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Extraction of Alumina from Local Clays by Hydrochloric Acid Process

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Abstract. A bench work study was carried out to investigate the use of kaolinitic clay containing 29.4% Al_2O_3 extremely abundant in Saudi Arabia for the production of pure alumina by calcination at 700°C for 1h (recommended by previous investigators) then leached by hydrochloric acid.

The effects of leaching temperature (25°C to boiling temperature), period of activation (10-150 minutes), acid concentration (1M – 6M), particle size (–8 to –200 standard Tyler screen mesh), acid to clay weight ratio (4:1 to 15 :1ml acid/gm clay) on alumina extraction were investigated.

The recommended leaching conditions are: 6 molar for acid concentration at boiling conditions under reflux, one hour for leaching time, –100 mesh standard Tyler screens for particle size of calcined clay and 10 ml acid/gm clay for acid to clay weight ratio. Leaching this local clay sample under these conditions resulted in 32% alumina extraction.

Local kaolinitic clay were calcined at temperatures varying between 400°C and 800°C at different calcination periods (5 to 120 minutes). The calcined clay was then leached with 3M HCl acid under the above-recommended leaching conditions. The optimum calcination conditions were 600°C and 1 hour for calcination temperature and time period, respectively. The corresponding alumina extraction from local clay sample is about 63%.

Keywords: Alumina extraction, Hydrochloric acid leaching, kaolinitic clay, Calcination.

1. Introduction

The raw material for manufacture of alumina, *i.e*. 'bauxite' has been discovered in the Kingdom of Saudi Arabia only in limited amounts. It is natural to look for the production of this important material through other available resources of raw materials that contain high alumina and low iron oxide content. One of the numerous aluminous raw materials distributed on a large scale in the Kingdom's land that contains a high percentage of aluminum oxide and low percentage of impurities is the kaolinitic clays. It is thought as a suitable substitute for bauxite from which alumina of high purity can be obtained.

Several sintering and acid-extraction processes have been investigated for the production of alumina from kaolin and other clays. The French Pechiney-Ugine Kuhlmann process treats clays and shales with concentrated sulfuric acid. Hydrochloric acid is added during the crystallization step to form aluminum chloride which crystallizes readily. Much raw material must be handled in the process, because the clays and shales have lower alumina content than bauxite[1]. Other methods involve the treatment of clays with different mineral acids or the continuous electrolysis of aluminum chloride[2].

It is reported in the literature that some of the more important advantages of using hydrochloric acid over other acids for leaching alumina are the ease of filtration of slurries, the ease of iron removal and the insolubility of titanium dioxide, which is present in many clays. The most serious problem connected with the use of hydrochloric acid is the severe corrosion; however, the development of corrosion resistant plastics and rubbers partially solved this problem so that the corrosion is no longer a prohibitive factor[3]. Both hydrochloric and sulfuric acids extract approximately the same quantity of alumina from each ton of clay[4-7]. It has been reported also that the silica residue is easily separated from the chloride solution, which filters rapidly, and a number of procedures have been proposed for eliminating iron from aluminum chloride solution[8, 9].

Bakr and El-Abd described in several papers the extraction of alumina from Egyptian kaolin by hydrochloric acid leaching[10, 11]. Optimum conditions have been worked out in respect of the variables involved such as fineness of kaolin, period and temperature of calcination, concentration of hydrochloric acid, acid to clay ratio and period and temperature of extraction. The production of a crude alumina from clay was also investigated on a pilot plant scale[12]. Weston described in several patents[13] the production of a purified alumina-silica product and substantially pure aluminum chloride from iron-containing bauxites, bauxitic clays, kaolinitic clays and mixtures thereof. The substantially iron free alumina-silica products were made by mixing the previous raw materials, agglomeration, calcining the mixture at approximately 650-900^{o}C and subjecting the calcined material to differential chlorination stages to produce a substantially iron-free product. The optimization of the crystallization process and concentration of impurities was controlled by $AlCl_3$ concentration in the feed solution, HCl gas flow rate, temperature and concentration of phosphorus and magnesium in the feed solution. Shanks[14] reported later that improvements were made by decreasing the initial leaching acid concentration from 25 to 20%, decreasing the leaching time 1 to 2 hour to 15 to 30 min eliminating the solvent extraction step for iron removal and eliminating the step to recover the aluminum content of the bleed-stream circuit.

