

Chemical leaching of rare earth elements from highly REY-rich mud

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Seafloor sediment rich in rare earth elements and Y (REY-rich mud) has received attention as a new resource for REY. During research cruise KR13-02 of R/V *Kairei*, mud containing more than 5,000 ppm total REY was collected near Minamitorishima Island, northwestern Pacific Ocean. We conducted a series of chemical leaching experiments on this material, varying the acid concentrations, leaching times, and temperature to determine the optimum conditions of REY leaching from REY-rich mud. The highest extraction efficiency of REY other than Ce was 95.1% using hydrochloric acid and 81.3% using sulfuric acid. Extraction efficiency of REY was highest under conditions of relatively low acid concentrations (0.25–0.5 mol/L), short leaching times (2–5 min), and room temperature (25°C). REY extraction amount decreased with increasing acid concentration, leaching time (only in the case of sulfuric acid), and temperature, apparently because of precipitation of calcium sulfate, rare earth phosphate, and rare earth-Na double sulfate. Although further research is needed, the leaching properties we determined are generally favorable for industrial exploitation of REY-rich mud.

Keywords: rare earth elements, REY-rich mud, deep-sea mineral resource, chemical leaching

INTRODUCTION

Rare earth elements (REEs) and Y, collectively called REY in this paper, are essential materials for contemporary technology. However, the production of REY relies heavily on China (about 90% of world mine production in 2013), and diversification of the REY supply is an urgent issue for many countries (U.S. Geological Survey, 2014). With the discovery of large bodies of REY-rich mud in the Pacific Ocean (Kato *et al.*, 2011), this material is attracting attention as a new REE resource (Szamalek *et al.*, 2013; Papavasileiou, 2014). Following this discovery, in 2013, extremely REY-rich mud, defined as mud with more than 5,000 ppm total REE concentration (Σ REY), was discovered in the western Pacific Ocean off Minamitorishima Island, Japan (Iijima *et al.*, 2015;

Fujinaga *et al.*, 2015).

In previous studies of marine sediments, potential host minerals of REY have been identified as iron oxyhydroxides/oxides, manganese oxide, and apatite. Iron oxyhydroxides/oxides from hydrothermal fluids adsorb many elements, including REY, from surrounding seawater, and precipitate as metalliferous sediments (Ruhlin and Owen, 1985; German *et al.*, 1991a, b; Rudnicki and Elderfield, 1992; Feely *et al.*, 1994; Mills and Elderfield, 1995; German and Von Damm, 2007). Marine manganese/ferromanganese oxides such as Mn nodules and Mn crusts are also enriched in many metals of economic interest, including REY, and may represent a future resource for these elements (Hein *et al.*, 2013). Biogenic apatite in pelagic sediment is known to be enriched in REY (Elderfield and Pagett, 1986; Toyoda *et al.*, 1990; Toyoda and Tokonami, 1990). Recently, Kashiwabara *et al.* (2014) determined by high-energy X-ray analysis that lanthanum (La) in REY-rich mud from piston core samples of sites 597 and 75 of the Deep Sea Drilling Project (DSDP) is concentrated in apatite. Kon *et al.* (2014) demonstrated that the total REY contents of apatite in REY-rich mud from near Minamitorishima Island averaged 21,000 ppm.

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Kato *et al.* (2011) established that chemical leaching is effective for REY extraction from REY-rich mud. More specifically, Takaya *et al.* (2014) demonstrated that dilute hydrochloric acid and sulfuric acid can leach most REY from standard deep-sea sediment (reference material JMS-2 from the Geological Survey of Japan, in which $\Sigma\text{REY} = 916$ ppm) rapidly (<5 min) and at room temperature (25°C). However, some questions, such as the effect of seawater on REY extraction and the possible secondary precipitations in the leaching solution, are still uncertain. It is imperative to elucidate more detailed leaching characteristics of rare earth elements in order to design the development system and to perform the economical evaluation. For this study, we conducted chemical leaching experiments under conditions similar to actual hydrometallurgical process with highly REY-rich mud ($\Sigma\text{REY} = 2,000\text{--}5,000$ ppm) collected from near Minamitorishima Island and determined the optimum leaching conditions toward the exploitation of REY-rich mud.

MATERIALS AND METHOD

For this study, we prepared a 60 g sample of REY-rich mud by mixing the samples from core PC05, collected during cruise KR13-02 of R/V *Kairei*. Core PC05, collected at N21°59'03", E153°56'35" and 5,735 m water depth, had ΣREY concentrations exceeding 7,000 ppm (Iijima *et al.*, 2015; Fujinaga *et al.*, 2015; Ohta *et al.*, 2015). We combined samples from 0.67 to 3.24 m below the seafloor and mixed them thoroughly in an agate mortar. In our whole-rock chemical analysis using inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS), ΣREY of this mixed mud sample exceeded 3,500 ppm (Table 1). X-ray diffraction (XRD) analysis revealed that the main constituent minerals were phillipsite-Na, quartz, fluorapatite, halite, illite, and muscovite. This mixed sample is classified as apatitic silty clay.

We conducted a series of chemical leaching experiments using hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) at various concentrations, leaching times, and temperatures to determine the most efficient extraction condition of REY. We diluted the acids with "Aquamarine" synthetic seawater (Yashima Pure Chemicals Co., Ltd.; composition in Supplementary Table S1) to simulate the actual leaching processes.

Samples were dried at 60°C for over 24 h prior to the leaching experiments. A mud sample weighing 0.1 ± 0.001 g was combined with 1.5 mL of the leachate solution (hydrochloric acid or sulfuric acid diluted with synthetic seawater) in a PFA vessel. We shook the vessel to agitate the mud and leachate and placed it in a temperature-controlled bath. After the prescribed reaction time, we again shook the vessel and collected the leaching solution. The

Table 1. Whole-rock chemical composition of REY-rich mud used in this study

	\bar{X}	SD
Na (wt %)	3.21	0.12
Mg	1.32	0.05
Al	6.84	0.27
P	2.20	0.07
K	2.54	0.09
Ca	5.08	0.19
Sc (ppm)	64.1	2.2
Ti (wt %)	0.41	0.02
V (ppm)	120	4
Cr	34.3	2.7
Mn (wt %)	1.34	0.05
Fe	4.76	0.16
Co (ppm)	182	5
Ni	376	14
Cu	341	15
Zn	152	7
As	18.9	0.6
Se	below detection limit	
Rb	66.6	2.4
Sr	401	15
Y	1046	37
Zr	149	5
Nb	11.4	0.4
Mo	69.1	2.1
Ru	0.00161	0.00028
Rh	0.00305	0.00089
Pd	below detection limit	
Ag	below detection limit	
Cd	0.26	0.02
In	0.21	0.01
Sn	2.19	0.16
Sb	3.27	0.08
Te	1.30	0.08
Cs	4.59	0.18
Ba	245	8
La	514	17
Ce	282	11
Pr	149	5
Nd	733	28
Sm	152	6
Eu	37.8	1.4
Gd	173.7	6.4
Tb	25.9	1.0
Dy	162	6
Ho	33.0	1.2
Er	93.5	3.5
Tm	12.5	0.4
Yb	76.2	2.8
Lu	11.5	0.4
Hf	3.93	0.17
Ta	0.65	0.03
W	5.43	0.20
Re	below detection limit	
Ir	0.0437	0.0296
Pt	0.0152	0.0031
Au	below detection limit	
Tl	3.82	0.10
Pb	42.3	1.5
Bi	1.31	0.04
Th	24.8	0.9
U	5.91	0.19

solution was immediately filtered with a 0.45 μm mesh filter and then diluted 400 times for analysis by ICP-QMS (Agilent 7500c, the University of Tokyo). Details of the ICP-QMS analysis are given in Kato *et al.* (2005, 2011).

The experimental conditions included eight different acid concentrations, four leaching times, and three leaching temperatures as follows.

Acid concentration:

HCl: 0.5 mol/L, 1.0 mol/L, 2.0 mol/L, 3.0 mol/L

H₂SO₄: 0.25 mol/L, 0.5 mol/L, 1.0 mol/L, 1.5 mol/L

Leaching time: 2 min, 5 min, 15 min, 60 min

Leaching temperature: 25°C, 50°C, 75°C.

In order to compare the experimental results between different acid solutions (HCl and H₂SO₄), the concentrations of these acids are set to the same normality (0.5 N, 1.0 N, 2.0 N and 3.0 N). To cover all combinations of these conditions, we conducted 96 leaching experiments. In addition, we performed 24 experiments using Milli-Q water instead of synthetic seawater with leaching times of 5 min that is sufficient for high extraction efficiency of REY in the experiments using synthetic seawater.

We calculated the extraction percentage of each element by the following equation and discuss the leaching characteristics.

$$\text{Extraction}[\%] = \frac{(A_i - B_i) \times R}{C_i} \times 100.$$

A_i : concentration of each element in the leaching solution (after the leaching);

B_i : concentration of each element in the leaching solution (before the leaching);

R : water/mud weight ratio (≈ 15);

C_i : concentration of each element in the mud sample.

