Recovery of Fine Aluminum Hydroxide with High Whiteness Index from Low Quality Bauxite Using Caustic Roasting and Water Leaching

Su Jin Kim1, Jeong Il Lee2, Kyu Sung Han1, So Yeong Byun1, Tam Tran1, and Myong Jun Kim1,*
1Department of Energy & Resources Engineering, Chonnam National University, Gwangju 61186, Republic of Korea
2Water Quality Analysis Division, Jeollanam-do Institute of Health and Environment, Muan 58568, Republic of Korea

Abstract: A bauxite of low quality containing 6.75% reactive silica and 37.4% Al2O3 as gibbsite was roasted with additives including NaOH (caustic/total alumina molar ratio of 2-4:1) and CaO (CaO/total SiO2 molar ratio of 0.5-3:1) at 300-1000 °C, producing calcines containing sodium aluminate (Na2O.Al2O3), silicates and hematite. Optimum conditions included roasting at 350-400 °C with CaO added at a CaO/total SiO2 molar ratio of 1:1 for 2-3 h. Dissolving the calcine in water at 90 °C produced a sodium aluminate liquor from which aluminum hydroxide (Al2O3.3H2O – alumina trihydrate or ATH) was precipitated. The addition of CaO reduced the silica extraction to <15% at optimum conditions, whereas the total organic carbon (TOC) was ~200 mg/L as carbon in all cases. Losses of alumina and caustic were experienced, as different phases of Al-Ca-Si or Na-Ca-Al-Si minerals were formed during roasting and/or leaching. The extracted alumina in the leached solution produced was precipitated at 60 °C for 20 h to produce a fine aluminum hydroxide having D50 of 1.9-2.8 µm with a whiteness index of 96.8-97.5, better than commercially available products.

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1. INTRODUCTION

Specialty alumina (Al2O3) and aluminum hydroxide (Al2O3.3H2O or alumina trihydrate abbreviated as ATH), which have a fine particle size, low soda and high whiteness have been used in many applications in ceramics and electrical industries [1,2]. Almost all of these commercial products are made from sodium aluminate liquors produced by the Bayer processing of bauxite.

The Bayer processing of bauxite to produce smelter grade alumina involves digestion of the bauxite ore at temperatures in the range 135-250 °C. The digestion produces a saturated sodium aluminate liquor from which ATH is crystallized (as gibbsite) by cooling in the presence of large quantities of seeds. In this context, a poor bauxite as defined by commercial practice [3] would have a Total Available Alumina/Reactive Silica (TAA/reactive SiO2) ratio of <10 (TAA is the total alumina extractable under Bayer digestion conditions). The processing of bauxites containing high soluble/reactive silica will cause losses of alumina and NaOH due to the formation of sodalite desilication products (DSP) containing sodium-aluminum silicate [4,5], whereas a high alumino-goethite feed will produce a red mud which is hard to settle or filter [6].

Typically, gibbsite is precipitated from a saturated Bayer liquor having a composition of 140-150 g/L Al2O3 and 180-220 g/L NaOH, reported as Na2CO3, with a large quantity of the fresh precipitate recycled as seeds [7]. It is well-known that the extraction and solubility of alumina in a sodium aluminate solution is dependent on the alumina/caustic (A/C) ratio [8], where A is measured as g/L Al2O3 and C is caustic concentration reported as g/L Na2CO3. The A/C ratio varies between 0.7 at the start and 0.4-0.5 at the end of the precipitation of ATH [6,9-12].

