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ORIGINAL ARTICLE

The production of rare earth elements group via tributyl phosphate extraction and precipitation stripping using oxalic acid

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Abstract In this study, solvent extraction and precipitation stripping were used to produce rare earth elements (REEs). Tributyl phosphate (TBP) was used to extract yttrium, lanthanum, cerium, and neodymium from an aqueous solution produced by nitric acid leaching of apatite concentrate. In the extraction stage, the effects of TBP concentration, pH, contact time, temperature, and phase ratio were investigated. The results show that about 95%, 90%, 87% and 80% of neodymium, cerium, lanthanum, and yttrium, respectively, can be extracted in optimum conditions of extraction. Hot, deionized water was used to scrub the impurities from the loaded organic phase. The results showed that three stages of scrubbing with a phase ratio (Va/Vo) of five removed about 80%, 30%, 27%, and 15% of Ca, Mg, Fe, and P, respectively, from loaded TBP, while less than 9% of total REEs was lost. The effects on precipitation stripping of oxalic acid concentration, contact time, and phase ratio were investigated. The results showed that precipitation stripping is a viable alternative to traditional acid stripping in the REEs production process. Mixed REEs oxide with an assay of about 90% can be achieved as a final product.

1. Introduction

The rare earth elements (REEs) are the group of 17 chemical elements, including scandium and yttrium with atomic num-

bers of 21 and 39, respectively, and the lanthanides with atomic numbers 57–71 (Gschneidner and Eyring, 1978).

The REEs are typically soft, malleable, ductile, and usually reactive. They have an ever-increasing variety of applications in modern technology. These applications range from mundane applications (lighter flints, glass polishing) to high-technology applications (phosphors, lasers, magnets, batteries, magnetic refrigeration) and futuristic applications (high-temperature superconductivity, safe storage, and transport of hydrogen in the post-hydrocarbon economy) (Haxel et al., 2002).

Some of the most common minerals that contain REEs are apatite, monazite, and xenotime. The general formula for apatite is $Ca_{10}(PO_4)_6X_2$, where X can be a fluorine ion, a chlorine

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ion, or a hydroxyl group (Kanazawa and Kamitani, 2006). Calcium can be substituted mainly by Na, Sr, Mn, and the REEs; the most common replacement for P is Si, coupled with a substitution of Ca by trivalent REE ions. Apatite, which contains an average of 0.1–0.8% of rare earth oxides, is the main source of phosphate fertilizers and phosphoric acid (Li et al., 2006).

Nitric, sulfuric, and hydrochloric acids have been used as leaching agents for the extraction of rare earth elements from apatite. When apatite is leached with HNO_3, all the rare earths substituted in the apatite lattice for calcium ions are dissolved, and several processes are available to recover them from the pregnant leach liquor (Li et al., 2006).

Usually, the rare earths are recovered from leach liquor by solvent extraction and finally precipitated from the strip solution as rare earth oxalates. The oxalates are calcined in a furnace to yield a mixture of rare earth oxides. Also, fractional crystallization, fractional precipitation, ion exchange, and selective oxidation or reduction are used for separating individual rare earths (Gupta and Krishnamurthy, 2005).

Different solvents, such as di(2-ethylhexyl)phosphoric acid (D2EHPA) (Xu et al., 1992; Giles et al., 1996; Nucciarone et al., 2001; Geist et al., 1999), tri-*n*-butyl phosphate (TBP) and tri-*n*-octylphosphine oxide (Cecconie and Freiser, 1990; Majdan, 1994; Mathur and Choppin, 1998), carboxylic acid derivatives (Zheng et al., 1991; Du Preez and Preston, 1992), amines (Gorski et al., 1991; Hirai and Komasawa, 1991; Preston, 1996), and ketones (Hirai and Komasawa, 1991; Abbruzzese et al., 1992), were used to extract REEs from aqueous solutions.