Extraction levels of REY, major elements (Al, P, K, Ca, Ti, Mn, Fe), valuable metal elements (V, Co, Ni, Cu, Mo), and the radioactive elements Th and U from the leaching experiments are reported in Figs. 1–8 and Supplementary Table S2. We subdivided REY extraction into Y, Ce, light REE other than Ce (LREE: La, Pr, Nd, Pm, Sm, Eu), and heavy REE other than Y (HREE: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Extraction levels of Na and Mg are excluded because the amounts leached were so small relative to the amounts in seawater that their accuracy was low.

RESULTS

Experiments using hydrochloric acid and synthetic seawater

Increasing the HCl concentration increased the extraction levels of most major elements (Al, K, Ti, Mn, Fe), valuable metals (V, Co, Ni, Cu, Mo), Th, and Ce (Fig. 1). For instance, Th and Ce extraction percentages at 25°C

and 5 min leaching time were 18.0% and 28.5% with 0.5 mol/L HCl, respectively, but increased to 75.4% and 68.2% with 3.0 mol/L HCl (Fig. 1b). At 75°C, extraction of Mn, Fe, V, Co, and Mo increased greatly with increasing acid concentration; for example, with 60 min leaching time, extraction percentages increased from 3.4% to 87.5% for Mn, from 4.7% to 48.4% for Fe, from 7.6% to 55.8% for V, from 2.4% to 85.6% for Co, and from 1.2% to 71.7% for Mo as acid concentration rose from 0.5 to 3.0 mol/L HCl (Fig. 11). Extraction levels of P, Ca, U, Y, LREE, and HREE was high ($>80\%$ for most) at all acid concentrations, which suggests that these elements are hosted in the same mineral phases. The highest total extraction efficiency of REY other than Ce was 95.1% (Y: 100%, LREE: 91.3%, HREE: 96.5%) and was obtained under conditions of 0.5 mol/L HCl, 5 min leaching time, and 25°C.

Increasing the leaching time increased the extracted amount of Al, K, Ti, Mn, Fe, Co, Ni, and Cu at all acid concentrations and temperatures (Fig. 2). This effect was particularly strong for five of these metals (Mn, Fe, Co, Ni, and Cu) at higher HCl concentrations and higher temperatures. Although extraction levels of V, Mo, and to lesser extent Th and Ce varied little with leaching time at lower temperature (25°C) or lower HCl concentrations (0.5 and 1.0 mol/L), their extraction improved with time at higher concentrations and higher temperatures. Extraction levels of P and Ca, and to a lesser extent U, Y, LREE, and HREE, were high at 2 min leaching time and changed only slightly with time at all temperatures.

Increasing the leaching temperature increased the extraction levels of Al, K, Ti, Mn, Fe, Co, Ni, and Cu under all combinations of HCl concentration and leaching time (Fig. 3). This increase was relatively large for Mn, Fe, Co, Ni, and Cu, especially at higher HCl concentrations and longer leaching times. Extracted amount of V, Mo, Th, and Ce decreased with rising temperature at low HCl concentrations and short leaching times, but increased with temperature at higher acid concentrations and longer leaching times. Extraction levels of P, Ca, Y, LREE, and HREE decreased significantly with rising temperature except in two experiments (HCl concentration 3.0 mol/L, leaching times 15 and 60 min). In the case of 0.5 mol/L HCl and 2 min leaching time, extraction percentages decreased from 100% to 88.6% for P, from 100% to 83.0% for Ca, from 99.2% to 82.1% for Y, from 89.5% to 76.4% for LREE, and from 94.4% to 81.8% for HREE between 25 and 75°C (Fig. 3a).

In the experiments using hydrochloric acid, the elements fell into three groups with respect to their dissolution behavior, suggesting that each group favors specific host minerals. The first group (Al, K, Ti, Mn, Fe, Co, Ni, Cu) tended to dissolve increasingly with increasing acid concentration, temperature, and leaching time. The sec-

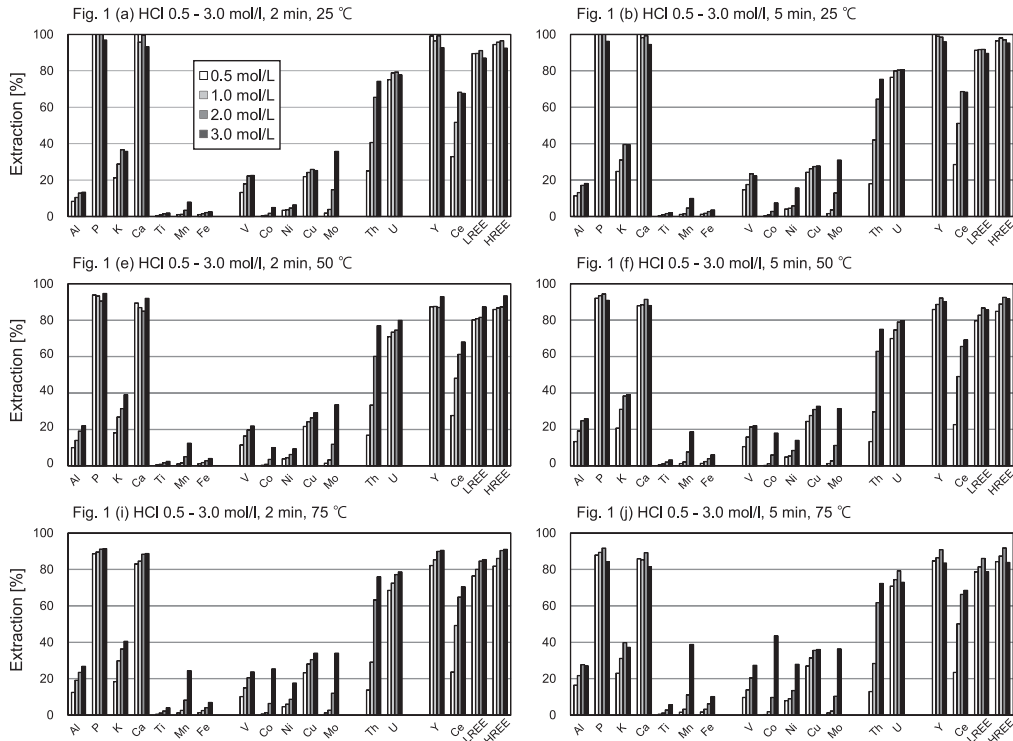


Fig. 1. Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of HCl concentration using seawater as the diluent.

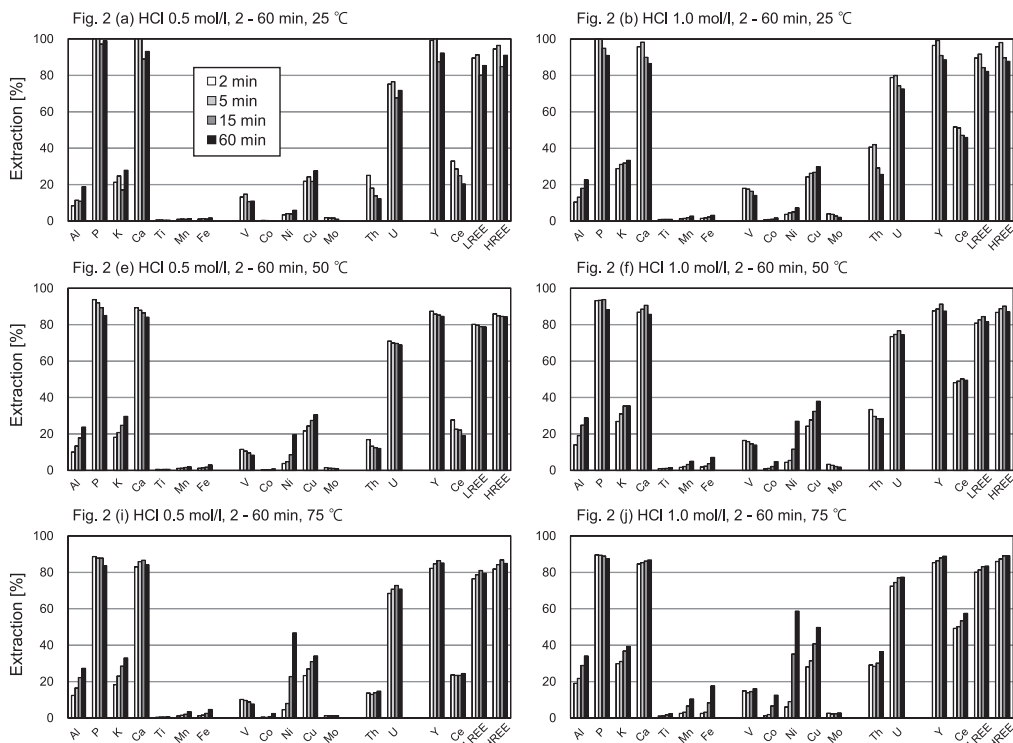


Fig. 2. Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of leaching time using HCl and seawater as the leaching solution.

