

Sulfuric Acid and Ammonium Sulfate Leaching of Alumina from Lampang Clay

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Received 14 August 2011; Accepted 24 September 2011

Abstract: The rapid development of the global alumina industry has led to a considerable increase in the production alumina and processing of alumina from non-bauxitic sources. Lampang clays comprise various minerals that contain about 22.70 wt% of extractable alumina. Local clay was ground, activated by calcination and treated with sulfuric acid to extract alumina. In the activation step, the effects of temperature and time on the extraction of alumina and iron were investigated. The leaching experiments were performed on clay samples with particle sizes less than 200 mesh. The samples were calcined at different temperatures, ranging from 450°C to 1050°C, and for different periods, ranging from 30 to 150 min. The optimum conditions for the extraction of alumina from Lampang clay include grinding the clay to pass through a 200 mesh sieve, calcining the ground clay at 750°C for 30 min, extracting the alumina from the calcined clay by leaching with 3M sulfuric acid, and using an acid to clay ratio of 80 wt% at 100°C for 120 min. An aluminum dissolution efficiency of 95.1 % was achieved under the conditions that resulted in the maximum dissolution efficiency of iron (26.6 %).

Keywords: Lampang clay, alumina, sulfuric acid leaching, ammonium sulfate leaching.

Introduction

Alumina is a white powder that is normally produced from bauxite ores through alkali leaching by the Bayer process. Many investigators have also tried to modify the Bayer process to utilize raw materials other than bauxite ore¹⁻⁷. Examples of non-bauxite raw materials include alunite, sillimanite, alusite, kyanite, kaolin, mica, and fly ash. Sulfuric acid is commonly used as a leachant for the recovery of alumina from ores, particularly for the direct acid leach process. Nitric acid and hydrochloric acid leaching processes for the recovery of alumina and other metals were developed decades ago. However, these processes have found few practical applications. In addition, hydrochloric acid and nitrate acid are expensive lixiviants in terms of acid cost, and large evaporative losses make these processes highly uneconomical. In contrast, sulfuric acid is cheaper than nitric acid or hydrochloric acid and can be easily obtained. Different concentrations of sulfuric acid have been reported for the extraction of alumina from calcined clays⁸⁻¹⁰. In general, the extraction

of alumina from calcined clays reportedly increases with increasing extraction time at a fixed temperature and also increases with increasing temperature at a fixed duration of extraction. A concentration of about 70 wt% sulfuric acid has been patented to produce aluminum sulfate¹¹. The aluminum sulfate can be precipitated from the solution by evaporation and cooling¹². When clay was heated to 1100–1200°C for 60 min; and then boiled with sulfuric acid with a concentration of 5–7 wt% for 60 min, alumina was extracted to 80 %. Leaching with sulfuric acid was carried out at 90°C and reached an acid concentration of 10–20 %¹³. Another patent reported 30 wt% as the recommended acid concentration¹⁴. A temperature of 105°C has been reported as a recommended extraction temperature¹¹. Another researcher recommended a temperature of 80°C for 858 min with 1M sulfuric acid to extract 90 % of alumina¹⁵. Other reports have detailed the production of ammonium aluminum sulfate, which represents a potential starting material for the preparation of alumina^{16–17}. Ammonium aluminum sulfate is commonly synthesized as an intermediate product for the production of alumina from Al-containing non-bauxitic raw materials¹⁸.

The purpose underlying the present work is the facilitation of alumina extraction from clays. Hence the influence of standard sulfuric acid processing and leaching via intermediate product processing has been investigated. This work details our investigation of the activation of Lampang clay by the calcination method and the leaching of alumina from the calcined clay by treatment with sulfuric acid. The effect of different variables on both the activation and leaching steps is investigated to allow a recommendation to be made for the most effective conditions for both processes.