Solvents are used to extract the rare earth ions, which are usually stripped by mixing the solutions with aqueous mineral acids (typically, hydrochloric acid or nitric acid). This removes the rare earth ions from the organic phase, draws them into the aqueous acids, and, in turn, regenerates the extractant. Oxalic acid is added, and the rare earth elements are precipitated from the strip solution as oxalates. Then, the oxalates are calcined at high temperature to convert them into rare earth oxides (Smith, 2007).

In precipitation stripping, the stripping and precipitation steps are combined by mixing the organic phase, which is loaded with REEs, with an aqueous solution of a precipitating agent, usually oxalic acid. The rare earth elements are stripped from the organic phase directly as solid oxalate salts, as shown in Eq. (1):

$$2REEs(HR_2)_{(org)} + 3H_2C_2O_{4(aq)}$$
$$\rightarrow REEs_2(C_2O_4)_{3(S)} + 6H_2R_{2(org)} \qquad (1)$$
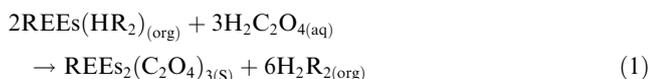
Precipitation stripping, as an alternative to traditional acid stripping, can be feasible in industrial counter-current, solvent extraction processes and can reduce the amount of aqueous waste generated in an industrial facility (Smith, 2007).

Iran imports REEs. One of the by-products of the Chadormalu iron ore beneficiation plant in Iran is the apatite concentrate, which is rich in REEs (Jorjani et al., 2007, 2008, 2011).

The objectives of the present work are to: (1) optimize the TBP concentration, pH, contact time, temperature, and phase ratio to extract yttrium (Y), lanthanum (La), cerium (Ce), and neodymium (Nd) ions from the aqueous solution produced by nitric acid leaching of apatite concentrate; (2) optimize the type of scrubbing agent, the phase ratio, and the number of

scrubbing stages; (3) optimize the oxalic acid concentration, contact time and phase ratio for precipitation stripping of the loaded organic phase and the preparation of oxalate salts of REEs. To our knowledge, no studies of the production of rare earth elements via precipitation stripping with TBP have been published.

2. Materials and methods

### 2.1. Sampling and preparation of pregnant liquor

The sample used in this study was prepared from apatite concentrate obtained from the Chadormalu plant; the apatite concentrate is a byproduct of iron-ore production in the Chadormalu iron-ore beneficiation plant. A representative sample, for which 80 wt.% of the sample was made up of particles that were less than 50 μm in diameter, was used for the characterization and leaching studies without any further size reduction. The results of the assay of the light and heavy rare earth elements in the apatite concentrate are shown in Table 1. As can be seen, La, Ce, Nd, and Y were the major rare earth constituents, so the evaluation of their recovery is the subject of the current work. The apatite sample was leached using a solution of 60% nitric acid at 60 °C and a solid-to-liquid ratio of 30% with agitation for 30 min at 200 rpm (Jorjani et al., 2008). The main chemical reaction that occurs when apatite is leached with nitric acid is shown in the following equation:

$$Ca_{10}(PO_4)_6F_{2(s)} + 20HNO_{3(aq)}$$
$$\rightarrow 6H_3PO_{4(aq)} + 10Ca(NO_3)_2 + 2HF_{(g)} \qquad (2)$$
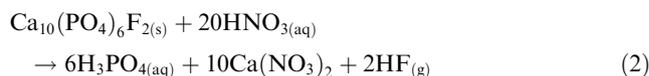
The slurry was filtered to remove the insoluble constituents, and the pregnant liquor (phosphoric acid), which contained the dissolved rare earth elements, was recovered. The chemical analysis of the pregnant liquor is shown in Table 2.

