



Extraction of Rare Earth Elements from Iraqi Phosphate Ore by Using of Tributyl Phosphate

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ABSTRACT

Iraqi phosphate ore deposits have been ascertained to be the second global reserve after Morocco, it has been utilized successfully at Al-Qaim phosphate fertilizers complex in the period 1983-2009. The deposit has valuable content of rare piles of earth and uranium, which is expected to have a good impact on the Iraqi economy if they are recovered from the ore. In the present study, solvent extraction was employed for the extraction of the rare earth elements (REEs), tributyl phosphate (TBP) in kerosene was utilized for extracting ytterbium, yttrium, erbium, and lanthanum from an aqueous solution made via the nitric acid (HNO₃) leaching of the concentrate of the Iraqi apatite ore. In the extraction stage, the effect of the concentration of TBP (1, 2, 3, and 3.5) M, contact time (1, 3, 5, 7, 9, and 11) min, and the phase ratio (organic/aqueous) (1/4, 1/3, 1/2, 1/1, 2/1, 3/1, 4/1) were studied. The outcomes manifested, that around 92.9%, 98%, 90.4%, and 98.3% of yttrium, ytterbium, erbium, and lanthanum, respectively were extracted at the best extraction conditions of 3M TBP, 4/1 organic to aqueous phase ratio and 7 min contact time.

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1. Introduction

Rare earth elements are the set of seventeen chemical elements, involving scandium and yttrium with atomic numbers of (21) and (39), as well as the lanthanides with the atomic numbers 57–71 [1]. REEs are distinctively ductile, malleable, soft, and normally reactive. These elements have owned an ever-rising diversity of uses in recent technology. Such uses are ranging from the mundane uses (glass polishing, and lighter flints) to the higher technology uses (magnetic refrigeration, batteries,

magnets, lasers, and phosphors) and futuristic uses (safe storage, hydrogen transport in the economy of post-hydrocarbon, and high-temperature superconductivity) [2].

Certain usual minerals, including rare earth elements are xenotime, monazite, and apatite. The normal apatite formula is $(Ca_{10}(PO_4)_6X_2)$, where X is the ion of fluorine, hydroxyl or chlorine ion [3]. Calcium can be replaced chiefly via (REEs), (Mn), (Sr) and (Na); the highly usual substitution for (P) is the (Si), engaged with a (Ca) replacement via trivalent ions of rare earth elements. Phosphate rock contains on average 0.1 to 0.8% estimated as lanthanide oxides (rare earth) [4]. The phosphate rocks are considered as a secondary source of uranium and REE, depending on the phosphate type and origin [5]. Due to the rising need for lanthanides with their compounds in various technological uses in the electronic instruments, superconductors, laser equipment, super magnets and batteries, the recovery and recycling of lanthanides from various secondary resources have been received in recent time an extensive attention. In such merits, various methods were conducted for separating lanthanides from phosphogypsum or phosphate rocks as the secondary origin of the elements of lanthanides [6].

HCl, H₂SO₄, and HNO₃ have been utilized as leaching agents for the extraction of (REEs) from the apatite. If the apatite is leached by the nitric acid, the whole (REEs) replaced in the apatite lattice for the ions of (Ca) will dissolve, many operations exist for recovering the (REEs) from the "pregnant leach liquor" [7]. Normally, solvent extraction is utilized for recovering the (REEs) from leach liquor; moreover, ion exchange, fractional crystallization, fractional precipitation, and chosen oxidation or reductions are utilized to separate the single elements of the rare piles of the earth [8].

