The Leaching Process of Alumina from Red Mud for Synthesis of Mesoporous Alumina

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Abstract. Alumina was leached from red mud by hidrometallurgy method. Alumina from red mud was leached by desilication process, separation of iron oxide process, and formation of alumina salt process. Residu of each step was characterized by X-ray diffraction (XRD), X-ray florence (XRF), scanning electron microscopy-energy dispersive x-ray analysis (EDX). From X-ray diffraction result. The composition of red mud from Bintan was determined by characterization process with X-ray diffraction (XRD) and X-ray fluorescence (XRF) that show red mud from Bintan contains hematite (Fe₂O₃), gibbsite (Al(OH)₃), boehmite (γ-AlO(OH)), anatase (TiO₂) dan quartz (SiO₂). After desilication process, SiO₂ on residue of red mud were collected 38.85 wt.%. From separation of iron oxide process, the residue of leaching process was Fe₂O₃ 81.80 wt.%. The product from formation of alumina salt process was characterized by scanning electron microscopy-energy dispersive x-ray analysis (EDX) that showed the leaching process of alumina from red mud had element oxygen and aluminium in its salt amounted to 64.94 wt.% and 26.40 wt.%. The product could be the source of alumina to synthesis of mesoporous alumina.

1. Introduction
Red mud is a reddish brown colored solid waste product produced in huge amounts from Aluminium industries. The production of 1 ton of alumina generates between 1 and 1.5 tons of red mud [1]. Globally, there are about 4 billion tons based upon its current rate production [2]. For solid waste, red mud will be found in the form of wet or dry mud which is collected in a pond. The red mud produced from these industries is generally stockpiled in open yard, which leads serious problem in soil, air and water because its highly caustic in nature [3]. There have been many strategies implemented for improving the management of red mud, but none of them was cost-effective methods.

It is essential to know the characteristic of red mud before working on red mud for any use. The minerals from Red mud are Fe₂O₃ (48-54%), Al₂O₃ (17-20%), SiO₂ (4-6%), TiO₂ (3-4%), Na₂O (3-5%) and CaO (1-2%) depending on the country of origin [4]. The recovery of a significant quantity of valuable components from the red mud is difficult, as they are locked up in complex mineral phases which are very fine grained and quite alkaline. Recovery of alumina from red mud can be done through several methods such as the addition of MgO + Na₂CO₃ through sintering process [5], mild hydro-chemical processes [6], the addition of acid (HCl, H₂SO₄, and HNO₃) [7], hydrothermal processes [1], and the process of reduction sintering [8]. The researches included recovery of
important elements such as Fe, Al, Na and rare earth elements like Sc, Y, La, Ti and V [9]. As known that red mud contains high value of aluminum more than 15% depending on source of origin. Therefore, red mud can be source of aluminum to manufacture mesoporous alumina.

Mesoporous Al₂O₃ has excellent properties such as highly uniform channels, large surface area and narrow pore size distribution. It has been widely used as adsorbents, catalysts supports, ceramics, heat insulating materials, and reinforcements for composite materials [10]. Because of such excellent properties, many attempts have been made to prepare mesoporous alumina by using different methods, such as evaporation-induced self-assembly (EISA) [11], hard or soft template self-assembly [12] etc. Some expensive aluminum alcoxide or inorganic salts as aluminum sources were used in the mentioned methods. However, among these synthesis routes, the processes were either complicated or uneconomical, which limits large-scale application in industry.

2. Methods

2.1 Materials

The raw material powders of Red Mud were obtained from Bintan Island of Indonesia, its chemical composition was (mass%): SiO₂, 20.21; Al₂O₃, 28.87; Fe₂O₃, 44.66; TiO₂, 3.03; CaO, 0.28; K₂O, 0.37; P₂O₅, 0.51; V₂O₅, 0.07; Cr₂O₃, 0.101; NiO 0.62; ZrO₂, 1.3 and ignition loss, 20.59. Cetyltrimethylammonium bromide (CTAB), sodium hydroxide (analytical grade), chloride acid (analytical grade), De-ionized water.

