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EXTRACTION OF RARE EARTH METALS FROM MONAZITE MINERAL USING ACID METHOD

EKSTRAKSI LOGAM TANAH JARANG DARI MINERAL MONASIT DENGAN METODE ASAM

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ABSTRACT

There are two types of REE-bearing mineral in Indonesia, namely monazite and xenotime. Those minerals have not been further processed to obtain pure REEs or to obtain its oxides. The objective of this study is to study the performances of the REE extracted from monazite in acid method. The results show that the highest REE-extraction (28.41%) is achieved when the comparison between of sulfuric acid and water (v/v) is 1:2 with leaching temperature 220°C and leaching time 150 minutes. The process employed hydrogen peroxide as an oxidizer. Pregnant solution was then precipitated using sodium hydroxide and then was calcined at 900°C for 3 hours to produce RE-oxide. Characteristic of the RE-oxide contains such elements of Ce, Gd, Y, Nd, La, Dy and Sm within 29.10, 1.54, 1.53, 11.53, 14.02, 0.489 and 1.85%, respectively.

Keywords: monazite, REEs, RE-oxide, extraction, acid method

SARI

Di Indonesia terdapat dua jenis mineral yang mengandung unsur tanah jarang (UTJ) yaitu monasit dan senotim. Mineral–mineral tersebut belum diolah lebih lanjut untuk memperoleh logam tanah jarang murni atau dalam bentuk oksidanya. Penelitian ini bertujuan untuk melihat kondisi proses ekstraksi UTJ dari monasit dengan metode asam. Dari percobaan diketahui bahwa persen ekstraksi UTJ tertinggi (28,41%) dicapai pada perbandingan volume asam sulfat dengan air (v/v) 1:2 pada suhu dan waktu proses masing-masing 220°C dan 150 menit serta penambahan hidrogen peroksida sebagai oksidator. Larutan hasil ekstraksi diendapkan dengan natrium hidroksida, selanjutnya dikalsinasi pada suhu 900°C selama 3 jam yang akhirnya menghasilkan oksida tanah jarang. Karakteristik oksida tanah jarang yang dihasilkan mengandung: 29,10% Ce; 1,54% Gd; 1,53% Y; Nd 11,53%, La 14,02%, Dy 0,489%; dan Sm 1,85%.

Kata kunci: monasit, unsur tanah jarang (UTJ), oksida tanah jarang, ekstraksi, metode asam

INTRODUCTION

Rare earth elements or REEs are a group of seventeen chemical elements there together as commonly listed in the periodic table. Its existences are normally associated with other metals in small quantity. The REEs belong to Lanthanide Group that consists of 14 elements, namely Ce-Pr-Nd-Pm-Sm-Eu-Gd-Tb-Dy-Ho-Tr-Tm-Yb-Lu. Three other elements (Sc-Y-La) are found in the same REE-bearing minerals and shows similarity in chemical properties with lanthanides (Gupta, 2005). It can be classified into light REEs that affiliates to Cerium group (Ce, Pr, Nd, Pm, Sm, Eu) and the other is heavy REEs that include Gd, Tb, Dy, Ho, Tr, Tm, Yb, and Lu. The light one is available in great quantities compared to the heavy one. Actually, the existence of REEs within

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the earth crust is not really rare. Compared to lead and silver; the availability of cerium, lanthanum, neodymium and yttrium is more common (Castor and Hendrick, 2011). REEs are used in many applications especially for high technology materials such as permanent magnet, superconductor, optoelectronics, transistor, ceramics, ferro-magnetic, laser, etc. Based on such a fact, the REEs are named as 21st-century materials (Soepriyanto and Buchari, 2010). The potential monazite deposits in Indonesia are found in Bangka Belitung, Karimata/Ketapang, Rirang-Tanah Merah (Atmawinata, 2011).