2.2. Extraction, scrubbing, and precipitation experiments

TBP supplied by Merck was used as the extracting agent. As an organophosphorus ester, TBP can extract rare earth ions (RE^{3+}) from nitrate media according to the following reaction:

$$RE^{3+}_{(aq)} + 3NO^-_{3(aq)} + 3TBP_{(org)} \rightarrow RE(NO_3)_3 \cdot 3TBP_{(org)} \qquad (3)$$
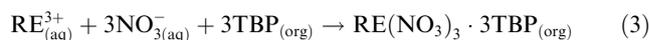
Kerosene was used as diluent. Different concentrations of extractant were prepared by dissolving various amounts of TBP in kerosene. The concentration of extractant, pH, temperature, contact time, and phase ratio were studied and optimized. The organic and aqueous phases were mixed in beakers with mechanical stirring at 200 rpm. When mixing was completed, the mixtures were transferred to a conical separating funnel for two-phase separation, and the aqueous phase was used for the analysis. All the elements in the aqueous phase, except fluorine and sulfur, were analyzed by inductively-coupled plasma atomic emission spectrometry (ICP–AES), Perkin Elmer Optima 7300 DV model; fluorine and sulfur were analyzed by ion chromatography, Metrohm 733 model and atomic absorption, Varian spectra AA 200 model, respectively.

Ammonium nitrate solution and deionized hot water were used to purify the loaded TBP and to remove undesirable loaded elements, such as calcium, iron, magnesium, and phosphorus.

Table 1 Assay of light and heavy REEs in the apatite concentrate.

Heavy rare earth elements	Assay (ppm)	Assay (%)	Light rare earth elements	Assay (ppm)	Assay (%)
Gd	233	16.61	La	1514	18.39
Tb	28.9	2.07	Ce	4204	51.1
Dy	145	10.34	Pr	455	5.52
Ho	24.2	1.73	Nd	1738	21.12
Er	63.2	4.51	Sm	293	3.58
Tm	7.76	0.55	Eu	24.5	0.29
Yb	40.9	2.9	Total	8229	100
Lu	4.94	0.35			
Y	855	60.94			
Total	1403	100			

Table 2 Chemical analysis of pregnant liquor.

Element	La	Ce	Nd	Y	Ca	Fe	Mg	P
Assay (ppm)	223.2	670.8	392.2	161.2	28,055	1621.8	1621.8	55,939

The rare earth-loaded organic solution was scrubbed and then mixed with oxalic acid solution. The mixtures were allowed to settle until three distinct phases were noticeable (solid rare earth oxalate, aqueous precipitating solution, and stripped organic solution). The rare earth oxalate precipitates were separated from the two other phases and stirred in 10 ml of 2-propanol for 10 min to remove any organic contaminants. Finally, the washed oxalate was calcined at 800 °C in ceramic crucibles for one hour, producing the rare earth oxides as a white powder. The powders were weighed and dissolved in 10 mL of 60% nitric acid solution and then analyzed for impurities.

3. Results and discussion

3.1. Extraction of rare earth elements

3.1.1. Effect of TBP concentration
Y, La, Ce, and Nd were extracted by varying the concentrations of TBP from 0.73 to 3.65 mol L^{-1} dissolved in kerosene. The extraction experiments were conducted using 10 ml of the pregnant liquor and 10 ml of the organic phase (phase ratio of 1:1) at a temperature of 25 °C, a contact time of 5 min, and initial $[H^+]$ of the aqueous solution of 6.3 mol L^{-1}. Fig. 1 shows the effect of TBP concentration on the extraction of REEs. It is apparent that the extraction of REEs increases as the concentration of TBP increases. As it was mentioned by Habashi (1999) the distribution coefficient increases with increasing extractant concentration in the organic phase. Thus, the optimum concentration of TBP was considered to be 3.65 mol L^{-1}.

