Minerals Engineering 122 (2018) 113–121

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Extraction of rare earth elements from Abu–Tartour wet process phosphoric acid using synthesized salicylaldehyde azine

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ARTICLE INFO

Keywords:
Rare earth elements
Abu-Tartour, extraction
Wet process phosphoric acid
Salicylaldehyde azine

ABSTRACT

Background: Total rare earth elements (REEs) are often associated with uranium and thorium. In order to satisfy application for many different industries, REEs should be separated from uranium and other elements. One way to achieve an applicable separation scheme is to employ an extractant that will economically and selectively bind to REEs in the presence of potential interfering ions.
Objective: This work was designed to selectively recover REEs from the Abu-Tartour phosphoric acid solution using synthesized salicylaldehyde azine (SAA).
Results: The operating extraction and stripping conditions of REEs extraction from phosphoric acid have been experimentally optimized. From the acid and extractant effects, 0.024 M SAA was suitable for the separation of REEs at 30% acid, which is similar to Abu-Tartour wet process phosphoric acid solutions (WPPA). The extraction isotherm predicts the separation of REEs at an aqueous-to-organic (A/O) phase ratio of 1/2 in three stages using 0.024 M SAA. From the stripped liquor using 2 M HCl, the stripped (REEs) were precipitated as rare earth oxalate. The extraction studies showed the best fit with the first order rate equation.

1. Introduction

The total rare earth elements (REEs) are of special interest and are very important due to their many industrial uses. The vigorous demand for these elements leads to exploitation of primary rare earths ores which are being exhausted step by step in the world and secondary sources must be found with the potential to fill this need. Phosphate rocks could be one of the secondary sources.

Phosphate rock is the major source of phosphorus in nature. It exists mainly in the form of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] and fluoroapatite [$Ca_{10}(PO_4)_6F_2$] or a mixture of both and is mainly used for the production of fertilizers and elemental phosphorus. Nile Valley, Red Sea coast and New Valley in the Western Desert represents the main regions of phosphate in Egypt (El-Ramly et al., 1970). The sedimentary phosphate rock contains 100–200 ppm of uranium, 2–20 ppm thorium and about 0.5% rare earth elements (REEs). Phosphoric acid produced by the wet process method has many heavy trace elements which lead to environmental calamities (Becker, 1989).

Phosphoric acid is used in many different industries such as detergents, food products, medical, environmental protection and electronic industries (Guirguis et al., 2008; El-Asmya et al., 2008; Ma et al., 2009; Ren and Duan, 2013) so it must be of high purity and free from uranium and REEs. If these elements are not separated from phosphoric acid, they will be lost and accumulate in soil, or they will be adsorbed by plants, which represent a health hazard.

Rare earth elements could be recovered from different leaching processes of phosphate rock. These include; sulfuric acid, nitric acid and hydrochloric acid leaching processes (Lokshin et al., 2013, 2015).

Solvent extraction is the conventional hydrometallurgical technique used to recover rare earth elements from phosphoric acid because of its simplicity, versatility, and ease of scale-up of processes (Tunley and Nel, 1974; Lunt and Holden, 2006). Studies on solvent extraction of REEs using organo-phosphorus reagents from phosphoric acid reported that REEs (major yttrium) were recovered as fluorides (Bunus and Dumitrescu, 1992; Bunus et al., 1994). Preston et al. developed a solvent extraction process for separation of cerium dioxide, heavy, middle REEs oxides and light REEs fraction concentrates from a phosphoric acid by-product by using di-butylphosphonate, tri-n-butyl phosphate, and Di-(2-ethylhexyl)phosphoric acid (D_2EHPA) (Preston et al., 1996).

The essential and applied aspects of the extraction of the REEs using D_2EHPA were discussed and the industrial flowsheets were described (L. Wang et al., 2010; G. Wang et al., 2010). Systematic solvent

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https://doi.org/10.1016/j.mineng.2018.03.037
Received 21 November 2017; Received in revised form 15 March 2018; Accepted 28 March 2018

extraction studies on yttrium and separation possibilities among REEs from phosphoric acid using organo-phosphorus reagents and ion exchange resins like Tulsion CH-96, Tulsion CH-93, Tulsion CH-90 and T-PAR resins were reported (Reddy et al., 2009, 2010; Radhika et al., 2012).

The TOPS 99 an equivalent to di-2-ethylhexyl phosphoric acid, (2-ethylhexyl) phosphonic acid mono-(2-ethylhexyl) ester [PC-88A], and Cyanex 272 were mentioned by Radhika et al. (2010, 2011). Also, using primene JMT (Guirguis et al., 2014), PX-107 and Chelok® polymers (Laurino and Mustacato, 2015), Tributyl phosphate (Jorjani and Shahbazi, 2016), emulsion liquid membrane (ELM) with di(2-ethylhexyl) phosphate (D2EHPA) (Zhang et al., 2016), Di octyl phenyl phosphoric acid (DOPPA) and Tri octyl phosphine oxide (TOPO) (Rollat, 2016), [methyltrioctyl ammonium][(2,6-dimethylheptyl) phenoxy acetic acid] (Wang et al., 2017), Cyanex 272 + Alamine 336 (Liu and Lee, 2016) and the systems containing acid–base coupling bifunctional ionic liquids (ABC-ILs) were highlighted (Dong et al., 2016).

