Effect of Mechanochemical and Roasting Techniques for Extraction of Rare Earth Elements from Indonesian Low-Grade Bauxite

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Abstract. In this research, the extraction of lanthanides from low-grade bauxite via mechanochemical and roasting methods has been studied. The addition of NaOH during mechanochemical process significantly increased the yield of collected rare earth elements. The effect of roasting process at temperatures in the ranges from 400°C to 1100°C was analyzed. The highest recovery values of lanthanide that extracted from low-grade bauxite at various temperatures and ratio low-grade bauxite and NaOH solid, with variations in the ratio of 1: 1 and 2: 1 were obtained for yttrium (~95.6%), lanthanum (~79.6%), cerium (~54.7%), neodymium (~81.8%), and samarium (~80.0%) from the theoretical value.

1. Introduction

Bauxite is important raw material for Indonesia economic development. However, seeing how much bauxite tailing produced, bauxite processing may give problem to surrounding environment such as plant grows abnormally, broken land structure, and may emit dangerous pollutants that endanger human life [1]. Therefore, there is a need to utilize residue bauxite for other applications rather than damaging the environment.

Utilization of low-grade bauxite can be categorized in three different field applications, namely (a) construction and chemical applications consist of civil and building construction, catalyst and adsorbent, ceramic, plastic, coating, and pigment; (b) environment and agronomic applications that consist of waste water and effluent treatment, waste gas treatment and agronomic applications; (c) metallurgical applications that consist of recovery of major metals, steel making and slag additive and recovery of minor metals (rare earth elements, REEs) [2]. Price of rare earth elements and rare earth elements oxide increased significantly, such as price of dysprosium was $300/kg in 2010 and increase in 2011 with $3600/kg [3], and lead many industries to investigate how to recover REEs in more effective way. Therefore, Indonesia, with a lot of natural resources, has to utilize this opportunity to increase economic value.

To increase REEs content that contains in low-grade bauxite, major elements such as aluminum, silica, and the other have to be downgraded. In this case, major elements considered as impurities in low grade bauxite. Removing impurities can be conducted by mechanochemical treatment through subjecting mechanic force and chemical activation which caused not only physically but also chemically changes on the low-grade bauxite. In other research had been conducted experiment that
mechanochemical treatment on bauxite with soda ash (CaO and Ca(OH)₂) addition along with leaching process and then compared by bauxite without those treatments. This study aims to look at changes in the structure of bauxite and determine the recovery value of alumina. The results show that the particle size of bauxite decreased very rapidly in the first three minutes and the next minute not decrease significantly. In contrast to the particle size, the degree of amorphous increased as the length of time milling increase. In addition, comparison of bauxite with mechanochemical treatment, only mechanical force, and without treatment mechanochemical obtaining results that bauxite without mechanochemical treatment resulted in recovery of alumina values of the lowest 84.3%. For bauxite that given only mechanical force (milling) without giving reagent produced a slightly higher recovery compared to bauxite without mechanochemical treatment which was 86.65%. As for the treatment of bauxite performed mechanochemical obtain the value recovery of alumina which was 87.41% [4].

In another study also examined the effect of mechanochemical treatment of the bauxite which has a high silica content with the addition of limestone (CaO) with various concentrations. The results of these studies indicate that with the addition of limestone (CaO) can reduce levels of silica (quartz) from bauxite. The more the addition of CaO on mechanochemical process of bauxite, the more silica content decreased. In addition, when compared with the decrease of silica with and without the addition of CaO milling, result silica that decrease was greater if given the commission of milling [5]. In another research, there was also a study of mechanochemical on low grade bauxite as a result of Bayer process with adding NaOH and CaO as reagents. Based on the research, on the same ratio of reagent and red mud with constant milling time, was obtained that recovery of alumina got higher or more effective with NaOH rather than CaO as the reagent. When CaO added as reagent, value point of alumina recovery was 9%, while NaOH added as a reagent, value point of alumina recovery was 18% [6].