3.1.2. Effect of $[H^+]$
The extractions of REEs were conducted with $[H^+]$ ranging from 0.5 to 6.3 mol L^{-1}. The $[H^+]$ of the aqueous solution was adjusted using nitric acid and ammonia solutions. The precipitate forms when $[H^+]$ reaches approximately 0.3 mol L^{-1}. Experiments to determine the appropriate $[H^+]$ were performed under the conditions of an extractor concentration of 3.65 mol L^{-1}, a contact time of five minutes, a phase ratio of 1:1, and a temperature of 25 °C. Fig. 2 shows the results, which indicate that, the extraction of REEs decreases as the $[H^+]$ increases. As shown, the optimum $[H^+]$ can be selected as 0.63 mol L^{-1}.

3.1.3. Effect of contact time
In this stage, the extraction of REEs was performed by mechanical stirring of two phases for various times, ranging from 1 to 9 min. The other parameters, i.e., TBP concentration of 3.65 mol L^{-1}, $[H^+]$ value of 0.63 mol L^{-1}, and phase ratio of 1:1 at a temperature of 25 °C, were used in this stage of the experiments. Fig. 3 shows the results, and it can be seen that the extraction of REEs increased as the contact time increased up to 5 min. However, when the contact time exceeded 5 min, the extraction of REEs was constant; therefore, the required time for extraction of REEs was determined to be 5 min.
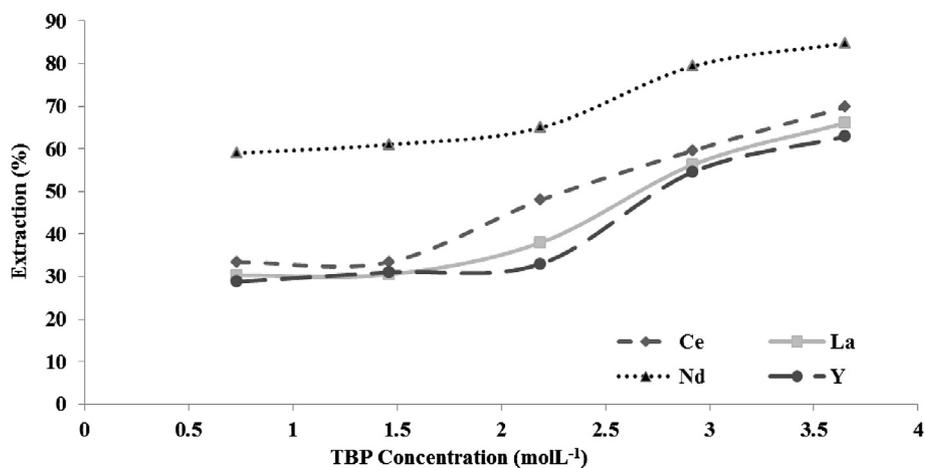
3.1.4. Effect of temperature
The extraction of REEs is usually a rapid, exothermic reaction at ambient temperature (Habashi, 1999). In the current work, the effects of different temperatures, i.e., 25, 35, 45, and 55 °C, on the extraction of REEs were examined. The TBP concentration of 3.65 mol L^{-1}, $[H^+]$ value of 0.63 mol L^{-1}, phase ratio of 1:1, and contact time of 5 min were used in this stage of the experiments. Fig. 4 shows the results, and it can be seen that the extraction of REEs decreased slightly when temperature was increased; so, a temperature of 25 °C was selected as the suitable temperature.
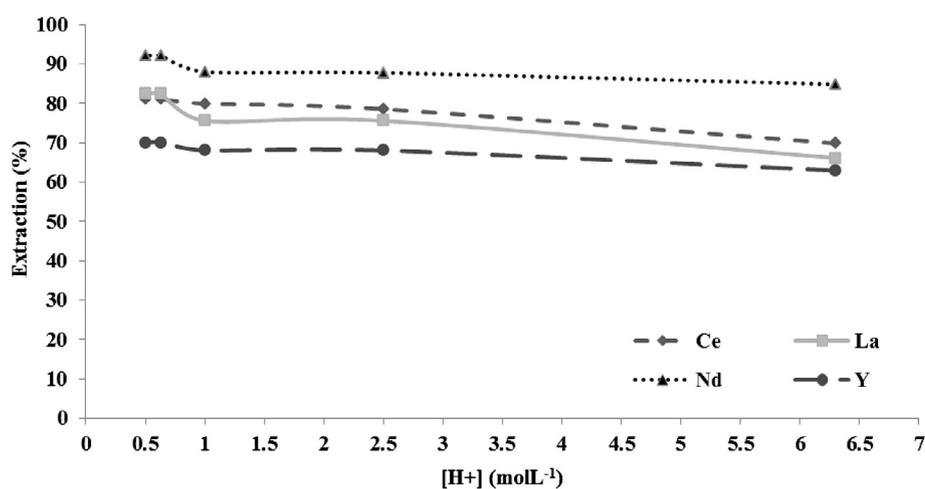
3.1.5. Effect of phase ratio
The volume ratio of the two phases plays an important role in the extraction process. The ratio of organic to aqueous phase (Vo/Va) was changed from 1:4 to 3:1. The results are shown in Fig. 5, and it can be seen that the extraction of REEs increased as the phase ratio increased from 1:4 to 2:1, after which it did not change significantly; so, a phase ratio of 2:1 was selected for the extraction stage.