Ozdemir and Cetisli[15] studied the extraction kinetics of alunite in sulfuric acid and hydrochloric acid in a batch reactor. The effects of reaction temperature, acid concentration, particle size, calcination temperature, calcinations time and acid/Al_2O_3 molar ratio on the extraction process were investigated. The calcination temperature was the most important parameter affecting the extraction process followed by reaction temperature. Other work reported in the literature on the extraction of alumina from clay by hydrochloric acid treatment include the work of Ziegenbalg *et al*.[16, 17], Poppleton and Sawyer[18], Eisele *et al*.[19, 20] and Shanks, *et al*.[21].

The aim of this paper is to investigate the possible manufacture of alumina from local Saudi clays, which are extremely abundant in the Kingdom, rather from the much scarcer bauxite. A bench scale study will be carried out to investigate the extraction of alumina from local clay by calcination and hydrochloric acid leaching of alumina. The effects of leaching temperature, period of activation, acid concentration, particle size acid to clay weight ratio and temperature and duration of calcination on alumina extraction were investigated to recommend the most suitable conditions.

2. Materials and Method

2.1 Materials

The clay sample selected for investigation was a kaolinitic clay obtained from Riyadh area (N: 24^o 00`36``, E = $47^o$ 44` 03``).

The chemical composition of the clay sample is given in Table 1. The analysis of local clay was done at the Chemical & Materials Engineering Department, College of Eng., KAU[22].

Table 1. Chemical composition of the local kaolinitic clay.

Compound	Natural local clay (%)
SiO_2	47.25
Al_2O_3	29.4
Fe_2O_3	2.87
TiO_2	1.17
MgO	0.35
CaO	0.59
K_2O	0.17
Na_2O	2.11
MnO	< 0.05
SO_3	< 0.05
P_2O_5	< 0.05
L.O.I.	16.02

2. 2 Methods

2.2.1 Grinding

The average size of the diameter of the raw local clay sample was about 2 to 3 inches. The clay sample was ground using a ball mill to –149 μm (100 mesh). The ground clay sample was placed on the sieve, and then mechanically shacked for 5 min. The oversize was further ground followed by sieving on the same sieve. The procedures were repeated till the entire clay sample passed through the sieve.

2.2.2 Calcination Experiments

Ground clay sample passing 100 mesh was subjected to calcination. A muffle furnace (Carbolyte) with a maximum temperature of 1200°C was used. The heating is carried out at 700°C for 1 h to activate the clay before acid treatment, which is reported in some previous work to be the recommended conditions for activation of local Saudi kaolinitic clays[22, 23].

2.2.3. Acid Leaching Experiments

Five grams of the calcined clay sample passing 100 mesh were leached using 3M hydrochloric acid for different periods of time (10-150 min) and at different leaching temperatures (25°C to boiling temperature) using a constant temperature shaking water bath at a fixed shaking rate of 160 cycles/min and using boiling under reflux. By the end of leaching, the resulting slurry was filtered to separate undissolved materials, washed three times with 10 ml portions of distilled water. The filtrate and washings were continued to a constant volume of 250 ml in a volumetric flask. The resulting solutions were diluted, analyzed for aluminum ion using solar MS Atomic Absorption Spectrophotometer[23].

The effects of leaching period, leaching temperature, and acid concentration on alumina extraction were investigated.

3. Results and Discussion

3.1 Effect of Extraction Time and Leaching Temperature

The effects of leaching time and temperature on the yield of alumina extracted from –100 mesh clay sample calcined at 700°C for one hour using 3M hydrochloric acid under different leaching temperatures ranging from 25°C to boiling under reflux at fixed acid to clay weight ratio of 10 are shown in Fig. 1. The figure shows that the percent of extraction of alumina from the clay is approximately constant after one hour at all leaching temperatures. Also, It shows that a relatively large increase in the percentage extraction of aluminum oxide is observed with increasing leaching temperature from 25°C to boiling temperature. Therefore, a reaction time and temperature were selected to be one hour and boiling temperature, respectively.