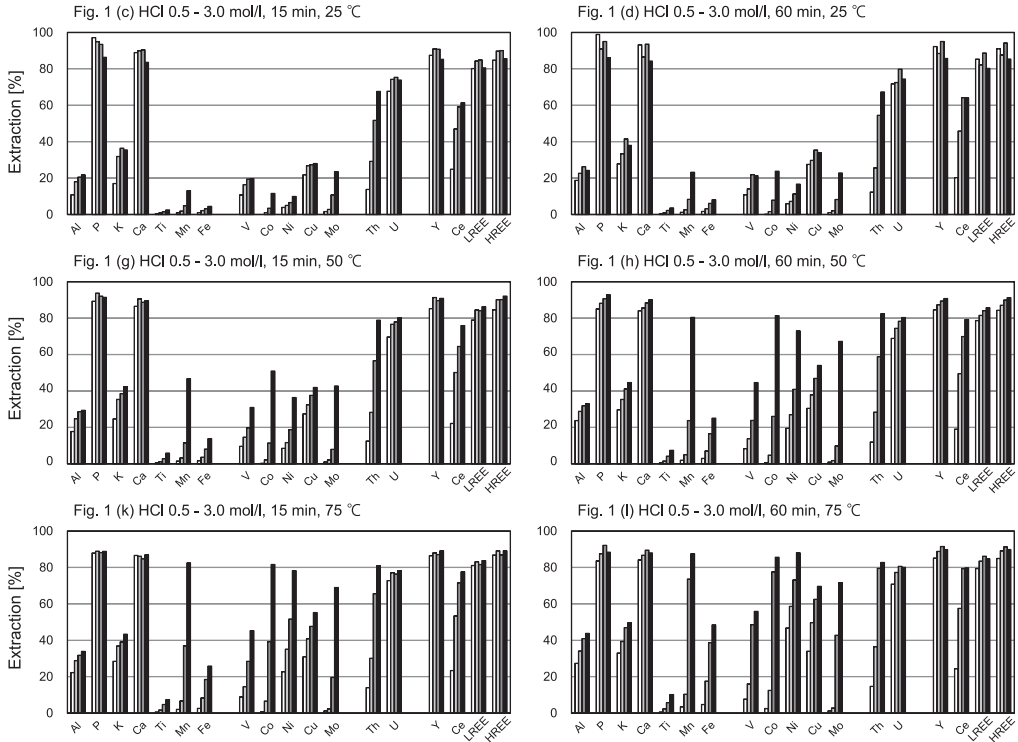


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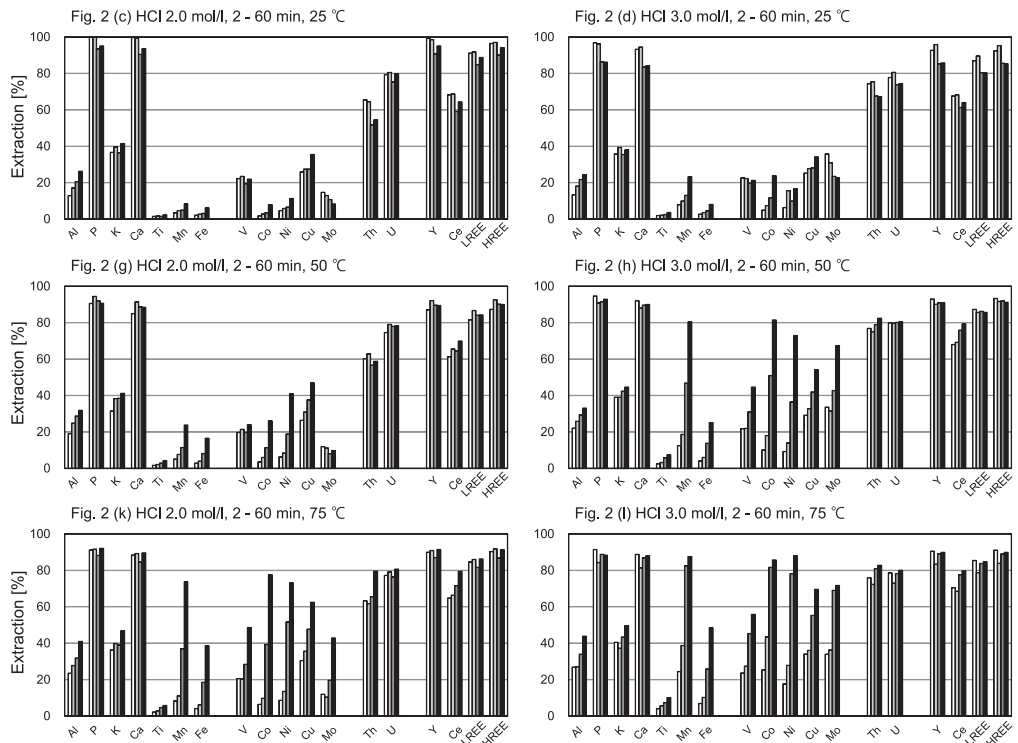


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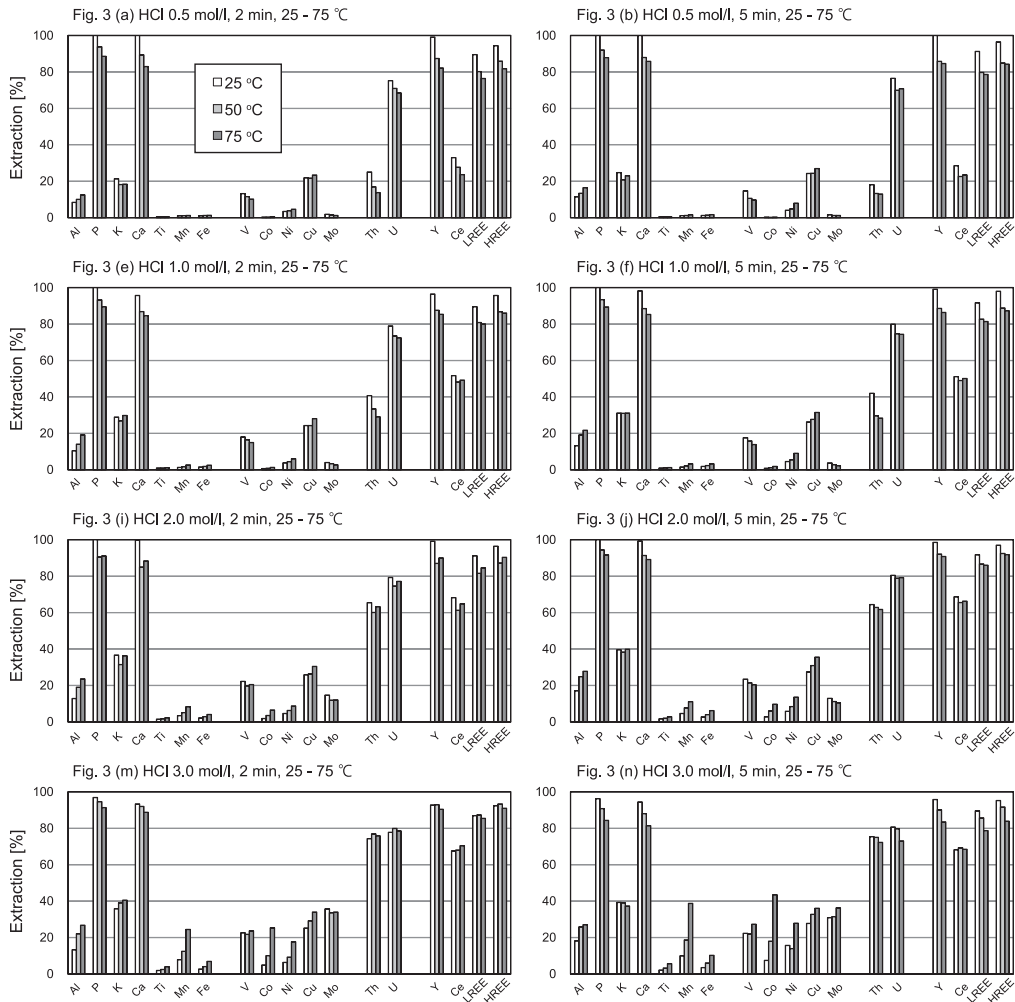


Fig. 3. Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of leaching temperature using HCl and seawater as the leaching solution.

ond group (V, Mo, Th, Ce) tended to be strongly affected by the concentration of HCl. The third group (P, Ca, U, Y, LREE, HREE) had high extraction levels even at low acid concentrations, short leaching times, and low temperatures.