Peppard et al. (1953, 1957) studied the extractability of rare earths from an aqueous HCl phase and from an aqueous phase

Figure 1 Extraction behavior of REEs as a function of TBP concentration; $[H^+]$: 6.3 mol L^{-1}, contact time: 5 min, temperature: 25 °C, phase ratio: 1:1.
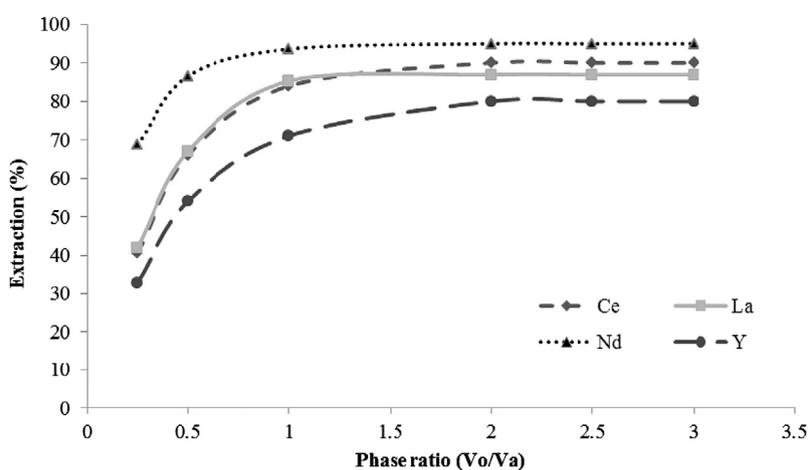