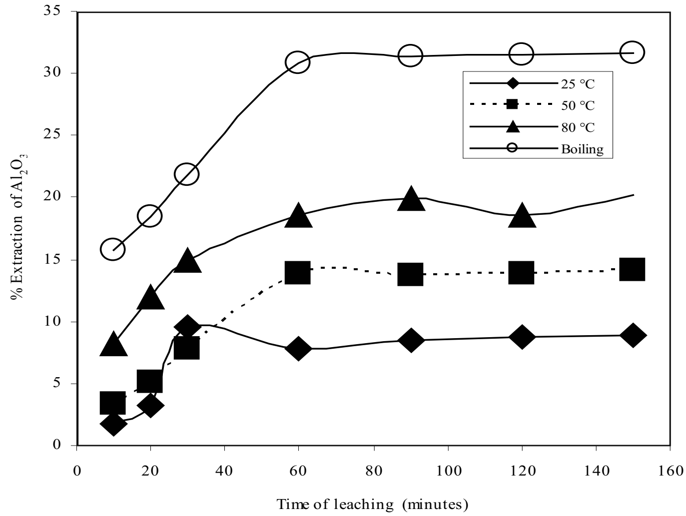

Fig. 1. Effect of leaching time and temperature on alumina extraction at acid to clay weight ratio of 1.

3.2 Effect of Acid Concentration

Results on the effect of varying acid concentrations from 1M to 6M on dissolution of alumina are illustrated in Fig. 2. It indicates that although alumina extraction increases with increasing acid concentration up to a value of 3M, the percent of alumina extracted using an acid concentration of 6M, however, decreases below that obtained at 3M acid concentration. It is expected that the diffusion rates of Al^{+++} ions from the solid to the solution increase as the concentration and diffusion of hydronium ion rise, a maximum is reached at concentration of 3 M HCl. The extraction rate at 6M HCl decreases. This may be due to the kaolin structure collapsing at this concentration or may be due that Al^{+++} species blocking H^+ diffusion. Similar behavior was also observed in other studies[18 – 21, 24].

Maximum alumina extraction observed from this specific local clay was still in the range of 31-32%.

3.3 Effect of Acid to Clay Weight Ratio

Results on the effect of varying acid to clay weight ratio on dissolution of alumina are illustrated in Fig. 3.

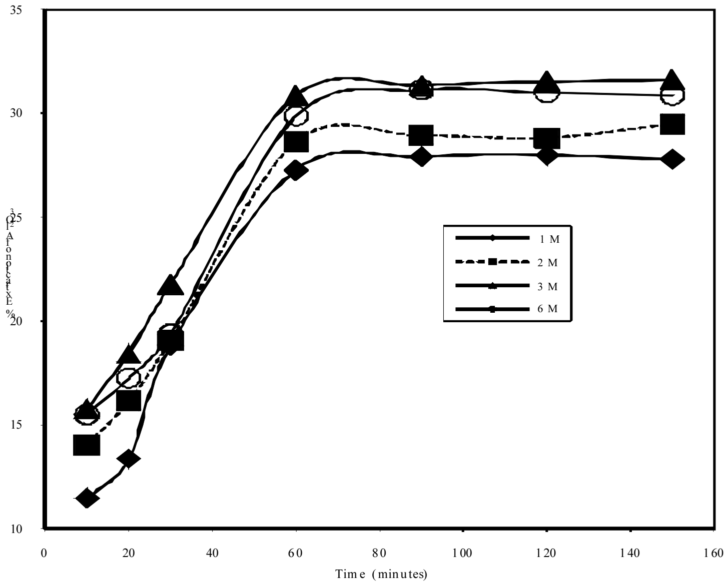

Fig. 2. Effect of leaching time and acid concentration on extraction on Al_2O_3 extraction at acid to clay ratio weight ratio of 10 and boiling temperature.

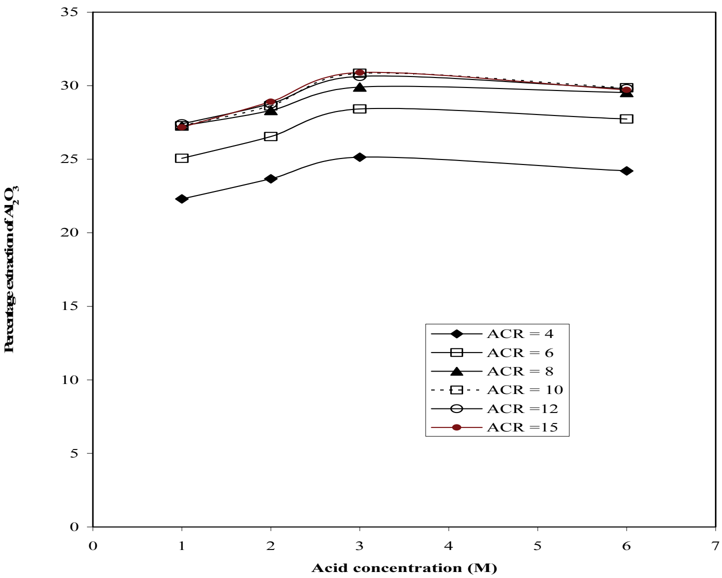

Fig. 3. Effect of acid to clay weight ratio on alumina extraction at different acid concentrations.

