Processing of Local Bauxite to Obtain Highly Purified and Fine Alumina Powder

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Abstract. A study on local bauxite was conducted at Mineral Research Centre, Ipoh to produce highly purified fine alumina (Al₂O₃) powder by using Bayer process as a basis. The study was conducted on a local bauxite from Johor. The raw material being classified having the specific gravity of 2.42 and the major constituent of mineral was identified as gibbsite in which indicates of having 58.7% Al₂O₃. Moreover, this raw material being classified as high silica content of bauxite ore because of the presence amount of SiO₂ was slightly more than 7.0%. Four (4) major processes were performed at Mineral Research Centre such as sample preparation, characterization of raw material, precipitation and characterization of product. In order to produce highly purified and fine alumina, some alternative on leaching and precipitation processes were studied. These due to leaching process tends to pre-determine the rate of recovery and the purity of alumina whereas a very effective precipitation process can be applied to produce fine size of alumina powder. This paper presents some results of leaching and precipitation processes and probably help to show how various processing parameters will affect the effectiveness of alumina recovery, purity as well as its sizes.

1. Introduction

Until today, The Hall-Heroult and Bayer discoveries developed more than 100 years ago are the only main technologies being practiced worldwide for production of aluminium. Aluminium hydroxides from Bayer process are being utilized to obtain metal grade alumina or alumina for non-metallurgical purposes. Aluminium hydroxides produced from the Bayer process are generally yellowish in colour and coarser in size. Apart from that it is used in aluminium manufacturing, these products are mainly used as chemical feed stock. But, as many non-metallurgical applications of aluminium hydroxides varies (commonly called aluminium trihydrate, ATH) and aluminium oxides require finer size particles and higher purity, the production of these materials from the Bayer precipitate may not be suitable [1].

Non-metallurgical ATH/oxides have a wide range of applications such as in glass ceramics, refractories, fire retardant products, cosmetics and catalyst. To be used in those kinds of purposes, special grade of hydroxide/oxides are required for any particular applications. The major considerations are particle size and purity as well as the brightness of the product [2].

Malaysia has produced bauxite from Pengerang, Johor for export purposes. There are also some known deposits such as in Jabor, Kuantan that have potential to be exploited [3]. However, in 2016 there was a significant drop of bauxite production in this country due to enforcement of moratorium for bauxite starting in January 2017. This is due to unprocessed bauxite (raw material) has created the environmental issues of bauxite mining include, air, water and soil pollution due to bauxite dust. For
example, 20 bauxite new bauxite mines were closed in Pahang. There was a huge production decrease of bauxite in 2016 which is 95% to 324,924 tonnes valued at RM35.49 million compared with 7,164,956 tonnes valued at RM832.21 million in 2015 [4].

As an alternative in solving the environmental issue, a technology to value-add these local resources has to be developed. In a near future, it may be beneficial for the manufacturing sectors in this country. In the present study, an attempt was made in order to produce high grade and fine particle of alumina oxide from local bauxite taken from Pengerang, Johor. The process mainly utilizes Bayer process as a basis for leaching and subsequently, the pregnant solution obtained was then precipitated within a short period of precipitation time. In the event of leaching, various parameters such as the effect of particle size, concentrations of leachants, leaching time, leaching temperature and applied pressure were studied. Furthermore, to produce high purity and fine size, the precipitation processes were carried out by varying some parameters such as conditioning time, amount of seed and its particles size, precipitation time and usage of a modifier. Changing in conditioning temperature during initial precipitation processes were also being studied.

Alumina trihydrate is used as a flame retardant both within and outside in the interiors of automobiles, commercial upholstered furniture, draperies, wall coverings. It is also used in detergents, antiperspirants, and cosmetics, and used therapeutically as an antacid (e.g., Maalox) and to control phosphate levels [2].

1.1. Aluminium Hydroxides, \( \text{Al(OH)}_3 \) Gibbsite (monoclinic)
Gibbsite is an aluminium hydroxide mineral of the oxides and hydroxides group, with structural formula \([\text{Al(OH)}_3]\). Gibbsite’s structure is made up by the stacking of octahedral sheets of aluminium hydroxide. Each layer consists of octahedrally (six-fold) coordinated \( \text{Al}^{3+} \) cations sandwiched between two closed-pack layers of \( \text{OH}^- \) ions. Because \( \text{Al} \) is a trivalent cation, each of the hydroxyls is bonded to only two aluminium elements, and thus, only two-thirds of the available octahedral sites are occupied. This type of octahedral occupancy is called dioctahedral [5].