Experiments using sulfuric acid and synthetic seawater

Increasing the H_2SO_4 concentration increased the extracted amount of five major elements (Al, K, Ti, Mn, Fe) and all valuable metal elements (V, Co, Ni, Cu, Mo) at all leaching times and temperatures (Fig. 4). Extraction levels of Th and Ce was highest at intermediate acid concentrations (0.5 or 1.0 mol/L), perhaps because precipitation of Th and Ce in response to increasing acid concentration offset their dissolution. Extracted amount of P showed no clear relation with H_2SO_4 concentration, except that at short leaching times and low temperatures the amount tended to decrease slightly with acid concen-

tration (Figs. 4a and b). Extraction level of Ca decreased with increasing acid concentration at 25°C and 50°C, but at 75°C extraction level differed depending on leaching time: it decreased with rising acid concentration at 2 min, remained almost constant at all acid concentrations at 5 min, and increased with the acid concentration at 15 and 60 min leaching time. The highest extraction percentage for Ca was only 66.3% with H_2SO_4 , significantly lower than its extraction with HCl, which was never lower than 81.4%. Extraction levels of Y, LREE, and HREE decreased significantly with increasing acid concentration in all conditions, and their extraction levels with H_2SO_4 were lower than the results with HCl. The highest extraction efficiency of REY other than Ce was 81.3% (Y: 87.4–90.5%, LREE: 73.8–75.6%, HREE: 85.3–85.8%) at acid concentration of 0.25 mol/L, 2 min leaching time, and 25°C or 75°C.

Increasing the leaching time increased the extracted

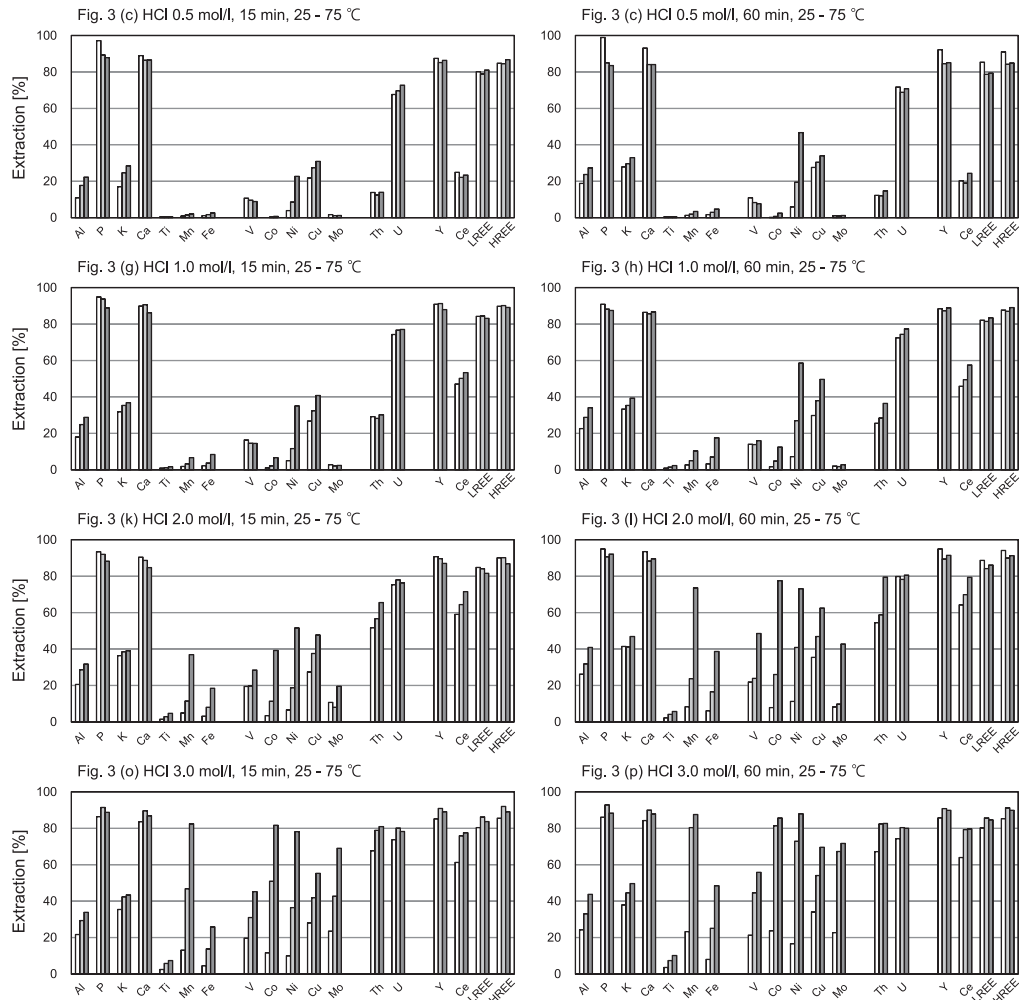


Fig. 3. (continued).

amount of Al, K, Ti, Mn, Fe, Co, Ni, and Cu under all conditions (Fig. 5). For Mn, Fe, Co, Ni, and Cu this effect was especially strong at higher acid concentrations and temperatures. Extraction of P was little affected by leaching time and was over 80% in almost all experiments. Extracted amount of Ca decreased with time, and that of V was almost constant with time, except for the cases of 1.0 mol/L or 1.5 mol/L acid concentration and 75°C, when the amount of both elements increased with time. Extraction level of Mo showed no dependence on leaching time. Extracted levels of Th and Ce generally decreased with time at lower acid concentrations (0.25 and 0.5 mol/L) and increased with time at higher concentrations (1.0 and 1.5 mol/L). Extraction levels of U, Y, LREE, and HREE were almost constant with time at lower acid concentrations and clearly increased with time at higher concentrations.

Increasing the leaching temperature increased the ex-

tracted amount of Al, K, Ti, Mn, Fe, Co, Ni, Cu, and P (Fig. 6). Extraction level of Ca increased with temperature except at lower H₂SO₄ concentration (0.25 mol/L) and short leaching times (2 and 5 min), when the extraction level decreased slightly with increasing temperature. Extraction of V was almost constant or decreased slightly with rising temperature at 0.25 and 0.5 mol/L acid concentrations, but increased with temperature increases at high concentrations (1.0 and 1.5 mol/L). Extraction level of Th decreased slightly with rising temperature in almost all conditions, U extraction increased slightly with temperature, and REY extraction was almost constant or decreased slightly with rising temperature in most experiments.

In the experiments using sulfuric acid, as with those using hydrochloric acid, extraction levels of eight elements, Al, K, Ti, Mn, Fe, Co, Ni, and Cu, increased with increasing acid concentration, temperature, and leaching

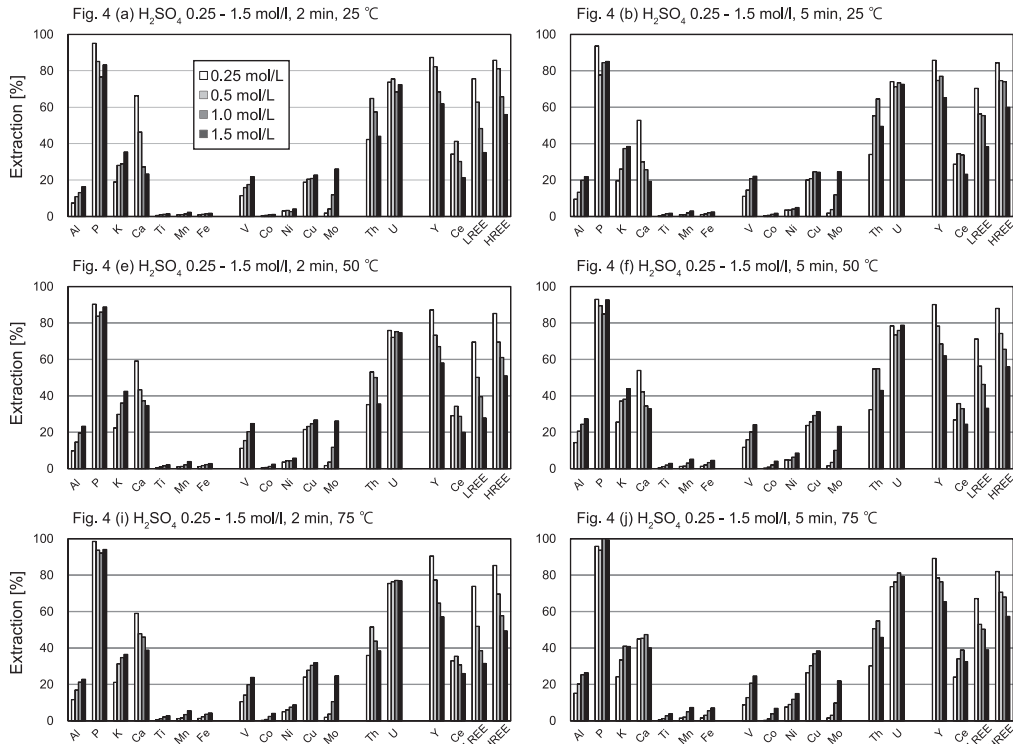


Fig. 4. Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of H_2SO_4 concentration using seawater as the diluent.