Act No. 4 Year 2009 on Mineral and Coal Mining as well as Regulation No. 1 Year 2014 from the Ministry of Energy and Mineral Resources states that all minerals raw materials should be processed within the own country so does monazite must be processed as well. Currently, Indonesian monazite has not been yet further processed to be pure REEs or its oxide forms nevertheless study of extracting REE has been conducted by some researchers in Indonesia and many other countries. Thailand Institute of Nuclear Technology and Center for Nuclear Minerals Technology and National Nuclear Energy Agency of Indonesia had conducted REEs extraction from monazite using alkaline method to separate its radioactive elements and yielded some REE-oxides (Pichestapong, 2010). Shwe et al. (2008) had successfully acquired cerium oxide from solvent extraction using tributyl phosphate and got 96% of CeO_2. Another study to separate other REEs from its oxide was accomplished by Soe et al. (2008) through a three-stage precipitation and employed ammonium hydroxide.

Another method for separating the REEs is conducted by acid technique. Janubia et al. (2010) had succeeded in separating thorium and uranium from REEs available within monazite through solvent extraction using sulphuric acid. Center for Accelerator Science and Technology (CAST) in National Nuclear Energy Agency of Indonesia was also successful in splitting each REE through acid method. The REE-oxides came from CAST research comprise Ce-, La-, Nd- and Sm oxides (Bintari et al., 2003). Therefore, the objective of this present research is to study the performances of REEs extraction from monazite mineral using acidic technique and how does the effect of an oxidizer to the process.

METHODOLOGY

Pressure leaching in an autoclave using a solvent of sulfuric acid was conducted at leaching temperature of 200 - 220°C. The studied parameters comprised of such effect of solvent type, solvent concentration, dissolving time, amount of an oxidizer of hydrogen peroxide (H_2O_2). Thorium was precipitated from the leachate by addition of ice. Into the filtrate that was obtained from thorium precipitation, was then added sodium hydroxide to get the REE-OH. The next step, the REE-OH was calcined to derive REE-oxides which then analyzed by ICP to assume its REEs contents. Instruments used during the experiments were hot plate, beaker glass, magnetic stirrer, graduated cylinder, thermometer and volumetric flask. For safety reason, a mask and a pair of gloves were required. Figure 1 shows the flow chart regarding the present REEs extraction.

RESULTS AND DISCUSSION

Raw material (monazite sand containing minerals) used in this study derived from PT. Mutiara Prima Sejahtera (MPS) at Bangka island. The material was ground into less than of 325 mesh for both of processed tests sand material and XRF analysis. The XRF analysis was conducted at Center of Geological Survey. Figure 2 shows the monazite sand as the raw material while XRF analysis is shown in Table 1.

Primarily, monazite sand of sized less than of 325 mesh was leached by sulphuric acid. The values of experimental parameters were employed in variation as well as in a fixed value. The varied parameters include solvent type of H_2SiF_6, HCl, H_2SO_4, and HNO_3, comparison between solvent and water in v/v of 1:1, 1:2; 2:1, 1:3 and 3:1, leaching time of 15, 30, 45, 60, 90, 120 and 150 minutes, an oxidizer addition of H_2O_2 (5%) and leaching temperature of 220°C. Such a figure referred to previous experiments by CAST in National Nuclear Energy Agency of Indonesia that provided the highest % extraction (Helaly, et al., 2012). Experiment results are presented in Figure 3.

It is clear that sulphuric acid provides the highest derived REEs (Figure 3). Sulphuric acid addition will develop stable REE-sulphate. On the contrary, the addition of nitrate, chloride, fluorosilicate will

