Recovery of Fine Particles of Rare Earth Minerals by Liquid-Liquid Extraction Method

by Eishi Kusaka†, Yoshitaka Nakahiro† and Takahide Wakamatsu†

ABSTRACT

In order to recover fine particles of rare-earth minerals from beach sand by the liquid-liquid extraction method, fundamental studies were carried out using several kinds of surfactants such as oleate, alkylsulfate, alkylbenzenesulfonate and alkylammonium salts. Isooctane and water were used as two liquid phases. Monazite, xenotime, zircon and quartz were chosen as test samples. The percent recovery of each of these minerals was determined in terms of pH of aqueous solution, type of surfactant and concentration of surfactant.

Zeta potential variations were measured as a function of pH for each of these minerals to determine its isoelectric point (IEP). In the pH range below the IEP of the mineral where the mineral particles were positively charged, high recoveries were obtained when the anionic surfactant was used at its proper concentrations.

To evaluate an oil-wettability of the mineral surface, contact angles in the monazite/isooctane/water system in the presence of the surfactant were measured. Interfacial tensions between isooctane and surfactant solution were also measured. Work of adhesion was then determined. The recovery variations were closely correlated with the work of adhesion.

Key Words: Liquid-liquid extraction, Fine particles, Rare earth minerals, and Work of adhesion.

INTRODUCTION

Monazite, (Ce, La)PO₄, xenotime, (Y)PO₄, and zircon, (Zr)SiO₄, are important minerals in producing rare-earth and related elements. These minerals are often found in the tin placer deposit of Southeast Asia together with cassiterite, ilmenite rutile, garnet, hematite, barite, quartz and so on. The ores are treated by a combination of the electrostatic, magnetic and gravity separation techniques to get valuable concentrates. However, the finer mineral particles become, the more difficult is the mutual separation among them. Consequently, fine particle fractions including lots of useful minerals are waste or dumped because they cannot be recovered by the conventional techniques.
As a fine particle processing, the froth flotation is well known and applied to improve the recovery of fine minerals. But it is even in flotation that the feed size to the flotation cells should be restricted to over ten microns because the presence of an energy barrier in the vicinity of the air/water interface prevents fine particles from making contact with bubbles. Therefore, the liquid-liquid extraction method has been studied to recover ultrafine particles and to remove mineral matter particles from coal.

In this study, the applicability of the liquid-liquid extraction for recovering fine mineral particles such as monazite, xenotime and zircon was investigated in terms of pH of aqueous solution, type of surfactant and electrokinetic property of the particle. In addition, quartz, a typical gangue mineral, was also used in the investigation to discuss the optimum condition for the mutual separation among those minerals by the liquid-liquid extraction technique.

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials

Monazite (from Malaysia), xenotime (from Brazil), zircon (from Vietnam) and quartz (from Japan) were used in this investigation. High grade pieces of these minerals were selected and ground in a vibratory ball mill for a few hours. The ground products were confirmed as pure mineral samples by the X-ray diffraction analysis. The specific surface area of the monazite, xenotime, zircon and quartz samples, as determined by the B.E.T. method, were 3.8 m²/g, 8.2 m²/g, 2.5 m²/g and 15.8 m²/g, respectively.

Reagent grade isooctane (2,2,4-trimethylpentane) was used as an oil phase throughout the experiments. In order to control the oil-wettability of the mineral surface and to stabilize the oil-in-water emulsion system in the extraction process, sodium oleate (NaOl), sodium dodecylbenzene-sulfonate (SDBS), sodium dodecylsulfate (SDS) and dodecylammonium acetate (DAA) or dodecylammonium chloride (DAC) were used as surfactants. All the surfactants were reagent grade. The pH in the suspension was adjusted with hydrochloric acid and sodium hydroxide. Sodium chloride was used as a supporting electrolyte for the measurement of electrophoretic mobility.

Experimental procedure

The mineral sample and surfactant solution both in their desired amounts were put into a 100-cm³ pyrex separatory funnel. The funnel was then shaken for 20 min. After shaking, isooctane was added to make up an oil-water-particle mixture. The weight ratio of solid, oil and aqueous solution was kept constant throughout the tests. The mixture was further shaken for 20 min to form the oil-in-water emulsion. During the emulsion forming operation, most of the particles were collected at the oil-water interface, while some were transferred into the oil phase according to the hydrophobicity of particle surfaces. The oil-water-particle mixture was allowed to stand for several minutes in order to separate the dense emulsion phase from the water phase. The two phases were drained into separate beakers, filtered, and dried. The dried solids were weighed to determine the recovery of the fine particles at the oil/water interface and in the oil phase.