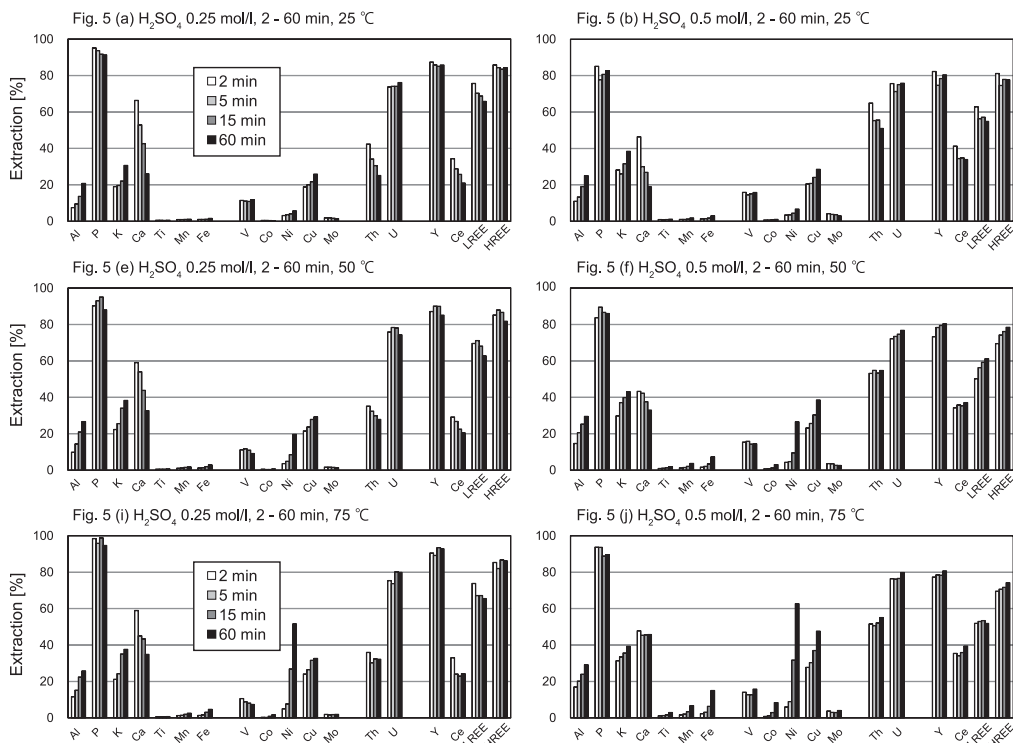


Fig. 5. Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of leaching time using H_2SO_4 and seawater as the leaching solution.

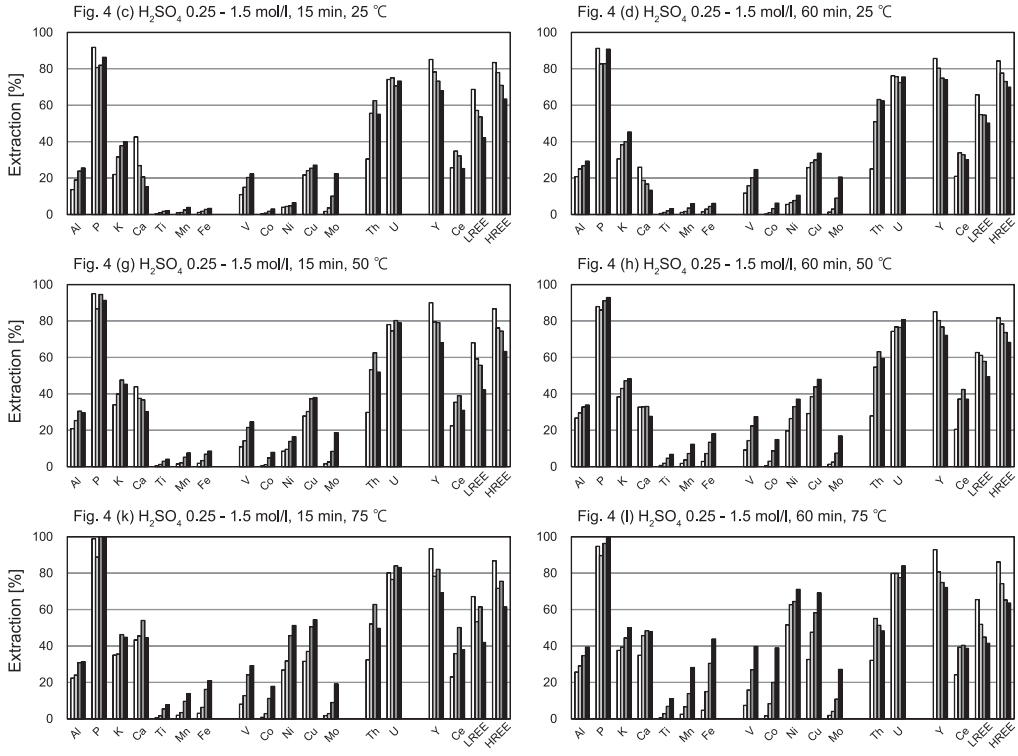


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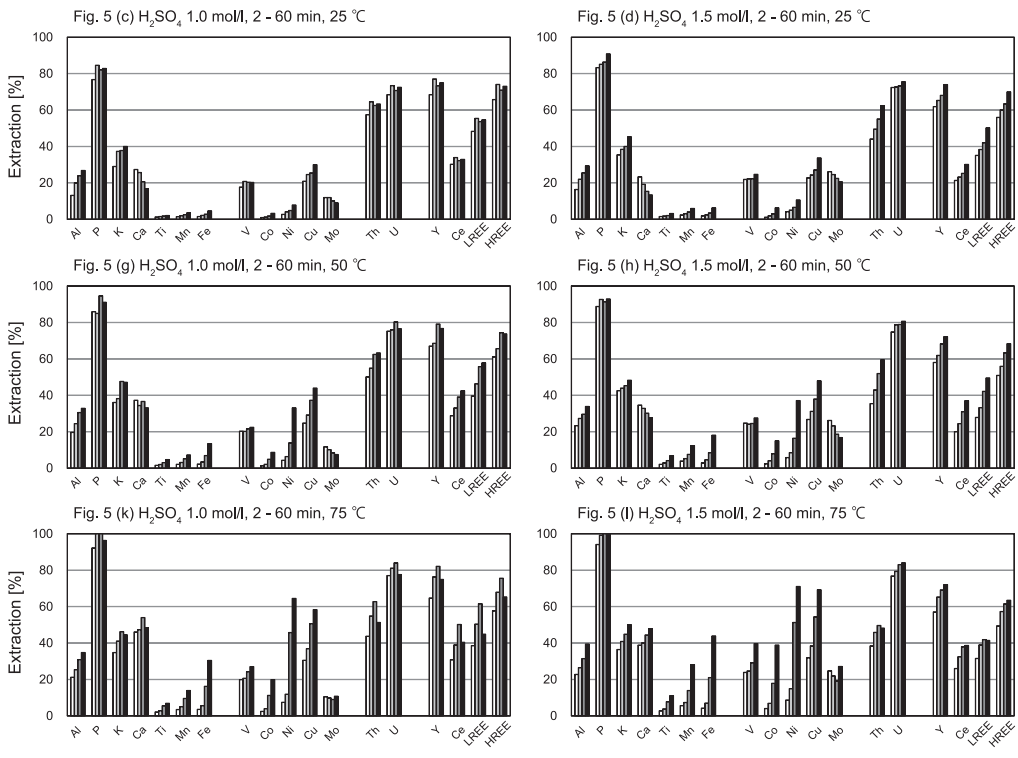


