EXTRACTION OF ALUMINA FROM BAUXITE RESIDUE FOR PREPARATION OF ALUMS AND POLY ALUMINUM CHLORIDE

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ABSTRACT

The chemical composition of West Kalimantan bauxite is 45 pct Al_2O_3 and 16 pct Fe_2O_3 that has been extracted to produce alumina and bauxite residue (red mud). The residues contains Al_2O_3 20 pct and Fe_2O_3 about 37 pct, wich was furthermore processed by roasting or lime-soda sinterization at temperature of 800-1100˚C. The sintered product was leached with sodium carbonate solution to produce soluble sodium aluminate ($2NaAlO_2$). The solution obtained was then precipitated to produce hydrated alumina ($Al(OH)_3$. Hydrated alumina was then sulfateized by adding ammonium hydroxide, and followed by crystallization to produce high purity of ammonium aluminum sulfate crystals (alums). In addition, hydrated alumina was also chlorinated in stoichiometric amount at mol ratio of OH/Al = 0.5 – 1.5 to form polyaluminum chloride (PAC). The residue obtained from leaching was concentrated by 1000 gauss of magnetic separator to produce iron concentrate as a by product. As the results, sulfatation of hydrated alumina with addition of ammonium hydroxide results high grade of ammonium aluminum sulfate ($NH_4Al(SO_4)_2 .12H_2O$) crystals. Chlorination of hydrated alumina in stoichiometric amount at mol ratio of OH/Al = 1.0 results polyaluminum chloride (PAC) that quality is adjacent to the first type of PAC. Through the soda-lime sinter process, it can also produce iron concentrate having grade of 66 % Fe_2O_3 with 40 % of recovery.

Keywords : bauxite residue, lime-soda sinter process, hydrated alumina, alums, PAC.

INTRODUCTION

Indonesia has potential bauxite resources, especially in West Kalimantan, Bintan island and surrounding of the area. West Kalimantan bauxite ore contains main compounds of $Al\text{-}_2O_3$ 44,79 %, Fe_2O_3 15,76 %, SiO_2 1,56 % and TiO_2 1,11 %. The processing of bauxite (Bayer Process) has been applied in producing alumina, however, the bauxite residue still contains significant Al_2O_3 20 % and Fe_2O_3 37 %.

Many ways have been tried and keep being developed for reusing bauxite residue by many countries which have alumina industries, one is Australia. In Australia, it is not less than 30 million ton of bauxite residue accumulates every year (40% from world production) [Sharif, 2005].

Research on extraction of alumina (Al_2O_3) from West Kalimantan bauxite residue was done by soda-lime sintering process that consists of sintering to the red mud with soda-lime at 800-1200^{O}C resulting sintered sodium aluminate solution ($2NaAlO_2$). Separation of sodium aluminate solution from residue followed by precipitation of sodium aluminate solution result hydrated alumina ($Al(OH)_3$). Hydrated alumina can be used as a raw material (aluminum resources) for alums and polyaluminum chloride (PAC). Then the residue of solution can be concentrated by magnetic separator to result iron concentrate as a by product.

The aim of this research is to produce hydrated alumina from West Kalimantan bauxite residue by soda-lime sintering process as raw materials for making alums and poly aluminum chloride (PAC). It also results iron concentrate from residue of leaching as a by product. Alums and PAC was selected because these products are currently required for water treatment. As known that the community is often difficult to obtain clear water in dry season. Besides alums, Indonesia still imports PAC (in the form of hydrated alumina).

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FUNDAMENTAL

Alumina

- Alumina from aluminosilicate minerals
  Padilla (1985) and Alp (2002) used lime-soda sinter process method to get alumina from aluminosilicate materials. In this process, aluminosilicate was reacted with lime (CaO) or calcium carbonate ($CaCO_3$) and sodium carbonate (Na_2CO_3) at high temperature (800-1200 ^oC) to form sodium aluminate ($Na_2O.Al_2O_3$ or $2NaAlO_2$) that is soluble in alkaline solution (Na_2CO_3 or NaOH) and to form dicalsium silicate (Ca_2SiO_4) which is not soluble in alkaline solution.

  The sintering reaction of clay materials can be stated as below [Padilla, 1985] :

  $Al_2Si_2O_7 + Na_2CO_3 + 4CaCO_3 \rightarrow 2NaAlO_2 + 2Ca_2SiO_4 + 5CO_2$ .... (1)

- Alumina from aluminous ores and bauxite residue
  Aluminous ores (Al_2O_3) was reacted with Na_2CO_3 at temperature about 1000 ^oC to form sodium aluminate. SiO_2 in aluminous ores causes sodium carbonate to react with SiO_2 during sintering process to form dissolved sodium silicate (Na_2SiO_3). The equation for that reaction [Habashi, 1997] :

  $Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$ .... (2)

  $SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2$ .... (3)