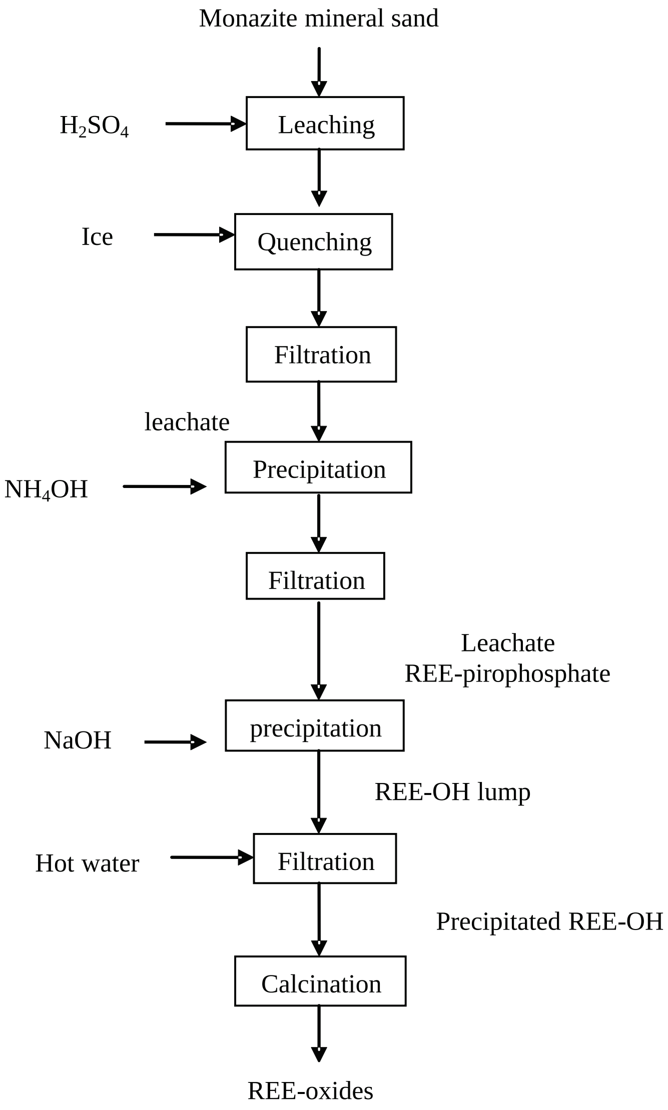

Figure 1. A flow chart for REE extraction using acid method

Figure 2. Monazite sand from Bangka used for study purposes

Table 1. XRF analysis of PT. MPS monazite sand

Element name	Element Content (%)	Oxide content (%)
La	11.34	19.10
Ce	18.27	30.67
Nd	8.64	14.33
Pr	0.54	0.91
Th	6.47	10.00
Others (Si, Zr, Sn, Y, Gd, Dy, U)	-	24.99

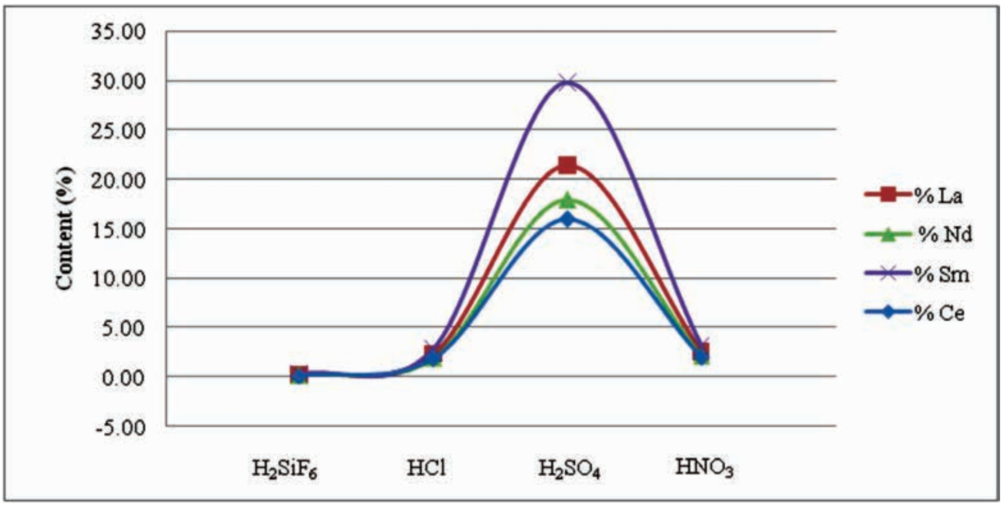

Figure 3. Effect of acid and its concentration on the derived REEs

form unstable REE-nitrate, REE-chloride and REE-fluorosilicate. Such reactions dealing with REE-sulphate are:

$2(REE)(PO_4) + 3H_2SO_4 \rightarrow (REE)_2(SO_4)_3 + 2H_3PO_4$
$ThSiO_4 + 2H_2SO_4 \rightarrow Th(SO_4)_2 + SiO_2 + H_2O$
$Th_3(PO_4)_4 + 6\ H_2SO_4 \rightarrow 3Th(SO_4)_2 + 4H_3PO_4$
$SiO_2.xH_2O + H_2SO_4 \rightarrow SiO_2 + H_2SO_4.xH_2O$