The zeta potential at various pH's and NaCl concentrations was electrophoretically measured by means of a zeta-meter. Values of the zeta potential were obtained by the use of the Smoluchowski equation.

The contact angle measurement was carried out by means of a tilting method, and the
EXPERIMENTAL RESULTS AND DISCUSSIONS

Zeta potential

Figs. 1 (a) to 1 (d) show the effect of pH on the zeta potential of monazite, xenotime, zircon and quartz in the presence of NaCl. From the results, monazite has its IEP at pH 4.9, xenotime at pH 3.9 and zircon at pH 3.7, which are determined by the pH of the solution and are independent of the NaCl concentration. Quartz is negatively charged within the pH range tested at 1.0×10⁻³ mol/dm³ NaCl.

Effect of NaOIr

Figs. 2 (a) to 2 (d) show the effect of pH on the liquid-liquid extraction recovery of the fine particles of monazite, xenotime, zircon and quartz at various concentrations of NaOIr.

High recoveries of monazite particles by the liquid-liquid extraction are obtained at pH 5 to 9 with
Fig. 2 Recovery of (a) monazite, (b) xenotime, (c) zircon and (d) quartz as a function of pH in the presence of sodium oleate (NaOl).

Low NaOl concentrations of $3.3 \times 10^{-5}$ and $1.6 \times 10^{-4}$ mol/dm$^3$. When NaOl concentration increases up to $3.3 \times 10^{-4}$ mol/dm$^3$, the optimum pH for high recoveries ranges from pH 3 to 10. In acidic solution, the recovery increases as NaOl concentration increases, while this tendency is less pronounced in alkaline solution. The shape of the recovery-pH curve for xenotime, as shown in Fig. 2(b), is similar to that for monazite. High recoveries for zircon, as presented in Fig. 2(c), are obtained in the pH range from 5 to 7 with low NaOl concentration of $1.7 \times 10^{-5}$ mol/dm$^3$ NaOl and in the pH range from 4 to 8 with $1.7 \times 10^{-4}$ mol/dm$^3$. An increased NaOl concentration brings about an increase in the recovery at any pH’s. As shown in Fig. 2(d), oleate surfactant has an effect on the recovery of quartz particles.

Comparing Fig. 2 with Fig. 1, it can be considered that oleate species adsorb somewhat chemically on the surface of each of these minerals in the pH range beyond each of their IEP’s where the particles are negatively charged. In the pH range below each of their IEP’s where the particles are positively charged, the electrostatic attraction between oleate anion and mineral surface may enhance the oleate adsorption.
Effect of SDBS

Figs. 3(a) to 3(d) present the effect of pH on the liquid-liquid extraction recovery of monazite, xenotime, zircon and quartz at different SDBS concentrations.

The recovery of monazite, as shown in Fig. 3(a), is at a maximum around pH 6 with SDBS concentrations of $4.0 \times 10^{-6}$ and $2.0 \times 10^{-5}$ mol/dm$^3$. With $1 \times 10^{-4}$ mol/dm$^3$ SDBS, high recoveries are obtained below pH 7. The recovery decreases rapidly beyond pH 7, independent of the SDBS concentration. Fig. 3(b) shows that the xenotime recoveries with $1.7 \times 10^{-6}$ and $1.7 \times 10^{-5}$ mol/dm$^3$ SDBS reach maxima at pH 6.5 and rapidly decrease below and beyond pH 6.5. With $1.7 \times 10^{-4}$ mol/dm$^3$ SDBS, high recoveries are obtained in the pH range below 7. The zircon recovery (Fig. 3(c)), whose pH-dependence is similar to those of monazite and xenotime, tends to decrease with increasing pH beyond 6 at any SDBS concentrations, and to increase with increasing the SDBS concentration in the pH range below 6. The addition of SDBS does not give significant effect on the quartz recovery as shown in Fig. 3(d).
Fig. 4 Recovery of (a) monazite, (b) xenotime, (c) zircon and (d) quartz as a function of pH in the presence of sodium dodecylsulfate (SDS).

Effect of SDS

Figs. 4 (a) to 4 (d) show the effect of pH on the recovery of monazite, xenotime, zircon and quartz at various concentrations of SDBS. The recovery-pH curves obtained here are similar to those in the case of SDBS because the chemical nature of SDS is analogous to that of SDBS.

Effect of dodecylammonium salt

Figs. 5 (a) to 5 (d) show the effect of pH on the recovery of monazite, xenotime, zircon and quartz at different concentrations of DAA or DAC. As the dodecylammonium salt is a cationic surfactant, the pH-dependence of the recovery curve with cationic surfactant is disimilar to those with anionic surfactants of SDBS and SDS.