  If sintered feed is added with CaO, sodium silicate will react with CaO and Al_2O_3 to form soluble sodium aluminate compound and unsoluble dicalsium silicate. The reaction is [Padilla, 1985] :

  $Na_2SiO_3 + 2CaO + Al_2O_3 \rightarrow 2\ NaAlO_2 + Ca_2SiO_4$ .... (4)

  Calcium can replace sodium to form calsium aluminate ($3CaO.Al_2O_3$) with chemical reaction [Habashi, 1997] :

  $4Al_2O_3 + Na_2CO_3 + 3CaO \rightarrow 2NaAlO_2 + 3CaO.\ Al_2O_3 + CO_2$ .... (5)

- Sinter Leaching
  Leaching of the sinter with sodium carbonate solution causes calsium aluminate to react with sodium carbonate to form sodium aluminate and solid residue of calsium carbonate ($CaCO_3$). [Habashi, 1997] :

  $3CaO.Al_2O_3 + 3Na_2CO_3 + H_2O \rightarrow 2NaAlO_2 + 4NaOH + 3CaCO_3$ .... (6)

Aluminum Sulfate Forming

Sulfatation of aluminum hydrate results aluminum sulfate, and sulfatation with adding ammonium hydroxide results ammonium aluminum sulfate.

$Al(OH)_3 + H_2SO_4 + H_2O \rightarrow Al_2(SO)_3.18H_2O + H_2O$ .... (7)

$Al(OH)_3 + H_2SO_4 + H_2O + NH_4OH \rightarrow NH_4Al(SO_4)_2.12H_2O + H_2O$ .... (8)

Ammonium aluminum sulfate solution can be crystallized in room temperature.

PAC FORMING

The mechanism of forming Poly Aluminum Chloride (PAC) can be explained by the reaction of $AlCl_3$ (aluminum chlorides) with $Al(OH)_3$ at mol ratio of OH/Al = 0.5 – 1.5 (Magnus, 1990). Aluminum chlorides are resulted through chlorination of $Al(OH)_3$. Furthermore, the reaction of $AlCl_3$ with $Al(OH)_3$ proceeds like 'polymerization' to form 'poly aluminum chlorides'.

EXPERIMENTAL

Red mud from bauxite processing residue was prepared and mixed with CaO and Na_2CO_3 both in stoichiometric amount of 10 % excessive, it was formed as pellets and need to be dried. Sintering of the dried pellet was done at variation of the temperature of 800 - 1100 ^oC. Sintered product was leached in 2 % wt. of sodium carbonate solution at room temperature with agitation to get sodium aluminate solution ($Na_2O.Al_2O_3$). The solution was then separated from its residue by filtration, and the residue was washed with aquades twice. Filtrate and residue were analyzed by atomic adsorption spectrometry (AAS) for the chemical composition.

The chemical composition of residue, filtrate and washed filtrate were used to calculate the recovery of alumina. Hydrated alumina was added sulfuric acid and ammonium hydroxyde to produce ammonium aluminum sulfate compound, and then was crystalized (Husaini, 2008). In addition, hydrated alumina was chlorinated with HCl to form $AlCl_3$, and then it was reacted by excess of hydrated alumina (*polymerization*) at mol ratio of OH/Al = 0.5 – 1.5 to form poly aluminum chloride. The residues of filtration was concentrated by magnetic separator (1000 Gauss) results iron concentrate as a by product, and it was analyzed by AAS for its chemical composition and recovery. Figure 1 shows the simplified scheme of the research.

