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ALKALINE FUSION OF MALAYSIAN MONAZITE AND XENOTIME FOR THE SEPARATION OF THORIUM AND URANIUM

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ABSTRACT

Thorium and uranium content in monazite and xenotime can be retrieved through extraction method. However, these elements need to be separated before extraction could be done. The purpose of this research was to study the effectiveness of thorium and uranium separation technique in monazite and xenotime via alkaline fusion method as well as to determine the suitability of this method towards the two minerals. The alkaline fusion process required the minerals to be fused in sodium hydroxide pellet at 300 - 350°C for about three hours before leaching with 6M hydrochloric acid. Two stages of selective precipitation were conducted using solutions of oxalic acid and ammonia to form oxalate complexes and hydroxide complexes respectively. Both solid complexes were later analysed for its elemental content using Energy Dispersive X-ray Fluorescence (EDXRF). The result obtained shows that thorium was separated in the oxalate complexes, while uranium separated in the hydroxide complexes. However, the conditions used in this technique were found to be more suitable for xenotime.

Keywords: Alkaline fusion, monazite, separation, thorium, uranium, xenotime

INTRODUCTION

Monazite and xenotime are known to be as phosphate-rich minerals due to high content of phosphate. In Malaysia, both minerals can be found in alluvial deposits and often retrieved from processing the waste produced in tin mines. Granitic rocks were also reported to be another resource to contain these minerals in Peninsular Malaysia (Sanusi et al., 2017). Apart from phosphate, the minerals become the source for rare earth elements. Monazite differs from xenotime in terms of rare earth elements that are present in the mineral. Light rare earth elements; cerium, lanthanum, and neodymium are mostly found in monazite meanwhile heavy rare earth elements such as yttrium, europium, gadolinium, and terbium are mostly found in xenotime. Often, these minerals are written in a formula represented by the abundant element presence which is (Ce, La) PO_4 for monazite and YPO_4 as for xenotime. Currently, these minerals are processed for its rare earth contents.

Other than rare earth elements, monazite and xenotime also contain radioactive elements, thorium and uranium. The reason thorium and uranium are often present in rare earth minerals are due to the similarity in their chemical structures to the rare earth elements (Kanazawa and Kamitani, 2006). This has become one of the problems that arise when these minerals were processed for rare earth element, whereas thorium and uranium are being treated as waste. One example that happened years ago, in Malaysia, monazite was processed for yttrium in a processing plant in Bukit Merah, Perak. The waste produced was known as thorium hydroxide residues that contain 32 - 33.5% thorium oxide, 1.1 - 1.4% uranium oxide and 27 - 28% uncovered rare earths (Badrulhisham and Meor Yusoff, 2014). Due to high amount of radioactive radiation emitted, this factory faced several protests from the public. Added with losses and higher cost of plant maintenance, this factory was forced to cease its operation in 1994. Rare earth industry on the other hand can become a source for the economy sector. Hence, a better way in managing the waste is greatly needed, perhaps through extracting the radioactive elements can reduced the amount of radiation that can be harmful to the environment.

The stages needed for obtaining thorium and uranium from minerals is basically similar to a processing rare earth element. It started with mining and comminution, followed by ore beneficiation and lastly the hydrometallurgical stage. In this last stage, it requires digestion of the concentrated mineral for the dissolution in aqueous media, which is involving the process of cracking the minerals. The term “cracking” refers to mineral decomposition in which the breaking down of the mineral can be done in several methods such as acid digestion and alkaline or caustic soda cracking. There were several methods conducted in processing these minerals. Kumari et al. (2015) summarized that monazite can be processed via digestion in sulphuric acid, nitric acid, hydrochloric acid, sodium hydroxide, and ammonium carbonate. Amer et al. (2013) reported that sulphuric acid digestion is very common in the United States of America, while India and Brazil favor in using caustic soda for mineral decomposition.

Alkaline fusion method differs from caustic soda in terms of higher temperature needed (Alex et al., 1998) and solid sodium hydroxide for cracking was used, whereas caustic soda method required concentrated sodium hydroxide solution in much lower temperature. The advantage of The alkaline fusion technique is that it uses more dilute acid to dissolve rare earth as (Badrulhisham and Meor Yusoff, 2014) apart from the being able to recover phosphate as by-product. As for this study, alkaline fusion as the new alternative method (Meor Yusoff et al., 2015) was used for the same purpose prior to the separation process of thorium and uranium. The separation process of thorium and uranium from local monazite and xenotime that were digested using the alkaline fusion technique was the main objective for this study. Other than that, the suitability for this process for the two local minerals was also being investigated.