For similar structures with divalent cations (e.g., brucite), each hydroxyl is bonded to three cations and all octahedral sites are filled. This is called a trioctahedral mineral. This arrangement result is a neutral sheet with no charge excess or deficit. Therefore, there is no interlayer charge to retain ions between the sheets and to strongly hold the sheets together. The sheets are only held together by weak hydrogen and van der Waals bonds and this results in a very soft and easily cleavable mineral [5].

In normal gibbsite, the hydroxyl ions are facing each other in successive layers. Layers are slightly offset, to produce monoclinic symmetry. Minor substitutions of \( \text{Fe}^{3+} \) for \( \text{Al}^{3+} \) are common in gibbsite. Crystals of gibbsite are typically-very small (< 2 µm in diameter), tabular and often, foliated, showing pseudo hexagonal outline. They may occasionally be granular. Compact lamellar aggregates, or rarely fibrous masses, may occur as whorls or as stalactitic forms. The colour may be white, grey, yellow, red, and brown, though most colours other than white or grey are due to traces of iron (hydr)oxides [5].

1.2. The Bayer Process
The process dissolves the aluminium component of bauxite ore in sodium hydroxide (caustic soda). Under pressure of 3500 kPa and high temperatures the chemical reactions are rapid [6] e.g.:

| Reaction | Equations |
|----------|-----------|
| Gibbsite | \( \text{Al}_2\text{O}_3.3\text{H}_2\text{O} + 2 \text{NaOH} \rightarrow 2 \text{NaAlO}_2 + 4 \text{H}_2\text{O} \) (135 – 150°C) |
| Boehmite | \( \text{Al}_2\text{O}_3.\text{H}_2\text{O} + 2 \text{NaOH} \rightarrow 2 \text{NaAlO}_2 + 2 \text{H}_2\text{O} \) (205 – 245°C) |
| Diaspore | \( \text{Al}_2\text{O}_3.\text{H}_2\text{O} + 2 \text{NaOH} \rightarrow 2 \text{NaAlO}_2 + 2 \text{H}_2\text{O} \) (high temperature and pressure) |

Then, the dissolved alumina is precipitated from the sodium aluminate solution in the form of \( \text{Al}_2\text{O}_3.3\text{H}_2\text{O} \) (alumina trihydrate), e.g.:
2 NaAlO$_2$ + 4 H$_2$O $\rightarrow$ Al$_2$O$_3$.3H$_2$O + 2 NaOH

The precipitation process is carried out by adding alumina trihydrate seed crystals. The size of the seed must be fine to form new alumina crystals. For gibbsite, the seeded precipitation from caustic aluminate solutions is accomplished by a combination of three crystallization processes i.e.; secondary nucleation, agglomeration and ordered growth. Secondary nucleation is the generation of new particles in the presence of seed material while agglomeration is the aggregation and cementation by growth of small particles. In the Bayer process, both require practically to be a high aluminate supersaturation in the liquors. Ordered growth is the slow deposition of new gibbsite on crystal faces in a manner that heals surface defect, resulting in a smoothing of surfaces. The three processes usually occur together during precipitation but the contribution of each process to the whole is dependent on the precipitation condition [7].

Although the phenomenon of precipitation has long attracted the interest of chemist, fundamental information concerning the mechanism of the process remains incompletely understood. It is certain, however, that the particle size of the solid that forms is influenced in part by such experimental variables as the temperature, the solubility of the precipitate in the medium in which it is formed, reactant concentrations, and the rate at which the reactants are brought together. The influence of these variables on the particle size of precipitates can be accounted for by a single property of the system called its relative supersaturation as shown in equation 1 [8].

\[
\text{Relative supersaturation} = \frac{Q - S}{S}
\]

Where Q – concentration of the solute at any instant
S – its equilibrium solubility

The objective of the study is to produce highly purified fine alumina (Al$_2$O$_3$) powder by utilizing local resource. Apart from that, the other objectives are to identify the mineralogy inside the ore and to optimize some parameters of the leaching and precipitation process.