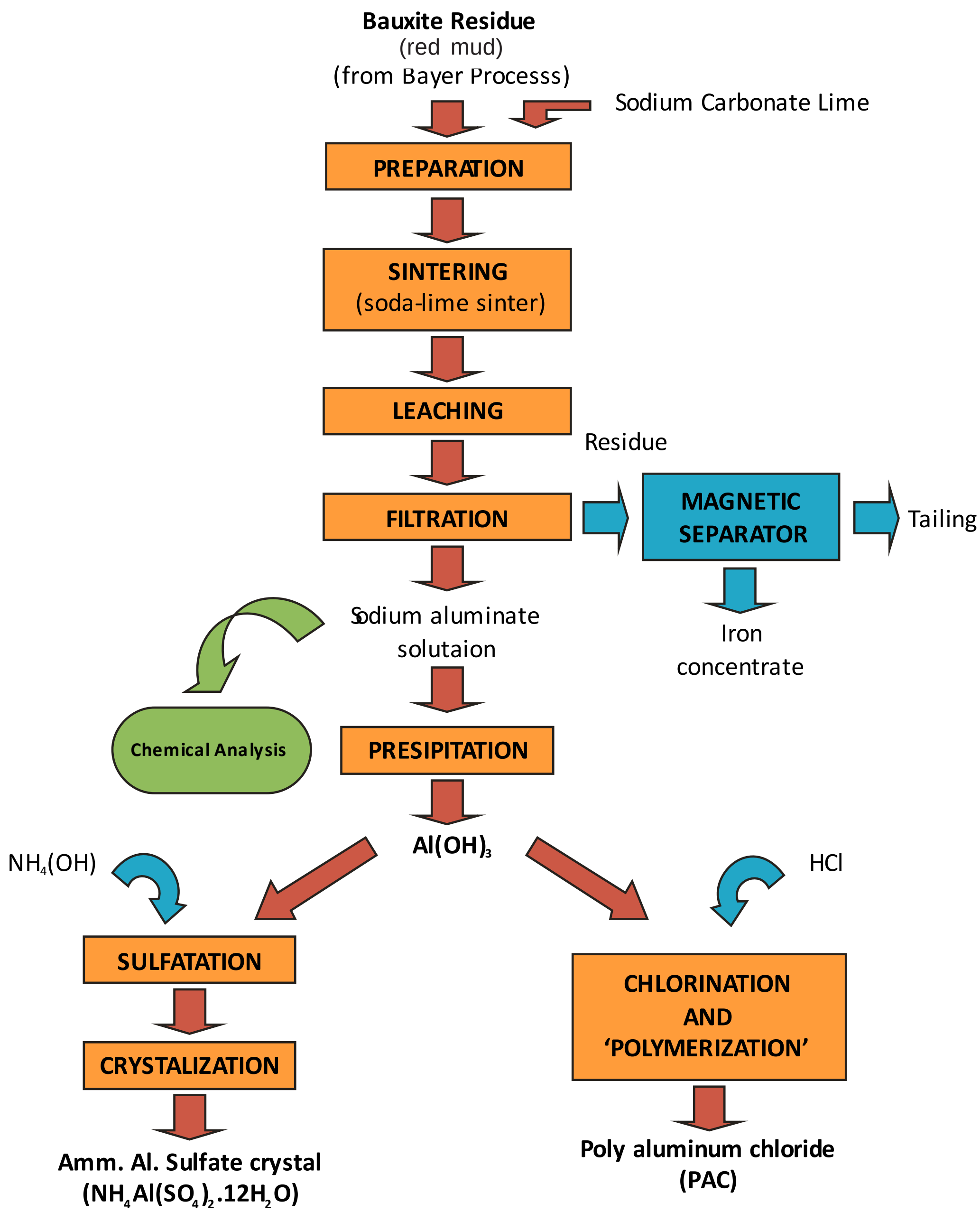


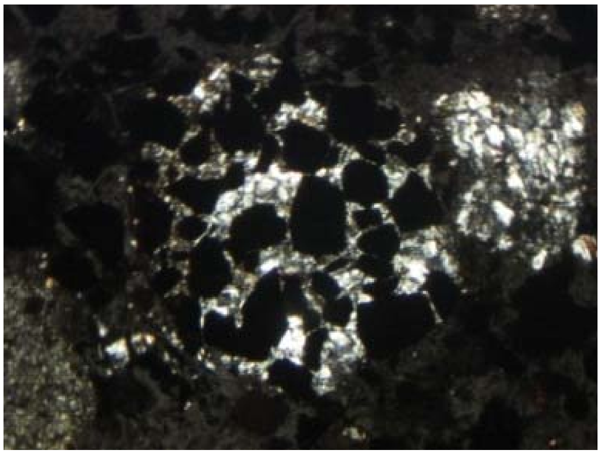
Figure 1. Scheme of bauxite residue processing to produce hydrated alumina $Al(OH)_3$), ammonium aluminum sulfate ($NH_4Al(SO_4)_2 .12H_2O$) and poly aluminum chloride (PAC)

RESULTS AND DISCUSSION

Bauxite Residue

Microscope optic examination shows a part of iron still interlock in gibsite particle (0.6 mm) and the other has already been liberated (Sutanto, 2008) shown in Figure 2.

Figure 3 shows the XRD graphic of West Kalimantan bauxite residue, it contains dominantly gibbsite ($Al(OH)_3 . 3H_2O$), the others are hematite (Fe_2O_3) and goethite ($Fe^{+3}O(OH)$). Gibbsite is required as source of alumina for alums and PAC after being extracted from bauxite residues.



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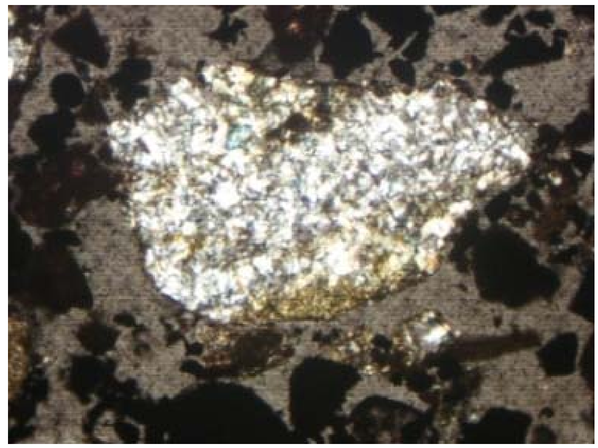


b

Figure 2. Photomycrograph of bauxite; (a) a particle of gibsite (white) 0.6 mm interlock with iron particles (black), (b) a particle of gibbsite has already been liberated (white)

The chemical composition of West Kalimantan bauxite and its residue are shown in Tabel 1. Bauxite residue resulted from alumina extraction of bauxite ores by Bayer process still contains alumina 20% and iron 37 %.