MATERIALS AND METHODS

The chemicals used for this study were of analytical grade, while monazite and xenotime minerals used were obtained from a mining factory in Perak. Local xenotime was recorded to contain about 0.96 to 1.24% uranium and 0.68 to 0.75% thorium (Meor Yusoff, 2010) while monazite has 5 to 7% thorium and uranium. 200 g of each mineral was mixed well with sodium hydroxide pellet in the ratio of 1:2. The mixture was then fused in Carbolite RHF1400 furnace at high temperature of around 300 - 350°C for 3 hours. After the fusion process, the fused products were washed with deionised water and filtered to remove the loose phosphate particles. The hydrous cakes were then leached in 6 M HCl for six hours at temperature 70 - 80°C. The leached solutions obtained were then undergoing two stages of precipitation conducted at pH 0.2 then continued at pH 6.0 by using oxalic acid and ammonia solution, respectively. The oxalic acid used was prepared by dissolving oxalic acid dehydrate in deionized water in ratio of 1:10. Ammonia solution, on the other hand was diluted with deionized water from 30% ammonia solution in ratio of 1:6. The precipitation products were dried in oven and the chemical compositions were determined by electron dispersive X-ray fluorescence spectrometry using Shimadzu EDX-7000.

RESULTS AND DISCUSSION

The percentage of thorium and uranium element analysed using ED-XRF in monazite and xenotime were as presented in Table 1. It was shown that xenotime contained less than 1% of thorium and uranium, while monazite had a slighter higher percentage of thorium as compared to uranium.

Table 1. Percentage of thorium and uranium analysed from xenotime and monazite

Mineral	Thorium (%)	Uranium (%)
Raw xenotime	0.62	0.57
Raw monazite	5.19	0.19

The phosphate content in both minerals was converted into soluble trisodium phosphate. This occurrence can be explained in Equation (1) by taking $REPO_4$ as the general formula for monazite and xenotime.

$$REPO_4 + 3NaOH \rightarrow RE(OH)_3 + Na_3PO_4 \quad (1)$$

Other remaining elements, including rare earths, thorium and uranium were still contained in the hydrous mineral cakes. Upon addition of the concentrated hydrochloric acid, these elements were dissolved in the acidic solution. The reaction for this stage can be described as in Equation (2) below.

$$RE(OH)_3 + 3HCl \rightarrow RECl_3 + 3H_2O \quad (2)$$

After dissolution of the elements, selective precipitation conducted at pH 0.2 by adding an oxalic acid solution forming oxalate complexes that contain thorium and other rare earth elements. Precipitation with ammonia solution followed next, in which hydroxide complexes containing uranium and other elements created. The results for the percentage of thorium and uranium in oxalate and hydroxide complexes obtained from both minerals were as presented in Table 2. The analysis showed that no trace of thorium found in the hydroxide complexes and also no trace of uranium found in the oxalate complexes. These findings support the studies done by Amer et al. (2013) and Farzaneh et al. (2017) in which 98% of thorium separated via precipitation using oxalic acid. The unreacted solid obtained after the leaching process was treated as waste.

Table 2: Analysis of thorium and uranium in oxalate and hydroxide complexes and in the residues

Precipitate Complexes	Monazite		Xenotime	
	Th (%)	U (%)	Th (%)	U (%)
(Th + REE) oxalate	3.98	-	0.78	-
(U + REE) hydroxide	-	0.60	-	0.94

The percentages of recovery for thorium and uranium element were calculated in reference to Equation (3). In both complexes from the two minerals, the percent recovery of thorium and uranium were reported in Table 3. In xenotime, uranium was recovered as much as 83.63%, while thorium was 62.15%. Monazite showed lower recovery percentage, that is 62.15% for thorium and 41.40% for uranium.

$$\% \text{ recovery} = \frac{(\text{Weight of Th or U in the complexes})}{(\text{Weight of Th or U in the mineral})} \times 100 \quad (3)$$

Table 3: Percent recovery of Th and U in oxalate and hydroxide complexes

Mineral	Monazite (%)	Xenotime (%)
Th	62.15	69.47
U	41.40	83.63

CONCLUSIONS

In this process, thorium and uranium can be separated from the ore minerals through cracking and acid leaching. Selective precipitation using oxalic acid solution allows thorium to be separated in the form of oxalate complexes from acidic leaching solution that contains uranium. Meanwhile, precipitation using ammonia solution form hydroxide complexes that included uranium. Upon calculation for the percent of recovery for both elements of the minerals, the recovery of uranium and thorium were more favorable in xenotime compared from monazite. This indicates that the parameters used in this process are more suitable for xenotime.

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