2.2 Procedure

Red mud was placed into beaker glass for 100 g in 2 L water stirred at low speed to remove some Fe₂O₃ contain by of gravitational principle. 50 gr solids from top layer was collected and treated in 6N HCl solution (solid/liquid ratio 1:5, g/ml) at 90 °C for 2 h with stirring. The obtained suspension was filtered and the filtrate was collected as Al source for synthesis of mesoporous alumina. NaOH solution (5N) was dropped into filtrate from previous procedure with vigorous stirring until AlCl₃ transformed into NaAlO₂ completely. Some impurity elements (Fe³⁺, Mg²⁺, etc.) formed precipitates that could be removed by filtering, and then NaAlO₂ solution was obtained. Subsequently, HCl solution (6N) was added to the NaAlO₂ solution with magnetic stirring until the pH was 7. The precipitate was collected and washed with deionized water.

2.3 Characterization

Powder X-ray diffraction pattern was collected on Phillips Expert with CuKα radiation (λ = 1.54056 Å), voltage 40 kV, 30 mA and 2θ = 5-50°. The surface area (calculated by BET method), pore size distribution (calculated by BJH method) and pore volume were obtained at -196 °C using a Quantachrome Instrument. Solids were characterization by Scanning electron microscope (SEM) images operated at an acceleration voltage of 20.00 kV and work distance of 9 mm. Compositional analysis were performed using energy-dispersive X-ray analyzer attached to the microscope (SEM-EDX) for Al, Fe, Si, Na, O, Br.

3. Result and Discussion

3.1 Measurement of composition of Bintan red mud

Composition determination of Bintan red mud used XRF and the results are presented in Table 1. Based on XRF result, the major compound composition are Fe₂O₃ (44.659%); Al₂O₃ (28.870%); SiO₂ (20.209%) and TiO₂ (3.026%). Several publication provide detailed information on characterization of red muds like [14] who reported composition of red mud from Tayan, West Kalimantan.
Table 1. Composition of red mud from Bintan, Riau Island.

| Compositions | Weight (%) |
|--------------|------------|
| Fe₂O₃        | 44.659     |
| Al₂O₃        | 28.870     |
| SiO₂         | 20.209     |
| TiO₂         | 3.026      |
| ZrO₂         | 1.294      |
| Other        | 1.942      |

Several researches have been studied about characterization of phase and element analysis in red mud, but data analysis for red mud composition which obtaining is not uniform. It is caused by the different composition of red mud each other places [14]. Fig. 1 shows that red mud comprises mineral in phase hematite (Fe₂O₃), gibbsite (Al(OH)₃), boehmite (γ-AlO(OH)), anatase (TiO₂) dan quartz (SiO₂). The diffraction peak of hematite at 2θ : 26°, 40°, 47°, 58° and 64°; gibbsite at 2θ : 20° and 24°; boehmite at θ = 18°, 33°, 45° and 58°; anatase at 2θ = 28° and 55°; quartz at 2θ = 21°, 26° and 50° [14].

![X-ray patterns](image)

Figure 1. X-ray patterns of (a) quartz, (b) anatase, (c) boehmite, (d) gibbsite, (e) hematite and (f) red mud

3.2 Leaching of Red mud

3.2.1 Desilication Process

Desilication process using hydrochloric acid was aimed to soluble of Al₂O₃ in red mud solid. Reaction in this process are below:

\[
\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O}(s) + 3\text{HCl}(l) \rightarrow 2\text{AlCl}_3(l) + 2\text{SiO}_2(s) + 5\text{H}_2\text{O}(aq) \quad (1)
\]

\[
\text{Fe}_2\text{O}_3(s) + 6\text{HCl}(l) \rightarrow 2\text{FeCl}_3(l) + 3\text{H}_2\text{O}(aq) \quad (2)
\]

\[
2\text{TiO}_2(s) + 8\text{HCl} \rightarrow 2\text{TiCl}_4(l) + 4\text{H}_2\text{O}(aq) \quad (3)
\]

Fig. 2 shows that residue (RSD-1) has quartz phase at 2θ : 20° and 26°. In addition, Table 2 shows that contain of SiO₂ in residue is 38.85 %wt. Several other elements in red mud are Fe, Al, Ti, Zr and P.
Table 2. XRF data of Residue (RSD-1)

| Compositions | Weight (%) |
|--------------|------------|
| Fe₂O₃        | 20.56      |
| Al₂O₃        | 27.90      |
| SiO₂         | 38.85      |
| TiO₂         | 8.36       |
| ZrO₂         | 2.89       |
| Other        | 1.44       |