Tabel 1. Chemical composition by AAS of West Kalimantan bauxite and its bauxite residue

Compound	Bauxite (%)	Bauxite residue (%)
SiO_2	1,56	3,40
Al_2O_3	**44,79**	20,17
Fe_2O_3	**15,76**	37,48
MnO	0,06	0,16
MgO	ttd	0,14
CaO	0,02	0,06
Na_2O	ttd	3,03
K_2O	ttd	ttd
TiO_2	1,11	3,43
P_2O_5	0,09	0,09
H_2O	36,04	31,21

Note: ttd means undetected

Sodium Aluminate Solution

Alumina was extracted from sinter by leaching with 2 % wt. of sodium carbonate solution. The result is shown in Figure 4. Sintering process in various temperature (800, 900, 1000, 1100^{O}C) show that the highest amount of extracted alumina is 75% occured at 800^{O}C with solid percentage of 11.8%. Between temparature of 900-1100^{O}C, the extraction is downword to become 50% at 900^{O}C and 45 % at 1100^{O}C. The present results of leaching are more accurate than that of the last (Aziz, et.al., 2009) because the process used sodium carbonate solution 1 % wt. The present leaching however, uses 2 % wt. of sodium carbonate solution in order to leach as much as calcium from calcium aluminate compounds ($3CaO.Al_2O_3$) to form sodium aluminate solution (Alp, 2002).

Extracted alumina as function of sintering time is shown in Figure 5. Sintering temperature at 800^{O}C results the highest extracted alumina of 85.20 %, occured in ½ hours. However, within time interval of 1-4 hours the extraction tends to reduce. The alumina extraction is decreasing to become 47%

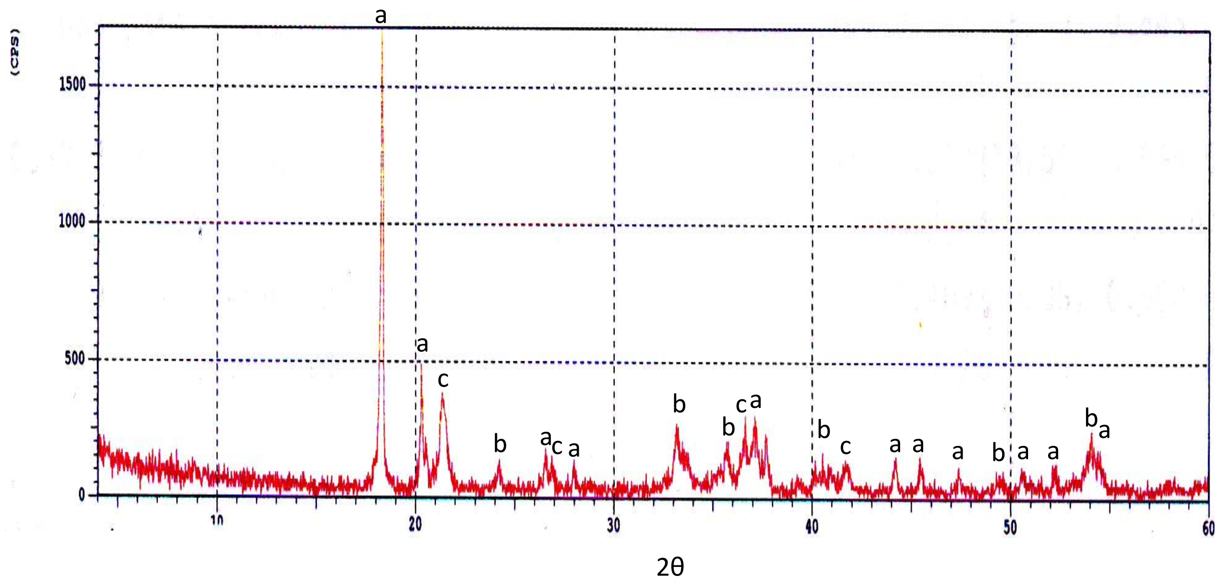


Figure 3. XRD graphic of West Kalimantan bauxite residue (note: a=gibbsite; b=hematite; c=goethite)