Kraikaew et al. [8] investigated the (REEs) solvent extraction from a medium of nitrate via tributyl phosphate (TBP) and di-(2-Ethylhexyl) phosphoric acid (D2EHPA) mixture dissolved in kerosene. The use of isomolar blends of (D2EHPA) and (TBP) in kerosene at room temperature (35±10°C) for the extractive separation of the single rare piles of earth from the blended nitrate feed solution of rare earth in comparison with the (50%TBP) in kerosene was investigated. Distribution coefficients (K_d) and the synergistic coefficients $[S=(K_{d,a}TBP, D2EHPA)/\{(K_{d,a}TBP+ (K_{d,a}D2EHPA)\}]$ were also investigated. The data obtained has revealed that the K_d of heavy rare piles of earth were greater if the solvents were (1.5 M) and (1.0 M) isomolar blends of (D2EHPA) and (TBP) in kerosene in comparison with the (50%TBP) in kerosene. Habashi [9] studied the hydrometallurgy of phosphate rock and recovery of uranium. The lanthanides extraction was feasible via the tributyl phosphate separately at leach solution having pH=0.3, also at (1/1) phase ratio within a single stage of the organic/aqueous, (100%) lanthanides were transferred into the organic phase. They were re-extracted from the organic phase via dilute HNO₃ solutions in double stages at (1/1) ratio of aqueous/organic. Precipitation was achieved selectively via (12%) oxalic acid, which was then calcined at temperature 1200°C for one hour to yielding a concentrate containing (88%) CaO plus (12%) Ln₂O₃. Nascimento et al. [10] studied the separation of rare piles of the earth via the solvent extraction utilizing (DEHPA). The study has introduced the outputs of the process variable analysis for the separation of the heavy REE from light REE in chloride media via solvent extraction. The di-(2-Ethylhexyl) phosphoric acid in isoparaffin extraction system was employed; synthetic solutions of REE oxides were formulated via dissolution in HCl solution for simulating the media of leaching initiating from the monazitic ores beyond the cerium.

The aim of the current investigation is to study the extraction parameters of the (TBP) concentration, contact time and phase ratio for extracting the ions of ytterbium (Yb), yttrium (Y), erbium (Er) and lanthanum (La) from the aqueous solution made via the (HNO₃) leaching of the apatite concentrate from Akashat Quarry in Anbar Governorate at western Iraq.

2. Materials Used and Procedures

1. Materials

The sample that is utilized in the present work was made from the concentrated of apatite obtained from Akashat Quarry in Anbar Governorate in western Iraq collected by the Iraqi geological survey. A representative sample of (106 μm) was selected after crushing and sieving. Characterizing and leaching investigations were commenced; Tables 1 and 2 list the outputs of the (REEs) assay for the apatite concentrate.

Table1: The XRF analysis for Iraqi phosphate ore

Element oxide	Concentration (%)
MgO	2.2
SiO ₂	2.621
P ₂ O ₅	14.86
CaO	52.48
SO ₃	1.291
Fe ₂ O ₃	0.27

Table 2: The AAS analysis for the REEs in the Iraqi phosphate ore

Elements	Concentration (%)	Concentration (ppm)
Y	0.0049731	49.731
La	0.0001799	1.799
Er	0.0004693	4.693
Yb	0.0001878	1.878

The above data indicates that (Y), (La), (Yb), and (Er) are the main rare earth components that could be assayed accurately by the flame atomic absorption spectrometry used in this work, thus their recovery development is the issue of the present work. The sample of apatite was leached utilizing a (2M) HNO₃ solution at (25°C) and a (1/4) solid: liquid ratio as well as agitation at (400 rpm) for (30 min). The selection of the parameters was based on a set of experiments conducted for every single parameter when the others kept constant during the process of leaching; however, the rate of mixing was selected due to previous work [5]. The principal chemical reaction that takes place if the apatite is leached by HNO₃ can be elucidated by equation 1 [11]:



The slurry was then filtered for removing the non-dissolved components, the separated of the pregnant liquor, i.e., phosphoric acid, which contains the dissolved REEs was conducted for the next extraction procedure. Table 3 displays the pregnant liquor chemical analysis. The analysis was performed at the laboratories of the Ibn Sina State Company (ISSC) using flame atomic absorption spectroscopy (AAS) (Nova AA 350) made in Germany, model 2012 supplied with a hydride – system. The calibration curves of elements are depicted in Figure 1.