Figure 2 Effect of $[H^+]$ on extraction of REEs by TBP; TBP concentration: 3.65 mol L^{-1}, contact time: 5 min, temperature: 25 °C, phase ratio: 1:1.
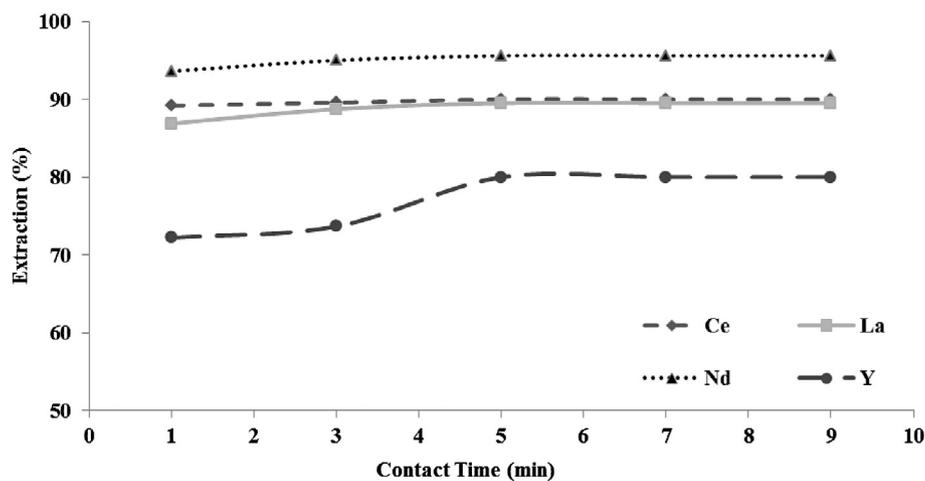
Figure 3 Effect of contact time of TBP and aqueous solution on extraction of REEs; TBP concentration: 3.65 mol L^{-1}, $[H^+]$ value: 0.63 mol L^{-1}, phase ratio: 1:1, and temperature: 25 °C.
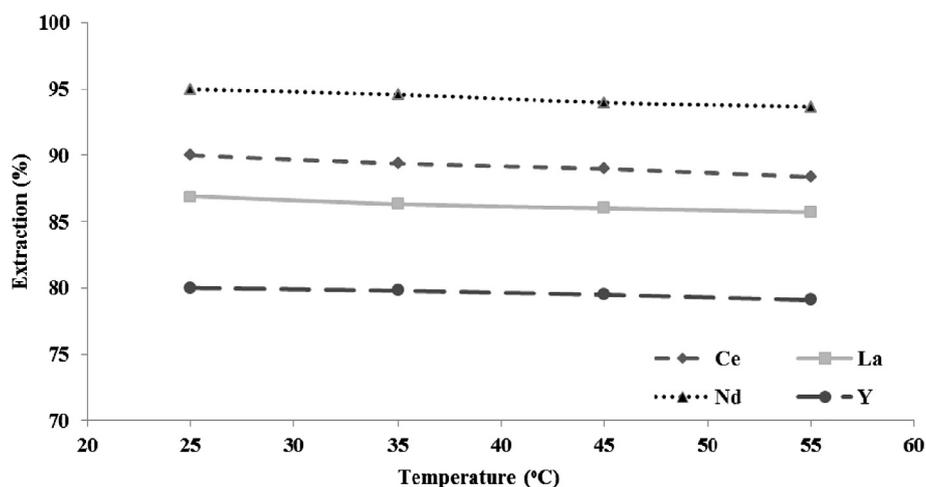
Figure 4 Effect of temperature on extraction of REEs by TBP; TBP concentration: 3.65 mol L^{-1}, [H$^+$]: 0.63 mol L^{-1}, phase ratio: 1:1, and contact time: 5 min.


Figure 5 Effect of phase ratio on extraction of REEs by TBP; TBP concentration: 3.65 mol L^{-1}, [H$^+$]: 0.63 mol L^{-1}, contact time: 5 min, and temperature: 25 °C.

containing 8 to 15.6 M HNO$_3$ by diluted and pure TBP and is shown to increase with increasing atomic number (Peppard et al., 1957, 1953); their result is compatible with the current work results which is presented in Figs. 1–5.

