	51.9	48.1
Y (%)	52.3	47.7

Table 58 Concentrations of important elements of the water and emulsion layer products (1.125x calcium chloride, 2x sodium silicate)

	Water	Emulsion	Reconstituted
Mass (%)	34.1	65.9	
Ca (ppm)	12270	15655	14500
Fe (ppm)	297800	278950	285380
Ce (ppm)	9480	11775	10992
La (ppm)	5050	6590	6065
Pr (ppm)	1760	2175	2033
Nd (ppm)	3005	3795	3526
Y (ppm)	970	1180	1108

Table 59 Recovery of elements from emulsion separation (1.125x calcium chloride, 2x sodium silicate)

	Water	Emulsion
Mass (%)	34.1	65.8
Ca (%)	28.9	71.1
Fe (%)	35.6	64.4
Ce (%)	29.4	70.6
La (%)	28.4	71.6
Pr (%)	29.5	70.5
Nd (%)	29.1	70.9
Y (%)	29.9	70.1

Table 60 Concentrations of important elements of the water and emulsion layer products (1.25x calcium chloride, 2.25x sodium silicate)

	Water	**Emulsion**	**Reconstituted**
Mass (%)	16.3	83.7	
Ca (ppm)	12810	15240	14845
Fe (ppm)	293750	276650	279433
Ce (ppm)	9225	11070	10770
La (ppm)	5285	6555	6348
Pr (ppm)	1675	2050	1989
Nd (ppm)	2870	3535	3427
Y (ppm)	925	1100	1072

Table 61 Recovery of elements from emulsion separation (1.25x calcium chloride, 2.25x sodium silicate)

	Water	**Emulsion**
Mass (%)	16.2	83.7
Ca (%)	14.0	86.0
Fe (%)	17.1	82.9
Ce (%)	13.9	86.1
La (%)	13.5	86.5
Pr (%)	13.7	86.3
Nd (%)	13.6	86.4
Y (%)	14.0	86.0

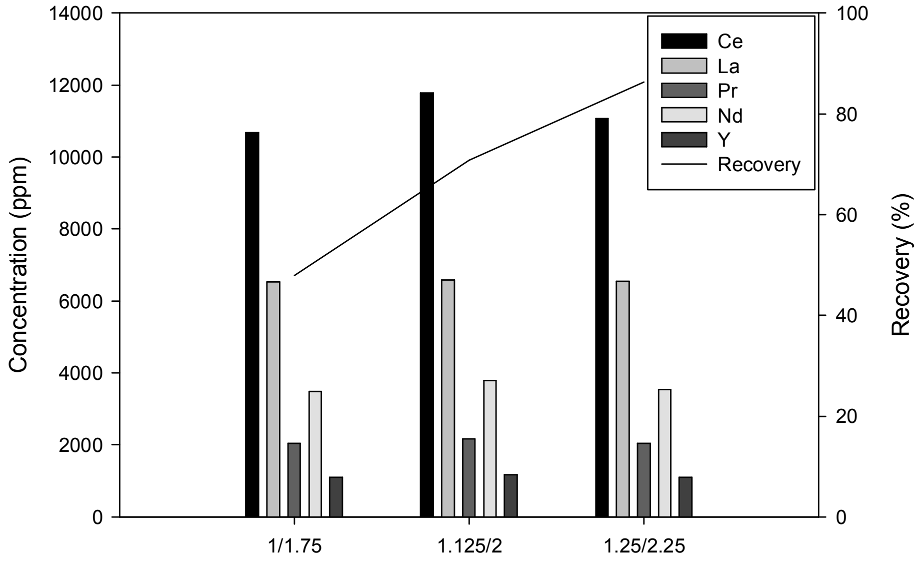


Figure 17 Concentrations and recovery of REEs for various dosage of calcium chloride and sodium silicate (volume ratio of slurry:oil = 2:1, pH 9.5, 2x sodium oleate, deslimed feed)

Chapter 5. Conclusions

Emulsion separation tests of REE ore samples were conducted to determine the optimum conditions for REE ore samples, and flotation tests were conducted to compare results. For emulsion separation, the volume ratio of slurry to oil, pH of slurry, particle size, type of oil, type and dosage of the collector, type and dosage of the depressant and the dosage of the activator were varied to identify the optimum conditions. Based on ICP-OES results, the value of the values of TREE (emulsion)/TREE (water) and TREE (emulsion)/TREE (feed) were calculated for comparison.

