



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

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

Esmaeil Jorjani *, Malek Shahbazi

Department of Mining Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received 9 September 2011; accepted 4 April 2012

KEYWORDS

Rare earth elements;
Tributyl phosphate;
Precipitation stripping

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 (V_a/V_o) 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.

© 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

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

* Corresponding author. Tel.: +98 912 1776737.
E-mail address: esjorjani@yahoo.com (E. Jorjani).

1878-5352 © 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

Peer review under responsibility of King Saud University.
<http://dx.doi.org/10.1016/j.arabjc.2012.04.002>



Production and hosting by Elsevier

Some of the most common minerals that contain REEs are apatite, monazite, and xenotime. The general formula for apatite is $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where X can be a fluorine ion, a chlorine 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).

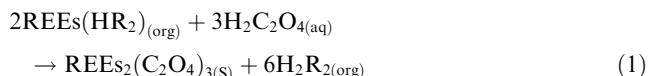
Nitric, sulfuric, and hydrochloric acids have been used as leaching agents for the extraction of rare earth elements from apatite. When apatite is leached with HNO_3 , all the rare earths substituted in the apatite lattice for calcium ions are dissolved, and several processes are available to recover 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 (Ceconie 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 Komasa, 1991; Preston, 1996), and ketones (Hirai and Komasa, 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):



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).

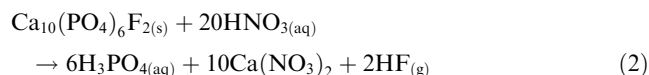
The objectives of the present work are to: (1) optimize the TBP concentration, pH, contact time, temperature, and phase ratio to extract yttrium (Y), lanthanum (La), cerium (Ce),

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

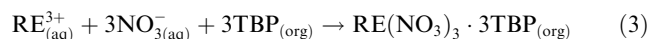
The sample used in this study was prepared from apatite concentrate obtained from the Chadormalu plant; the apatite concentrate is a byproduct of iron-ore production in the Chadormalu iron-ore beneficiation plant. A representative sample, for which 80 wt.% of the sample was made up of particles that 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:



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:



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

Download English Version:

<https://daneshyari.com/en/article/5142263>

Download Persian Version:

<https://daneshyari.com/article/5142263>

[Daneshyari.com](https://daneshyari.com)