II. Extraction of REEs

Tributyl phosphate (TBP); a technical grade of (99%) purity and 266.32 g/mol molecular weight was used as an extraction agent and was obtained from Ibn Sina State Company. The (TBP) is able to extract the ions (RE³⁺) of the rare earth from the nitrate media according to the following reaction [3]:



$$D = C_{\text{metal in org.}} / C_{\text{metal in aq.}} \quad (3)$$

Where: C represents metal concentration in the organic phase calculated from the difference between the C of metal in the aqueous phase before and after solvent extraction.

$$\% E = \frac{100 D}{D + \left(\frac{V_a}{V_o} \right)} \quad (4)$$

Where: E is the extraction percent, D is the distribution coefficient, C is the concentration of metal, V_a is the volume of aqueous phase (ml), V_o is the volume of the organic phase (ml).

The result of the best experiment is used to explain the distribution coefficient and the percentage of extraction (E %) for yttrium.

$$D = 36.59 \text{ ppm} / 11.53 \text{ ppm} \longrightarrow D = 3.173$$

$$E \% = (3.173 * 100) / [3.173 + (1/4)] = 92.7 \%$$

Kerosene was used to dilute TBP, which is a product of the Sigma Aldrich Company. The effects of concentration of TBP, contact time, and phase ratio on the extraction efficiency were investigated,

while the temperature was kept constant at room temperature ($25 \pm 5^\circ\text{C}$) depending on previous research [3]. Aqueous and organic phases were mixed in a glass beaker using a mechanical stirring of 400 rpm. Separation of the mixed phases was accomplished in a conical glass funnel. REEs analysis was made in the aqueous phases by AAS.

Table 3: The pregnant liquor chemical analysis by AAS

Elements	Heavy or light	Concentration (ppm)
Y	Heavy	48.12
Yb	Heavy	1.197
La	Light	1.32
Er	Heavy	4.32

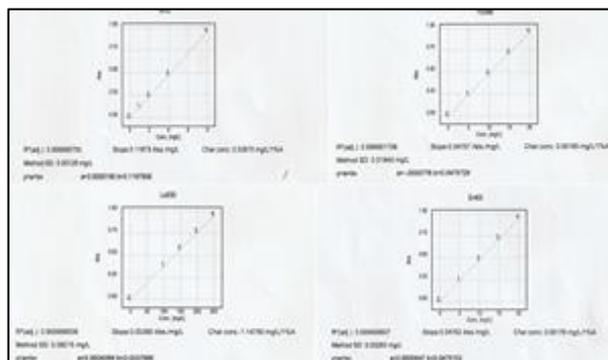


Figure 1: Calibration curves of yttrium (Y), ytterbium (Yb), lanthanum (La) and Erbium (Er) respectively

3. Results and Discussion

I. TBP concentration effect

Er, Yb, Y, and La were extracted via changing the (TBP) concentrations from (1 M) to (3.5 M) using kerosene as diluent. Extraction experiments were achieved utilizing (20 ml) of the organic phase with 1:1 phase ratio at 25°C , 20 ml pregnant liquor, 5 min contact time at room temperature of 25°C . (TBP) concentration influence on the (REEs) extraction is depicted in Figure 2. It's clear that the (REEs) extraction increased when the (TBP) concentration reached the level of 3 M, where after getting decreased [12]. Molecular TBP interactions in the organic phase might be ascribed to the decreasing extraction percent after 3M [13].

II. Effect of organic to the aqueous ratio

The two-phase volume ratio takes a significant role in the extraction process. This ratio (O/A) varied from 1:4 up to 4:1, and other parameters were remained at (3M TBP and 5 min time). Figure 3 illustrates the results, it can be seen that the (REEs) extraction raised with the increase of the phase ratio from (1:4) to (4:1), as a result, the (4:1) phase ratio was chosen for the next stage of extraction. Declining at less than 1:1 ratio might be ascribed to the mutual solubility of phases accompanied by various molecular and ionic interactions [14].

