

Alkali pug bake process for the decomposition of monazite concentrates



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ARTICLE INFO

Article history:

Received 27 August 2016

Revised 26 December 2016

Accepted 20 February 2017

Available online 9 March 2017

Keywords:

Alkali pug

Monazite

Rare earths elements

Leaching

ABSTRACT

An alkali pug bake-leach process was studied for the decomposition of monazite and extraction of rare earth elements (REEs), uranium, and thorium. Under the conditions studied, 4 h bake time and 210 °C with an alkali to concentrate ratio (A/C) of 4:1 allowed for relatively high REEs extraction while maintaining relatively low thorium and uranium extraction, which may allow for at least partial separation of REEs from thorium and uranium. At this level, and with an average particle size of 81 μm, more than 90% of REEs were extracted, uranium extraction dropped to ~38% by partly reporting to the water leach solution, and thorium extraction was consistently low at ~25%. Baking temperature (180–250 °C) was found to have a pronounced effect on the extraction of REEs, uranium, and thorium. The maximum extraction of REEs was achieved during the 210 °C, 3 h bake time test. Thorium extraction was greater than 90% in the 2 h bake time at 210 °C, then dropped drastically to 50% or less for the 3 and 4 h bake times. Uranium extraction preferred the 250 °C level, but remained fairly low for the vast majority of the levels tested. The effect of particle size (48–137 μm) was studied at 210 °C and was found to have some effect on the extraction in the 1 and 2 h tests. However, in the 3 and 4 h tests, extractions were of similar magnitude for all three particle sizes studied. Thorium extraction peaked during the 2 h test and then dropped in 3 and 4 h tests. Alkali consumption was calculated and found to increase with increasing temperature and decreasing particle size (0.01–0.22 g alkali/g concentrate). Alkali consumption was increased with increasing extraction. The drop off in extraction is attributed to the dehydration of the hydroxides produced and the formation of insoluble phosphate phases.

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1. Introduction

In the ongoing development of new technologies, the world is becoming more dependent on rare earth elements (REEs) to provide solutions for an ever-increasing population. The development of high strength magnets, lasers, superconductors, and fiber optics will ensure an increasing demand for REEs. Currently, world REE production is dominated by China, which supplies over 90% of the demand. The United States, Australia, and India also produce small amounts of REEs. Monazite sands were at one time the primary source of REEs until the development of bastnäsite resources, and remain a valuable resource for REEs.

Monazite may once again become the primary source of REEs, as it is distributed throughout many countries around the world, most notably in heavy sand deposits. These heavy sand deposits also hold other minerals of economic importance, namely ilmenite, zircon, and rutile. Because the sand deposits are of so much importance, monazite extraction methods may need to be developed and

improved upon quickly. Monazite is made up of approximately 20–30% Ce, 10–40% La, and appreciable amounts of heavy REEs, with REE oxides all-together accounting for approximately 70% of monazite's weight (Kilbourn, 1993).

Because monazite is a phosphate mineral, it is difficult to decompose by direct acid leaching. A suitable ligand is required to form complexes with the rare earth metals present. Sulfuric acid treatment, where the sulfate ion acts as the ligand forming REE sulfates, and phosphoric acid have been commonly utilized in the past. However, sulfuric acid process does not yield pure products and is no longer in use (Amer et al., 2013). A major disadvantage of sulfuric acid processing is the loss of the phosphate, which may have potential economic value. However, sodium hydroxide decomposition of monazite allows for the recovery of phosphate as tri-sodium phosphate, which can then be used in the production of fertilizer (Gupta and Krishnamurthy, 2005).

Monazite is most often decomposed by the sodium hydroxide process where finely ground (–325 mesh) monazite is reacted with sodium hydroxide in an autoclave under high pressure. Monazite concentrate is mixed with 40–70% sodium hydroxide solution at a 1:1 weight ratio and then reacted in an autoclave for 3–4 h. This usually results in at least 95% recovery of the REE values from the

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monazite, as well as separation of the phosphate as tri-sodium phosphate (Gupta and Krishnamurthy, 2005).

Val'kov et al. (2010) proposed an approach to make use of the large amount of phosphorus present in monazite by employing alkali decomposition with potassium hydroxide as an alternative to sodium hydroxide. Potassium carbonate and nitric acid were utilized to separate REEs, thorium, and uranium in order to produce REE carbonates as well as potassium nitrate, which could then be sold as a fertilizer.

Abdel-Rehim (2002) acknowledged that sodium phosphate, a byproduct of sodium hydroxide decomposition of monazite, can also be used as a fertilizer. Simultaneous ball milling and alkali leaching was investigated in an autoclave rotated in a furnace. About 99.8% monazite was decomposed in 2.5 h at 150 °C using 150% of theoretical requirement of alkali at a concentration of 500 g/L. The continuous grinding utilized allowed for the hydroxide layer to be removed so that the alkali solution contacted the surface of the monazite more efficiently. Separation of thorium and uranium from REEs was obtained by processing the water leach residue using ammonium carbonate in an autoclave.

