RECOVERY OF THORIUM AND RARE EARTH ELEMENT (REE) FROM DIFFERENT PARTICLE SIZE OF XENOTIME MINERAL

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ABSTRACT

The present work describes the development of alkaline fusion process to recover thorium (Th) and rare earth elements (REE) from Malaysian xenotime. The steps investigated in the process to recover thorium and REE were: (i) milling of xenotime mineral with different speed, (ii) cracking process of xenotime mineral via alkaline fusion, (iii) washing process and (iv) leaching of mineral cake with hydrochloric acid (HCl). The influence of milling speed to particle size distribution and effect of particles size on recovery of thorium and REEs were investigated. Based on the results, the particle will be decrease from 220 µm to 17.12 µm as increasing the milling speed up to 300 rpm. However, not much reduction in the particle size upon milling at 400 rpm. The results revealed that the smallest particle size recover 77.02% of thorium, 68.08%, 58.95%, 53.69% and 51.67% of yttrium (Y), ytterbium (Yb), erbium (Er) and dysprosium (Dy), respectively. As compare to unmilling sample, the average Th and REE recovery were just in the range of 31.45% to 45.34%. The increase of surface area resulted in an increase of the Th and REE recovery by enhancing the reaction mineral surface area and HCl.

ABSTRAK

Kerja-kerja ini menerangkan perkembangan proses gabungan alkali untuk memulihkan torium (Th) dan unsur-unsur nadir bumi (REE) dari xenotime Malaysia. Langkah-langkah yang dikaji dalam proses untuk mendapatkan semula thorium dan REE adalah: (i) pengilangan mineral xenotim dengan kelajuan yang berbeza, (ii) proses retak mineral xenotim melalui gabungan alkali, (iii) proses pembersihan dan (iv) asid hidroklorik (HCl). Pengaruh kelajuan pengilangan kepada pengagihan saiz zarah dan kesan saiz zarah pada pemulihan torium dan REEs telah disiasat. Berdasarkan hasilnya, zarah akan berkurang dari 220 µm ke 17.12 µm sambil meningkatkan kelajuan penggilingan sehingga 300 rpm. Walau bagaimanapun, tidak banyak pengurangan saiz zarah pada penggilingan pada 400 rpm. Hasil kajian menunjukkan bahawa saiz zarah terkecil mengembalikan 77.02% torium, 68.08%, 58.95%, 53.69% dan 51.67% daripada yttrium (Y), ytterbium (Yb), erbium (Er) dan dysprosium (Dy). Seperti yang dibandingkan dengan sampel unmilling, purata pemulihan Th dan REE hanya dalam lingkungan 31.45% hingga 45.34%. Peningkatan kawasan permukaan mengakibatkan peningkatan pemulihan Th dan REE dengan meningkatkan kawasan permukaan mineral reaksi dan HCl.

INTRODUCTION

Malaysia has many potential mineral resources including some rare earth elements (REE) minerals such as xenotime. Xenotime mineral derived from by-product of tin mining industry which contain rare earth elements (REE dominant by Y, Dy and Gd whose content respectively 30-40% [1], 7.8% and 2.6% [2]. Xenotime (YPO4) is classified as a radioactive mineral as it contain small amount of radioactive element such as thorium (Th) and Uranium (U) but possessed highly enriched yttrium phosphate mineral. REE play critical roles in the applications of advanced materials.

Before chemical treatment, xenotime typically concentrated through physical processing which comprise floatation, magnetic, electrostatic separation and gravity separation methods. Then followed by beneficiation and physical separation. Currently two major routes of xenotime decomposition that have been established such as using sodium hydroxide (NaOH) or sulfuric acid to attack and break down the greatly stable xenotime structure [3]. Both of these techniques needed passionate extraction conditions for example elevated heat or pressures. NaOH was found environmentally friendly compared to sulfuric acid roasting due to radioactive free (Th or U) in the leach waste. Alkaline fusion with NaOH produces trisodium phosphate (TSP) as a by-product that can be sold as compost to assist alleviate the cost of NaOH. Even though Malaysia has a lot of rare earth resources, most of valuable mineral have to be imported because of the lack of expertise to extract these minerals into purified single element. Environmentally friendly methods is essential to increase the country towards power sources diversity and carter the demand for electricity source. In order to recover thorium from xenotime, 'breaking up' and cracking of this mineral is required [4].