The volume ratio of slurry to oil was adjusted to 1:2, 1:1, and 2:1, and the volume ratio of 2:1 was found to be optimal for emulsion separation. The pH was adjusted to 4, 7, 9.5 and 11, and the best results were achieved with pH 9.5. To evaluate the effect of particle size, the feed was separated with a micro sieve with a mesh of 10 μm. When the 10 μm over size product was used for the emulsion separation test, all of the particles moved to the water layer. However, the emulsion separation test of the 10 μm under size product showed that all of particles moved to the emulsion layer. There was no difference in concentration between the under products and over products. This finding indicates that fine particles play a role as a stabilizer of the emulsion, and help the coarse particles to stabilize the emulsion. In addition, only surface properties can affect the separation results for particles of the same size.

Two types of collectors, sodium oleate and salicylhydroxamic acid, were used. Sodium oleate was more effective for emulsion separation of REE ore sample with a molecular dosage of twice the number of moles of TREEs. Kerosene and decane was used as the oil phase in emulsion separation tests to find the appropriate oil for this test. Better results were achieved with kerosene as the oil phase. Two types of depressants, sodium silicate and starch (corn), were used for emulsion separation tests. Starch (corn) did not show selectivity and ability to depress; therefore, sodium silicate was selected for the depressant.

To determine the optimum conditions for emulsion separation, the dosages of the activator and depressant were varied. Calcium chloride was used as an activator and sodium silicate was used as a depressant. The original feed and deslimed feed were used for emulsion separation. For the original feed, 0.875x calcium chloride and 2.626x sodium silicate were the best conditions for emulsion separation. 75% of recovery was achieved. The value of TREE (emulsion)/TREE (water) was 1.465, and the value of TREE (emulsion)/TREE (feed) was 1.114. For the deslimed feed, the optimum conditions were 1.125x calcium chloride and 2x of sodium silicate. However, lower efficiency and selectivity were achieved with the deslimed feed. The size effect and degree of liberation are considered the main factors causing low performance of emulsion separation with deslimed feed compare with the original feed.

Emulsion separation is the separation process that separate minerals by difference of surface property of minerals. It is similar with froth flotation but hydrophobic phase is different. Flotation is the most abundant process for mineral separation and emulsion separation could replace the flotation. In this study, emulsion separation tests were conducted for REEs, however, emulsion separation could be applied to any other mineral separation.

References

1. Abaka-Wood, G. B., Addai-Mensah, J., & Skinner, W. (2017). A study of flotation characteristics of monazite, hematite, and quartz using anionic collectors. International Journal of Mineral Processing, 158, 55-62.
2. Arantes, R. D. S., & Lima, R. M. F. (2013). Influence of sodium silicate modulus on iron ore flotation with sodium oleate. International Journal of Mineral Processing, 125, 157-160.
3. Azizi, D., Larachi, F., & Latifi, M. (2016). Ionic-liquid collectors for rare-earth minerals flotation□ Case of tetrabutylammonium bis (2-ethylhexyl)-phosphate for monazite and bastnäsite recovery. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 506, 74-86.
4. Butler, C. J. (2014). Rare earth elements: China's monopoly and implications for US national security. *Fletcher F. World Aff.*, *38*, 23.
5. Castor, S. B., & Hedrick, J. B. (2006). Rare earth elements. Industrial minerals volume, 7th edition: Society for mining, metallurgy, and exploration, Littleton, Colorado, 769-792.
6. Chen, Q., Stricek, I., Gray, M. R., & Liu, Q. (2017). Influence of hydrophobicity distribution of particle mixtures on emulsion stabilization. Journal of Colloid and Interface Science, 491, 179-189.
7. Espiritu, E. R. L., & Waters, K. E. (2017). Flotation studies of monazite and dolomite. Minerals Engineering.
8. Fuerstenau, D. W. (2005). Zeta potentials in the flotation of oxide and

