

CRACKING OF MALAYSIAN XENOTIME CONCENTRATE IN SODIUM HYDROXIDE USING FUSION TECHNIQUE

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ABSTRACT

There are different methods for processing and breaking down minerals including acid baking, alkaline cracking and alkaline fusion digestion techniques. In this paper, xenotime was cracked via alkaline fusion digestion methods. Xenotime is one of the rare earth minerals that contain radioactive materials such as uranium (U) and thorium (Th). In this study, Malaysian xenotime undergo the process using sodium hydroxide (NaOH) and leached in 6M hydrochloric acid (HCl) followed by selective precipitations to obtain 1) mixed thorium and rare earth in the form of oxalates and 2) mixed uranium and rare earth in the form of hydroxide. The samples were characterized using Field Emission Scanning Electron Microscope (FESEM), X-ray Diffraction (XRD) and Energy Dispersive X-ray Fluorescence (ED-XRF) instruments to study their morphology, qualitative and quantitative value of elements obtained along the study. The percentage of recovery can be calculated from the mass of samples obtained with assist from ED-XRF results.

Keywords: Alkaline fusion, recovery, selective precipitation, thorium, xenotime

INTRODUCTION

Rare earth elements (REE) consist of scandium (Sc), yttrium (Y) and fifteen other elements in the lanthanide group. They have similar catalytic, optical and magnetic properties while possessing unique nuclear, physicochemical, chemical and electronic characteristics. The lanthanide elements are divided into two groups. REE from lanthanum to samarium (La, Ce, Pr, Nd, Pm, and Sm) are considered as light REE while europium to lutetium (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) are considered as heavy REE. Yttrium categorized as heavy REE due to resemblance with the heavy REE in term of ionic radius, mode of occurrence and their properties regardless of its low molecular weight (Gomes et al., 2018).

REE are crucial elements in the production of high-tech products due to their significant properties. In the example, lanthanum is used widely as components in catalysts in petroleum refining industries as well as in carbon lighting applications (Lucas et al., 2015). Yttrium is vital in computer and television screen production whilst cerium (Ce) is used in car's catalytic converters and plays a crucial role in the chemical reactions application (Bradley et al., 2014). The applications of REE not only bound in electronics, renewable energy sciences, or industrial engineering, but also extend into military applications (Hsu, 2010).

The values of REE inflate in these few years due to several factors. One of the factors is emerging of new technologies and innovation of products that demand for more REE. In addition, the characteristics poses by these elements are unique which hardly matched by any other metals

neither with artificial components. Currently there is a major REE-producing country decided to stop exporting their rare earth. Thus, it's becoming crucial for some countries being able to produce their own rare earth supplies. REE can be obtained from several types of minerals in the earth crust. A mineral that contains one or more REE is called as rare earth minerals. Major raw material for REE can be obtained from xenotime, monazite, basnasite and phosphate rocks (Habashi, 2012).

MATERIALS AND METHODS

The xenotime sample is obtained from a Malaysian Mining corporation plant in Kampar, Perak. This sample undergoes an alkaline fusion process where the minerals were decomposed. 100 g of sample was mixed with 200 g NaOH pellets and was fused in a furnace for 3 hours at 350°C. Then the complex was soaked in deionised water for washing purposes in order to remove loose phosphate components. The mechanical stirrer used was set at 350 rpm for 3 hours to wash the complex thoroughly.

After washing and drying, the remaining yttrium component was leached in 6 M HCl with sample to acid ratio 1:6 for 6 hours while heating at 70 - 80°C. The leached component was then filtered to remove undissolved materials. The undissolved material was then washed and dried. Mixed oxalate was precipitated by adding oxalic acid ($C_2H_4O_2$) into the after-leached solution until it reached pH 0.2. The precipitate was filtered, washed and dried. Remaining solution was then precipitated by addition of ammonia solution (NH_4OH) until pH 8 was reached. The precipitated hydroxide was filtered, washed and dried. All the sample was weighed and analysed using XRD, ED-XRF and FESEM.