REE contain in mineral have similarity in their ionic radii. Thus, make these REE interchangeable in most mineral and are causing difficulties to separate REE [5] into individual elements. Therefore, the present study aimed to evaluate the recovery of REE through alkaline fusion of xenotime mineral. A process consisting a alkaline fusion followed by hydrochloric acid leach has been examined with experimental parameters including particle size (20 – 220 µm. The current literature does not discussed in detail for this novel method for xenotime. In addition, NaOH has not been utilized commercially for REEs extraction from xenotime and just few report studies on its ability to extract Th and REE from xenotime. In facts, this study seeks to investigate the effect of particle size on cracking and further leaching process are highlighted in the present study.

METHODOLOGY

Experimental

In the present study, the xenotime ore from Lembah Kinta, Perak, Malaysia was used. Fritsch Pulverissette 6 (7 mm ball) with ball-to-solid ratio of 1:1 was used for xenotime ore grinding. The milling was conducted for 30 minutes at 100 to 400 rpm. Dry sieving was conducted for 5 minutes using a rotary sieve shaker and ASTM sieves of 45 to 180 μm, for determining the particle size distributions of the milled samples. Mineral cracking was done by mixed xenotime mineral with NaOH beads and fused in furnace at 350 °C for 3 hours. Sodium hydroxide was chosen as fusion agent due to its relatively lower fusion temperature requirement and also cheaper than most of other chemical available. After washing and filteration process, the sample undergo acid leaching process. The leaching was done in air atmosphere at 70-80 C for 6 hours. 6 M HCl was introduced in this step. Selective precipitation was done by adding oxalic acid to recover thorium oxalate and ammonium hydroxide to recover uranium hydroxide.

Characterization

The solid samples obtained after leaching step and co-precipitation were characterized using Honeywell, Microtrac X100 Particle Sizer for particle size analysis, Energy Dispersive X-Ray Fluorescence (EDXRF), EDX-7000, Shimadzhu for elemental analysis, Field Emission Electron Microscope (FESEM), Carl Zeiss, GeminiSEM for morphology and X-ray Diffraction (XRD), PANalytical, X'Pert PRO MPD PW 3040/60 for phase identification.

RESULTS AND DISCUSSION

Early characterization of xenotime ore was conducted to determine the composition using EDXRF. Table 1 indicates the chemical composition of the xenotime based on XRF analysis. As can see, the thorium is 1.18% and total REE 61.47% make it is significant to extract thorium and REE from this mineral. Also from this process, yttrium (Y), ytterbium (Yb), dysprosium (Dy), erbium (Er), neodymium (Nd) and holmium (Ho) could be recovered,. Even though REE contents in this ore are small, these ore minerals can be mine and process economically due to its vast application. More element exist in single particles would make forming process becoming more complicated [6]. Upon extracting this Th and REE via alkaline fusion, it is believe can enhance advanced materials properties. Chemical composition of raw ore are also important to distinguish method in recovering high yield of REE or Th.

Table 1 Elemental content of raw Xenotime mineral.