Experimental

The chemical composition and structural vibration conformation of the clay samples were determined by X-ray fluorescence (XRF; Philips Minipal) and Fourier transform infrared spectroscopy (FT-IR; Shimadzu model). The X-ray diffraction (XRD) analysis was carried out on a Philips PW 1830 X'Pert powder diffractometer. Alumina and iron concentrations were analyzed with a Perkin Elmer inductively coupled plasma atomic optical emission spectrometer (ICP-OES) model Optima 5300 DV. The clay sample was ground in an agate mortar to a particles size of less than 200 mesh. In general, two leaching methods can be used to prepare alumina; standard sulfuric acid processing and leaching via an intermediate product. To prepare the alumina by standard sulfuric acid leaching, the clay sample was calcined in air at 450°C to 1050°C with a heating interval of 100°C. The duration of calcination was varied from 30 min to 150 min. The calcined clay samples were extracted by sulfuric acid with a concentration of 1, 2, 3, 4, or 5M.

Leaching tests were performed using 2M sulfuric acid leachant to investigate the effect of the following variables on the extraction step: a) reaction time: the effect of reaction time was studied over a range from 15 min to 180 min at 60°C to 100°C b) acid to clay ratio: the effect of the acid to clay ratio was studied over a range from 20 wt% to 100 wt% and the acid to clay ratio is equal to the quantity of acid used divided by the stoichiometric quantity of acid required. After leaching, the residue, which consisted mainly silica was filtered and then washed with hot water. The filtration was completed to a constant volume of filtrate then diluted and analyzed for alumina and iron by ICP-OES. Leaching via an intermediate product was conducted by following the same procedure as that for sulfuric acid processing, except that the mixed powder consisting of calcined clay and ammonium sulfate (the ratios of calcined clay to ammonium sulfate were 1:4, 2:3, 3:2

and 4:1 wt%) was reacted at 300–700°C for 60–180 min. The reaction product was poured into 100 mL of 0.5M to 4M H₂SO₄ solution and reacted at 70 to 90°C for 60, 180, or 300 min. The filtered leach liquor was analyzed for alumina and iron by ICP–OES.

Results and Discussion

Characterization of Lampang clay

XRF analysis showed that a representative sample of Lampang clay used in this study consists of 66.30% SiO₂, 22.70% Al₂O₃, 4.05% K₂O, trace amounts of 0.63% Fe₂O₃, 0.03% TiO₂, 0.05% CaO, 0.15% MgO, 0.49% Na₂O and a loss of ignition (LOI) of 5.10 wt%. The FT–IR of the clay is shown in Fig. 1. The bands at 1115, 1030, 1009, 694, 472, and 426 cm^{−1} are attributed to Si – O stretching. The bands at 795, 756, and 536 cm^{−1} are assigned to Si–O–Al stretching. The appearance of the band at 914 cm^{−1} is related to Al–OH stretching^{19–21}.

Standard sulfuric acid process

Effect of temperature and time of calcinations

The effects of calcination temperature on the extraction of alumina and iron are indicated in Table 1 and Table 2 respectively. The data indicate the following points: in an inert zone at temperature less than 450°C and greater than 950°C, the percentage dissolution of alumina is small. The percentage dissolution of alumina increase in a zone from 550°C to 850°C. The percentage dissolution decreases sharply when the temperature exceeds 850°C. The highest alumina dissolution (52.2 %) is reached at a calcination temperature of 750°C and a duration of 30 min, as can be seen from the data in Table 1. Therefore, a temperature of 750°C and a duration of 30 min are recommended for future experimental work.

The XRD patterns of Lampang clay (Fig. 2) predominately showed minerals, such as quartz, illite, and kaolinite. The heat treatment of Lampang clay transforms it into activated clay. Dehydration by thermal treatment converts clay to activated clay, which is semi-crystalline and much more reactive than the local clay. The temperature needed to completely transform local clay into activated clay was at least 650°C.

Table 1. Effect of calcinations temperature and duration of on alumina dissolution. Acid to clay ratio: 40 wt%; concentration: 2M sulfuric acid; extraction temperature: 80°C; extraction duration: 30 min.

Temperature of calcination (°C)	450	550	650	750	850	950	1050
Time of calcination (min)	Alumina dissolution (%)						
30	22.3	46.2	50.4	52.2	46.1	12.0	6.8
60	22.0	44.8	49.2	50.9	45.8	11.4	6.5
90	21.8	44.9	49.3	50.8	45.6	11.8	6.5
120	21.9	44.9	49.4	50.6	45.7	11.9	6.4
150	21.8	44.8	49.4	50.4	45.8	11.8	6.5

Table 2. Effect of calcination temperature and duration of on iron dissolution. Acid to clay ratio: 40 wt%; concentration: 2M sulfuric acid; extraction temperature: 80°C; extraction duration: 30 min.