Several studies have been carried out investigating high temperature pretreatment of monazite with calcium carbonate, sodium carbonate, and sodium bicarbonate (Franken, 1995). Sodium bicarbonate was found to have a slight advantage over sodium carbonate at a roasting temperature of 815 °C. However, overall extractions of REEs were in the range of 15–30% with mineral acids in stirred reactors. When ultrasonic agitation was used, the extraction increased to ~93%. Thorium was still present with the REEs, and separation was not improved. This series of experiments was carried out in tube furnaces with 2 g samples, whether or not the process will scale up has yet to be tested (Franken, 1995).

A high temperature process was studied by Merritt (1990a,b), where monazite concentrate was roasted in an atmosphere that was both reducing and sulfidizing at the temperature range 980–1190 °C. Calcium chloride and calcium carbonate were both used as oxidizing agents. The process had some advantages in that fine grinding was not necessary, the reactions took place in minutes as compared to hours, and the thorium residue produced was virtually insoluble. However, this process has some limitations, and REE extraction was only ~89%. The process did not improve the thorium separation over sodium hydroxide or acid bake methods, and the phosphate value is unable to be recovered for fertilizer. Using sodium carbonate allowed for recovery of the phosphate value as tri-sodium phosphate by water leaching. However, thorium is converted to insoluble compounds by this method and is therefore more easily separated by leaching in 3.5% HCl (Merritt, 1990a,b).

Mechanical milling methods using calcium oxide and calcium chloride were studied by Zhang and Lincoln (1994). Extraction of REEs ranged from ~61 to ~99%; however, the process required extended milling times of ~15–24 h in an argon atmosphere. The process is unattractive commercially due to the slow kinetics (Zhang and Lincoln, 1994).

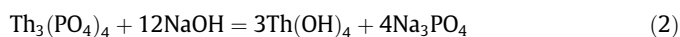
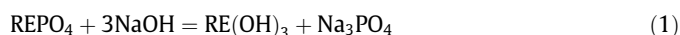
In a study by Panda et al. (2014), almost all of the phosphate value was recovered as well as ~95% of the REEs by autoclave digestion with 50% NaOH (w/v) at 180 °C and 100 g/L pulp density. Autoclave digestion is a proven method for decomposition of monazite and has been unchanged for many years. This method has its limitations, though. Fine grinding of the feed is required for complete dissolution of the monazite due to the formation of impermeable reaction products being formed on the surface of the particles.

This paper reports on a non-autoclave method for the decomposition of monazite and recovery of REEs. Alkali pugging process is a liquid-solid reaction that is adaptable to a rotary furnace, which would allow for continuous operation as opposed to the batch

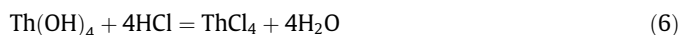
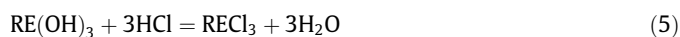
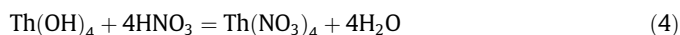
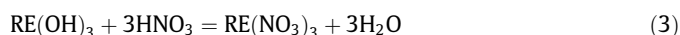
process in use today. In this study, the effects of experimental parameters including alkali to concentrate weight ratio, baking time, baking temperature, and particle size were investigated on REE extraction. The REE hydroxide cake that was formed was then leached in nitric acid solution for further processing.

2. Chemistry of leaching

In this study, sodium hydroxide was used as the lixiviant to solubilize and remove the phosphate. The chemical reactions for the alkali decomposition of monazite at elevated temperatures (reactions (1) and (2)) are as follows (Abdel-Rehim, 2002; Habashi, 2013):



The REE phosphates are converted to REE hydroxides and trisodium phosphate. The trisodium phosphate is washed from the bake residue along with the excess sodium hydroxide, while the REE hydroxides are insoluble and left in the leach residue. The water leach residue is then dissolved in either hydrochloric acid or nitric acid for further processing, depending on the subsequent operations or process goals. Reactions (3) and (4) are for the nitric acid system, while reactions (5) and (6) are for the hydrochloric acid system. In this study, the nitric acid system was utilized.



3. Materials and methods

3.1. Materials

The monazite concentrate, provided by Korea Institute of Geoscience and Mineral Resources (KIGAM), was first split using a Jones riffler and then milled using ceramic balls to generate finer particle size. After 90 min of milling, the concentrate was wet screened using a Rotap screen shaker. The generated particle sizes consisted of 44–53 µm, 74–88 µm, and 125–149 µm.

To determine the moisture content of the monazite concentrate, approximately 40 g of concentrate were carefully weighed and placed in a drying oven set at ~80 °C for several days. After the sample was allowed to cool, the weight of the sample was exactly the same as it was before drying. This shows that the monazite concentrate was completely free from moisture. X-ray diffraction (XRD) analysis (Rigaku Model Ultima +) was carried out on the monazite concentrate to determine the major mineral phases present (Fig. 1), and it was found that the monazite feed was mostly composed of monazite (Ce, La, Nd, Th(PO₄)), belovite (NaCeSr₃(PO₄)₃F), and florencite ((La,Ce)Al₃(PO₄)₂(OH)₆). An assay of the feed provided by KIGAM is shown in Table 1.

Certified ACS sodium hydroxide pellets (99% purity) and 69% pure nitric acid, both provided by Fischer Scientific, were used in the experiments. Deionized (DI) water was used in water leaching experiments.

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