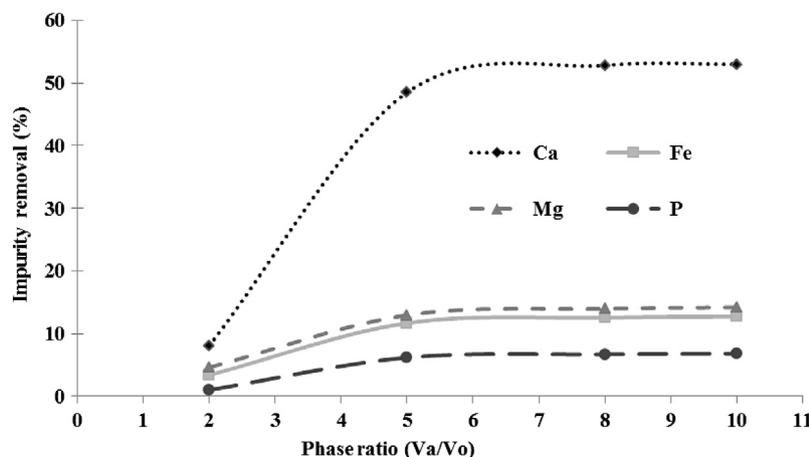### 3.2. Scrubbing of loaded organic phase

Ammonium nitrate solution (3 mol L^{-1}) and deionized hot water (70 °C) were used to scrub the loaded TBP. To compare these two scrubbing solutions, experiments were performed with an aqueous-to-organic phase ratio of 5 with a contact time of 5 min. The results are shown in Fig. 6, and it can be seen that the deionized hot water was more effective than the NH$_4$NO$_3$ solution, especially for calcium removal.

The effect of phase ratio (deionized water: loaded organic phase) on the removal of undesirable elements was studied with various phase ratios from 2 to 10. The results are presented in Fig. 7, and it can be seen that the removal of undesirable elements increased as the phase ratio increased from 2 to 5. But, when the phase ratio was increased above
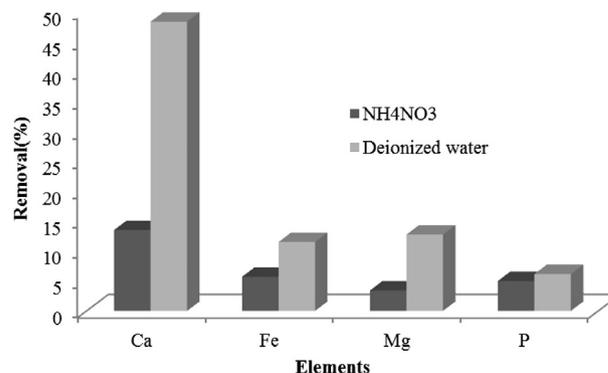
Figure 6 Effects of NH$_4$NO$_3$ and deionized water on the removal of impurities from the organic phase.

5, the removal of undesirable elements did not change noticeably; so, a phase ratio of 5 was selected for hot water scrubbing.

Figure 7 Effect of deionized water-to-loaded organic phase ratio on the removal of impurities.

Table 3 Removal of impurities for different scrubbing times.

| Element	Number of times scrubbing was conducted			
	1	2	3	4
Ca	48.5	69.56	81.83	85
Mg	13	22.21	30.48	32
Fe	11.72	20.15	27.82	29
P	6.2	11.06	15.62	17

With one stage scrubbing, the removal of impurities was inadequate. Therefore, in order to increase the removal of impurities, scrubbing was repeated from one to four times. The results are listed in Table 3. When the scrubbing was repeated three times, more than 81, 30, 27, and 15 wt.% of calcium, magnesium, iron, and phosphorus, respectively, were removed (Table 3), while the losses of REEs were not significant (2.6%, 1.5%, 3.2%, and 1.6% for Nd, Ce, Y, and La, respectively). When the scrubbing was done more than three times, the removal of harmful elements only increased slightly (Table 3), but the loss of REEs increased significantly; so, a total of three scrubbings with hot water (70 °C) were selected as the optimum condition for scrubbing.

3.3. Precipitation stripping

The effects of oxalic acid concentration, precipitation time, and phase ratio were evaluated, and the results are shown in Tables 4–6, respectively. Fig. 8 shows three distinct phases, i.e., solid rare earth oxalate, aqueous precipitating solution, and stripped organic solution produced after precipitation stripping. As shown in Table 4, increasing the concentration of oxalic acid increased the purity of rare earth oxides (REOs) in the precipitate. But, the effect of oxalic acid with concentrations greater than 10% was not impressive.