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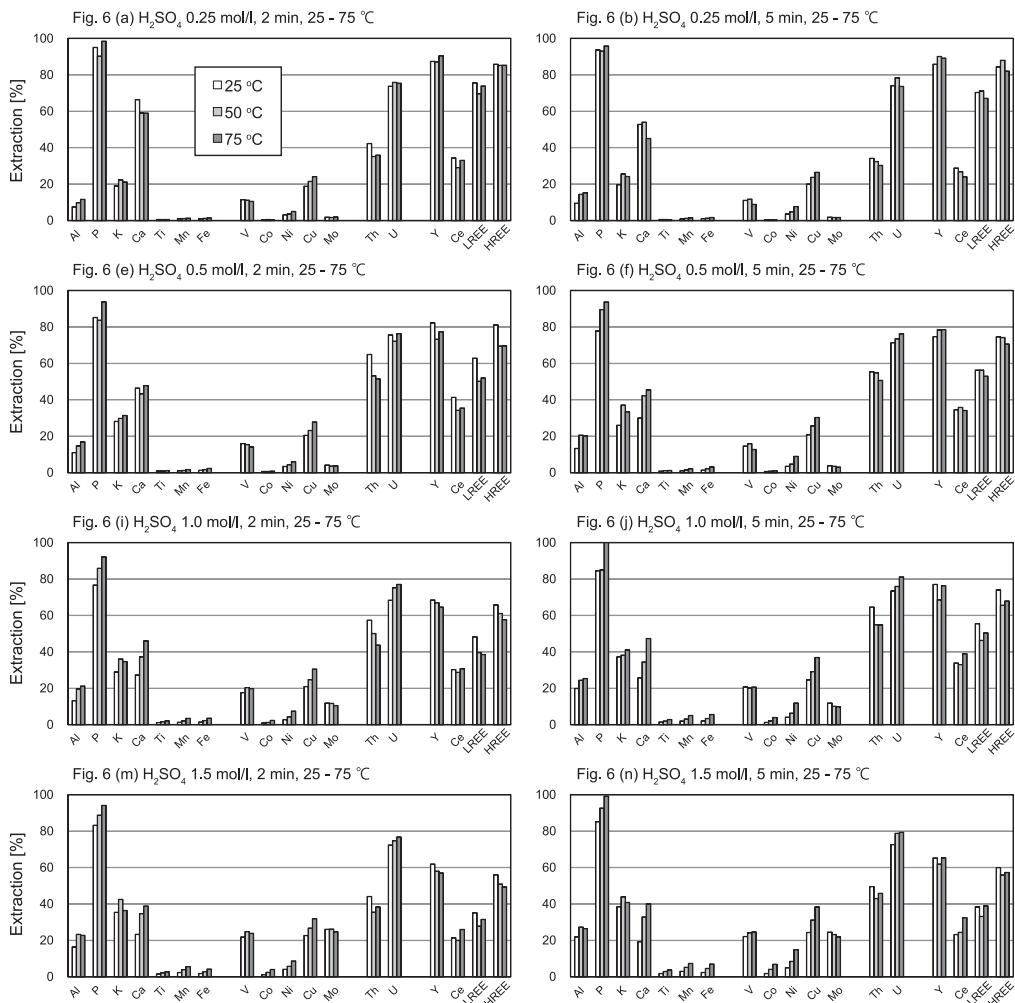


Fig. 6. Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of leaching temperature using H_2SO_4 and seawater as the leaching solution.

time. Extraction level of P was high in all cases and was not strongly affected by any leaching conditions. Extraction of V and Mo were consistently affected by acid concentration. Extraction levels of Th and Ce were highest at intermediate acid concentrations. Extraction levels of U and REY other than Ce were highest at lower acid concentrations, lower temperatures, and short leaching times.

Experiments using Milli-Q water

In experiments with HCl and Milli-Q water, as with those using seawater, extracted amount of Al, K, Ti, Mn, Fe, Co, Ni, and Cu increased with acid concentration and temperature (Fig. 7). Extraction levels of V, Mo, Th, and Ce increased with acid concentration and decreased with rising temperature, except in the experiments with 3.0 mol/L HCl (Fig. 7g). Extraction levels of P, Ca, U, Y, LREE, and HREE were high at all acid concentrations, were almost constant or increased slightly with acid con-

centration (Figs. 7a–c), and decreased with rising temperature (Figs. 7d–g). Extraction efficiency of REY other than Ce was highest at 96.1% (Y: 97.5%, LREE: 95.3%, HREE: 96.2%), slightly greater than results with seawater, at 1.0 mol/L HCl and 25°C.

In experiments with H_2SO_4 and Milli-Q water, extracted amount of P, Al, K, Ti, Mn, Fe, Co, Ni, and Cu increased with increasing acid concentration and temperature (Fig. 8). Extraction level of Ca was much lower than in the experiments with HCl, and it decreased with increasing acid concentration at 25°C and increased at 75°C (Fig. 8). Extraction levels of V and Mo increased with acid concentration (Figs. 8a–c), but were almost constant or decreased slightly with rising temperature (Figs. 8d–g). Extracted amount of Th, U, and REY increased with acid concentration (Fig. 8a), were almost constant with temperature at lower concentrations (Figs. 8d and e), and increased slightly with temperature at higher concentra-

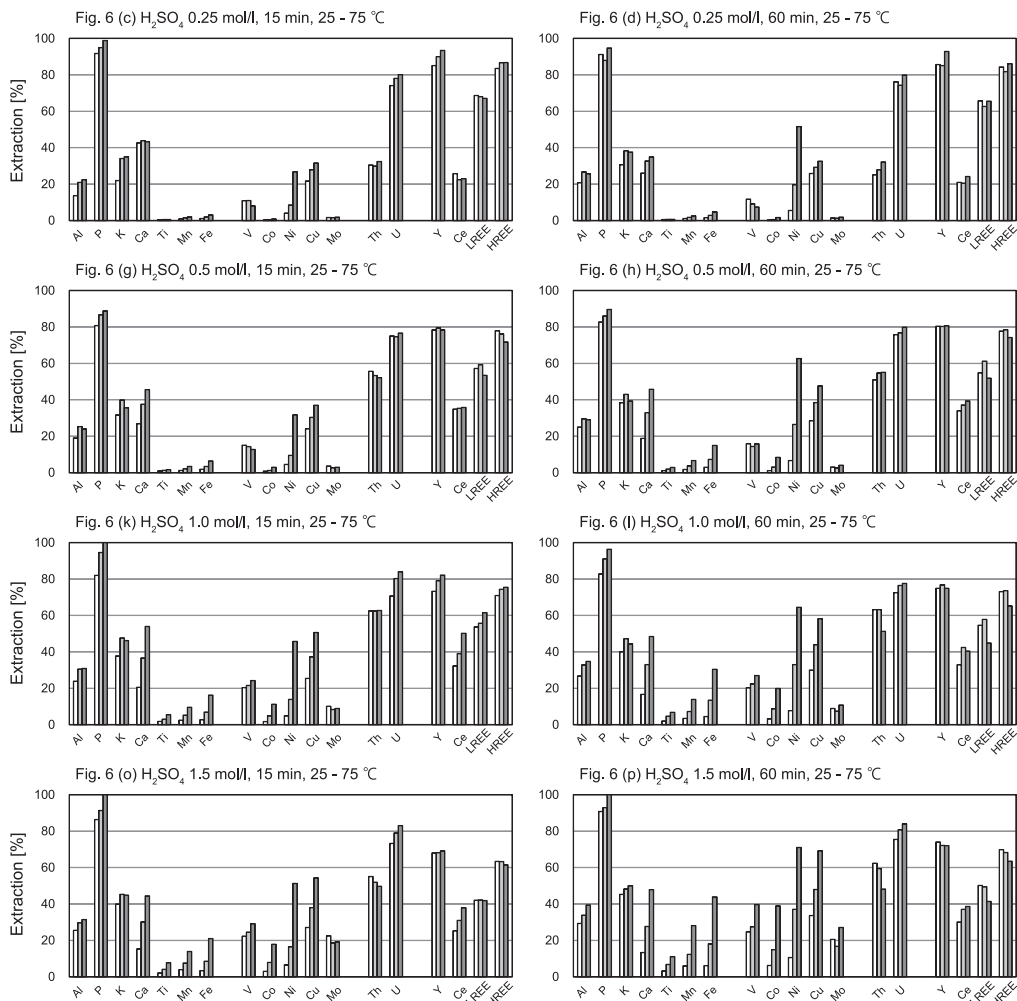


Fig. 6. (continued).

tions (Figs. 8f and g). In general, REY extraction efficiency was lower with sulfuric acid than with hydrochloric acid. The highest extraction efficiency of REY other than Ce was 89.4% (Y: 94.7%, LREE: 85.0%, HREE: 92.0%) at 1.5 mol/L H_2SO_4 and 75°C. Relative to the experiments conducted with seawater, REY extraction efficiency improved with increasing acid concentration.

DISCUSSION

Dissolution and precipitation behavior of REY and other elements

In our experiments, the extraction efficiency of REY other than Ce was highest at low acid concentrations, short leaching times (2 or 5 min), and at 25°C with hydrochloric acid and at 25°C and 75°C with sulfuric acid. Under these conditions, extraction percentage of P, the main constituent element of apatite, was nearly 100%. This sig-

nifies that almost all apatite grains in the mud sample dissolved in 2–5 min, and it appears that REY extraction is hampered by precipitation or adsorption associated with increasing acid concentrations, leaching times, and leaching temperatures.