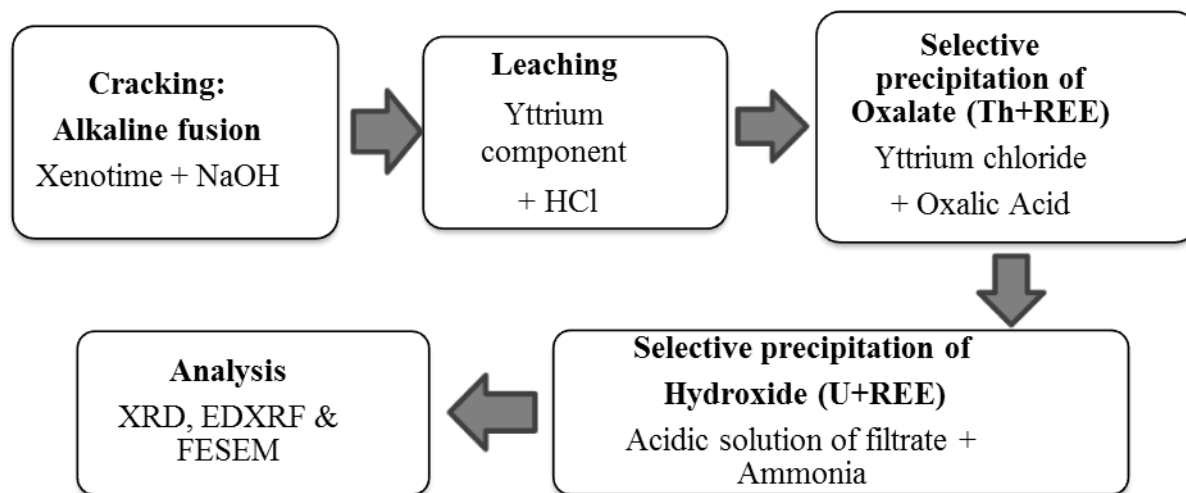


Figure 1: Flow chart of overall process

The mass of thorium and uranium in each sample was calculated using Equation (1). Whilst Equation (2) was used to calculate the percent recovery of elements, which in this study, we focused on thorium and uranium elements.

$$\text{Mass of elements (g)} = \frac{\text{Wt. \% of elements in sample from EDXRF} \times \text{Total mass of sample (g)}}{100\%} \quad (1)$$

$$\text{Percent recovery (\%)} = \frac{\text{Mass of element in sample} \times 100\%}{\text{Mass of element in xenotime}} \quad (2)$$

RESULTS AND DISCUSSION

XRD Analysis

The unprocessed sample of xenotime minerals shows peaks similar to reference pattern 98-006-3171 for xenotime (Yttrium) as shown in Figure 2. This indicates local xenotime is a yttrium-rich mineral. That is why xenotime are usually written as YPO_4 (yttrium phosphate). The undissolved xenotime that were filtered after leaching process was differentiated into coarse (larger than 130 μm) and fine (smaller than 130 μm) residue. The XRD analysis of coarse residue in Figure 3 indicates the presence of xenotime (Dysprosium) based on reference pattern of 98-002-2081. The XRD patterns of finer residue in Figure 4 shows similarities with unprocessed xenotime pattern which indicates incomplete xenotime decomposition of mineral. It also shows the presence of cerium oxide formula (98-005-4296).