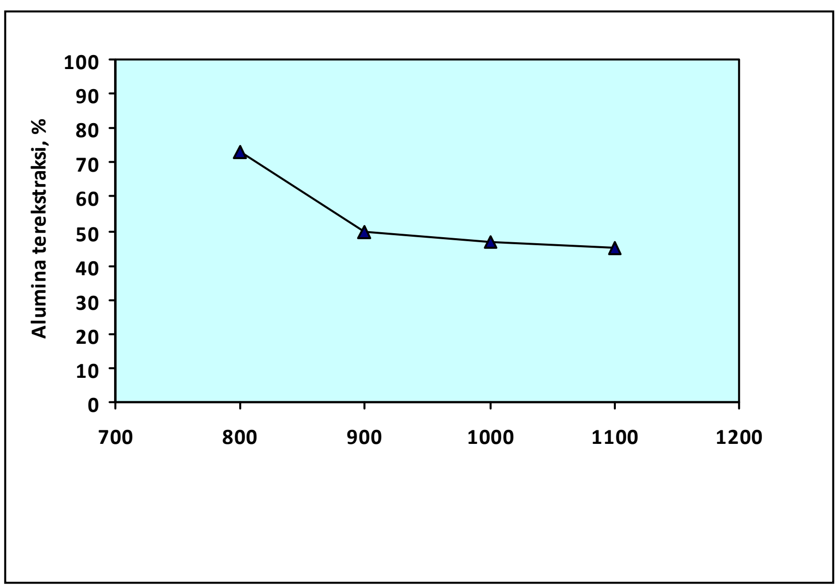


Figure 4. The effect of sintering temperature to the extracted alumina

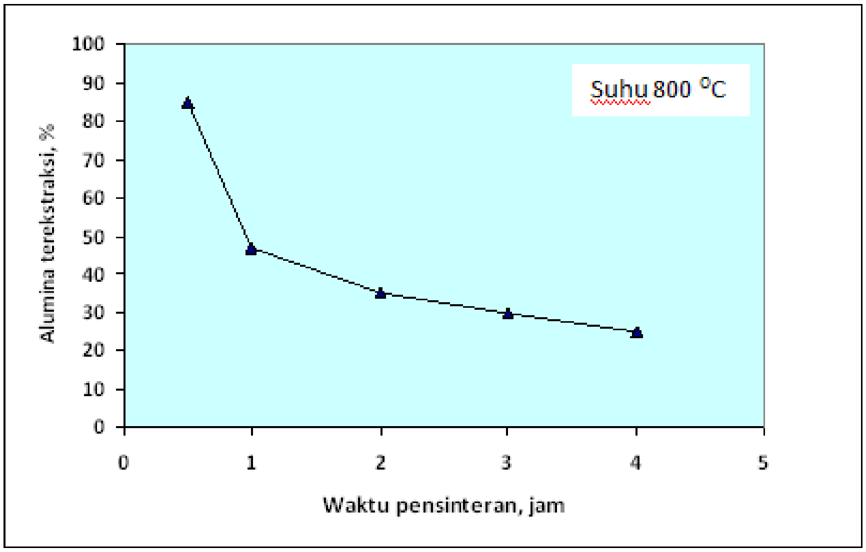


Figure 5. The effect of sintering time to the extracted alumina for sintering temperature of 800°C

Table 2. The concentration of main soluble elements in sodium aluminate solution, detected by AAS

No.	Al (10^3 ppm)	Na (10^3 ppm)	Si (ppm)	Fe (ppm)	Ca (ppm)
1.	50,41	32,39	0,37	1,95	1,74
2.	52,22	31,42	0,34	1,76	1,66
3.	51,71	36,11	0,32	1,54	1,77

in 1 hour and 25% in 4 hours of the sintering time. The concentration of soluble main elements (Al^+, Na^+, Si^+, Fe^+, Ca^+) in sodium aluminate solution is shown in Tabel 2.

The data show that sinter soda-lime process of bauxite residue produced sinter containing sodium aluminate ($NaAlO_2$) compound that is soluble in sodium carbonate solution, producing sodium aluminate ($Na_2O.Al_2O_3$) solution, and leaving the solid residue.

Precipitated Hydrated Alumina

Hydrated alumina was precipitated by carbonatation process. The chemical composition of hydrated alumina from precipitation of sodium aluminate solution and its anhydrated alumina after calcinations is shown in Tabel 3. The grade of alumina in hydrated alumina is 64.5 % Al_2O3 and the anhydrated alumina from calcination contains 98.67 % Al_2O_3.

Tabel 3. Chemical composition of hydrated alumina or aluminum hydroxyde ($Al(OH)_3$) and its anhydrated alumina from presipitation of sodium aluminate solution, detected by AAS

No.	Na_2O (%)	CaO (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	SiO_2 (%)	H_2O (%)	Al_2O_3 anhydrate (%)
1.	0,43	0,048	64,52	0,007	0,002	0,014	34,96	98,67
2.	0,45	0,047	64,53	0,008	0,003	0,012	34,95	98,69
3.	0,41	0,049	64,52	0,009	0,001	0,011	34,96	98,67

The chemical composition of imported alumina (from Australia) is shown in Table 4. The grade of Al_2O_3 resulted from extraction of bauxite residue is 98.67 % (Table 3), and it is likely similiar to the quality of imported alumina (Table 4).