We conducted X-ray diffraction (XRD) analyses of the dissolved matter (dried leachate solution) to identify the solvent chemical forms. The measurements were performed by Rigaku Ultima IV X-ray diffractometer at the University of Tokyo, using Cu $K\alpha 1$ radiation with 40 kV and 40 mA, and at a scanning speed of $2\theta = 3^\circ/\text{min}$ (step width 0.02°) over a range of $2\theta = 3^\circ\text{--}80^\circ$. These analyses showed three basic diffraction patterns corresponding to three experimental regimes (Fig. 9). Pattern I (seawater, 0.5 mol/L HCl, 2 min leaching, 25°C) displayed strong peaks for halite and weak peaks for calcium sulfate (hydrate) and rare earth phosphate. This result shows that Ca, mainly from apatite, combined with sulfate, mainly

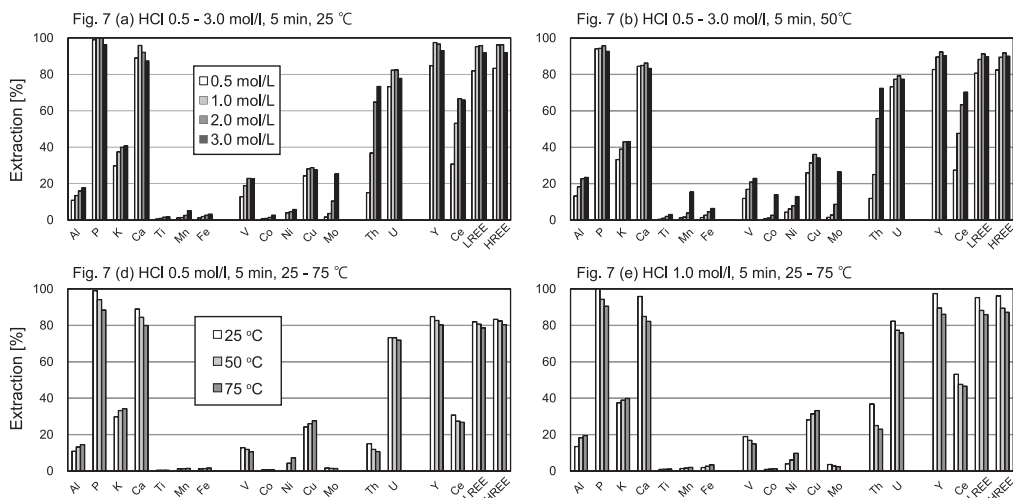


Fig. 7. (a–c) Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of HCl concentration using Milli-Q water as the diluent. (d–g) Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of leaching temperature using HCl and Milli-Q water as the leaching solution.

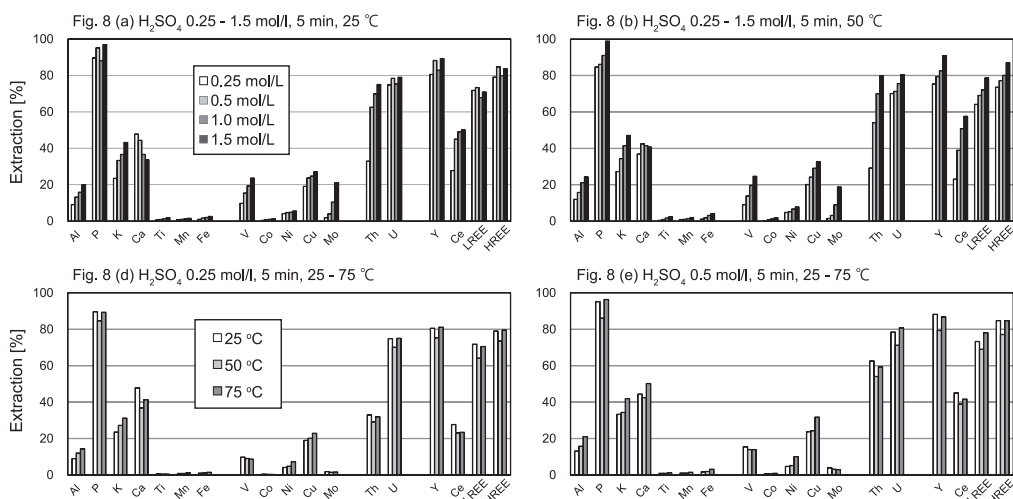


Fig. 8. (a–c) Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of H₂SO₄ concentration using Milli-Q water as the diluent. (d–g) Extraction percentages of major elements, valuable metals, radioactive elements, and REE from REY-rich mud as a function of leaching temperature using H₂SO₄ and Milli-Q water as the leaching solution.

from seawater, in the leachate solution and that REY recombined with phosphoric ions from apatite. Pattern II (Milli-Q water, 0.5 mol/L HCl, 2 min leaching, 25°C), in addition to the three materials of pattern I, displayed peaks for calcium hydrogen chloride phosphate hydrate. Because the experiments with Milli-Q water could not supply sulfate ions from seawater, dissolved Ca was likely to combine with phosphorus and chlorine ions. In pattern II, the calcium sulfate (hydrate) peaks were much weaker than those in pattern I because the sulfate ions were only

available from the small amount of seawater contained in the sample. Pattern III (seawater, 0.25 mol/L H₂SO₄, 2 min leaching, 25°C) displayed peaks similar to those of pattern I. From these results, the extraction efficiency of REY can be broadly explained by referring to the following three chemical mechanisms:

(1) Dissolution of apatite: In addition to Ca and P, the main constituent elements of apatite, the REY, Sr, U, and Th contained in apatite dissolve into the leachate solution.

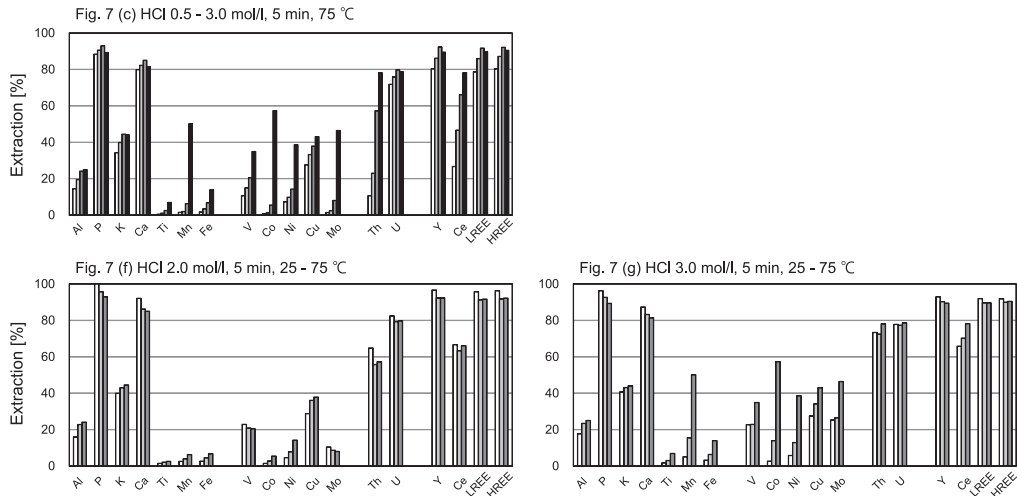


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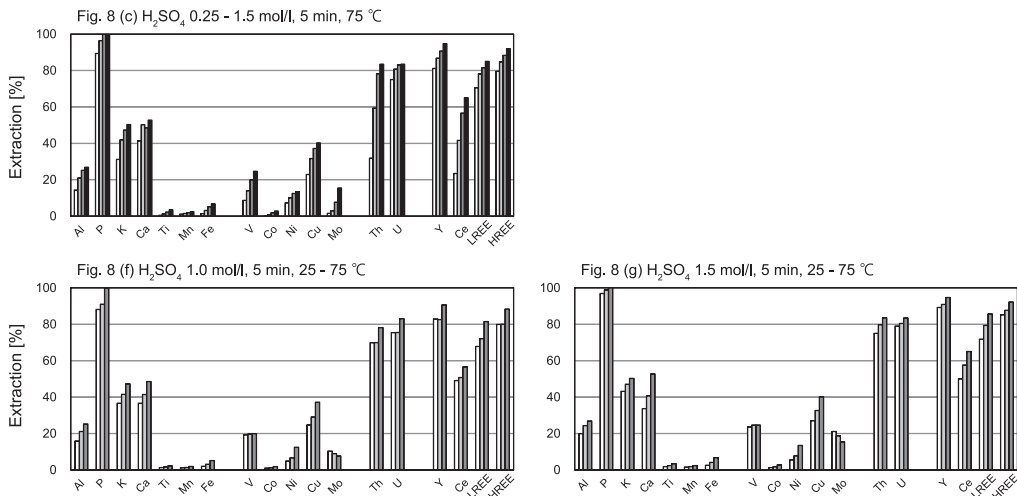


Fig. 8. (continued).

(2) Formation and precipitation of calcium sulfate (hydrate): This hampers Ca extraction, and REY coprecipitates with calcium sulfate because the ionic radii of the REY elements allow them to substitute for Ca.

(3) Formation and precipitation of rare earth phosphate: In this case, P and REY dissolved from apatite recombine and precipitate in the leachate solution.

We note two things about these chemical behaviors. The first is that the solubility of calcium sulfate (not calcium sulfate hydrate) diminishes with increasing temperature (Blount and Dickson, 1969). The second is that rare earth phosphate is more soluble in sulfuric acid than in

hydrochloric acid. With those stipulations, we can interpret the experimental results with the chemical properties mentioned above.