Figure 2. XRD pattern of Residue (RSD-1)

3.2.2 Separation of Fe₂O₃ and Other Impurities from Red mud

Filtrate was obtained from previous process then add NaOH 5N solution, simultaneously. In this process, AlCl₃ was converted into NaAlO₂. Reaction in this process are below:

\[
\text{AlCl}_3(l) + \text{FeCl}_3(l) + 6\text{NaOH}(l) \rightarrow \text{Al(OH)}_3(l) + 6\text{NaCl}(l) + \text{Fe(OH)}_3(s) \quad (4)
\]

Residue was obtained then denoted as RSD-2. It was characterized by XRD and XRF to know about its phase and composition. XRD pattern of RSD-2 (Fig. 3) shows the peaks at 20 : 18°, 20°, 32°, 40° and 45° which indicated that RSD-2 has halite phase (NaCl) at 20 : 32° and 45°. In other hand, the peak of Fe(OH)₃ is not obtained which means Fe(OH)₃ in amorf [15]. XRF result indicated that other impurities are not obtained in RSD-2. The high concentration of Cl in RSD-2 show high concentration of NaCl from residue.

Table 3. XRF data of Residue (RSD-2).

| Compositions | Weight (%) |
|--------------|------------|
| Fe₂O₃        | 81.80      |
| Al₂O₃        | -          |
| SiO₂         | -          |
| TiO₂         | -          |
| ZrO₂         | -          |
| Cl           | 18.20      |
3.2.3 Formation of Salt Alumina
The next stage is the process of neutralizing of Al(OH)$_3$ which obtained from previous process and then added HCl 6N simultaneously to obtain NaAlO$_2$. The precipitate formed from this process is a white alumina salt. Reaction that occurs in this process as follows:

$$\text{Al(OH)}_3(l) + 2\text{NaOH} (l) + \text{HCl} (l) \rightarrow \text{NaAlO}_2 (s) + \text{NaCl} (l) + 3\text{H}_2\text{O} (aq)$$  \hspace{1cm} (5)

Alumina salt (GM-AL) was washed with distilled water and separated by Buchner funnel. GM-AL obtained were then characterized by XRD to determine the phase and the SEM-EDX to know the morphology and composition were contained in the GM-AL. Based on the characterization by XRD(Fig. 4) shows that GM-AL is anamorphous solid. This is demonstrated by acts of the characteristic peaks in the XRD pattern of GM-AL.
Figure 5 shows morphology of GM-AL by SEM where GM-AL has an irregular shape and there are non pores on the surface of solids.

![Morphology of GM-AL](image)

**Figure 5. Morphology of GM-AL**

Fig. 6 displays the GM-AL spectra which showed the characteristic peaks elements contained in the GM-AL. These spectra indicate that the content of the elements contained in the GM-AL is oxygen, aluminum, sodium, and chlorine. Based on Table 4, it can be seen that the element oxygen and aluminum in GM-AL amounted to 64.94% wt and 26.40% wt.

![EDX spectra of GM-AL](image)

**Figure 6. EDX spectra of GM-AL**

**Table 4. EDX data of GM-AL**

| Compositions | Weight (%) | Atom (%) |
|--------------|------------|----------|
| O            | 64.94      | 76.40    |
| Al           | 26.40      | 18.42    |
| Cl           | 6.62       | 3.52     |
| Na           | 2.04       | 1.67     |
4. Conclusion
In conclusion, the leaching process of alumina from red mud for synthesis of mesoporous alumina was done by desilication process, separation of iron oxide process, and formation of alumina salt process. The residue from desilication process and separation of iron oxide process were characterized by XRF. Based on XRF result of these processes showed that the impurities were separated successfully from the product. The product from formation of alumina salt process was characterized by EDX that showed the leaching process of alumina from red mud had element oxygen and aluminium in its salt amounted to 64.94 wt.% and 26.40 wt.% . It is indicated that the product could be the source of alumina to synthesis of mesoporous alumina.

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