Temperature of calcination (°C)	450	550	650	750	850	950	1050
Time of calcination (min)	Iron dissolution (%)						
30	1.2	4.9	5.4	5.5	4.8	0.8	0.5
60	1.3	4.9	5.4	5.4	4.7	0.7	0.4
90	1.3	4.8	5.3	5.4	4.7	0.7	0.4
120	1.3	4.9	5.3	5.5	4.8	0.7	0.4
150	1.4	4.8	5.4	5.5	4.7	0.8	0.5

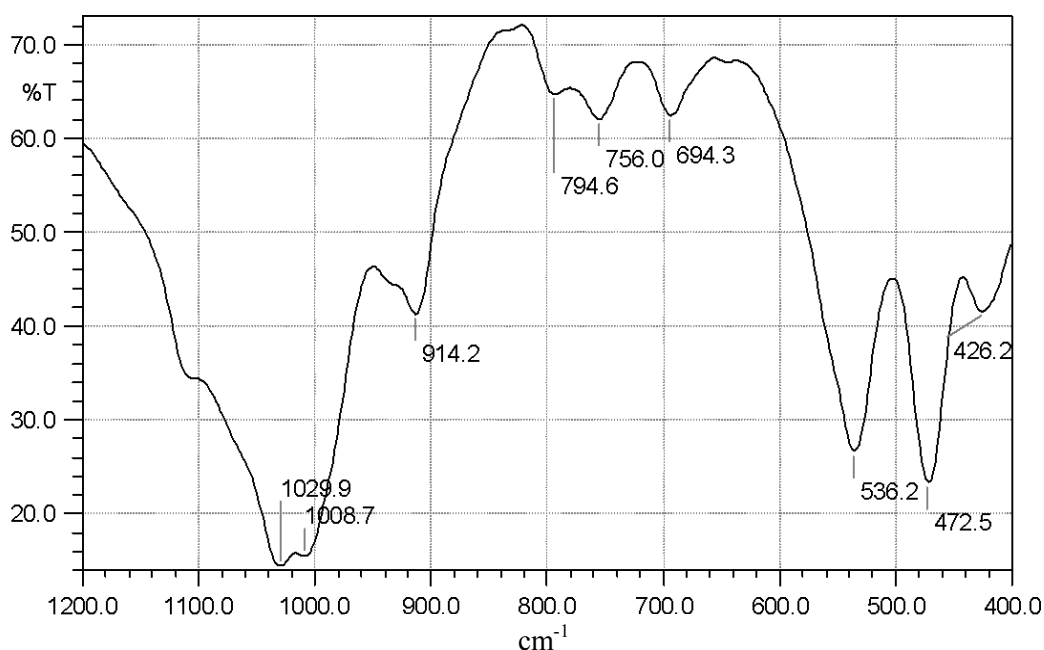


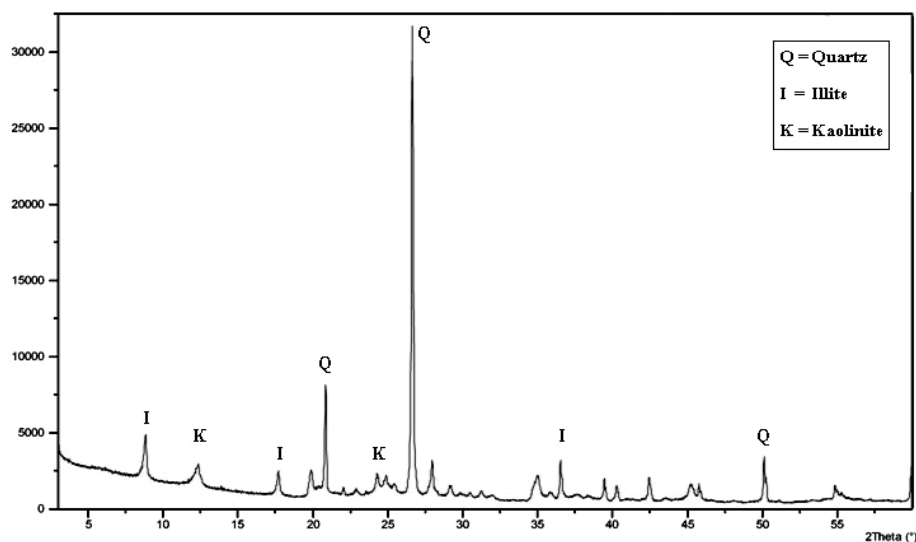
Figure 1. FT-IR spectrum of Lampang clay.

