Extraction of rare earth elements from low-grade Bauxite via precipitation reaction

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Abstract. The aim of this research was to determine the optimum hydrometallurgical parameters to extract the rare earth elements (REE) from low-grade bauxite through acid leaching and precipitation reaction. REE or lanthanide recovery by a precipitation method with sodium sulphate and sodium phosphate as precipitation agents is reported where the effect of pH and recovery of REE are described. The metal composition of REE in low-grade bauxite after treatment were analyzed by ICP-OES. The total recovery values of REE elements at the first precipitation reaction using sodium sulphate as the precipitation agent at pH 3.5 showed ~68.2% of lanthanum, ~18.9% cerium, and ~7.8% yttrium. Lanthanum was the rare-earth element present at the highest concentration in the low-grade bauxite after the series treatments. An optimum pH of 3.5 for precipitation of rare-earth elements using sodium sulphate was demonstrated where this method is recommended for the extraction of REE elements from low-grade bauxite.

1. Introduction
Indonesia is rich mineral resources such as coal, copper, nickel, gold, tin, silver, bauxite and petroleum [1]. In 2017, an estimated total export volume of 6636 tonnes of bauxite occurs from Indonesia. High demand of bauxite by the market has consequently produced a substantial amount of waste without any further use. Low-grade bauxite with alumina content is less than 50% from washing bauxite ore from abundant bauxite sources in Bintan Island, Indonesia. Low-grade bauxite is under-utilized and may pose a potential problem since bauxite mining occurs on open land that leaves unproductive and potential land hazards due to non-reclamation of tailings and disposal.

Demand for lanthanides has been increasing due to the unique luminescent properties and long-lived emission of these elements [2]. They have a very high economic value since they possess very good physical and chemical properties suitable for applications in advanced materials [3]. Therefore, some countries without lanthanides resources must develop the new material resources such as low-grade lanthanide sources. Previous research indicates that low-grade bauxite contains lanthanides, namely lanthanum oxide (La₂O₃) at 0.0052 wt% and yttrium oxide (Y₂O₃) at 0.0041 wt% [4]. Separation of lanthanides from low-grade bauxite is beneficial for both the environment and economy because of waste reduction from mining. Separation of lanthanides using solid-liquid extraction methods by acid, precipitation, crystallization, or ion exchange have been reported [5,6]. The alkaline cracking and acid baking methods for rare earth elements concentrate have been reported by Sadri and

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partners [6]. A study on the acid leaching of low-grade bauxite after mechanical-roasting treatment was reported to be useful for separation and further purification. A previous study found that substantial reserves of lanthanides exist in low-grade bauxite [4,7], where low-grade bauxite contains La ions with a concentration up to 0.0052% (w/w) [4].

Recently, extraction of lanthanides from Indonesian low-grade bauxite using acid leaching with oxalic acid has been reported [8]. Indonesian low-grade bauxite was pre-treated with mechanical-roasting processes, then followed by oxalic acid leaching at 40°C and concentration of 1 M for 2 hours. This approach has served as an argument for the need to develop a more effective and economical method to separate lanthanides from low-grade bauxite. Therefore, this study evaluates the extraction of lanthanide using a precipitation method with sodium sulphate and sodium phosphate. Precipitation occurs because the substance in compound has a sufficiently low solubility product (Ksp) to allow for phase separation from solution in the saturation-state. The lanthanide deposited was carried out by two stages of precipitation reaction by controlling pH and temperature, where the concentration of the lanthanide metal species exceeds the equilibrium condition according to the solubility product. The filtrate from a one-stage precipitation process still contains lanthanides so a second stage of precipitation is required [9]. The purpose of this work is to determine the optimum pH for lanthanides recovery using oxalic acid leaching [8], along with precipitation using sodium sulphate and sodium phosphate as precipitation agents.

2. Experimental

2.1. Materials
Low-grade bauxite was collected from Madong area, Bintan Island, Indonesia. Oxalic acid dihydrate (C₂H₂O₄·2H₂O) was purchased from Merck (Darmstadt, Germany). Other chemicals and materials were used without purification, namely 25% ammonia, 96% sulfuric acid, aquadest, 99% sodium hydroxide, tri-sodium phosphate dodecahydrate, and sodium phosphate.

2.2. Characterization
The metal composition of REE, Al and Fe were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) Agilent technology 7000. Samples were dissolved in aqua regia (HCl: HNO₃ = 3:1) solution.

2.3. Preparation of concentrated solution
Precursors for the precipitation were prepared according to the optimum condition as described by Kusrini et al. [8]. In this study, we used the most effective leaching condition at 40°C and a concentration of oxalic acid solution at 1 M. Low-grade bauxite was mechanically milled until it reached a particle size of 200 mesh. The material was roasted at 500°C in order to decompose the remaining organic fraction. Low-grade bauxite was dissolved in aquadest with ratio of solid: liquid at 1:4. The ratio of low-grade bauxite and oxalic acid solution of 1:15 was added into a 500 mL beaker where the mixture was stirred for 2 h on a hot plate at 40°C with 1 M oxalic acid solution.