As the suitable solvent was obtained, next experiments were took place by varying comparison between solvent of the sulphuric acid and water in v/v. The optimum condition by varying the v/v of the solvent and water is achieved by comparison of 1:2 (Figure 4). The comparison of 1:2 denotes the total REE around 28.41% whilst the higher comparison of H_2SO_4 and water (2:1) reveals drastically decreasing the content of REEs to 20.41%. High viscosity of the solvent may supposed to be the reason that was caused the acid does not completely react. Referring to the optimum conditions, next experiments were accomplished using hydrogen peroxide as an oxidizer. As a strong oxidizer, the reagent of H_2O_2 is very reactive and does to oxidize various organic as well as metal compounds. H_2O_2 can exothermally and spontaneously be decomposed into water and oxygen. The elements, notably Ce ion, retained two valences namely 3^+ and 4^+. The 3^+ ion is easy to dissolve and reacts with chlorides and metal. Therefore, to optimize REE solubility, the 4^+ ion is converted to the 3^+ one (reduction

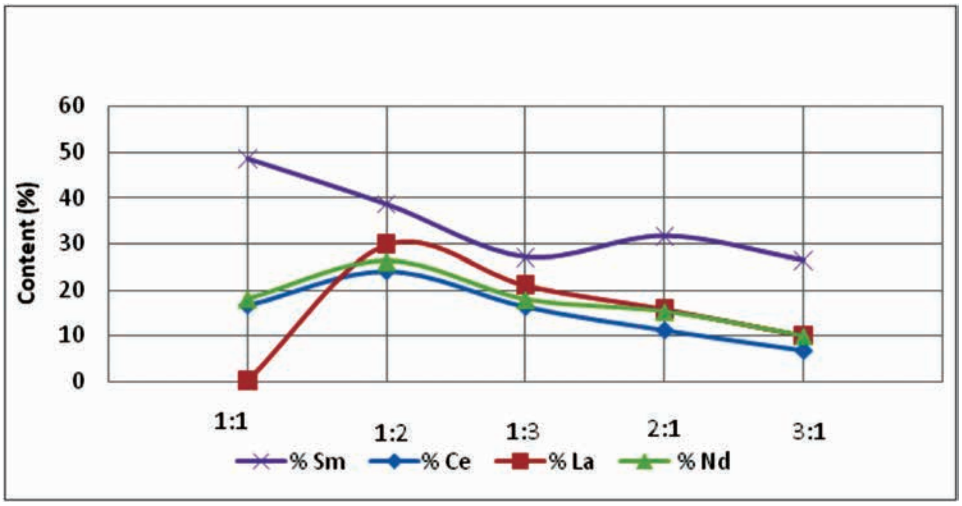

Figure 4. Effect of comparison between sulphuric acid and water in v/v on REE contents

process) as the H_2O_2 retains red-ox character (Tan and Vinh, 2011). The fact that the reagent is in liquid nature it means that the peroxide is easy to react as well as simple to handle compared to solid reductor. In addition, H_2O_2 will form H+ ion and O_2 during the process that keeps the product relatively clean. Other reductor and oxidizer that can be used within process are MnO_2 and NaOCl performing reaction of (Tan and Vinh, 2011):

$$2Ce^{4+}{}_{(aq)} + H_2O_{2(aq)} \rightarrow 2Ce^{3+}{}_{(aq)} + 2H^+{}_{(aq)} + O_{2(g)}$$

Figure 5 presents the experimental results using H_2O_2 as an oxidizer into the chloride-, sulphuric- and nitrate leaching type. For sulphuric leaching, it seems that oxidizer addition does not significantly affect to the percentage of Ce extraction due to the all reacted REEs with sulphuric acid are still mixed, it is not individually separated. Each REE maintain double valences of II and III while the Ce keeps double valences of III and IV. The oxidizer addition seems effective if it was conducted at REE separation stage, mainly for Ce separation. The addition of oxidizer into REE-nitrate will change Ce(III) to Ce(IV). The solubility of Ce-OH is relatively different with other REE-OH that has similar valence such as LaOH, NdOH etc. As a result, Ce precipitates faster than other REEs.