Lower yields of aluminum hydroxide precipitate from sodium aluminate liquors and its slow kinetics have prompted several researchers to look for new ways to improve this recovery, especially when the alumina...
products are not for smelter use [13]. Alternative processes (non-Bayer) have been developed in efforts to recover aluminum hydroxide from bauxite in an attempt to reduce the cost and energy required for the production of specialty alumina (low soda, fine and high purity alumina). To produce these more valuable specialty alumina or sodium aluminate, other processing techniques have been developed [14,15]. New research has also been conducted to develop alternative processes to recover alumina from “hard to treat” bauxites, including those containing high soluble silica or diasporne, alumino-goethite ores or calcium aluminate slags, which pose technical difficulties during Bayer processing [16]. Boehmite (aluminum monohydroxide or alumina monohydrate, Al$_2$O$_3$.H$_2$O or g-AlOOH) can be synthesized by hydrothermal processing at >160 $^\circ$C [17], or via crystallization from saturated sodium aluminate liquors by cooling [18,19]. Dash et al. reported that boehmite could be precipitated from a sodium aluminate solution having an A/C$_{Na_2O}$ of 1.0-1.1 at 85-93 $^\circ$C (which is higher than the conditions for gibbsite precipitation) using >300 g/L boehmite seeds. The addition of additives such as tartaric acid (50-300 mg/L) or precipitation at lower temperatures would favor the formation of gibbsite. A higher super-saturation also favors gibbsite formation [15]. Wang et al. used CO$_2$ to precipitate a mixture of gibbsite and boehmite from a sodium aluminate liquor as a method to recover aluminum hydroxide [32].

The use of flash calcination at 400-600 $^\circ$C was applied to pretreat a bauxite containing high alumino-goethite [6]. A thermal-chemical activation process was also developed by Smith and his co-workers to deal with high reactive silica bauxite [4,5,20]. The process involves the roasting of bauxites containing high reactive silica to ~950 $^\circ$C or above to decompose the kaolin component into amorphous silica and transitional alumina.

Roasting bauxite before its digestion can also potentially destroy most organic matter, which exist in the ore up to 0.5% w/w carbon [21]. Due to the cyclic nature of the Bayer process, most organic matter dissolves during pressure digestion, forming humate, oxalate, formate and other carboxylates, etc., which accumulate and can reach 20 g carbon/L or higher after several years of operation unless removed [21-23]. Apart from affecting the ATH yield during precipitation, the presence of organics, especially humates, darkens the Bayer liquor into a red-brown color, preventing the production of high quality specialty ATH or alumina with high whiteness [2,10,24].

Sodium hydroxide (NaOH) or sodium carbonate (Na$_2$CO$_3$) which are used for roasting zircon (ZrO$_2$.SiO$_2$) at 800-1000 $^\circ$C to produce sodium zirconate (Na$_2$O.ZrO$_2$), is required for the processing of zirconium products from zircon sand [25-27]. The roasting process can also convert silica into an inert form, as observed in the thermal-chemical activation process [4], and convert goethite to the more benign hematite for easier filtration of process residues [6].

This research therefore attempted to minimize the formation of sodium-aluminum silicate by adding CaO during roasting. Our ultimate aim was to produce a sodium aluminate (Na$_2$O.Al$_2$O$_3$) from roasting which is easily dissolved in water. Silica or other silicates would be rendered mostly insoluble during the water leaching stage. This paper reports the results of a study on the recovery of aluminum hydroxide from a bauxite containing high reactive silica and boehmite using NaOH roasting and water leaching.

### 2. EXPERIMENTAL PROCEDURE

A 20 kg high silica/boehmite Australian bauxite sample was received from Korea Chemicals (KC) Corp. operating a Bayer plant in Mokpo, South Korea. The sample was sub-divided into smaller proportions using a sample splitter. The characteristics of the bauxite were determined by KC Corp and are summarized in Table 1.

The sample contained a total available alumina (TAA) of 46.3%, which is the maximum extractable alumina during Bayer plant digestion at 250 $^\circ$C, as determined by bomb digestion by KC Laboratories. Of this TAA, 37.4% was identified as gibbsite or ATH.
(aluminum tri-hydroxide/alumina trihydrate) and 8.88% as boehmite/diaspore (aluminum monohydroxide or alumina monohydrate). The total Al\(_2\)O\(_3\) was 53.4%, implying 6.9% of the alumina was associated with clay (silicate) or other insoluble minerals. The reactive silica was 6.75% (of the total 8.65% SiO\(_2\)), representing a poor quality bauxite according to commercial practice, with the ratio of TAA/Reactive silica of <10) [3,28].