The data presented indicate that increasing acid to clay weight ratio from 4 : 1 to 8 : 1 increases the percentage of alumina extraction under the same calcination and leaching conditions, followed by a slight increase in the percentage of alumina extraction with increasing acid to clay ratio to 10 : 1, and approximately no change in the percentage of alumina extraction at higher ratios up to 15 : 1.

3.4 Effect of Particle Size of Calcined Clay

Figure 4 shows the effect of grain size of clay sample on the percentage of aluminum oxides extraction. All samples were calcined at fixed temperature of 700°C for a fixed period of one hour. Then the calcined samples were leached by 3M HCl using acid to clay weight ratio of 10 : 1 for one hour at boiling conditions under reflux and varying the mesh number of the clay sample over a wide range between –8 and –200 standard Tyler screen mesh. Figure 4 indicates that grinding the clay samples beyond –65 mesh has no significant effect on the extraction of alumina from the local clay sample. Therefore, a grain size of –100 Taylor mesh was selected for further work.

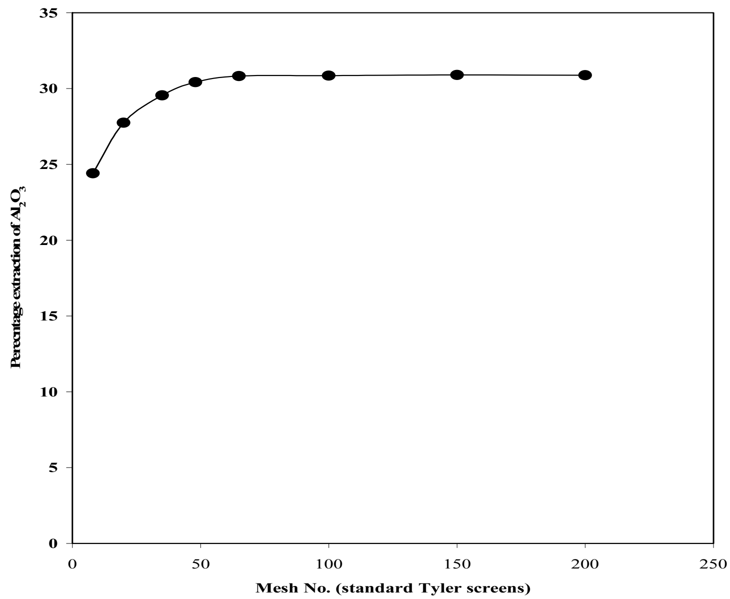

Fig. 4. Effect of particle size of calcined clay on alumina extraction using 3M HCl.

3.5 Effect of Temperature and Period of Clay Calcination

To investigate the effect of calcination temperature and time on the extraction of alumina, clay samples were calcined at different temperatures ranging from 400 to 800°C, each for different periods of time ranging from 5 to 120 minutes before leaching these –100 mesh calcined clay samples for 1 our under reflux. Figure 5 shows that the calcination temperature appears to be the most important parameter affecting alumina extraction. Below a calcination temperature of 450°C represent a negligible extraction zone exist. An active zone exists between 500 and 600°C and another inert zone exists after about 650°C. The alumina extraction yields increase from 17.02% to 62.94% over the range of 400 to 600°C for a calcination period of 60 min. The decrease in extraction beyond a calcination temperature of 600°C may be attributed to a total dehydration of clay samples at 600°C and to the solid phase transformation of alumina beyond 600°C. For this reason, the extraction yield of alumina continued to increase up to 600°C after which, the yield decreases. Similar behavior was also observed in previous studies[15, 24- 27]. These data also indicate that in the temperature range up to 650°C, alumina extraction yield increases with increasing calcination time, whereas, at calcination temperatures higher than 650°C, the alumina extraction yield decrease with increasing calcination time. This may be attributed to a partial sintering of clay subjected to larger periods of calcination at higher calcination temperatures. Therefore, the data shows that a calcination temperature of 600°C for 1 h gives the optimum conditions for alumina extraction from local clay samples. The corresponding alumina extraction is 62.94%. Similar results were observed by Ting[24].