2.4. Precipitation method
The pH of the leaching solution varies and results in challenges for the control of the acid levels after the roasting-leaching processes. The sample was washed with aquadest and then vacuum pumped until neutralization (pH 7). The lanthanide salt mixture was prepared using NaOH and the added sodium sulphate and sodium phosphate but it was unable to undergo complete precipitate formation. The pH of concentrate solution was adjusted using sodium hydroxide (NaOH) and ammonia solution (25 v/v %).

At pH 1.5, the concentrate was added sodium sulphate to avoid ferric hydroxide precipitation but no precipitate formed. The precipitation reaction continued and the pH was adjusted to pH 3.5 and 9 using NaOH. Both the yield of the lanthanide precipitate with sodium sulphate and/or sodium
phosphate was below 1 g. The metal REE element content in a low-grade bauxite was determined by ICP-OES.

In this study, Indonesian low-grade bauxite (200 mesh) after a magnetic separation process was used as raw material (1.5 kg). Based on the ICP-OES analyses, low-grade bauxite is composed of various lanthanide oxide, silicate, alumina and iron oxide. REE existing in low-grade bauxite is La of 0.00157% (0.02355 g), Ce of 0.00176% (0.02646 g) and Y of 0.00018% (0.00277 g). The metal REE element composition from the precipitation reaction using each sodium sulphate and sodium phosphate at each pH condition (pH 3.5 and 9) is shown in Table 1.

In Table 1, the recovery of mixed lanthanides (REE) from Indonesian low-grade bauxite after the precipitation reaction was calculated using equation 1 as follows:

\[
\% \text{ Recovery of REE} = \frac{m \text{ concentrate (REE)}}{m \text{ REE}} \times 100\%
\]

with \( m \) is mass (g) and REE is the metal rare earth elements.

**Table 1.** Elemental composition of REE after precipitation reactions using sodium sulphate and sodium phosphate at each pH 3.5 and 9.

| Sodium sulphate | pH 3.5 | pH 9 |
|-----------------|--------|------|
|                 | La     | Ce   | Y    | La   | Ce   | Y    |
| 1.55108%        | 0.48129% | 0.02098% | 0.00858% | 0.0315% | 0.00039% |
| (0.01606 g)     | (0.00498 g) | (0.00021 g) | (0.00405 g) | (0.00148 g) | (0.00018 g) |
| Recovery of REE (%) | 68.23 | 18.88 | 7.84 | 17.23 | 5.64 | 6.6 |

| Sodium phosphate | pH 3.5 | pH 9 |
|------------------|--------|------|
|                  | La     | Ce   | Y    | La   | Ce   | Y    |
| 0.9034 g         | 0.17297 | 0.01841% | 0.00440 | 0.00694% | 0.00017% |
| (0.00125 g)     | (0.00016 g) | (0.000164 g) | (0.00364 g) | (0.000089 g) |
| Recovery of REE (%) | 5.3 | 5.91 | 6   | 9.81 | 13.78 | 3.2 |

3. Results and Discussion

As shown in Table 1, the weight content (%) of Fe element in Indonesian low-grade bauxite before treatment and after magnetic separator process are shown [9] with minor changes observed. In this research, three types of lanthanides were studied; La, Ce and Y. The metal composition (%) of REE elements in low-grade bauxite before treatment is shown in Figure 2. Both La (18.4%) and Ce (19.3%) elements are the major components in low-grade bauxite before treatment. Cerium was the rare-earth element present at the highest concentration in low-grade bauxite before the magnetic separator process.
To examine the effect of pH on the two step precipitation reactions, the recovery of REE (La, Ce and Y) was calculated from weight content of REE (%) in Table 1. Figure 3 presents the lanthanide recovery for La, Ce and Y from the precipitation reaction. As shown in Figure 3, recovery of lanthanum (~68.2%) was achieved at pH 3.5 using sodium sulphate. On the basis of the total amount, the greatest recovery of lanthanides (~95%) from the low-grade bauxite was achieved using sodium sulphate as the precipitation agent at pH 3.5. The optimal result using sodium sulphate is in accordance with the previous acid leaching process using 1M oxalic acid at 40°C and pH 3.5 [8]. The metal composition of lanthanide species obtained from the second precipitation with sodium phosphate is low when compared with the first stage of precipitation using sodium sulphate. A similar effect was noted by acid leaching with sulfuric acid [9]. In this study, La was the rare-earth element present at the highest level in the low-grade bauxite and similar results were obtained for the leaching of REE slag from Hongcheon, Korea [2].
4. Conclusion
The leaching of lanthanum, cerium and yttrium in oxalic acid and precipitation reactions with sodium sulphate and sodium phosphate at pH 3.5 and 9 were studied. The optimum condition for recovery of La, Ce and Y was pH 3.5 using sodium sulphate as the precipitation agent. The recovery metal composition was analyzed using ICP-OES. The recovery of lanthanum (~68.2%), cerium (~18.9%), and yttrium (~7.8%) were achieved by the first of precipitation step of the reaction using sodium sulphate as precipitation agent.

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