In order to determine the appropriate time to allow for precipitation to occur, the loaded organic phase was mixed with an equal volume of 10% oxalic acid solution for 10, 15, 30, and 60 min. As Table 5 shows, increasing the mixing time from 10 to 30 min increased the assay of REOs in precipitate. Increasing the time further did not improve the purity of the precipitate.

To evaluate the effect of organic-to-oxalic acid solution phase ratio, the experiments were performed using a 10% oxalic acid solution and phase ratios of 0.5, 1, and 2 with a contact time of 30 min. The results are shown in Table 6, which shows that increasing the phase ratio from 0.5 to 1 increased the percentage of content of REOs in the precipitate, after which it did not change significantly. So, a phase ratio of 1:1 was selected. Table 7 shows the results of the analysis of the final
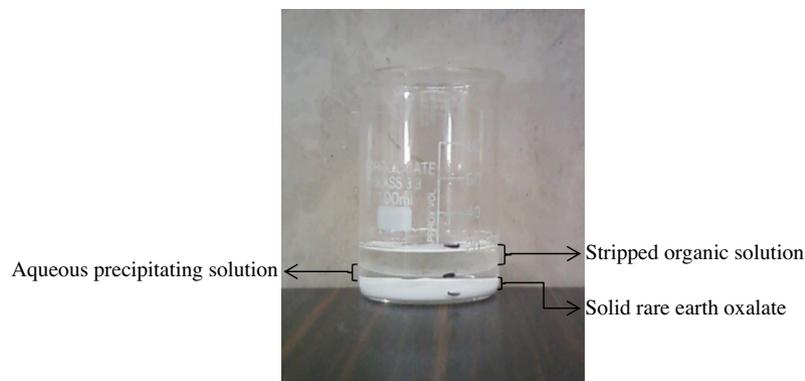
Figure 8 Three distinct phases after precipitation stripping.

Table 4 Effect of oxalic acid concentration on REOs assay produced in precipitation stripping.

Concentration of oxalic acid (%)	5	10	15	Saturated
REO (%)		61.23	89.28	89.12	89.27

Table 5 Effect of precipitation time on REOs assay produced in precipitation stripping.

Time (min)	10	15	30	60
REO (%)	85.21	87.17	89.28	89.11

Table 6 Effect of phase ratio on REOs assay produced in precipitation stripping.

Vo/Va	1:2	1:1	2:1
REO (%)	86.27	89.28	89.11

Table 7 Analysis of final REOs.

Element	Ca	Fe	Mg	P	S	REO
Assay (%)	10.51	0.06	0.04	0.05	0.06	89.28

REOs, indicating that the REOs with a purity of about 90% were achieved as the final product.

4. Conclusions

- The extraction of four rare earth elements, i.e., Y, La, Ce, and Nd, by TBP from pregnant liquor prepared from apatite acid leaching was studied.
- Under optimum conditions of TBP concentration of 3.65 mol L^{-1}, [H$^+$] of 0.63 mol L^{-1}, contact time of 5 min, organic-to-aqueous phase ratio of 2:1, and an ambient temperature (25 °C), about 95%, 90%, 87%, and 80% of neodymium, cerium, lanthanum, and yttrium, respectively, were extracted into the organic phase. The extractability of rare earths from HNO$_3$ aqueous phase rose with increasing atomic number.
- Scrubbing of the organic phase to remove impurities was performed three times using hot, deionized water (70 °C). About 80%, 30%, 27%, and 15% of Ca, Mg, Fe, and P, respectively, were removed from the loaded organic phase, while less than 9% of the REEs was lost.
- Precipitation stripping with 10% oxalic acid with a phase ratio (Vo/Va) of 1:1 and a contact time of 30 min, followed by calcination at 800 °C can produce the REOs with about 90% purity.

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