After the optimum conditions for solvent type and concentration as well as an oxidizer volume have been derived, the next step was seeking optimum condition for leaching time. Varying leaching time of 15, 30, 45, 60, 90, 120 and 150 minutes obtained the REEs as shown in Figure 6. Habashi (1997) stated that leaching time is a factor affecting the perfection of the process. The longer is the time, the better is the molecular interaction. The highest REE of 28,41% was achieved at leaching time of 150 minutes. Referring to a series of the present experiments, the optimum condition for extracting the REEs is obtained due to sulphuric acid as the best solvent, with comparison between solvent and water in v/v of 1:2, leaching time of 150 minutes and H_2O_2 as an oxidizer.

Quenching was the next step after leaching. Such a stage was conducted to precipitate thorium from the REE-sulphate. This radioactive element is always available in monazite mineral and dissolves during sulphuric acid leaching that performs such reaction as follows:

$$2REE_2(SO_4)_3 + 6H_3PO_4 \rightarrow REE_4(P_2O_7)_3 + 6H_2SO_4 + 3\,H_2O$$

$$Th(SO_4)_2 + 2H_3PO_4 \rightarrow Th(P_2O_7) + 2H_2SO_4 + H_2O$$

Based on the above reactions, thorium pyrophosphate will precipitate while the REE- pyrophosphate will dissolve in the solution. However, the REE-solution is considerably radioactive free (where Th content is less than 0.076%). The next step was precipitating the REEs by NH_4OH to get REEs concentrates as follow:

$$2REE_2(SO_4)_3 + 6H_3PO_4 \rightarrow REE_4(P_2O_7)_3 + 6H_2SO_4 + 3\,H_2O$$

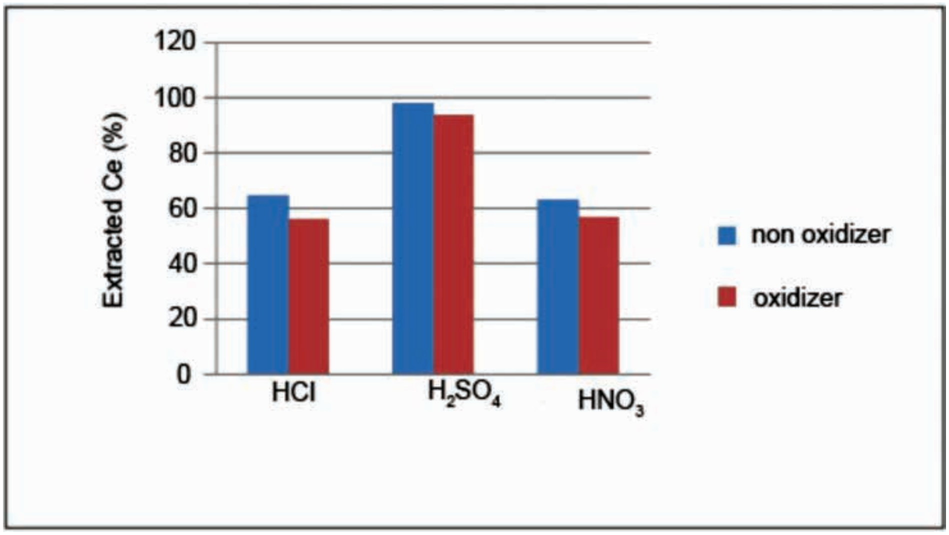

Figure 5. Effect of oxidizer on % Ce extraction

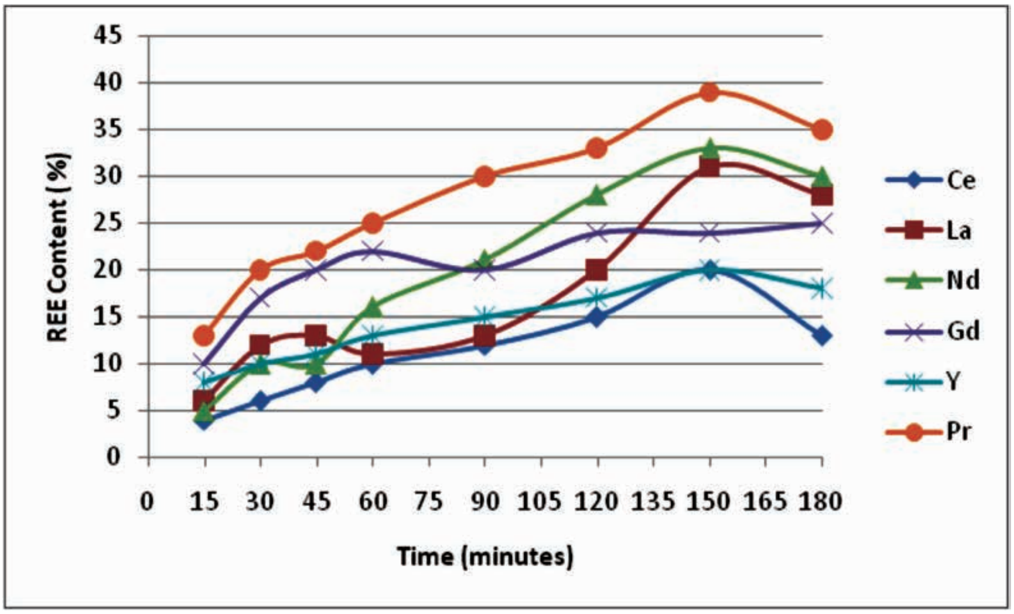

Figure 6. Effect of leaching time on REE concentration

$$REE_2(SO_4)_3 + 6NH_4OH \rightarrow 2REE(OH)_3 + 3(NH_4)_2SO_4$$

The precipitates were still as REE- pyrophosphate and REE-OH as shown in Figure 7.

From the images of Figure 2 and Figure 7, the form of REE-pyrophosphate and REE-OH look similar appearance, but in fact Figure 2 has shaped like sand, while Figure 7 has shaped like powder, moreover, the yellow color of Figure 2 looks brighter than the yellow color of Figure 7.

Figure 7. The form of REE- pyrophosphate and REE-OH (free from thorium)

Reacting both precipitates with NaOH will make up REE-OH concentrate and the concentrate was then calcined at 900°C for 3 hours to produce REE-oxide. The result is presented in Table 2 and 3.

The calcination process of REE-OH into REE-oxide apparently increases the grade of total REE from 26.55% up to 62.97%. This can be attributed during the calcination process, there were the

Table 2. The available REE within REE-OH

No.	Element	Symbol	Grade(%)
1.	Cerium	Ce	12.22
2.	Gadolinium	Gd	0.57
3.	Yttrium	Y	0.559
4.	Neodymium	Nd	4.93
5.	Terbium	Tb	0.0558
6.	Lanthanum	La	6.04
7.	Dysprosium	Dy	0.201
8.	Europium	Eu	0.0327
9.	Samarium	Sm	0.771
10.	Praseodymium	Pr	1.17
11.	Thorium	Th	0.0762
12.	Uranium	U	0.04
Total REE			26.55
Total impurities			73.45

Table 3. The available REE within REE-oxide

No.	Element	Symbol	Grade (%)
1.	Cerium	Ce	29.10
2.	Gadolinium	Gd	1.54
3.	Yttrium	Y	1.53
4.	Neodymium	Nd	11.53
5.	Terbium	Tb	0.124
6.	Lanthanum	La	14.02
7.	Dysprosium	Dy	0.489
8.	Europium	Eu	0.095
9.	Samarium	Sm	1.85
10.	Praseodymium	Pr	2.69
11.	Thorium	Th	0.165
12.	Uranium	U	29.10
Total REE			62.97
Total impurities			37.03

evaporation of the amount of impurities and water content reducing in the sample. The impurities contain large amount of P, Fe, Zr, Ti, Si and LOI.

CONCLUSIONS

Sulphuric acid can dissolve the REEs from monazite sand to make up stable di-sulphate solution. The performance of REEs extraction conditions to achieve the highest REEs extraction of 28.41% was found with sulphuric acid as the solvent in comparison with water of 1:2 (v/v); leaching temperature of 220°C; leaching time of 150 minutes; hydrogen peroxide as an oxidizer of 5%. The achieved REE-oxides by such method was 62.48%. In order to obtain grade of REE-oxide more than 90%, the next experimental work is suggested to be done in an autoclave pressure leaching using sulfuric acid.

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