III. The effect of contact time

At such a stage, the (REEs) extraction was achieved via mechanical mixing the phases at various time intervals, ranging from (1) to (11) minutes, the other parameters were kept constant, i.e., 3 M TBP and (4:1) phase ratio and room temperature. The results are clarified in Figure 4. It can be noted that the (REEs) extraction increased when the contact time has risen up to (7 min). Nevertheless, the effect is rather small compared with other studied parameters indicating fast extraction reactions of the REEs by TBP-Kerosene system [3].

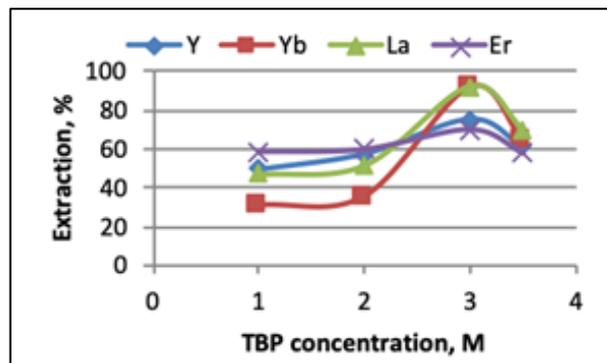


Figure 2: Concentration effect of (TBP) on the extraction of (REEs) at 1/1 Organic to Aqueous (O/A) Ratio and 5 min

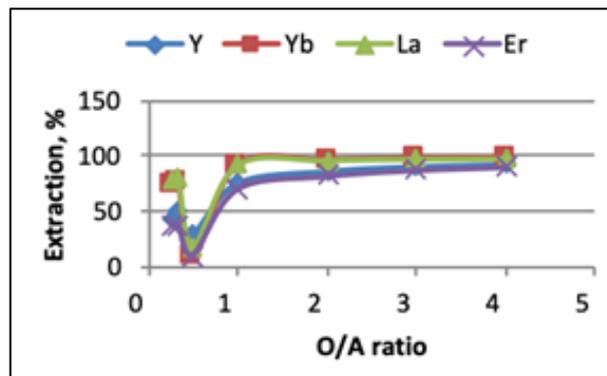


Figure 3: Effect of (O/A) ratio on the extraction of REEs at 3M TBP and 5 min

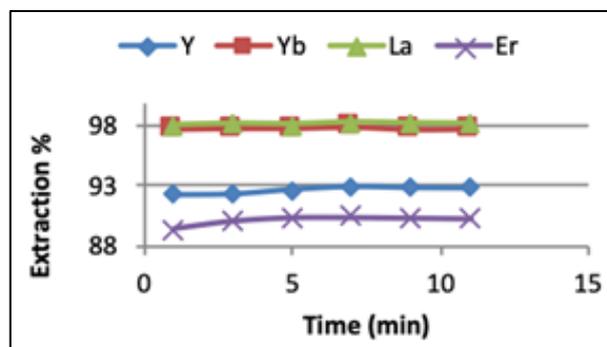


Figure 4: Influence of contact time on the (REEs) at 3M TBP and 4/1(O/A)

4. Conclusions

1. Chemical analysis of trace elements abundant at the Iraqi phosphate ore deposits have revealed the promising secondary source for uranium and rare piles of earth and many other metals.
2. Extraction of four (REEs), i.e., (YB), (Y), (Er) and (La), via Tributyl phosphate from the pregnant liquor made via nitric acid leaching of apatite was investigated.
3. At the best-studied conditions, including (3 M) concentration of (TBP) (7 min) contact time, and (4:1) organic-to-aqueous (O/A) phase ratio, the results manifested that about 92.9%, 98%, 90.4% and 98.3% of Yttrium, Ytterbium, Erbium, and Lanthanum, correspondingly were extracted into the organic phase.
4. The contact time had no significant influence on the percentage of extraction which indicates a fast kinetic reaction.

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