The decomposition of monazite and leaching of REEs using mechanochemical method has also reported by Kim and partners [7]. This process involves the mechanical milling of a mixture of monazite and NaOH [7].

To obtain high content of rare earth elements, it is necessary to conduct decomposition method because REEs don’t exist as a single element. The decomposition method using roasting with alkali addition is a good method to decompose REEs. For instance, decomposition of monazite with roasting treatment with alkali addition at different temperatures. The roasting process was compared with and without alkali addition. Ratio of ore and alkali was 1:1. After roasting process, washing and filtration were conducted. It was obtained that decomposition of rare earth element with alkali addition was more effective than the one without alkali addition. The higher temperature process, the higher decomposition of rare earth element obtained with optimum temperature 400°C [8].

In another study, chemical beneficiation could reduce alumina and soda content from low-grade bauxite that contained Fe₂O₃-Al₂O₃-Na₂CO₃.C. Chemical beneficiation step was roasting process of low-grade bauxite, soda, and carbon mixture that aims to reduce alumina content on Low-grade bauxite. It was obtained that roasting temperature <750°C had lower recovery of alumina (<50%). While roasting temperature >925°C obtained 70% of alumina recovery [9].

2. Experimental
2.1. Materials
Low-grade bauxite with alumina content is less than 44% was used. This sample was collected from Bintan Island, Indonesia. The sample was classified by its particle size distribution with sieving process with 25, 45, 100, 200 and 325 mesh.
2.2. Preparation
The next stage was the process of mechanochemical decomposition. In this process, low-grade bauxite and solid NaOH, with variations in the ratio of 1: 1 and 2: 1, mixed in a ball mill chamber. Ball mill used for this process was a variation of two balls tool steel 30 mm in diameter each weighing 111 g and 6 balls tool steel with a diameter of 20 mm weighing 32.5 g. Rotational speed applied in this process by 660 rpm or 11 Hz, and the milling time was 120 minutes. Then, the milling results sieved to determine the grain size of the low-grade bauxite which had milled with NaOH. Then, the results were roasted using a Carbolite Furnace with temperature variation 400°C, 500°C, 1000°C and 1100°C. The total sample was 12, which was comprised of three samples at each temperature variations. One sample was the result of milling with a ratio of low-grade bauxite and NaOH 1: 1, one sample was the result of milling with a ratio of low-grade bauxite and NaOH 2: 1, and a sample is a sample that does not do the milling process but only do the roasting process without performing the process of mechanochemical.

After those stages, samples of roasting were washed with hot water at 70°C with agitation for 30 minutes. Then the ore that had finished washing was filtered and dried in an oven with a temperature of 120°C for 2 hours until the water contained evaporates.

In this study, characterizing the process was conducted before and after the samples were undergo the process. The process of characterizing the samples to determine the effect of temperature differences in the addition of NaOH and roasting on mechanochemical decomposition process of the phase transformation occurring on low-grade bauxite. To determine the effect of variables on the process used some tools such as XRD (X-Ray Diffraction), XRF (X-Ray Fluorescence) and SEM (Scanning Electron Microscope).

3. Results and Discussion
3.1 Particle Distribution Before and After Sieving
In this study, low-grade bauxite was collected from Bintan Island, Indonesia which was by product of crushing and washing process from alumina mining. Distribution of sieving results before and after treatment was shown in Figure 1. Distribution particle size of low-grade bauxite was ranging from 0.044 to 0.707 mm. In Figure 1 above showed that the size distribution of the particle diameter of 0.074 mm or 200# had the most dominant distribution percentage that equal to 39%. As for the other particle diameter 0.044 mm, 0.149 mm, 0.354 mm, and 0.707 mm were 4.9%, 10.7%, and 15.4% respectively.

The results of the sieving process conducted a quartering process where homogenization process of distribution of particles occurred and then tested initial characterization using X-ray fluorescence (XRF) to determine content of the elements contained in the low-grade bauxite, X-ray Diffraction (XRD) to determine the compounds contained and Scanning Electron Microscope/Energy Dispersive Spectrometer (SEM/EDS) to determine the morphology of the low-grade bauxite.