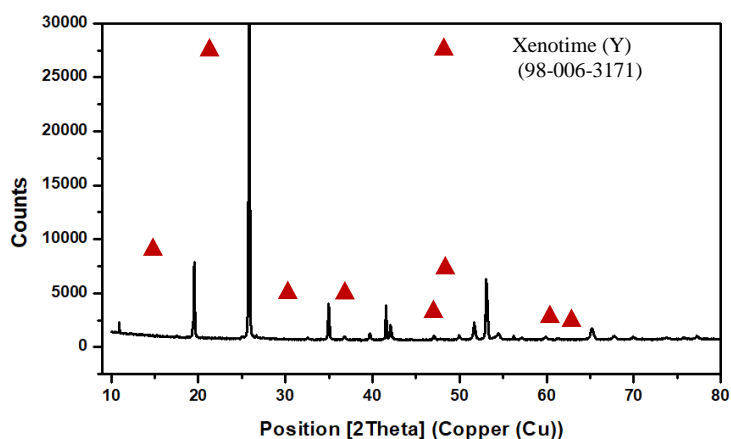


Figure 2: XRD pattern of unprocessed xenotime

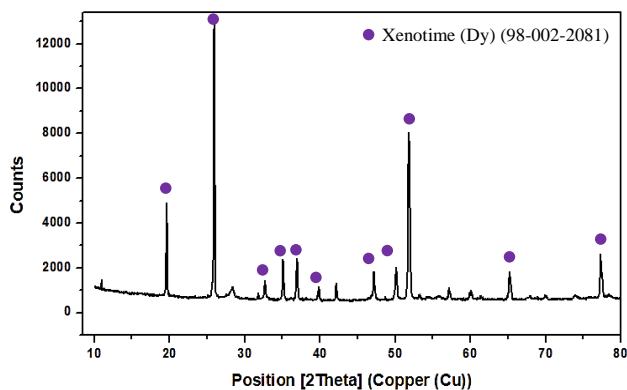


Figure 3: XRD pattern of undissolved coarse sample

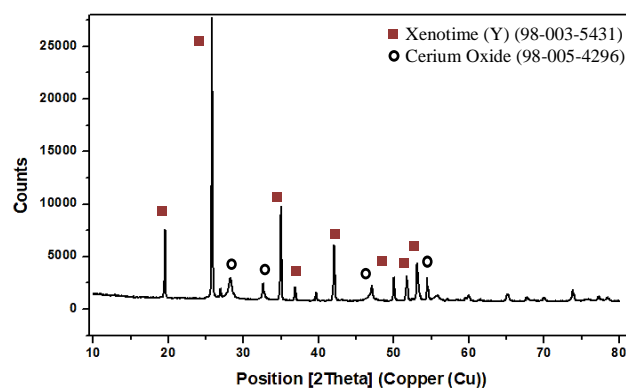


Figure 4: XRD pattern of undissolved fine sample

ED-XRF Analysis

ED-XRF results indicates yttrium as the highest percent in local xenotime which supports the XRD analysis. It was estimated that yttrium content in local xenotime is between 30 - 40% (Meor Yusoff, 2010). REE that is contained in this sample includes heavy REE such as ytterbium (Yb) which present in highest amount, gadolinium (Ga), holmium (Ho) as well as some light REE such as Ce and neodymium (Nd). The weight percent of uranium and thorium are small which is about 0.63 wt.% and 0.57 wt.% respectively as shown in Table 1. The mixed oxalate obtained through selective precipitation using oxalic acid shows high percentage of yttrium and most of REE in the lanthanide group.

Table 1: The wt.% of elements content in unprocessed xenotime

Elements	wt.%	Elements	wt.%
Y	33.90	Ba	1.46
P	20.05	Nd	1.40
Fe	12.91	Ho	1.39
Yb	7.11	Ce	1.16
Hf	1.83	Th	0.63
Ti	1.80	U	0.57
Gd	1.68	Nb	0.04

Thorium content appears only in a minimum amount which is about 0.78 wt. % as shown in Figure 5. Same goes to mixed hydroxide sample which have higher yttrium content followed by phosphorus (P). The percentage of uranium is only 0.94% as shown in Figure 6. It can be said that the precipitation method successfully separates thorium from uranium. ED-XRF analysis also indicated that there are uranium and thorium still present in both undissolved xenotime prior to leaching process. Yttrium still present in the largest portion of the filtrate for both coarse and fine samples. REE such as Dysprosium (Dy), Yb, Nd and Gd also can be observe from the analysis as shown in Table 2.