Tabel 4. Chemical composition of imported alumina

Na_2O (%)	CaO (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	SiO_2 (%)
0,42	0,043	98,7	0,010	0,002	0,016

Figure 6 shows the XRD graphic of hydrated alumina which is resulted from precipitation of sodium aluminate solution. It contains bayerite ($Al(OH)_3$) and sodium aluminum carbonate hydroxide ($NaAlCO_3(OH)_2$). This hydrated alumina can be used as raw material for alums and PAC.
Sulfatation of Hydrated Alumina

Hydrated alumina obtained from extraction of bauxite residue was reacted with sulfuric acid, then it is added ammonium hydroxide and crystallized to produce ammonium aluminum sulfate crystals ($NH_4Al(SO_4)_2 .12H_2O$) with high purity as shown in Figure 7.

From above figures (Figure 6 & 7), we can see that all aluminum hydoxide has already changed to ammonium aluminum sulfate hydrate (alums) by sulfatation process. No iron detected in this alums, so that is physically shown of transparent alums. Husaini (2008) prepared alums who applied direct sulfatation of bauxite powder, however it produced brown colour of alums. The brown colour may be due to dissolved iron and other impurities from bauxite. This method needs next process after reducing the impurities from alums.

Chlorination of Hydrated Alumina

Hydrated alumina was chlorinated with HCl in stoichiometric amount to produce aluminum chloride ($AlCl_3$), then it was reacted by excess of hydrated alumina at mol ratio of OH/Al = 0.5 – 1.5 to form poly aluminum chloride ($Al(OH)_{1.2}$ $Cl_{1.8}$). Table 5 shows the products on chlorination of hydrated alumina at various mol ratio of OH/Al.

There are 2 (two) types of PAC in applications (Anonimous, 2010); the first type can be used for most applications, its contains Al_2O_3 18-20 % (9.5-10.6 % Al) and Cl 21-22 %, the second type mostly uses for drinking water treatment, its contains Al_2O_3 8.8-9.2 % (4.6-4.9 % Al) and Cl 9.8-11 %. The PAC resulted from this experiment (Code No.2) is considerably adjacent to the first type of PAC.

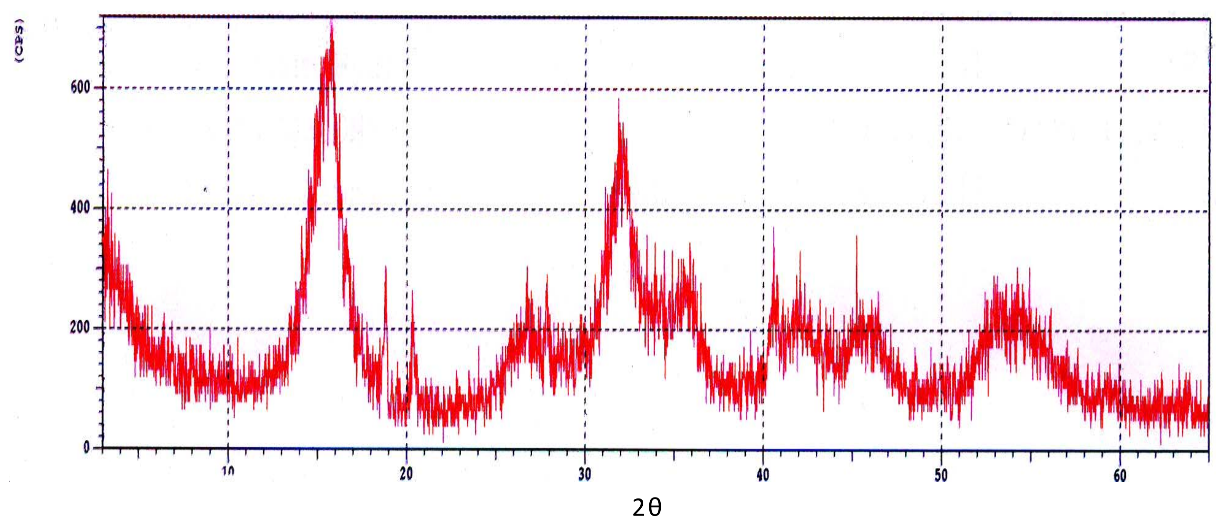


Figure 6. XRD graphic of hydrated alumina
(note: a=bayerite (aluminum hydroxide); b=sodium aluminum carbonate hydroxide)