After the initial characterization, the samples were subjected mechanochemical treatment in a planetary ball mill for two hours and then conducted a sieving process. Percentage of distribution particle size of low grade bauxite after mechanochemical process was shown in Figure 1.
Figure 1 Particle Distribution before (left) and after sieving process (right), where $A =$ particle distribution and $B =$ distribution cumulative

In Figure 1, it showed that after being given the commission of mechanochemical, the particle size became smaller when compared to before by the commission of mechanochemical. When compared before and after given mechanochemical treatment, the percentage of 0.044 mm particle size distribution increased from 5% to 28% indicating that a reduction in size of the particle diameter of the low-grade bauxite. This was caused by the collision between the steel ball with ore due to the force of compression, shear, impact caused by the rotation of the planetary ball mill [10,11].

3.2. Morphology of low-grade bauxite before and after Mechanochemical and Roasting Treatment

From electron microscopy analysis, the low-grade bauxite showed variation of the particle diameter in the range of 0.074 to 0.354 mm. Overall Low grade bauxite samples were fine enough due to 0.074 mm particle size distribution was large enough for about 39%. However, there were still many coarse particles that present in low-grade bauxite.

Figure 2 was the result of the SEM characterization after mechanochemical process that indicating that the process of mechanochemical can refine and reduce the size of the grains. It can be seen in Figure 2 results low-grade bauxite particle after milling with a magnification of 100X shown that with the addition of NaOH mechanochemical bauxite became finer and smaller in size and had irregular shape. This was caused by collisions between particles of low-grade bauxite with steel balls in a planetary ball mill chamber that collided with one another, generating more impact and compression force capable of destroying the grain into smaller sizes and irregular shape. However, while looking in Figure 2, the sample residues shown the fine particles and clumping (agglomeration). The particles in the low-grade bauxite samples that have undergone a process of mechanochemical size will be smaller and then agglomerated thus reintegrated into more solid particles, then the particles low-grade bauxite will be very fine [12].
3.3. Elemental composition

Low-grade bauxite was characterized using X-ray Diffraction (XRD) which aims to determine the contained of compounds and transformation prior treatment and after the roasting process at a temperature of 400°C, 500°C, 1000°C, 1100°C. The XRD test result prior treatment was shown in Figure 3. It was shown that the most dominant compound contained in the low-grade bauxite was corundum (Al₂O₃) as much as 49%, 7% quartz (SiO₂) and 44% calcite (CaCO₃). Other minerals contained was very little quantity which was not detected by XRD. Fe₂O₃ which is usually contained in the low-grade bauxite, but in the XRD results, it did not appear. In addition to the initial characterization using XRD, in this study also use X-ray fluorescence to determine the chemical composition in quantitative or thoroughly into the low-grade bauxite sample which shown in Table 1. In addition to the initial characterization, XRF is also used to determine the chemical composition of the residues bauxite after mechanochemical treatment and the roasting process.

![Figure 2 Morphology of low-grade bauxite (a) before and (b) after mechanochemical process with 100X Magnification](image)

![Figure 3 X-ray Diffraction pattern of low-grade bauxite before treatment](image)

In the results of initial characterization XRF in Table 1 show that the dominant element contained in the low-grade bauxite was aluminum (Al) as much as 32.92%, 27.568% silicon (Si) and 36.383% iron (Fe) which indicated that the compositions usually contained in low-grade bauxite, a by-product...
processing of bauxite crushing and washing from waste Wacopek, Bintan. In this case, impurities such as aluminum, silica and other dominant element needed to be removed to increase the content of rare earth metals. As for the rare-earth metals contained in the low-grade bauxite, such as yttrium (Y) and cerium (Ce) in very low concentrations. Yttrium levels is 0.008% and for the concentration of cerium is 0.119%.