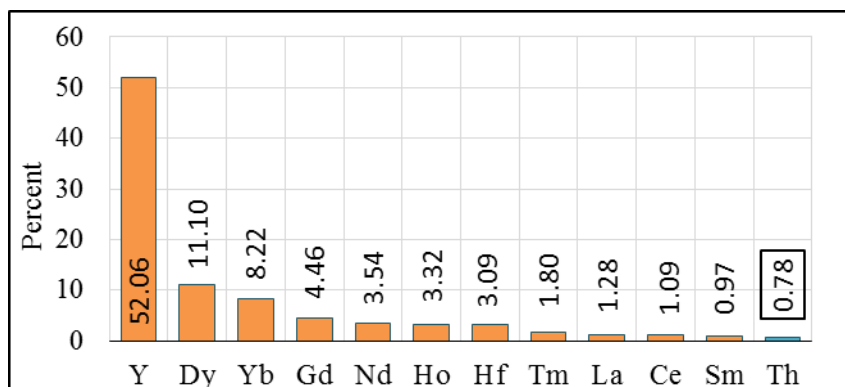


Figure 5: The wt. % of elements in mixed oxalates after selective precipitation using C₂H₄O₂

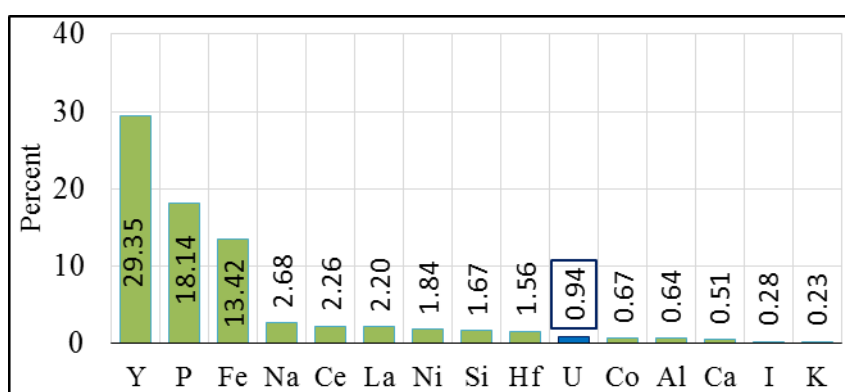


Figure 6: The wt. % of elements in mixed hydroxides after selective precipitation using NH₄OH

Table 2: The wt.% of elements in the filtrate after leaching process

Elements	Coarse	Fine	Elements	Coarse	Fine
	wt. %			wt. %	
Y	31.90	30.60	Ce	2.18	9.20
P	24.91	19.58	Hf	1.68	1.67
Dy	6.62	3.64	Gd	1.58	1.78
Yb	6.38	-	U	0.56	0.50
Si	5.73	12.75	Th	0.69	1.44
Nd	2.86	1.44	Ho	0.94	1.32
Ti	2.81	2.84	Zr	0.30	2.12
Tm	2.73	2.71			

FESEM Analysis

The unprocessed xenotime consist of particles with average size of 150 to 250 μm as shown in Figure 7. When compared the particle size between the mixed oxalate and mixed hydroxide, the size differs significantly. Particle size of oxalate and hydroxide sample is less than 10 μm (Figure 8(a)) and between 20 - 150 μm (Figure 8 (b)) respectively.