Element	Raw xenotime mineral (wt%)	Element	Raw xenotime mineral (wt%)
Y	45.29	P	28.71
Yb	5.24	Fe	9.72
Dy	4.73	Si	6.36
Er	2.99	Ba	4.19
Nd	1.64	Mn	2.56
Ho	1.58	Co	1.10
Th	1.18	S	0.86
U	1.17	Zr	0.63
Ti	4.22	Ca	0.46

Additionally, particle size analysis was done and presented in Figure 1. The range of particle size for raw xenotime mineral is 200 - 400 μm. As discussed, individual samples were prepared by dry grinding at 100, 200, 300 and 400 rpm for 30 minutes. Based on particle size analysis in Figure 1, grinding more than 400 rpm had no significance effect on the fineness of the prepared powder. 60% of samples have less than 29.5 μm upon milling at 300 rpm.

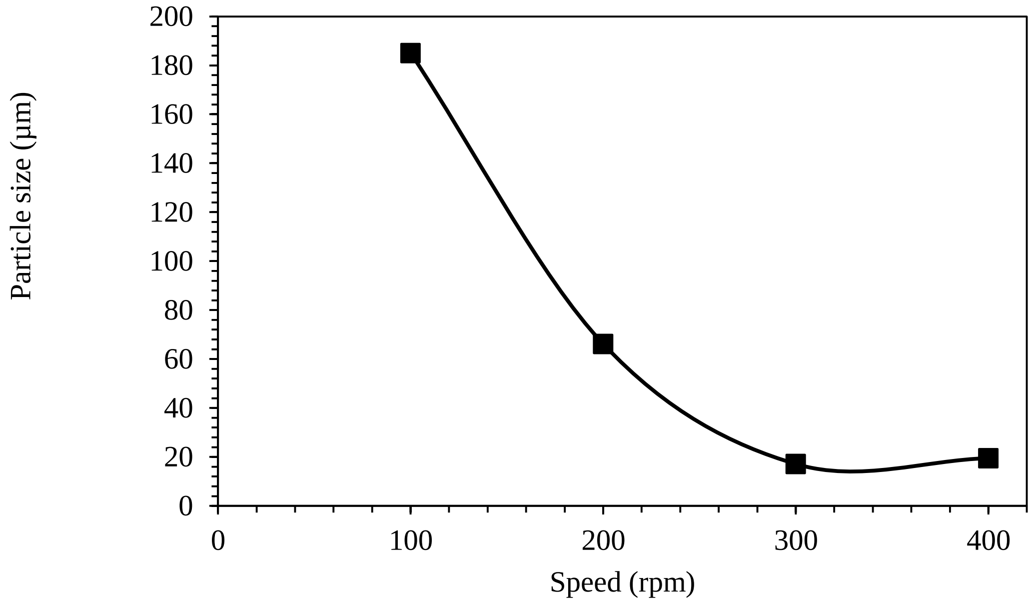

Figure 1. Median diameter of xenotime sample after milling at different speed.

Moreover, the raw and grind particle were analysed using FESEM and shown in Figure 2 Figure 2a shows a particle from raw xenotime mineral via FESEM and the average size is 220 µm. For all grind sample, small powder were tendency to adhere on bigger particle surface.