| Element | Content (%) | Element | Content (%) |
|---------|-------------|---------|-------------|
| Na      | 0.055       | Ti      | 1.188       |
| Al      | 32.92       | Fe      | 36.383      |
| Si      | 27.568      | Zr      | 0.086       |
| S       | 0.392       | Nb      | 0.007       |
| Cl      | 0.377       | Y       | 0.008       |
| K       | 0.379       | Ce      | 0.119       |
| Ca      | 0.518       |         |             |

3.4. Effect of Roasting Temperature on Total Content and Total Recovery of REEs

After the roasting process, washing and X-ray Fluorescence (XRF) characterization were conducted to determine the chemical composition of the low-grade bauxite quantitatively. Figure 4 shows graph of grade and recovery of roasting results. Figure 4 shows the effect of roasting temperature of total content and recovery of REEs for each temperature. It is shown that to increase the levels of rare earth metals optimal occurred at 1100°C by the addition of NaOH 33% and a grade for the lowest place at a temperature of 500°C with the addition of NaOH 0% or the sample residue bauxite without mechanochemical process. Overall, at a temperature of 1100°C with the addition of NaOH 33.3% or the ratio of low-grade bauxite and NaOH 2 : 1 had the most optimum grade value.

At 400°C, the addition of NaOH 50% (ratio of low-grade bauxite and NaOH 1 : 1) gave higher value grade than at the temperature of 1100°C without addition of NaOH. Variation of temperature resulted highest grade at 1100°C. This is true also for the case of NaOH 0%, NaOH 33.3% and NaOH 50% addition. These results shown that in those temperature rare earth elements started to appear. While in the same NaOH addition with temperature of 500°C resulted in lowest grade value for NaOH 0% and NaOH 50% addition. This implied that roasting in higher temperature gave better effect on the recovery of rare earth elements.

As for the addition of NaOH same with different temperature values obtained the highest grade in either the addition of NaOH 1100°C temperature of 0%, 33.3% and NaOH 50% addition. This shows that at 1100°C, the rare-earth metal elements began to appear. As for the addition of NaOH same with different temperatures lowest grade values obtained at a temperature of 500°C for the addition of NaOH 0% and 50% NaOH. This shows that roasting at a low temperature did not effectively enrich the rare earth metals content.

Figure 4 shown that the highest recovery value was obtained at a temperature of 500°C and 1100°C and with the addition of NaOH 33.33% while the lowest recovery values obtained at 500°C with the addition of NaOH 0%. In general, the greatest recovery value obtained on the addition of NaOH 33.33% for each temperature. In addition to the recovery value through mechanochemical process has a higher recovery value than the value of recovery is not through mechanochemical process. This was because the process of mechanochemical of alumina contained dissolved [13] and also reduce levels of CaO [6] so that the levels of rare earth metals contained can be increased. In this highest total recovery, from XRF we were obtained for yttrium (~95.6%), lanthanum (~79.6%), cerium (~54.7%), neodymium (~81.8%), and samarium (~80.0%) from the theoretical value.
4. Conclusion
Mechanochemical process of low-grade bauxite with NaOH using a planetary ball mill could reduce and refine the grain size. On the low-grade bauxite by addition of NaOH 33% produced the highest overall grade value of rare earth metal element is obtained. In the roasting process at various temperatures, the recovery value residual got vary results. For the element yttrium (Y) has highest recovery value with the addition of NaOH 33.3% at a temperature of 400°C with the recovery value of 95.6%, for the element cerium (Ce) by addition of NaOH 33.3% at temperatures of roasting 1100°C had the recovery value of 54.7%, for the elements lanthanum (La) to NaOH 50% addition roasting temperature 1000°C had recovered value of 79.6%, for the element neodymium (Nd) with the addition of 50% NaOH at a temperature roasting 1100°C had recovery value of 81.8% and the element samarium (Sm) with the addition of NaOH 33.33% at the roasting temperature 1000°C had 80% recovery value.

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