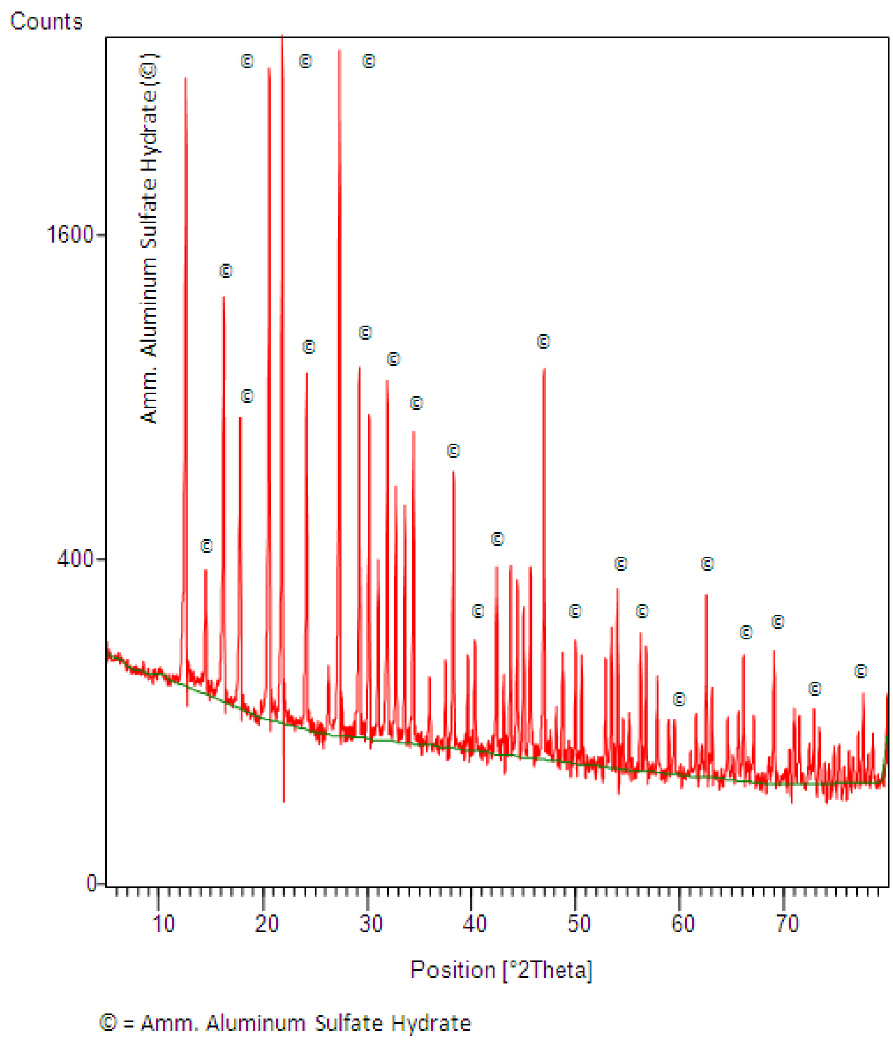


Figure 7. XRD graphyc of ammonium aluminum sulfate hydrate

Tabel 5. The reactans and products on chlorination of hydrated alumina with HCl at mol ratio of OH/Al = 0.5, 1.0, and 1.5 in PAC forming, detected by AAS

CodeNo.	$Al(OH)_3$ g	HCl 12 % weight (ml)	mol ratio OH : Al	Product,Al and Cl content in liquid PAC ($Al(OH)_{1,2}Cl_{1,8}$)	
				% Al	% Cl
1.	229	681	1.5	12.9	19.35
2.	235	732	1.0	10.1	19.33
3.	241	782	0.5	8.1	19.3

Figure 8 shows comparison floc setting time between experimental PAC (code-2) and imported PAC from Taki Chemicals, Japan. The figure shows that both of them have the same trend by pH, but experimental PAC resulted from this research has floc setting time little bit slower than that of imported one, it means that application of experimental PAC need more time to form floc and settle down to the bottom.