4. Conclusion

Approximately 62.9% of alumina present in a local Saudi clay can be extracted by calcination followed by a leaching step using hydrochloric acid. The recommended extraction procedure is ‘a’ first step calcination at 600°C for a period of one hour, followed by a leaching step of the calcined clay after grinding and sizing to a 100 standard Taylor screen. Leaching should be carried out using 3M solution of HCl at boiling conditions under total reflux for a period of one hour using a

10 : 1 liquid to solid weight ratio. Leaching this local clay sample under theses conditions result in 62.94% extraction of alumina.

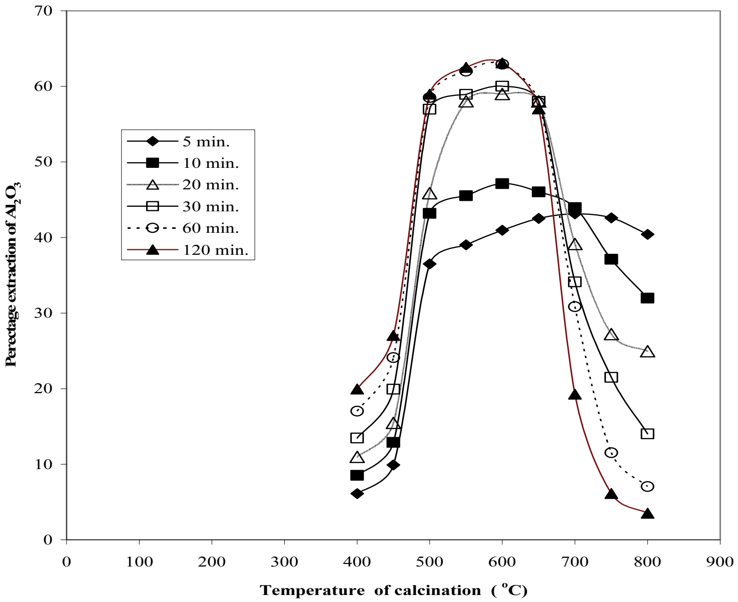

Fig. 5. Effect of temperature and period of clay calcination on alumina extraction using 3M HCl.

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إنتاج الألومينا من الطفلة الوطنية بالمعالجة بحامض الأيدروكلوريك

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المستخلص. تم إجراء دراسة معملية حول استخدام خامات الطفلة من النوع الكاوليني تحتوي على ٢٩,٤٪ المتوفرة بكميات كبيرة في أراضي المملكة لإنتاج الألومينا النقية بالتحميص عند درجة ٧٠٠ مئوية لمدة ساعة، ثم الاستخلاص بحامض الأيدروكلوريك. وقد تمت دراسة تأثير درجة الحرارة (من ٢٥ مئوية إلى درجة الغليان) وزمن المعالجة (١٠ إلى ١٥٠ دقيقة) وتركيز الحمض (١– ٦ مولار) وحجم الحبيبات (٨ – ٢٠٠ مناخل تايلر) واستخدام نسبة وزنية من الحامض إلى الطفلة تساوي (١ : ٤ إلى ١: ١٥ حامض الأيدروكلوريك\جم طفلة) على نسبة استخلاص الألومينا.

وقد وجد أن الظروف المثلى للعوامل السابقة والتي تؤدي إلى أعلى نسبة استخلاص هي: ٣ مولار لدرجة تركيز الحمض ودرجة حرارة مماثلة لتلك تحت ظروف الغليان وساعة واحدة لزمن تفاعل و –١٠٠ لمقاس حبيبات الطفلة و١٠ (ملل حامض الأيدروكلوريك \جم طفلة) لنسبة محلول حامض الأيدروكلوريك إلى الطفلة. وقد كانت النسبة المئوية لاستخلاص الألومينا عند معالجتها بالحمض تحت الظروف السابقة مساوية ٣٢٪.

وقد تم تحميص خامات الطفلة من النوع الكاوليني تحت درجات حرارة تتراوح بين ٤٠٠ الى ٨٠٠ درجة مئوية لمدد

زمنية تتراوح من ٥ إلى ١٢٠ دقيقة ثم تمت معالجتها بالحمض تحت الظروف المثلى السابقة. وقد وجد أن الظروف المثلى لتحميص الطفلة هي ٦٠٠ درجة مئوية لمدة ساعة حيث أعطت نسبة استخلاص مقاربة ٦٣ ٪.