2. Materials and Methods

2.1. Characterization of Sample

At the preliminary stage of mineral processing, the characterization tests on any sample is very important. It determines the chemical composition (oxide elements), mineral content, phase presence and its morphology before further processing can be carried out. Identification of mineral through characterization also facilitates in selecting suitable processing equipment and techniques. In characterization process, the samples taken from the field were then analysed to identify the components of its feed material. Minerals can be only identified absolutely by its chemical and physical properties. From the information gathered, the appropriate testing could be planned smoothly and can contribute directly to the beneficiation techniques for the alumina upgrading.

The rock samples (coarser than 10 cm in diameter) were crushed using a jaw and a cone crusher and subsequently, ground in a grinding mill. Then, it was mixed thoroughly and split into various portions, to be used for further tests and analysis. The materials were analyzed using gravimetric assay, x-ray fluorescence (XRF), x-ray diffraction (XRD), laser particle size analyser (LPSA), image analysis, scanning electron microscope (SEM) and energy dispersive x-ray (EDX). Besides that, the specific gravity tests on the sample were also being carried out. All the information for characterization of the sample are shown in Table 1.

2.2. Magnetic Separation

Wherever required, magnetic separator was employed to remove iron content (Fe$_2$O$_3$) in the mineral sample. For the sample with the size range of $\sim$600 µm +250 µm, a dry magnetic separator was used.
For the finer size range (~250 µm), the removal was carried out by means of high intensity wet magnetic separator.

2.3. Leaching process

The leaching process techniques namely activated was carried out on the sample. In this technique, sodium aluminate solution was prepared by dissolving gibbsite minerals in a boiled sodium hydroxide solution [9]. In this study 3.0 M of sodium hydroxide (NaOH AR grade) solution was prepared as the leaching agent. A magnetic stirrer was used for mixing. Then, 17 g of bauxite sample powder with the size range of ~600 µm (the d₈₀ of the sample was about 175 µm), was mixed with the 100 mL of NaOH solution using a hot plate with magnetic stirrer equipped with thermometer (IKA® RCT Basic C, Germany). The mixing temperature, stirring speed and mixing time were at 93 ± 1°C, 400 rpm and 60 mins, respectively. The pH of mixing solution was maintained at 12. It was recorded by a pH meter (Thermo Scientific™ Orion Star A121, Fisher Scientific, UK) and using H₂SO₄ (1% conc.) to adjust its pH. After the leaching process, the sample solution was filtered using filter paper (Whatman, φ12 cm and pores size of 2.7 µm) and a vacuum pump (VELP Scientifica, Italy). The residue was dried under a hot lamp whereas the pregnant solution was used in precipitating process. The experimental work flowchart is illustrated in figure 1.

2.4. Precipitation process

Precipitation process was performed on pregnant solution which was obtained from the activated leaching process [10]. Several tests were carried out by varying the precipitation parameters. The effects of changing parameters such as the amount of alumina seed, conditioning time, temperature setting and the usage of modifier (H₂SO₄) on the characteristics of ATH product were studied. Some of the results of precipitation experiments with selected operational conditions are shown in Table 1.

3. Results and Discussions
3.1. Characterization

From the results of XRF analysis revealed the presence of chemical composition of bauxite from Johor in their respective compositions of SiO$_2$ (7.2%), Al$_2$O$_3$ (58.7%) and Fe$_2$O$_3$ (3.71%), TiO$_2$ (0.51%) and K$_2$O (0.09%), LOI (29.81%) and CaO (0.03%). The Al$_2$O$_3$ content was found to be 58.70% which is not exceeding 65.4% gives an indicator that the bauxite mineral as gibbsite [11]. Besides SiO$_2$ content (7.20%) which is more than 7% is considered that the material contains highly SiO$_2$ [12]. Gravimetric method was carried out and hence it showed the grade of Al$_2$O$_3$ dan Fe$_2$O$_3$ in feed sample were 60.56% and 4.26% respectively. The particles size distribution of sample was reported as a cumulative percentage passing 80% for sample –600 μm gives (d$_{80}$) 175 μm. The SG of sample was 2.42 indicates that this value is Gibbsite.