Iron Concentrate as By Product

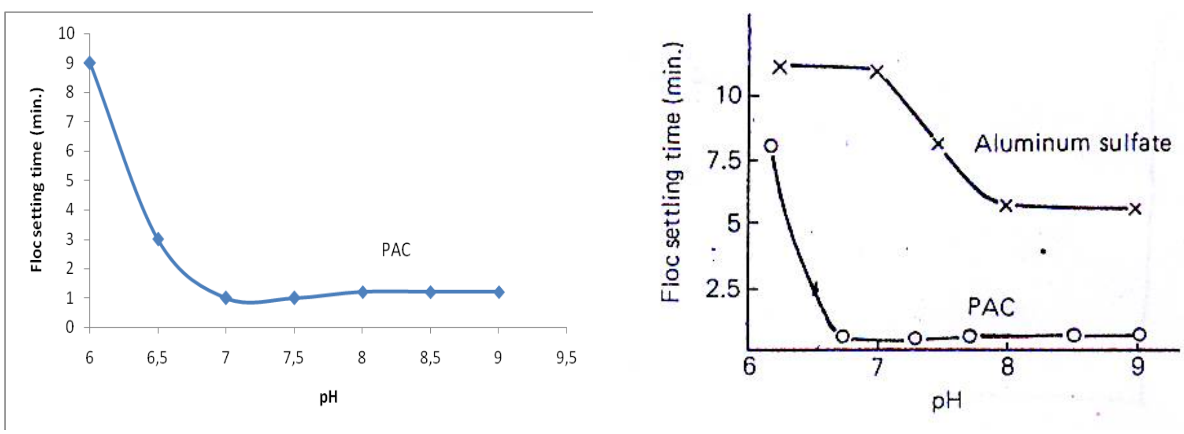
Iron content in leached residue was separated by magnetic separator at intensity of 1000 gauss to produce iron cocentrate 58-62 % Fe_2O_3. Table 6 shows the chemical composition of main compounds in iron concentrate. The value and recovery of Fe_2O_3 in iron concentrate for various sintering time were shown in Figure 9. At time interval of 1-4 hours, the iron content and recovery tend to decrease, the highest iron recovery (40 %) is occured at ½ hours of sintering time. To get better result, the iron concentrate need to be up graded by higher magnetic intensities.

CONCLUSION

– Amount of 75-85 % alumina could be recovered from bauxite residue by soda-lime sinter process at 800 ^{O}C, followed by leaching with sodium carbonate at room temperature.

– The highest extraction of alumina from bauxite residue is 85.20%, it is formed in such experimental condition (sintering temperature 800^{O}C, sintering time is ½ hours, leaching with 2 % wt. of sodium carbonate solution at room temperature, solid percentage is 11.8%, and agitation time is 2 hours). The value of alumina results up to 98,67 % Al_2O_3, it shows the same quality as imported alumina.

– Sintering temperature and time are very influenced to the recovery of alumina from bauxite residue. Higher sintering temperature would decrease the alumina extraction, and sintering time more than ½ hours reduces the extraction result.



(a) (b)

Figure 8. Floc setting time of resulted PAC code-2 (a); and imported PAC (b)

Table 6. Chemical composition (major compound) in iron concentrate, detected by AAS

No.	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	TiO_2 (%)
1.	61,91	17,79	3,53	9,70
2.	59,16	18,81	4,22	8,91
3.	58,23	21,04	4,14	9,33

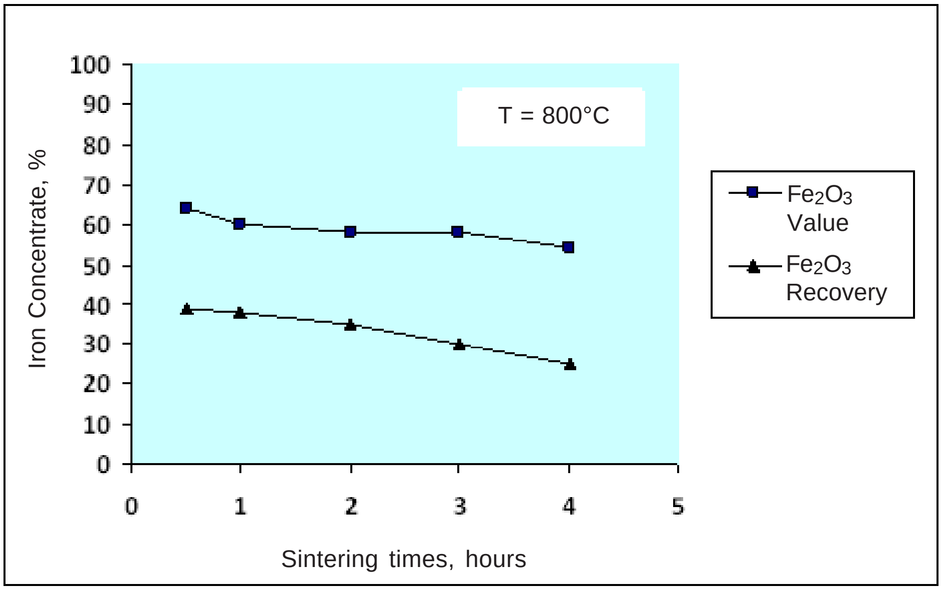


Figure 9. Iron concentrate from leaching residue of sinter at 800°C, separation by magnetic of 1000 gauss

– Sulfatation of hydrated alumina with adding of ammonium hydroxide results in high grade of ammonium aluminum sulfate $(NH_4Al(SO_4)_2 .12H_2O)$ crystals.

– Chlorination of hydrated alumina in stoichiometric amount at mol ratio of OH/Al = 1.0 results poly aluminum chloride (PAC) which is adjacent quality to the first type of PAC.

– Through the soda-lime sinter process it can also produce iron concentrate having grade of 66 % Fe_2O_3 with 40 % of recovery.

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PAC, Taki Chemicals Co., Ltd.