As shown in Fig. 5, it is noted that high quartz recoveries by the liquid-liquid extraction can be achieved with a cationic surfactant of DAA in the pH range beyond its IEP where quartz surfaces are negatively charged. Furthermore, an increase in the DAA concentration in the pH range beyond the IEP produces an increase in the recovery. Similar results are obtained with other mineral samples. Taking
Recovery of Fine Particles of Rare Earth Minerals
by Liquid-Liquid Extraction Method

![Graphs showing recovery of different minerals as a function of pH](image)

Fig. 5 Recovery of (a) monazite, (b) xenotime, (c) zircon and (d) quartz as a function of pH in the presence of dodecylammonium acetate (DAA) or dodecylammonium chloride (DAC).

The zeta potential of the particle (Fig. 1) into account, it can be considered that electrostatic attraction between dodecylammonium ion (RNH$_3^+$) and the negatively-charged mineral surface enhances the surfactant adsorption sufficient to make the surface hydrophobic, which contributes to high recoveries in the pH range beyond the IEP of each of these minerals.

**Oil-wettability of mineral surface**

In order to understand surface-chemical aspects of the liquid-liquid extraction, the relationships between the recovery, the surfactant concentration and the oil-wettability of mineral surfaces are discussed specially in the system composed of monazite particles, isooctane and water in the presence of SDBS.

Fig. 6 shows the effect of the SDBS concentration on the recovery of monazite particles at a given pH of 5. As shown in Fig. 6, the recovery tends to increase as the SDBS concentration increases up to $1 \times 10^{-4}$ mol/dm$^3$. High recoveries over 95% are obtained in the SDBS concentration range from $4 \times 10^{-4}$ to $2 \times 10^{-4}$ mol/dm$^3$. However, the addition of SDBS above $2 \times 10^{-4}$ mol/dm$^3$ results in a rapid
The Young-Dupré equation regarding work of adhesion at the mineral/oil interface in the water phase can be expressed as follows:

\[
W_a = Y_{ow} (1 - \cos \theta_{w/o})
\]

where \(W_a\) is work of adhesion for the mineral/oil interface in the water phase, \(Y_{ow}\) is the oil/water interfacial tension, and \(\theta_{w/o}\) is contact angle of the oil droplet on the mineral surface in the water phase as schematically presented in Fig. 7. If the interfacial tension, \(Y_{ow}\), between SDBS solution and isooctane and the contact angle, \(\theta_{w/o}\), of the isooctane/water interface on the monazite surface are experimentally determined, it is possible to calculate the work of adhesion, \(W_a\), of isooctane on the monazite surface in the water phase.

The result of the isooctane/water interfacial tension measurement is presented in Fig. 8 as a function of SDBS concentration. SDBS is fully ionized in an aqueous solution since it is a strong electrolyte. Under the experimental conditions used, it was confirmed that no sulfonate should be extracted into the isooctane phase. The interfacial tension remains approximately constant at any pH's. As shown in Fig. 8, a linear relationship is obtained between the interfacial tension and the logarithm of the SDBS concentration above \(2 \times 10^{-4}\) mol/dm³.

Fig. 9 shows the effect of the SDBS concentration on the contact angle at pH 5.0. The contact angle curve shown in Fig. 9 can be divided into three regions, as suggested by Somasundaran et al.
The contact angle increases gradually with SDBS concentration when the concentration is less than $2 \times 10^{-5} \text{ mol/dm}^3$. Within the range of SDBS concentration from $2 \times 10^{-5}$ to $1 \times 10^{-4} \text{ mol/dm}^3$, the contact angle increases rapidly with increasing SDBS concentration. When the SDBS concentration is more than $1 \times 10^{-4} \text{ mol/dm}^3$, the contact angles increase again slightly.

Fig. 10 shows the relationship between the work of adhesion, $W_a$, and the SDBS concentration. The work of adhesion, $W_a$, in the monazite/isooctane/water system can be evaluated from the contact angle (in Fig. 9) and the interfacial tension (in Fig. 8) by the use of Equation 1. $W_a$ increases more than 50 mJ/m$^2$ as the SDBS concentration increases up to $1 \times 10^{-4} \text{ mol/dm}^3$. The increased SDBS concentration over $1 \times 10^{-4} \text{ mol/dm}^3$ leads to a rapid decrease in $W_a$. In view of the work of adhesion, it is considered that the SDBS concentration of $1 \times 10^{-4} \text{ mol/dm}^3$ should be an optimum condition at pH 5.