From the image analysis as shown in figure 2, it has pointed out that the grey colour is gibbsite. The XRD analysis (figure 3) showed that this mineral contains quartz, hematite, kaolinite, illite and montmorillonite in traces amount.

![Figure 2. Polish section observation of sample shows grey colour of gibbsite.](image)

![Figure 3. XRD diffractogram of bauxite sample contains the major minerals of gibbsite and minor minerals such as quartz, hematite, kaolinite, illite and montmorillonite.](image)
3.2. Magnetic Separation
The iron content, Fe$_2$O$_3$ in fresh sample was determined to be 4.26%. However, it was reduced to 1.49% after passing through the magnetic separator.

3.3. Precipitation Process
The sodium aluminate solution was prepared by dissolving gibbsite minerals in a boiled sodium hydroxide solution. The precipitation days, percent of Al$_2$O$_3$ precipitated and grade of Al$_2$O$_3$ before calcination are shown in Table 1. From the results presented in Table 1, it can be focussed that:

3.4. Effect of Seed Added
Under the similar precipitation conditions and assuming that the process is completed after 45 days, when the consumption of seed increased from 2 g (test 4) to 6 g (test 8), the recovery of Al$_2$O$_3$ was also increased from 33.0% to 57.0%, respectively. When the pH increased from 13 to 14, Al$_2$O$_3$ recovery obtained (test 5) was only 4.5% by using 4 g of seed and, its recovery rose to 20.1% after consuming 6 g of alumina seed. The seed provides surface area for the deposition of alumina from the supersaturated liquor. By increasing the amount of seed could increase the adhesive interaction force between particle and nuclei, control secondary nucleation and hence enhance agglomeration.

3.5. Effect of pH
Tests 7 and 8 show the effect of pH on the sodium aluminate solution at room temperature resulting in recovery of ATH. At pH 14 the precipitation was completed within 45 days with Al$_2$O$_3$ recovery of 20.1% (Test 7). However, its recovery rose to 57.0% (test 8) when pH decreased to13. When the pH was lowered to 12.5 (Tests 13 and 14), the completion of precipitation process was faster. The precipitation process at much lower pH was not selected because at that condition the other impurities in the solution had also started to precipitate and affected the purity on the intended product. The significant effect of pH shown that pH 11.8 was optimum in precipitation of ATH. It is suggested that at lower pH (pH 11.8) of species region gave highly supersaturated of alumina, and apparently the adhesive interaction force between particle and nuclei can enhance agglomeration process of alumina.

3.6. Effect of Conditioning Temperature
The results show that the precipitation process was sensitive to the temperature introduced during conditioning period. Generally, increasing temperature of a solution increases the solubility of the ionic compounds, improving the likelihood of precipitate formation. From the test results, the precipitation of the particles was active when the temperature for conditioning was increased to 70°C compared to 50°C. It is seen that for 5 days period of precipitation for 70°C (Test 12) has shown a greater number ATH recovery of 41.66% compared to 30.11% at 50°C (Test 9). In case where the precipitation temperature was as a general rule, the more heat is added to a system, the more soluble a substance becomes. Therefore, at higher temperatures (70°C), more solute can be dissolved than at lower temperatures (50°C). Thus, the precipitation of alumina hydrate from higher supersaturation sodium aluminate would also be higher.

3.7. Other Effects
Even though, other parameters such as changing the ambient temperature during precipitation and prolong the precipitation time will affect the final recovery and the purity of the product, it was found out that their contribution were less compared to the above-mentioned parameters. It may worth to be noted that the experimental results proved the relation between the particles size range of the product and its purity with the final precipitation time. Results from the particles size distribution analysis test carried out on several products show that, if a precipitation process can be completed faster, the particles size range of the product are smaller and the purity are also higher. However, the limitation for this statement is yet to be known as various aspects such as the kinetics of the various processes involves are still being studied.
Generally, the results also show that the grade of $\text{Al}_2\text{O}_3$ in all of the white ATH powder obtained before calcination were remarkably high (which is in the range of 63.8% to 69.5%). From test 16, firstly results of XRD analysis revealed the ATH is gibbsite as $\text{Al(OH)}_3$ as shown in figure 4. Further analysis on the ATH produced by LPSA (figure 5) has shown that the particle size of ATH was less than 10 $\mu$m. It is followed by SEM micrograph (figure 6) and EDX analyser (figure 7) has proven that the fine particles size range and considerably high purity ATH product with hexagonal platelet in shape.