All reagents used in this study (sodium hydroxide, oxalic acid) were of analytical grade and supplied by Duskan Pure Chemicals Co Ltd. (Korea).

Mixtures of bauxite and NaOH (at different NaOH/total Al\(_2\)O\(_3\) molar ratios (2, 3 and 4:1). After mixing the mixtures were placed inside ceramic crucibles and roasted at various temperatures in the range 300-1000 °C for a fixed time (either 1, 2 or 3 hours). Cooled calcines were then leached at 90 °C water using different volumes using a reflux flask to yield sodium aluminate liquors of different alumina and caustic concentrations. Samples were taken at 30, 60, 90 and 120 min of leaching and analysed for alumina and caustic to confirm the completion of the dissolution (generally within 1 h). After leaching, the slurry was made up to the original weight (due to minor evaporation), filtered and the residues washed thoroughly and the liquor analyzed for final alumina and caustic analysis. These analyses were then used to calculate the overall extraction (%) of alumina and caustic based on accurate mass balance. The produced aluminate liquors were then subjected to precipitation experiments to produce fine alumina having high whiteness using primary seeds produced by mixing aluminum sulphate solutions (H\(_2\)SO\(_4\) 23%, Al\(_2\)O\(_3\) 8%) with sodium aluminate solutions (A/C 0.65). The seeds were added at different amounts (0.5-2% seeding) to the pregnant sodium aluminate liquors (148.2g/L Al\(_2\)O\(_3\), 223.6g/L caustic as Na\(_2\)CO\(_3\)) and the precipitation of fine alumina was conducted at 60 °C for 20 hr. The procedures to make fine alumina were detailed in our earlier study [2].

### 3. RESULTS AND DISCUSSION

#### 3.1 HSC modelling of roasting conditions

The experimental program was based on thermodynamic modelling using HSC software [30]. The modelling was based on 100 g of raw bauxite roasted with NaOH, sodium carbonate or sodium oxalate. The HSC modelling was conducted to determine the temperature required to achieve the maximum yield of sodium aluminate (Na\(_2\)O.Al\(_2\)O\(_3\)) at a minimum use of reagents (NaOH, sodium carbonate or sodium oxalate). The stoichiometry of the NaOH were thoroughly hand-mixed with sodium hydroxide (NaOH) added at different NaOH/total Al\(_2\)O\(_3\) molar ratios (2, 3 and 4:1).
roasting reaction to form sodium aluminate $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3$ is equivalent to 2:1 molar ratio of NaOH/total $\text{Al}_2\text{O}_3$. For both sodium carbonate ($\text{Na}_2\text{CO}_3$) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) the reaction stoichiometry is equivalent to 1:1 molar ratio of carbonate or oxalate/total $\text{Al}_2\text{O}_3$. For this modelling, the input amounts of alumina, silica, iron oxide, etc. in 100 g of bauxite were calculated from their contents in the bauxite (Table 1). CaO was also added at 1:1 molar ratio with respect to silica, to evaluate the formation of various Ca-silicates during roasting.

Figure 1 shows results for the roasting of bauxite with NaOH (at 2:1 NaOH/$\text{Al}_2\text{O}_3$ molar ratio) representing the stoichiometric requirement for the roasting to convert all alumina into sodium aluminate. The results indicate that for NaOH roasting, the formation of sodium aluminate at a maximum yield of 89% starts at 300 °C. An increase in roasting temperature up to 800 °C did not change the sodium aluminate yield much. Within this temperature range, the loss (at ~10%) of alumina is predicted mainly to form a Ca-Al-silicate ($\text{CaAl}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$). At a temperature higher than 800 °C, more losses of alumina are expected due to the formation of other Ca-Al or Ca-Al-Si compounds (mainly $2\text{CaO}.\text{Al}_2\text{O}_3$.SiO$_2$, $\text{NaAlSiO}_4$, $\text{CaO}.\text{Al}_2\text{O}_3$, etc.).