Comparing Fig. 10 with Fig. 6, a good correlation between $W_a$ and the monazite recovery is obtained. The recovery of monazite decreases rapidly within the SDBS concentration range where $W_a$ is markedly reduced within the SDBS concentration range where $W_a$ is markedly reduced. Fig. 11 shows the relationship between work of adhesion, $W_a$, and the monazite recovery given in Fig. 4(a) and Fig. 6. The calculations of $W_a$ in this figure were made using additional results of contact angle measurements at various pH's and SDBS concentrations. As shown in Fig. 11, an increase in $W_a$ results in an increase in the monazite recovery. $W_a$ of 50 mJ/m$^2$ gives a monazite recovery of more than 80%, whereas $W_a$ of 30 mJ/m$^2$ gives around 20%. Hence, it has been confirmed that work of adhesion is of great importance since it determines the liquid-liquid extraction recovery regardless of pH in aqueous suspension and concentration of the surfactant used.

CONCLUSIONS

As a fundamental study for recovering fine rare-earth minerals from beach sand by the liquid-liquid extraction method, the concentrations of fine mineral particles such as monazite, xenotime, zircon and quartz at the oil/water interface have been investigated in the presence of surfactant. The summaries obtained are as follows:
Eishi KUSAKA, Yoshitaka NAKAHIRO and Takahide WAKAMATSU

(1) High recoveries of monazite, xenotime and zircon by the liquid-liquid extraction are obtained in the neutral and alkaline pH range with NaOl as surfactant. An increased NaOl concentration results in an increase in the recoveries over a relatively wide pH range of the suspension. Comparing these results with their IEP's, it is considered that oleate species should adsorb somewhat chemically on these mineral surface. Oleate surfactant has no effect on the liquid-liquid extraction of fine quartz particles.

(2) Regarding the liquid-liquid extraction of monazite, xenotime and zircon with an anionic surfactant such as SDBS and SDS, an increased concentration of the surfactant increases the mineral recovery in the pH range below the IEP where the mineral particle is positively charged, while the recoveries decrease rapidly when the pH increases beyond the IEP where the particles are negatively charged. From the results obtained, it is considered that electrostatic attraction between the particle surface and the surfactant anion may contribute to an increase in the surfactant adsorption onto mineral surface, rendering particles more hydrophobic. Quartz is not amenable to the liquid-liquid extraction using SDBS or SDS.

(3) The addition of a cationic surfactant of dodecylammonium salt gives high quartz recoveries by the liquid-liquid extraction method in the pH range beyond its IEP where the quartz particle is negatively charged. An increased amine concentration brings about an increase in the quartz recovery in the same pH. Similar results have been obtained with each of the rare-earth minerals used. From the results obtained above, it is considered that the electrostatic adsorption of dodecylammonium cation on the mineral surface may produce the particle surface hydrophobic and play an important role in mineral recovery of liquid-liquid extraction.

(4) The effect of the SDBS concentration on the monazite recovery at pH 5 was determined. The recovery increases with the SDBS concentration and reaches a maximum over 95% within the SDBS concentration range below $1 \times 10^{-4}$ mol/dm$^3$. However, the recovery decreases rapidly with increasing SDBS concentration over $1 \times 10^{-4}$ mol/dm$^3$. To evaluate the oil-wettability on the monazite surface, the contact angle in the monazite/isooctane/water system and the isooctane/water interfacial tension was also determined in terms of the SDBS concentration. The work of adhesion based on the Young-Dupre equation being then calculated, a characteristic correlation is obtained between the work of adhesion and the monazite recovery independent of the pH of aqueous suspension and the surfactant concentration.

REFERENCES

6) Shergold, H.L. and Mellgren, O., "Concentration of mineral at the oil-water interface: hematite-

7) Shergold, H.L. and Mellgren, O., "Concentration of hematite at iso-octane-water interface with

8) Marinakis, K.I. and Kelsall, G.H., "Adsorption of dodecylphosphonate on wolframite,
(Fe, Mn)WO₄, and their use in the two liquid flotation of fine wolframite particles," J. Colloid

9) Marinakis, K.I. and Kelsall, G.H., "Effect of lattice cations, silicate ions and fluorosilicate ions on

10) Zambrana, G.Z., Medina, R.T., Gutierrez, G.B. and Vargas, R.R., "Recovery of minus ten micron

11) Kusaka, E., Nakahiro, Y. and Wakamatsu, T., "Recovery of fine monazite particles by liquid-liquid

12) Kusaka, E., Nakahiro, Y., Wakamatsu, T. and Sri Murdiati, "Recovery of fine ilmenite particles


(1941).

15) Somasundaran, P. and Fuerstenau, D.W., "Mechanisms of alkyl sulfonate adsorption at the