### Table 1. Results of precipitation.

| Experimental condition | Test No. | Temp (°C) | Seed (g) | pH | Precipitation (days) | $\text{Al}_2\text{O}_3$ precipitated (%) | Grade of $\text{Al}_2\text{O}_3$ before calcination (%) |
|------------------------|----------|-----------|-----------|----|----------------------|----------------------------------------|---------------------------------------------------|
| **Condition 1:**       |          |           |           |    |                      |                                        |                                                   |
| Sodium aluminate solution was kept in an oven at controlled temperature of 80°C for 24 hours. Then, alumina seed and $\text{H}_2\text{SO}_4$ were added, stirred at 150 rpm for another 24 hours at 50°C and poured the solution into Teflon beaker and allowed for precipitation at room temperature³. | 1  | 50  | 6  | 14 | 20                  | 48.0                                   | 65.6                                         |
| Step 1: Alumina seed was added to the aluminate solution, stirred at 150 rpm for 24 hours at 50°C and observed it for 7 days before filtration. | 2  | 50  | 2  | 13 | 45                  | 58.1                                   | 66.5                                         |
| Step 2: $\text{H}_2\text{SO}_4$ and alumina seed were added to the filtrate. Then, the mixture was stirred at 150 rpm at the at 50°C for another 24 hours before the precipitation process was allowed to occur at room temperature³. | 3  | 50  | 2  | 14 | 45                  | 53.0                                   | 65.4                                         |
| **Condition 2:**       |          |           |           |    |                      |                                        |                                                   |
| The appropriate amount of $\text{H}_2\text{SO}_4$ and alumina seed were added to the aluminate solution. The mixture was then stirred at 150 rpm at fixed temperature for 24 hours. After that, the precipitation process was allowed to occur at room temperature³ (except for ³). | 4  | 50  | 2  | 13 | 45                  | 33.0                                   | 63.8                                         |
| 5  | 50  | 4  | 14 | 45 | 4.5                  | 64.1                                   |                                        |
| 6  | 50  | 4  | 14 | 45 | 4.2³                 | 63.3                                   |                                        |
| 7  | 50  | 6  | 14 | 45 | 20.1                 | 66.2                                   |                                        |
| 8  | 50  | 6  | 13 | 45 | 57.0                 | 66.4                                   |                                        |
| 9  | 50  | 6  | 13 | 5  | 30.11                | 65.0                                   |                                        |
| 10 | 50  | 6  | 13 | 10 | 40.63                | 66.1                                   |                                        |
| 11 | 50  | 6  | 13 | 15 | 52.63                | 63.6                                   |                                        |
| 12 | 70  | 6  | 13 | 5  | 41.66                | 64.3                                   |                                        |
| 13 | 70  | 6  | 12.5 | 8 | 41.18                | 65.7                                   |                                        |
| 14 | 70  | 6  | 12.5 | 10 | 49.21                | 66.4                                   |                                        |
| 15 | 70  | 6  | 12.0 | 5 | 59.0                 | 68.2                                   |                                        |
| 16 | 70  | 6  | 12.0 | 9 | 65.0                 | 69.5                                   |                                        |
| 17 | 70  | 6  | 11.8 | 3 | 63.88                | 68.6                                   |                                        |

³Room temperature from 28°C to 29°C.
³Kept in a refrigerator.
Figure 4. XRD diffractogram of ATH contains the major minerals of gibbsite.

Figure 5. Particle analysis of ATH < 10 µm.

Figure 6. Particle morphology of ATH as hexagonal platelet.

Figure 7. EDX analysis of white powder shows the peak line of Al, Si and K from test 16.
4. Conclusion
The leaching process and precipitation performance of bauxite deposits from Pengerang, Johor, Malaysia have been demonstrated to produce high purity and fine particles size of ATH (subsequently alumina powder) by removing iron mineral before pursuing the leaching process. The precipitation parameters such as temperature (70°C), pH (11.8) and amount of seed (6 g) has given significance affect to recovery, purity and particles size of ATH. The significant effect of pH shown that pH 11.8 was optimum in precipitation of ATH with 63.88% of Al₂O₃ precipitated.

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