Effect of acid concentration on the extraction of alumina

The percentage dissolution (Table 3) efficiency initially increases, reaches a maximum and then decrease. The dissolution maximum occurs at an acid concentration of approximately 3M. An acid concentration of 3M corresponds to 65.1 % dissolution of alumina and to 6.0 % dissolution of iron. Therefore, an acid concentration of 3M is recommended for future experimental work.

Table 3. Effect of acid concentration on the dissolution of alumina and iron from clay calcined at 750°C for 30 min using an acid to clay ratio of 40 wt% at 80 °C for 30 min.

Concentration of H ₂ SO ₄ (M)	Dissolution (%)	
	Alumina	Iron
1	44.1	3.6
2	52.2	5.5
3	65.1	6.0
4	61.7	5.3
5	57.2	5.0

**Figure 2.** XRD pattern of Lampang clay.

Effect of time of extraction

Table 4 indicates that nearly 79.3 % of alumina dissolves during a 120 min extraction. By increasing the extraction time to 180 min, the efficiency increased to 80.1 % but this represent only slight increase in the efficiency achieved after 120 min. Therefore, a reaction time of 120 min is recommended. The corresponding results for iron are almost constant with respect to calcinations time.

Table 4. Effect of extraction time on the dissolution of alumina and iron from clay calcined at 750°C for 30 min using acid to clay ratio of 40 wt% under 3M sulfuric acid, 80°C and different extraction durations

Extraction duration (min)	Dissolution (%)	
	Alumina	Iron
15	60.3	4.2
30	65.1	6.0
60	72.1	9.9
120	79.3	10.5
180	80.1	10.0

Effect of acid to clay ratio

Table 5 shows that the alumina dissolution increases moderately as the acid to clay ratio increases. The percentage dissolution of alumina is almost constant when the acid to clay ratio exceeds approximately 80. Therefore, an acid to clay ratio of 80 wt% is recommended for future experimental work.

Table 5. Effect of acid to clay ratio on the dissolution of alumina and iron at different acid to clay ratios, with calcination at 750°C for 30 min and leaching with 3M sulfuric acid at 80°C for 120 min.

Acid to clay ratio (wt%)	Dissolution (%)	
	Alumina	Iron
20	74.6	5.7
40	79.3	10.5
60	81.6	14.2
80	84.6	16.4
100	83.7	17.4

Effect of the temperature of extraction

Table 6 shows that the extraction of alumina increases as the temperature increases. The increase in the alumina extraction when temperature is increased from 60°C to 100°C is about 39.9 %. This temperature is limited by the need to conduct the extraction below 100°C, to hydrolyze and therefore precipitate any dissolved titanium salts. The extraction of alumina from calcined clay at temperatures below 100°C renders titanium impurities present in the clay soluble in solution. However, at 100°C, soluble titanium sulfate is hydrolyzed to the insoluble form, which contaminates the product. The iron contaminant can be separated from the solution using hydrochloric acid^{1, 22}. Therefore, a temperature of 100°C (boiling temperature) is recommended.

Table 6. Effect of temperature on the extraction of alumina and iron from clays calcined at 750°C for 30 min, and leached with 3M sulfuric for 120 min at an acid to clay ratio is 80 wt%.

Temperature of extraction (°C)	Dissolution (%)	
	Alumina	Iron
60	55.2	12.3
70	74.4	15.0
80	84.6	16.4
90	91.9	24.8
100	95.1	26.6

*Leaching via intermediate product process**Effect of temperature and time*

The alumina extraction is almost constant for all calcinations temperatures although increases with temperature and time. The alumina dissolution increases for powders consisting of calcined clay (450 °C for 30 min) and ammonium sulfate mixed in a ratio of 2:3 that have been calcined at 400°C for 120 min in preparation for the next step of leaching.