In the experiments using hydrochloric acid, with either Milli-Q water or synthetic seawater, extraction levels of P, Ca, and REY other than Ce were highest at only 5 min and at 25°C. Extraction levels clearly decreased with rising temperature at all leaching times, in response to increasingly rapid formation and precipitation of calcium sulfate or rare earth phosphate. The effect of leaching time was small, and therefore it appears that the precipitated calcium sulfate and rare earth phosphate were

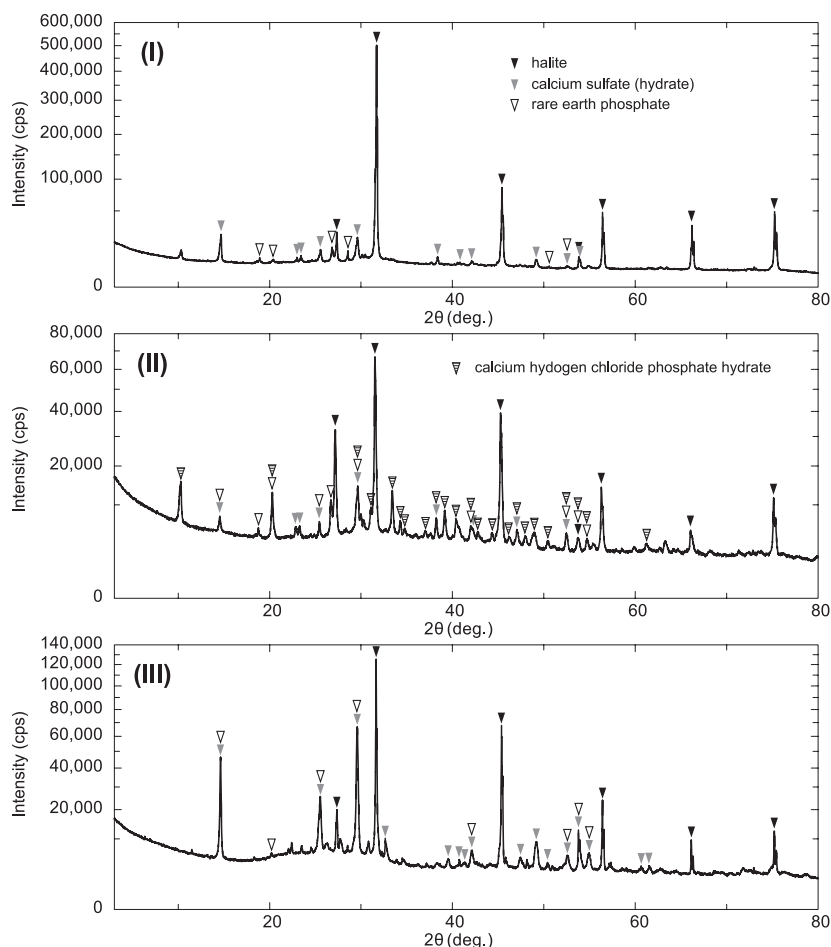


Fig. 9. Typical X-ray diffractograms of dissolved chemical compounds in leachate solution showing basic profiles resulting from three experimental regimes: (I) dilution with seawater, 0.5 mol/L HCl, leaching time 2 min, leaching temperature 25°C; (II) dilution with Milli-Q water, 0.5 mol/L HCl, leaching time 2 min, leaching temperature 25°C; and (III) dilution with seawater, 0.25 mol/L H₂SO₄, leaching time 2 min, leaching temperature 25°C.

not redissolving in hydrochloric acid. We believe that the decrease in extracted amount of Ca, Y, LREE, and HREE with increasing temperature reflects the diminishing solubility of calcium sulfate. It appears that U also coprecipitated with calcium sulfate or rare earth phosphate, because its behavior was very similar to that of Ca, Y, LREE, and HREE. On the other hand, extraction of Th and Ce was significantly affected by HCl concentration because, we suggest, Th and Ce were being liberated not just from apatite but from silicate minerals in terrigenous clasts and clay and from manganese/ferromanganese oxides. This suggests that industrial processing of REY-rich mud can reduce extraction amount of Th, which is commonly avoided as a radioactive contaminant, through the use of dilute acid. As with Mn and Fe, extraction levels of valuable metals significantly improved with increasing HCl concentration, time, and temperature. It appears that those conditions promote disso-

lution of manganese oxide and iron oxyhydroxide/oxide, releasing their content of valuable metals into solution.

In the experiments using sulfuric acid, extraction levels of both Ca and REY were lower than with hydrochloric acid. This indicates that a significant amount of Ca precipitated as calcium sulfate that incorporated REY. Furthermore, the difference between seawater and Milli-Q water was telling, in that REY extraction increased with increasing acid concentration in Milli-Q water, but decreased in seawater. We suggest that REY extraction decreased in seawater owing to the formation and precipitation of the double sulfate of rare earths and Na (REE-Na double sulfate), or NaREE(SO₄)₂, incorporating the Na from seawater. In industrial REE production, this substance is obtained by adding Na₂SO₄, NaCl, and NaOH to a sulfuric acid solution containing REY and phosphate ions (Abreu and Morais, 2010). Formation of REE-Na double sulfate may also account for the difference in ex-

traction of Th and Ce between experiments using Milli-Q water (in which Th and Ce extraction levels increased with increasing H₂SO₄ concentration) and seawater (in which extraction levels were highest at intermediate acid concentrations). This may be because coprecipitation of Th and Ce with REE-Na double sulfate offsets their dissolution. Extracted amount of P and Ca increased with rising temperature, because of the solubility increase of phosphate minerals with temperature in the case of P and because of hydration and redissolution of calcium sulfate with rising temperature in the case of Ca. Extraction of V and Mo clearly increased with H₂SO₄ concentration, but it was little affected by leaching temperature and decreased with time in some cases at lower temperature. We infer that this result reflects re-adsorption of V and Mo onto manganese oxide and iron oxyhydroxide/oxide.

Optimum conditions for REY leaching from REY-rich mud

In the experiments using seawater as a diluent, extraction efficiency of REY other than Ce was highest at lower acid concentrations and short leaching times with both acids. Furthermore, increasing acid concentration and leaching time enhanced the elution of elements considered undesirable in the REY refining process, such as Mn and Fe. In addition, extraction levels of REY other than Ce decreased slightly with increasing temperature in most experimental conditions. In sum, the optimum leaching conditions for REY are as follows:

(1) The lowest acid concentration that can fully extract REY in REY-rich mud.

(2) The shortest leaching time, about 5 min, that can fully dissolve apatite grains in REY-rich mud.

(3) Room temperature (25°C).

It appears that REY elution (apatite dissolution) proceeds preferentially and promptly to other elements; thus, the optimum acid concentration of a leaching solution is the lowest concentration corresponding to the Σ REY of the REY-rich mud. If all of the phosphorus in our mud sample is assumed to be in apatite (Ca₅(PO₄)₃(OH,F,Cl)), the concentration of acid required to dissolve all apatite is about 0.16 mol/L for hydrochloric acid (mud/leachate ratio 1:15) and about 0.08 mol/L for sulfuric acid. Although the minimum acid concentrations in our experiments were 0.5 mol/L hydrochloric acid and 0.25 mol/L sulfuric acid, it may be that even lower concentrations would be sufficient to fully dissolve the apatite and achieve high REY extraction efficiency. Each of the optimum condition mentioned above—low acid concentration, short leaching time, and room temperature—is strong advantage that encourages the development of REY-rich mud. On the other hand, valuable metals had high extraction levels under different conditions: high acid concentration, long leaching time, and high temperature. This means it may be possible to leach valuable metals sepa-

rately from REY, depending on the economics of the situation.

Our experiments using sulfuric acid and seawater showed that REY can precipitate as REE-Na double sulfate; this precipitation would be a serious disadvantage of using sulfuric acid. To avoid precipitation of REE-Na double sulfate, it is necessary to use freshwater instead of seawater and to lower the acid concentration. No difference in REY extraction efficiency was seen between seawater and Milli-Q water in the case of hydrochloric acid; moreover, hydrochloric acid offers the advantages of higher REY extraction efficiency and a residual mud that is easily detoxified with a sodium hydroxide solution.

CONCLUSIONS

We conducted a series of chemical leaching experiments on REY-rich mud using hydrochloric acid and sulfuric acid to investigate leaching conditions for hydrometallurgical process of REY from this material. The highest REY extraction occurred with either acid under conditions of low acid concentration (hydrochloric acid: 0.5 mol/L, sulfuric acid: 0.25 mol/L), short leaching time (~5 min), and room temperature (25°C). The experiments identified two chemical mechanisms that could interfere with processing, particularly in sulfuric acid leaching with seawater: precipitation of REY in rare earth phosphate and REE-Na double sulfate, and coprecipitation of REY with calcium sulfate. REY extraction level was generally much higher with hydrochloric acid, and the optimum conditions for REY leaching were low concentrations (~0.5 mol/L) of hydrochloric acid leachate, short leaching times (~5 min), and room temperature (25°C).

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SUPPLEMENTARY MATERIALS

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Tables S1 and S2