The HSC modelling comparing predictions at NaOH/total $\text{Al}_2\text{O}_3$ ratios of 2:1 and 3:1 and CaO:SiO$_2$ molar ratio of 1:1 shows that an excess of caustic is required to form more sodium aluminate $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3$. At a temperature >400 °C and a NaOH/total $\text{Al}_2\text{O}_3$ molar ratio of 3:1, the formation of sodium aluminate increases slightly compared to that obtained at a molar ratio of 2:1, until reaching a steady state at ~800 °C. Calcium oxide will bind with SiO$_2$ to form $\text{CaAl}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ causing the potential loss of $\text{Al}_2\text{O}_3$ during extraction, as this mineral might not be soluble in water during leaching. Above 400 °C, however this
mineral decomposes releasing Si to form soluble sodium silicate. Such a formation will consume caustic and release silicate during leaching. Other minerals, such as Ca-Al silicate, Ca silicate or calcium aluminate, can also be formed at low levels as shown in Fig. 1c.

3.2 Effect of roasting temperature on TAA and total $\text{Al}_2\text{O}_3$ extraction

Roasting of NaOH-bauxite mixtures was then conducted within the temperature range 300-1000 °C, with the optimum range of 350-400 °C. A temperature higher than 400 °C did not improve the TAA extraction (>90%), but did extract more silica during leaching, confirming the predictions of the HSC modelling. Figure 2 shows little variation in the TAA extraction within this temperature range. As a result, most subsequent experiments were conducted at 350-400 °C and 3 hours roasting. A maximum TAA extraction of 90% was achievable under these conditions, implying that most gibbsite and a proportion of boehmite/diaspore are extractable, as long as excess NaOH is used during roasting. Leaching at a lower NaOH:$\text{Al}_2\text{O}_3$ molar ratio of 2:1 resulted in a lower TAA extraction (Fig. 3) as expected. Silica extraction slightly increased without CaO, whereas with CaO there was little variation in its extraction.

3.3 Effect of leaching time

The calcines produced after roasting at different conditions using a NaOH/$\text{Al}_2\text{O}_3$ molar ratio of 2:1 were subjected to leaching in different volumes of distilled water at 90 °C. Figure 4 shows that after 30 min all available soluble sodium aluminate was fully extracted into the solution. The extractions of both alumina and caustic were found to increase only slightly with temperature in the range 400–500 °C and roasting time 1–2 h. The results show that the molar ratios of caustic recovered in these tests as sodium carbonate/alumina are in the range 1.5-1.6:1, higher than 1:1 ratio for sodium aluminate. A mismatching of extractions of alumina and caustic was observed, indicating that either alumina re-precipitated after the sodium aluminate was dissolved in water, or some of it was lost forming water-insoluble Al-silicate compounds during roasting. To achieve a higher TAA extraction, a higher NaOH/$\text{Al}_2\text{O}_3$ molar ratio is required during roasting.

3.4 Effect of varying CaO addition

The effect of added CaO is shown in Fig. 4. By adding CaO at a CaO/SiO$_2$ molar ratio of 0.5-3, the extraction of Si is gradually reduced to <5% at the highest molar ratio. However, the TAA extraction decreases at a CaO/SiO$_2$ molar ratio >1:1. As a result, the optimum addition of CaO was set at a CaO/SiO$_2$ molar ratio of 1:1.
3.5 Effect of NaOH/Al$_2$O$_3$ molar ratio used for roasting