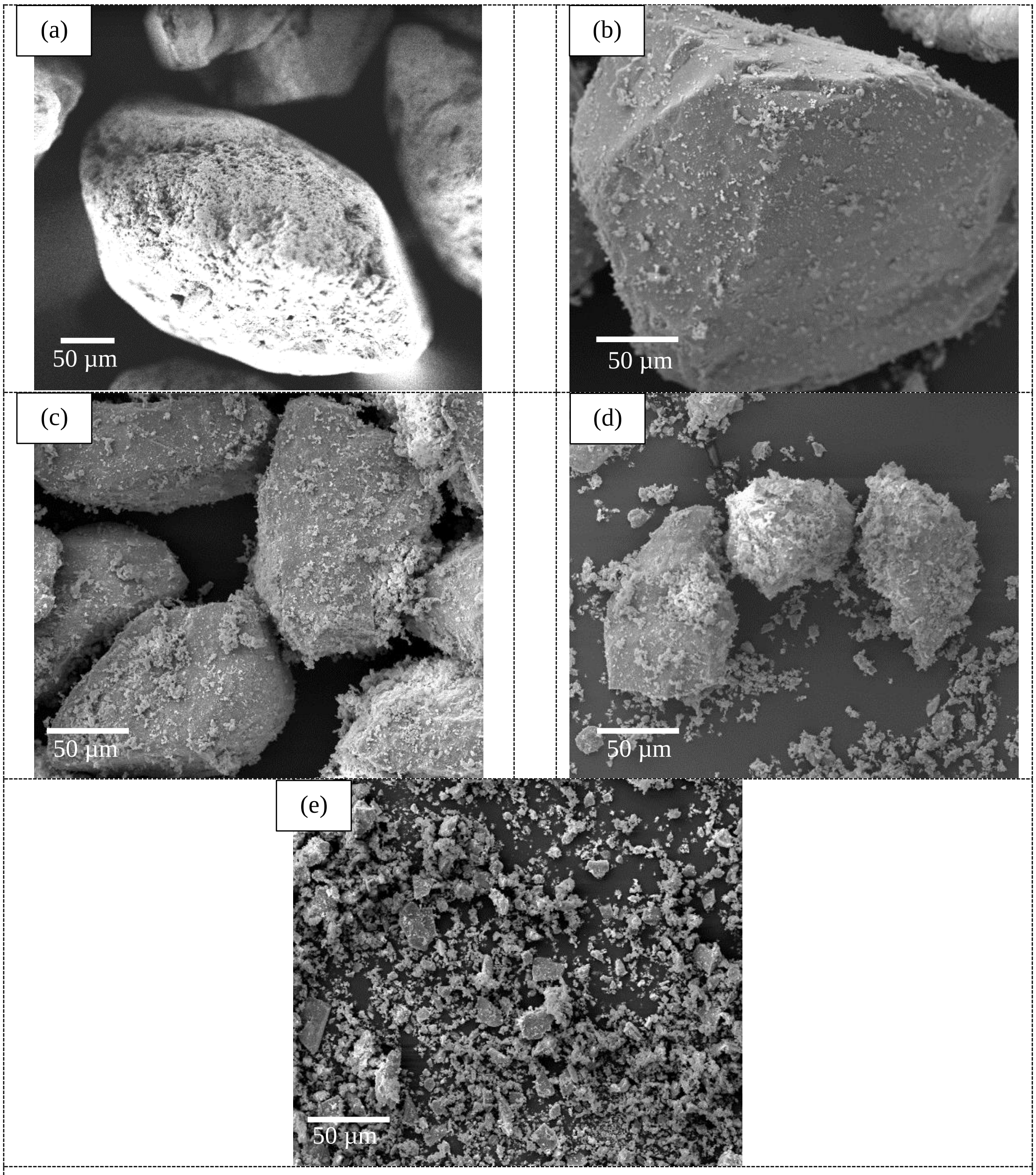

Figure 2. SEM micrographs of xenotime mineral with different range of particle size; (a) raw xenotime with average 220 µm, (b) more than 180 µm, (c) 90 -180 µm, (d) 45 – 90 µm and (e) less than 45 µm.

The results revealed that the smallest particle size recover 77.02%, 68.08%, 58.95%, 53.69% and 51.67% of thorium, yttrium (Y), ytterbium (Yb), erbium (Er) and dysprosium (Dy), respectively (Figure 3). As compare to unmilling sample, the average Th and REE recovery were just in the range of 31.45% to 45.34%. Figure 3 shows the data comparing the particle size to the Th recovery. The Th recovery from this reactions were 20-45 µm > 45-90 µm > 90-180 µm. The smaller the particles size, more Th content could be obtained. In a solid, only surface particles can interact with the other reactants. If the solid is divided into smaller pieces, then there is greater surface area; consequently, more particles are able to react, and the reaction rate increases. Relatively the raw mineral particle grains were isolated from different types of elements that have different behaviour. This can straining the reaction to occur. In the other hand, smaller particle size make the surface area larger. Therefore, higher Th recovery could be obtain with smaller particle size due to the exposure of larger surface area as a result of the finer grind used for alkaline fusion. By increasing of surface area of xenotime particle, Th and REE recovery enhanced through more reaction sites for digestiong to occur.