Effects of the concentration of sulfuric acid, the volume of sulfuric acid, temperature and time

The results are listed in Table 7-Table 9. The results in Table 7 indicate no significant change in the extraction of alumina between 0.5M and 4M sulfuric acid, where as the dissolution of iron ranges from 29.6 % to 34.6 %. This result indicates that an acid concentration of 0.5M is suitable for the extraction. Based on the results presented in Table 8, a volume of 100 mL produced the greatest extraction efficiency for alumina. The iron extraction decreased moderately as the volume of acid increased. Based on these results it is clear that a volume of acid greater than 100 mL presents unacceptably low extraction efficiencies for alumina. Table 9 shows that the extractions of alumina and iron from the intermediate products moderately increase as the temperature and reaction time increase. The efficiency increased to around 58 % for alumina and 38 % for iron when the reaction time was increased to 180 min. However, the efficiencies remained almost constant beyond 180 min. The difference in the percentage dissolution of alumina between 180 min and 300 min is small. The results of leaching via an intermediate product show that a high alumina extraction efficiency was obtained for the intermediate products (clays calcined at 450°C for 30 min; ammonium sulfate=2:3; calcination at 400°C for 120 min). Leaching with 100 mL of 0.5M sulfuric acid at 90°C for 180 min (58.3 %) represents the optimal conditions for the extraction of alumina from intermediate products.

Table 7. Effect of acid concentration on the extraction of alumina and iron with a 2:3 ratio of calcined clay to ammonium sulfate, calcination at 400°C for 120 min, and leaching with 200 mL of sulfuric at 90°C for 180 min.

Concentration of sulfuric (M)	Dissolution (%)	
	Alumina	Iron
0.5	49.4	34.6
1.0	47.2	32.7
2.0	45.7	32.3
3.0	44.7	30.4
4.0	43.1	29.6

Table 8. Effect of the volume of sulfuric acid (0.5M) on the extraction of alumina and iron with a 2:3 ratio of calcined clay to ammonium sulfate, calcinations at 400°C for 120 min, and a reaction temperature of 90°C for 180 min.

Volume of sulfuric acid (mL)	Dissolution (%)	
	Alumina	Iron
100	58.2	38.4
150	52.9	32.6
200	49.4	29.2
250	40.3	27.3
300	38.7	25.2

Table 9. Effect of temperature and time on the extraction of alumina and iron with a 2:3 ratio of calcined clay to ammonium sulfate, calcination at 400°C for 120 min, and leaching with 100 mL of 0.5M sulfuric acid.

Time (min)	Dissolution of alumina (%)			Dissolution of iron (%)		
	Temperature (°C)					
	70	80	90	70	80	90
60	47.2	51.6	56.0	34.3	35.6	36.6
180	51.6	55.1	58.3	36.5	37.4	38.4
300	52.5	56.9	59.2	36.7	37.8	39.2

Conclusion

The best conditions for the extraction of alumina from Lampang clay (standard sulfuric acid processing) include grinding the clay to pass a 200 mesh sieve (Standard Tyler screens), calcination of the ground clay at 750°C for 30 min, extracting the alumina from the calcined clay by leaching with 3M sulfuric acid, and using an acid to clay ratio of 80 wt% at 100°C (boiling condition) for 120 min. An aluminum dissolution efficiency of 95.1 % was achieved under the same conditions that produced the maximum dissolution efficiency of iron (26.6 %). The optimum conditions for leaching alumina via an intermediate product show that a high alumina extraction efficiency was obtained by the following steps: (a) preparation of the intermediate product (calcined clays at 450°C for 30 min:ammonium sulfate=2:3; calcination at 400°C for 120 min) (b) the extraction of alumina from the intermediate product by leaching with 100 mL of 0.5M sulfuric acid at 90°C for 180 min. The results indicated that 58.3 % of alumina could be extracted. The amount of alumina obtained using the standard sulfuric acid processing was higher than that obtained from an intermediate product.

Acknowledgments

The authors are grateful to the Center for Innovation in Chemistry (PERCH – CIC) and the National Research Council of Thailand (NRCT) for the financial support to carry out this work.

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