silicate minerals. Advances in Colloid and Interface Science, 114, 9-26.

9. Fuerstenau, D. W. (2013). Design and development of novel flotation reagents for the beneficiation of Mountain Pass rare-earth ore. Minerals & Metallurgical Processing, 30(1).
10. Hou, T., Xu, R., & Zhao, A. (2007). Interaction between electric double layers of kaolinite and Fe/Al oxides in suspensions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *297*(1), 91-94.
11. Humphries, M. (2013). Rare earth elements: The global supply chain. Congressional Research Service, 16.
12. Jordens, A., Cheng, Y. P., & Waters, K. E. (2013). A review of the beneficiation of rare earth element bearing minerals. Minerals Engineering, 41, 97-114.
13. Kar, B., Sahoo, H., Rath, S. S., & Das, B. (2013). Investigations on different starches as depressants for iron ore flotation. Minerals Engineering, 49, 1-6.
14. Liu, X., Luo, H., Cheng, R., Li, C., & Zhang, J. (2017). Effect of citric acid and flotation performance of combined depressant on collophanite ore. *Minerals Engineering*, *109*, 162-168.
15. Massari, S., & Ruberti, M. (2013). Rare earth elements as critical raw materials: Focus on international markets and future strategies. Resources Policy, 38(1), 36-43.
16. Napier-Munn, T., & Wills, B. A. (2006). Wills' mineral processing technology: An introduction to the practical aspects of ore treatment and mineral recovery. Elsevier.

17. Tohry, A., & Dehghani, A. (2016). Effect of sodium silicate on the reverse anionic flotation of a siliceous–phosphorus iron ore. Separation and Purification Technology, 164, 28-33.
18. Trahar, W. J. (1981). A rational interpretation of the role of particle size in flotation. International Journal of Mineral Processing, 8(4), 289-327.
19. Tranvik, E., Becker, M., Pålsson, B. I., Franzidis, J. P., & Bradshaw, D. (2017). Towards cleaner production–Using flotation to recover monazite from a heavy mineral sands zircon waste stream. Minerals Engineering, 101, 30-39.
20. Tyler, G. (2004). Rare earth elements in soil and plant systems-A review. Plant and soil, 267(1-2), 191-206.
21. USGS (2017). Mineral Commodity Summaries. 135.
22. Van Gosen, B. S., Verplanck, P. L., Long, K. R., Gambogi, J., Robert, R., & Seal, I. I. (2014). The rare-earth elements: vital to modern technologies and lifestyles (No. 2014-3078). US Geological Survey.
23. Yan, Z., Elliott, J. A., & Masliyah, J. H. (1999). Roles of various bitumen components in the stability of water-in-diluted-bitumen emulsions. Journal of colloid and interface science, 220(2), 329-337.
24. Ye, F., Miao, M., Jiang, B., Campanella, O. H., Jin, Z., & Zhang, T. (2017). Elucidation of stabilizing oil-in-water Pickering emulsion with different modified maize starch-based nanoparticles. Food Chemistry, 229, 152-158.
25. Zeng, T., Wu, Z. L., Zhu, J. Y., Yin, S. W., Tang, C. H., Wu, L. Y., & Yang, X. Q. (2017). Development of Antioxidant Pickering High Internal

Phase Emulsions (HIPEs) Stabilized by Protein/polysaccharide Hybrid Particles as Potential Alternative for PHOs. Food Chemistry.

