



Modified acidic leaching for selective separation of thorium, phosphate and rare earth concentrates from Egyptian crude monazite



E.H. Borai^a, M.S.Abd El-Ghany^b, I.M. Ahmed^a, Mostafa M.Hamed^a, A.M. Shahr El-Din^{a,*}, H.F. Aly^a

^a Hot Laboratory Center, Atomic Energy Authority, Cairo, Egypt

^b Nuclear Materials Authority, P.O. Box 530 El-Maadi, Cairo, Egypt

ARTICLE INFO

Article history:

Received 24 February 2015

Received in revised form 18 January 2016

Accepted 8 February 2016

Available online 12 February 2016

Keywords:

Monazite

Acid digestion

Rare earth elements

Thorium

Phosphate

ABSTRACT

The objective of the present work was oriented to develop a technological separation process of phosphate, thorium and rare earth element (REE) concentrates from Egyptian monazite. In this respect, monazite digestion was carried out in sulfuric acid media with low or high acid/monazite ratio. These two ratios were designed to explore the acid efficiency for leaching Th and REE in the presence of high phosphate media ($P_2O_5 \approx 25\%$). The original monazite sample (grade 50%) was analyzed by XRF to evaluate the existing elements and their concentrations. A series of experiments was firstly applied to remove various element impurities (such as Na, Ca, and Si) which exist in the monazite sample and create a series of interferences with the main product (REEs). The results are likely promising for removal of the interfering ions specially Na, Ca and Si. These elements usually complicate the separation of the main elements (REEs). A series of experiments was constructed to digest the monazite sample with a low amount of concentrated H_2SO_4 and to explore the separation possibility of Th from REEs in successive steps at different $BaCl_2$ weights that act as precipitating agent. The results demonstrated that, firstly selective thorium precipitation (99.3%) was obtained at pH 0.9. Secondly, the phosphate ions (83.3%) could be successfully separated from the mixed REE cake. Thirdly, separation of light REEs (LREEs) from the mixed cake was then performed by disodium sulfate. The precipitation efficiency of double sulfate for LREEs reached 92, 79 and 82% for Ce, Nd and La respectively. Finally, the remaining REE-phosphate was converted to REE-hydroxide precipitate at pH 7 then leached with dilute HCl at pH 3 and treated with 3% oxalic acid to precipitate Y and the other HREEs as HREE-oxalate. The results indicated that all Y and other REEs are completely precipitated.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Much attention has been paid to rare earth (RE) elements in the manufacture of a lot of functional materials such as high intensity magnets and electrical assemblies. Of the 200 best known minerals containing rare earth elements, only three contain significant amounts – bastnaesite, monazite and xenotime – monazite being the second most important and abundant source of rare earths (Thompson, 1980).

Monazite is a rare earth phosphate containing thorium and uranium as associated metals (Abrao, 1994; Loureiro, 1994; Miyawaki and Nakai, 1996; Sundaram, 1987; Wall and Mariano, 1996). Its structural group consists of arsenate, phosphate and silicate in addition to RE, Th, U, Ca, Bi, etc. (Fleischer et al., 1990; Toledo and Pereira, 2003). Monazite ($REPO_4$, RE: rare earth elements) is primarily composed of rare earth

phosphates especially those of low atomic numbers such as Ce, La, and Nd along with numerous other minor constituents such as Pr, Sm, and Gd. Th and U can be extracted from it as well as a by-product (Kanazawa and Kamitani, 2006; El-Nadi et al., 2005). The processing of monazite leads to the generation of RE concentrates containing thorium (Th), uranium (U) and phosphate (PO_4^{3-}).

Several technological methods are used for industrial processing of monazite. The decomposition of rare earth elements from monazite has been conducted in several methods. Commercially, these methods include the acid leaching in sulfuric or hydrochloric acid, alkaline leaching in sodium hydroxide, sintering with sodium phosphate or sodium hydroxide at high temperatures (Hughes and Singh, 1980; Gschneidner, 1981) and solid state reactions with suitable reactants at high temperatures (Kizilyalli and Welch, 1987). Both acid and alkaline leaching processes are commonly used, however, alkaline leaching is most preferable and widely used because it has some advantages. The most important advantage of them is the simultaneous removal of phosphorus during leaching, producing a

* Corresponding author.

E-mail address: ashahreldin@yahoo.com (A.M.S. El-Din).

by-product, sodium phosphate as fertilizer and regenerating alkali (Miao and Horng, 1988). During decomposition by strong alkali such as sodium hydroxide, the rare earth elements in the form of insoluble phosphates in monazite are transformed into rare earth hydroxides. The rare earth hydroxides obtained from the alkaline processing can be easily dissolved in acid after removal from supernatant solution of alkaline phosphates (Abdel-Rehim, 2002). The separation of thorium and uranium from lanthanides is carried out by selective neutralization of solutions with ammonia or alkali up to pH = 5.8–6. The result is nearly complete precipitation of thorium and uranium in the form of thorium concentrate, containing about 3% lanthanides (Cheng and Hou, 2007).

The recovery of mixed rare earths and the removal of thorium and uranium from monazite are accomplished through a variety of methods after chemically attacking the mineral with sulfuric acid or sodium hydroxide (Gupta and Krishnamurthy, 1992). Technological processes for the separation and purification of REEs from U and Th require repeated transition steps (Gupta et al., 1979).