By varying the amounts of calcines used during water leaching (i.e., the calcine/water mass ratio), various liquors of different concentrations of alumina and caustic could be produced. The results obtained from leaching the various calcines produced from roasting using NaOH/Al$_2$O$_3$ of molar ratios 2, 3 and 4:1 are shown in Fig. 5. Excellent linear relationships (with $R^2$: 0.88-0.99) exist between the concentrations of extracted Al$_2$O$_3$ and NaOH (as sodium carbonate), indicating the consistency of the calcines produced at different conditions. The A/C (Alumina/caustic as sodium carbonate) ratios as slopes of the plots at different conditions show 0.50 and 0.42 at caustic/alumina molar ratios of 3:1 and 4:1, respectively, irrespective of CaO addition. At a lower caustic/alumina ratio of 2:1 and a CaO/SiO$_2$ molar ratio of 1:1 (Fig. 1), the A/C ratio is 0.66 compared to 0.54 without CaO addition. This indicates that more alumina is extracted without excess NaOH if CaO is added under these conditions. At an A/C molar ratio of 0.66 the liquors yielded reach near saturation (maximum solubility), closely matching the equilibrium results reported by Li et al. at 90 °C (Fig. 5a).

The solubility of sodium aluminate in Bayer liquor is dependent on both temperature and NaOH concentration [31]. Data from Li et al.’s study plotted in Fig. 6a confirm that the calcines produced at a NaOH/Al$_2$O$_3$ molar ratio of 2:1 with added CaO yield...
liquors very close to saturation. For calcine produced at this molar ratio, alumina would start to precipitate during water leaching even at 90 °C, if the concentration of NaOH as Na₂CO₃ is below 100 g/L. At higher NaOH/total Al₂O₃ molar ratios, excess NaOH in the leached liquor would ensure the Al₂O₃ concentration to be below the solubility limit with A/C ratio in the range of 0.4-0.5.

3.6 Losses of alumina and NaOH

In order to have a clearer understanding of how the losses of alumina and NaOH occurred, samples of calcines and residues produced from the experiments using a NaOH/total alumina molar ratio of 2:1 were subjected to XRD analysis, and their patterns are shown in Fig. 6 a and b. The calcine roasted at 500 °C for 3 h using a NaOH/total alumina molar ratio of 2:1 has an XRD pattern (Fig. 6a) showing the presence of sodium aluminate, sodium aluminum silicon oxide, di-calcium silicate and unreacted gibbsite. This XRD pattern confirms that gibbsite was not fully converted to sodium aluminate, and some alumina was also lost via forming Na-Al-Si oxide at this level of caustic NaOH addition. After leaching at 90 °C for 2 h, the unreacted gibbsite was not detected in the residue. However, several phases of Ca-Al-Si and Na-Al-Ca-Si compounds are formed (tetranatrolite, katoite, sodalite), indicating losses of both caustic NaOH and alumina during leaching. Iron is detected as hematite in the residues confirming the results predicted by HSC modelling.

Instead of forming Ca-Al-Si oxide as predicted by HSC (Fig. 1), di-calcium silicate (2CaO·SiO₂) was also detected in the calcine (Fig. 6a), possibly due to the more favorable kinetics of di-calcium silicate formation. The formation of di-calcium silicate, however, was also found during calcination of high iron-bearing bauxite and alumina-containing slag using lime [16]. The leaching at 55-90 °C of calcium aluminate produced from this process also resulted in losses of alumina forming Ca-Al-silicate and Na-Al silicate [16]. The formation of various Al-Ca-Si and Na-Al-Ca-Si phases found in the residue’s XRD pattern of Fig. 8b (from the reaction of calcine di-calcium silicate with caustic during leaching) seems to follow the same pattern as that found by Sun et al. (2015).

3.7 Reduction of organic carbon

The advantage of this roast-leach process is that pure and colorless sodium aluminate liquors can be produced without any organic co-dissolved during leaching, as occurs in the Bayer process. A typical Bayer plant liquor will contain a total organic carbon (TOC) of 10-20 g carbon/L [22,23]. Figure 7 shows the measurements of TOC (total organic carbon) to be in the range 0.1-0.3 g/L TOC as carbon (within the error limit for the technique) over a wide range of roasting temperature. This is much lower than the level measured (4.6g/L TOC as carbon) when the original bauxite sample was stirred in a caustic solution at 90 °C. These liquors
are therefore more suitable for the production of ATH of high whiteness.