26. Zhang, W., Honaker, R. Q., & Groppo, J. G. (2017). Flotation of monazite in the presence of calcite part I: Calcium ion effects on the adsorption of hydroxamic acid. Minerals Engineering, 100, 40-48.
27. Zhang, X., Du, H., Wang, X., & Miller, J. D. (2013). Surface chemistry considerations in the flotation of rare-earth and other semisoluble salt minerals. Minerals & Metallurgical Processing, 30(1).

초 록

희토류는 많은 최첨단 산업 분야에서 매우 중요한 자원이다. 광석으로부터 희토류를 분리하기 위해 부유선별공정이 매우 자주 이용되었다. 그러나 희토류 광물의 부유선별공정은 낮은 선택성과 효율로 인하여 매우 어렵다. 이번 연구에선 이러한 문제를 해결하고자 희토류 광물을 위한 이멀젼 선별공정을 개발했다.

이번 연구에 사용된 광석의 경우 대부분의 희토류는 모나자이트로 존재했다. 그러나 철산화물 (침철석)의 함량이 50%가 넘을 정도로 많았다. 광석 시료의 d10, d50, d90는 각각 1.31μm, 11.105μm, 51.285μm 이다.

이멀젼 선별공정은 물질의 표면 특성을 이용하여 광물을 분리한다는 점에서 부유선별공정과 유사하다고 할 수 있다. 두 공정의 차이점은 부유선별공정의 경우 소수성 매체로 공기가 이용되며 이멀젼 선별공정의 경우는 기름이 사용된다. 부유선별공정과 마찬가지로 표면 특성을 이용하는 방법이기 때문에 포수제, 억제제, 활성제가 사용된다.

본 연구에서는 용액과 기름의 부피비, pH, 입도, 기름 종류, 포수제의 양과 종류, 억제제의 양과 종류를 바꾸어가며 실험을 진행했다. 최적의 용액과 기름의 부피비는 2:1 이었으며 pH 9.5에서 가장 좋은 결과를 보였다. 광석 시료를 10μm 마이크로시브를 이용하여 분리하였으며 분리된 시료를 통해 입도의 영향을 알아보았다. 이를 통해 미립자들이 이멀젼의 안정화에 중요한

역할을 한다는 것이 밝혀졌고 또한 미립자의 도움을 통해 조립자도 이멀젼을 안정화 할 수 있는 것도 알게 되었다. 입도 차이에 의한 원소 함량 차이가 없다는 것이 확인되어 같은 시료에서는 본 선별공정은 오로지 표면 특성에 의한 분리라는 것이 입증되었다. 사용 되었던 기름 중에선 케로진이 제일 효과가 좋았으며 sodium oleate 포수제를 썼을 때 가장 좋은 결과를 얻을 수 있었다. 투입된 포수제의 양은 시료에 존재하는 희토류의 몰수에 따라 정해졌다. Sodium silicate를 억제제로 썼을 때 가장 좋은 효과를 보였다.

최적의 조건을 찾기 위해 억제제 (sodium silicate)의 투입량과 활성제 (calcium chloride)의 투입량을 조절했다. 비교를 위해 원시료와 슬라임이 제거된 시료를 대상으로 실험을 진행했다. 원시료에서의 최적 조건은 희토류 몰수만큼의 포수제 양의 0.875배의 calcium chloride와 2.625배의 sodium silicate첨가 되었을 때 이다. 이멀젼층 희토류 함량이 물층 희토류 함량에 비해 1.465배 많았으며 원시료 희토류 함량에 비해 1.114배 많았다. 회수율은 75%를 기록했다. 슬라임이 제거된 시료에서는 원시료에서의 결과보다 안 좋은 결과를 보였으며 이는 입도의 영향과 낮은 단체분리도의 영향으로 보인다.

주요어: 이멀젼, 선별공정, 부유선별, 표면화학, 희토류
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