But, in the above solvents, the selective separation of total REEs from phosphoric acid, without contamination of uranium, is difficult to implement. These solvents also have lower efficiency of impurities removal and require high operating cost. Besides, some of these solvents require pH at or above 1.5, which needs either dilution or neutralization of most leaching solutions. Therefore, finding a suitable extractant for recovery of REEs from WPPA is an urgent task, solution of which has not been found previously. The interest in the study of hydralazine and hydrazone compounds has recently been growing up due to their coordination capacity (Ayman and Ahmed, 2011; El-Sherif et al., 2012). They have wide applications in the treatment of many diseases. Also, they can be used for copper (II), cobalt (II), Zn (II) and nickel (II) complexes (Ayman and Ahmed, 2011; El-Sherif et al., 2012). In addition, hydralazine compounds have not been previously used for extraction of REEs from acidic solutions. The preparation of a new hydrazone ligand was perhaps the most important step in the development of REEs complexes which exhibit unique properties and novel reactivity.

In this work, trials to find out new extractant were conducted as they have some advantages such as selectivity, low cost, stable composition, easy preparation, and lack of emulsification during extraction. In this context, salicylaldehyde azine as a synthesized organic solvent was used to extract REEs from prepared H_3PO_4 acid (30% P_2O_5 and 300 ppm REEs) to be used in the field of REEs extraction from real phosphate rock.

2. Experimental

2.1. Materials

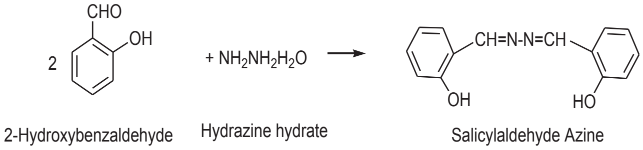
The use of synthesized azine for the recovery of total rare earth elements from Abu Tartur phosphate rock sample is the main concern of this work.

2.1.1. Preparation of synthetic phosphoric acid

The relevant factors affecting rare earth elements extraction and stripping with the synthesized azine have first been optimized using simulated synthetic rare earth elements-bearing phosphoric acid solution. The latter assaying 30% P_2O_5 has thus been prepared from Edwic 85% P_2O_5 phosphoric acid by proper dilution. In the latter, properly weighed samples of yttrium oxide, lanthanum (III) oxide and cerium (III) chloride hepta-hydrate are dissolved and made up to volume to give 1000 ppm of Yttrium, lanthanum and cerium stock solutions respectively. It is important to mention herein that Y(III), La(III) and Ce (III) are intended to represent the three categories of REE (light, medium and heavy). On the other hand, for studying the possible interference from other metal impurities that might be associated with rare earth elements in its solutions, proper weights of some of their compounds have been dissolved in the prepared synthetic 30% P_2O_5 solution in a manner to assay 100 ppm for each. The metal compounds used have involved the hydroxides of Fe, and Ca, the nitrate salts of Pb, Ni and Th and the chloride salts of Cu, Ce and Y while V from ammonium metavanadate.

2.1.2. Procedure of salicylaldehyde azine preparation

For the synthesis of salicylaldehyde azine, 2-hydroxy-benzaldehyde (0.1 mol) was dissolved in 95% ethanol (60 ml). Hydrazine hydrate (0.05 mol) was also dissolved in 95% ethanol (25 ml) and added slowly with constant stirring to the aldehyde solution. The reaction was usually exothermic and was driven to completion by refluxing the reaction mixture for about 2 h. cooling to room temperature led to the deposition of yellow crystals which were filtered off under suction and re-crystallized from ethanol/water (1:1) mixture and dried under vacuum (Salam and Chowdhury, 2001; Li et al., 2012).



2.1.3. Abu Tartur WPPA

Abu Tartur phosphate rock sample was chosen as a case study for studying the optimum rare earth elements extraction conditions. For this purpose, a sample of the former has kindly been provided from Abu Tartur phosphate ore material and has completely been analyzed for the present work. According to EL-Sayed and Abdel-Aal (2000), rare earth elements recovery of about 90% could be achieved using HCl with the following conditions:

Particle size: < 0.25 μm
Reaction temperature: 30 °C
Reaction time: 1 h.
HC1 concentration: 300 g/L
Liquid/solid ratio: 2:1

2.2. Experimental procedure

The extraction of total rare earth elements from the synthetic phosphoric acid was carried out by using salicylaldehyde azine extractant dissolved in toluene at proper molarities at 25 °C for the desired time. The relevant solvent extraction and stripping factors were studied including synthesized salicylaldehyde azine concentration, contact time, temp., settling time, phosphoric acid concentration, aqueous-to-organic (A/O) ratio as well as the effect of some interfering ions which are present in phosphoric acid. Besides, construction of isotherm to calculate the number of theoretical stages required for maximum loading and stripping of rare earths was also tackled.

2.3. Analytical procedures

2.3.1. Analysis of Abu Tarture ore material

The conventional wet chemical technique of Shapiro and Brannock (1962) was applied upon the prepared sample solutions for major elements determination using their relevant spectrophotometer methods. On the other hand, analysis of the metals of interest; e.g. the rare earth elements have spectrophotometerically been determined using Arsenazo-III as the chromogenic reagent (Marczenko, 1986). U was analyzed in the different aqueous stream solutions fluorometrically by using the laser fluorometer“UA-3” [Uranium Analyzer (Scintrex, Canada)].

Other elements in interfering study were analyzed using ICP-ES Teledyne technologies (Inductively Coupled Plasma Optical Emission Spectrometer).

Meanwhile, JASCO Spectrometer, model V-530 has been used to