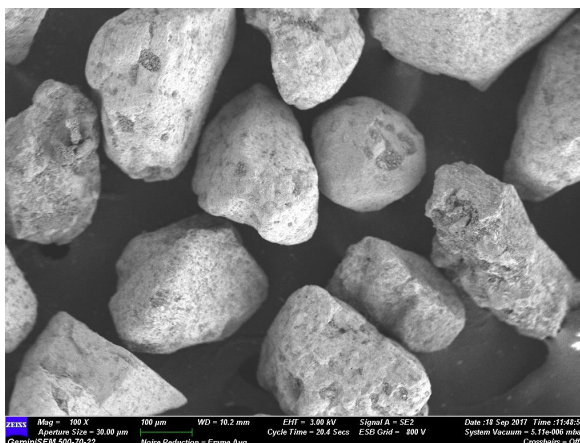


Figure 7: Morphology of unprocessed xenotime under FESEM

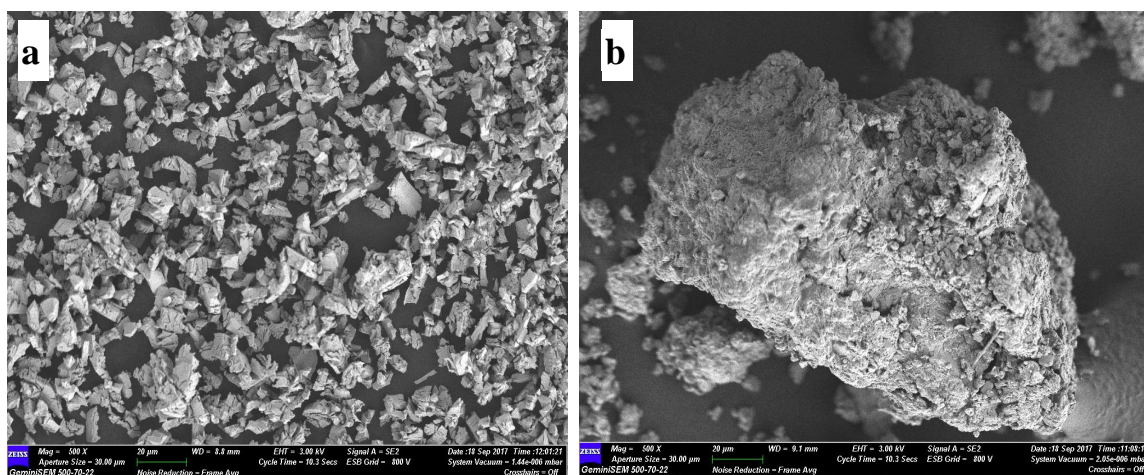


Figure 8: The particles of mixed oxalate (a) and mixed hydroxide (b) at 500X magnification

Percent Recovery

Table 3 shows the mass of thorium and uranium in each of the samples calculated from ED-XRF results using Equation (1). From here, the percent recovery was then calculated using Equation (2). Through calculations, 68.25% of thorium in forms of oxalate and 55.14% of uranium in forms of hydroxide were recovered from the 100 g of xenotime.

Table 3: Mass (g) of thorium and uranium in each of samples

	Sample Mass (g)	Th(g)	U(g)
Xenotime	100	0.63	0.57
Mixed Oxalate	55	0.43	-
Mixed Hydroxide	56	-	0.32
Residue (Coarse)	11	0.07	0.06
Residue (Fine)	27	0.39	0.14

CONCLUSIONS

All five samples which are unprocessed xenotime, mixed oxalate, mixed hydroxide and residue (coarse and fine) were analysed using XRD, EDXRF and FESEM. The elements that are deposited in xenotime minerals includes mainly yttrium, ytterbium, gadolinium, neodymium, holmium, as well as uranium and thorium but in smaller percent. The selective precipitation method is able to separating thorium from uranium successfully. By using EDXRF analysis, mass of thorium and uranium in 100 g of unprocessed xenotime were 0.63 g and 0.57 g respectively. After cracking, leaching and precipitation process, the mass of thorium calculated from mixed oxalate is 0.43 g whilst mass of uranium in mixed hydroxide is 0.32g. As a conclusion, the recovery percentage of thorium is 68.25% and 55.14% for uranium was achieved in this study.

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