Monazite can be attacked by strong acid (usually sulfuric acid), which essentially transforms the metal phosphate ion to dihydrogen phosphate salt and phosphoric acid and leaves the metal ions as water soluble salts (Katzin et al., 1986). In the acid treatment method, the sulfuric acid had been used depending on the acid/ore ratio, temperature and concentration. Either thorium or the rare earths can be selectively solubilized or both thorium and rare earths totally solubilized. Rare earths and thorium are subsequently recovered from the solution. Yttrium and the heavy rare earth double sulfates are quite soluble and go with thorium. The rare earths, however, are recoverable from the thorium fraction by solvent extraction for further purification of thorium and uranium. Amaral et al. (Amaral and Morais, 2010), proved that Primene JM-T (primary amine) can extract thorium with a concentration not exceeding 0.15 mol/L, in which increasing concentration of Primene JM-T causes an increase in extraction of rare earth elements, but this fact was not observed for Alamine 336 (tertiary amine) in the concentration range investigated which confirm that REEs can be extracted by primary amines not by secondary or tertiary amines. Other commercially significant processes essentially involve precipitation of thorium pyrophosphate or basic salts from the leach liquor and subsequent recovery of the rare earth in solution as double sulfates, fluorides, or hydroxides or even selective solubilization of thorium in the ore treatment stage itself. But, unfortunately, the sulfuric acid process does not yield pure products and is no longer in commercial use.

Thorium is of particular interest because of its potential usefulness as a fertile material for breeder reactors. Within this context, the present contribution is directed to separate thorium, phosphate and REE concentrate from Egyptian monazite by a modified acidic leaching.

2. Experimental

2.1. Chemicals and reagents

The monazite used in this work was obtained from the Nuclear Materials Authority, Egypt. All chemicals and reagents used were analytical reagent grade and their solutions were prepared with distilled water. All rare earth elements were obtained from Sigma Aldrich (99.9%). The pH of the solutions was readjusted using 0.1 mol/L H₂SO₄ and 0.1 mol/L NaOH.

2.2. Experimental procedure

The present paper was classified into two main parts to represent two different amounts of sulfuric acid (low or high acid/monazite ratio). This classification was designed to explore the acid efficiency

for leaching U, Th and rare earth elements (REEs) in the presence of high phosphate media (P₂O₅ ≈ 25%). A representative monazite sample (grade 50%) was firstly analyzed by XRF to evaluate the existing elements and their concentrations. The outstanding advantage of the sulfuric acid method is that it can be used for all types and grades of commercial monazite and does not require fine grinding (Kewswan, 1996). The measurements and detection of various element concentrations were carried out using optical emission inductively coupled plasma (OEICP, Hudson, New Hampshire, 03051, U.S.A.).

2.2.1. Washing of monazite

A series of experiments was applied to remove various element impurities (such as Na, K, Ca, Mg, and Si) that exist in the monazite sample and create a series of interferences with the main product (REEs). The effect of HCl concentration was tested by washing 2 g of monazite sample carefully with different HCl concentrations (0.1, 0.5 and 1 mol/L) and shaking for 1 h at room temperature. The effect of temperature was tested by shaking 2 g monazite with 100 mL 1 mol/L HCl for 1 h at different temperatures (25, 60 and 100 °C). The effect of shaking time was tested by shaking 2 g monazite with 100 mL 1 mol/L HCl for 30, 120 and 180 min, at 60 °C. The solution of each step was filtrated and the residue was subjected to XRF measurements.

2.2.2. Acidic processing of monazite

Firstly, monazite was digested at high monazite/acid ratio (1:3). This ratio was selected mainly based on our previously published work (Borai et al., 2002). In this respect, a 5 g monazite sample was mixed with 15 mL H₂SO₄. The mixture was stirred for 2 h at 200 °C, and then diluted with distilled H₂O to 50 mL. The slurry was filtrated and the filtrate was diluted with distilled H₂O to 100 mL (original solution).

A series of experiments was constructed to remove different radionuclide (U-series and Th-series) from the original solution. In this respect, different BaCl₂ weights (0.1, 0.5, 1 and 2 g) were added individually to 10 ml from the original solution and shaken for 5 min. The four samples were filtrated and the filtrate was subjected for ICP elemental measurements, while the radioactivity concentration in the residue was measured using multichannel NaI detector.

To separate U ions from both Th and REEs, the pH of the rest solution of the original filtrate (50 mL) was readjusted at pH 7.5 using NH₄OH solution to precipitate all the existing elements as (U, Th and REEs) sulfate/phosphate/hydroxide ppt. Then the concentrations of the existing elements in the filtrate after precipitation at pH 7.5 were measured.

Secondly, another trial to digest the monazite sample with low acid/monazite ratio has been performed to explore the separation possibility of radionuclides from REEs in successive steps of different batch processes. In this respect, 20 g of monazite sample (grade 50%) was mixed with 19 mL H₂SO₄ (98%), then heated for 2 h at 220 °C followed by adding 5 g BaCl₂ to separate radionuclides. The slurry is poured directly to 100 mL distilled H₂O. The mixture was stirred for another 2 h at room temperature.

The slurry was washed by 50 mL of 10% H₂SO₄. The slurry was filtrated and the filtrate diluted to 150 mL to represent the original solution then subjected to ICP measurements. The residue was weighed (12 g) and subjected to radioactive measurements by multichannel germanium–lithium detector.

2.3. Thorium separation

Thorium separation from the filtrate was performed by adding 100 mL NH₄OH (1:1) until the pH reached to 1.05. The solution was filtrated and the greenish white precipitate was analyzed by Ge-Li

Download English Version:

<https://daneshyari.com/en/article/213714>

Download Persian Version:

<https://daneshyari.com/article/213714>

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