3.8 Recovery of fine ATH having high whiteness

Several options exist to recover aluminum hydroxide values from a sodium aluminate liquor using non-Bayer precipitation techniques. The precipitation of aluminum hydroxide from a leach liquor produced from leaching of a diasporic ore yields boehmite [11,15] or a mixture of boehmite and gibbsite at $>85 \, ^\circ\text{C}$; gibbsite becomes more predominant at $<75 \, ^\circ\text{C}$ [32]. On the other hand, 80-90% of the sodium aluminate could also be recovered as a solid via crystallization at temperatures within the range 60-90 $^\circ\text{C}$ over 2 h from a concentrated leach liquor containing 575 g/L caustic as Na$_2$O + 333 g/L Al$_2$O$_3$ [14].

A process for recovering commercially-valuable fine ATH having high whiteness is presented in Fig. 8. In this process (right hand side paths) the high silica bauxite is first roasted using pure or recycled spent liquor from an existing Bayer plant. After recovering the sodium aluminate produced by water leaching of the roasted bauxite, fine ATH with discreet particles can be precipitated at 60 $^\circ\text{C}$ over 20 hr using primary seeds (0.5-2.0% seeding) produced by mixing a sodium aluminate solution with aluminum sulphate. These details were reported in our previous study [2]. After precipitation of fine ATH, the spent liquor contains low or no organic contaminants, as compared to the conventional Bayer process where the organics can reach 20 g/L carbon. The spent liquor can then be recycled for the next cycle of roasting. Excess liquors can also be recycled back to the main Bayer process, thus providing a means to reduce the overall organics of a Bayer refinery.

The novel process produces fine ATH products having high whiteness. The product morphology of discreet fine particles with little agglomeration, yielded a narrow range of particle sizes, as confirmed by SEM photos (Fig. 9).

The produced ATH from this study had a mean
particle size ($D_{50}$) of 1.9-2.8 µm. The finest (1.9 µm) at 2% seeding is comparable to commercial products currently produced by Korea Chemicals (KC) Corp (2 µm Superfine ATH) and Sumitomo Chemical [33], whereas whiteness at 96.8-97.5% is better than those commercially available, as shown in Table 2.

4. CONCLUSIONS

The roasting of a low quality bauxite containing 6.75% reactive silica and low gibbsite (37.4% $Al_2O_3$) at temperatures in the range 300-1000 °C with additives including NaOH (caustic/total alumina molar ratio of 2-4:1) and CaO (CaO/total SiO$_2$ molar ratio of 0.5-3) produces calcines containing sodium aluminate ($Na_2O.Al_2O_3$). At optimum conditions of roasting at 350-400 °C, or 2-3 h, adding CaO at a CaO/total SiO$_2$ molar ratio of 1:1 and then dissolving in water within 1 h at 90 °C, a colorless liquor with high clarity and containing no TOC was produced, suitable for the production of alumina with high whiteness. To achieve an extraction of ~90% of total extractable alumina (TAA) excess caustic (>1.5x stoichiometric requirement) is required. Losses of alumina and caustic were experienced as different phases of Al-Ca-Si or Na-Ca-Al-Si minerals were formed during roasting and/or leaching. The extracted alumina in the leached liquor produced can be precipitated as fine gibbsite/bayerite seeds produced by adding an acidic aluminum sulfate to the primary liquors. The residual liquor after product precipitation can be recycled to the Bayer process, where the spent liquor is extracted from or to the roasting stage. From the concentrated liquor produced, fine aluminum hydroxide products (mean particle size $D_{50}$ of 1.9-2.7 mm) with high whiteness index of 96.8-97.5 were produced. The proposed process presents an alternative method for processing specialty aluminum hydroxide from a low quality bauxite as a supplement to current Bayer alumina refineries.

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