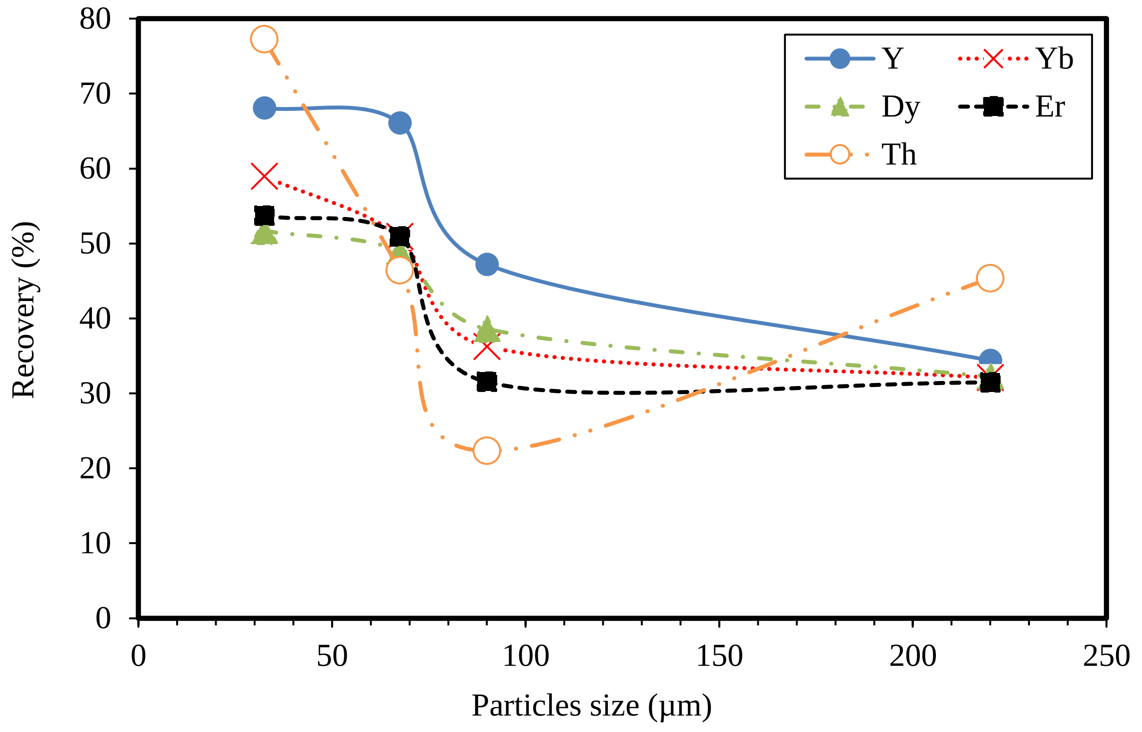

Figure 3. Th and rare earth recovery from alkaline fusion with different particles size of xenotime.

CONCLUSIONS

Cracking of raw xenotime mineral were successfully done using hydrothermal technique with various fusion duration. Through the experiment, the best parameter to recover most of thorium element from xenotime is smaller particle size (45 - 90 µm). In order to get smaller particle size (45 – 90 µm), the raw mineral of xenotime need to be milling with 7 mm milling ball size at 300 rpm for 30 minutes. Modification and optimization of the concentration process in xenotime cracking experiment should be undertaken to produce higher grade thorium. Further evaluation to select the extraction process of minerals concentrate into individual Th element should be undertaken based on their mineralogy, physical and chemical characteristics.

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