International Journal of Research in Advanced Engineering and Technology
Online ISSN: 2455-0876
www.engineersjournals.com
Volume 1; Issue 1; October 2015; Page No. 64-72

Kinetics studies of hydrochloric acid leaching of alumina from Agbaja clay

[1] Udeigwe Uchenna, [2] Okechukwu Dominic Onukwuli, [3] Ajemba Regina, [4] Ude Callistus Nonso

[1, 2, 3] Department of Chemical Engineering, Nnamdi Azikiwe University. P.M.B 5025, Awka, Anambra State, Nigeria.

[4] Projects Development Institute, PRODA, Emene-Enugu, Enugu State.

Abstract
Obtaining alumina from Agbaja clay was seriously hindered due to small surface area and presence of negative surface charges. The research was targeted towards the modification of the local clay by thermal treatment and investigation of the kinetic models. The clay was characterized using FTIR, XRD and SEM. The effects of temperature and time on the calcinations process was studied in the temperature range of 400-900 ^{o}C and at the time range of 30-180 minutes. Effects of particle size, concentration of the acid, acid-clay weight ratio, stirring speed and leaching temperature on alumina yield were studied. Results obtained revealed that with the exception of particle size, increasing all the process parameters increased the yield of alumina. The optimum calcinations conditions were found to be 700 ^{o}C for a period of 1hr.
The dissolution process followed the liquid-film diffusion controlled model and the kinetic equation was obtained as

$1-(1-x)^{2/3} = 0.0075C^{0.552}_{[HCl]}\,(dp)^{-0.482}\,(l/s)^{0.491}(sp)^{0.6388}\exp(-34/RT)t$

Activation energy was calculated to be 34KJ/mol.

Keywords: Dissolution, alumina, calcinations, kinetics, liquid film diffusion.

1. Introduction

Though alumina is known to be produced from bauxite, the bauxite is not present in commercial quantity in some countries to meet up with the increasing demand for alumina. This led to radical search for alternative raw materials from which alumina can be produced. One of the most abundant raw materials with high alumina content available in Nigeria is clay (Ogbuagu, *et al.,* 2007). Most Nigerian clays have been reported by some authors to have very large content of alumina. Ajemba and Onukwuli, (2012) reported that most Nigerian clays contain as much as 25-40% alumina which can be readily extracted for industrial uses.
Different acids are employed for the leaching of alumina from clays (Al-Zahrani and Abdul, 2009). The most important of these acids are hydrochloric acid and tetra-oxosulphate (vi) acid. Due to corrosion effect, there was a slight drop in the use of hydrochloric acid but recent development of corrosion-resistant plastics and rubber has partly solved this problem (Peters *et al.,* 1962). No matter the alumina content in particular clay, leaching the raw clay has not produced desirable results. Works by several authors (Ozdemir and Cetisli, 2005; Poppleton and Sawyer, 1977; Eisele, 1983) have reported greater yield of alumina for calcined clay samples over the raw clay samples. In the leaching of Saudi local kaolin in hydrochloric acid, an approximate yield of 62.9% was obtained by Al-Zahrani and Abdul, (2009). Ting, (1952) had obtained similar results. Hulbert and Hoff, (1970) studied the kinetics of alumina removed from calcined kaolin with nitric acid, sulpuric acid and hydrochloric acids and found that the leaching of alumina from clay in these acids could be described by a nucleation rate equation. Ajemba and Onukwuli, (2012) in their work in leaching of alumina from Ukpor clay with hydrochloric acid found that the leaching process could be described by product layer diffusion reaction controlled model and calculated the activation energy to be 39.009KJ/mol.
In the study of dissolution kinetics and leaching of Rutile ore in hydrochloric acid, Alafara *et al.,* (2009) reported that dissolution rate was greatly affected by hydrogen ion concentration, stirring speed, particle size and leaching temperature and the diffusion-controlled shrinking core model was reported to have explained the leaching process. Other works that reported alumina leaching in hydrochloric acid present in the literature include the works of Ziegenbalg and Discher, (1983); Eisele *et al* (1983); Christensen, (1943) and Bakr and El-Abd, (1969). Therefore, this study focused on kinetics studies of hydrochloric acid leaching of alumina from Agbaja clay.

2. Materials and methods

2.1 Sample preparation and characterization

The clay material was mined at Agbaja in Kogi State Nigeria. The mined clay was soaked in water for two days after which the impurities were removed and the clay sun-dried for 24 hours then oven-dried at 60 ^{o}C for 18hours. The sample was then grinded with porcelain mortar and pestle, sieved into various sizes and calcined in a furnace in the temperature range of 400 to 900 ^{o}C. The duration of calcinations was varied from 30 to 180 minutes.
The X-ray fluorescence spectrometer (XRF: Phillips) was used to determine the chemical composition, the Scanning Electron Microscope (SEM) was used to study the morphology of both the raw and activated clay and the structural vibration conformation of the clay sample were determined using the Fourier transform infrared spectroscopy (FTIR; Shimadzu FT S8400 model). The aluminum ion content in the leach solution

was analyzed with MS- Atomic Absorption Spectrophotometer (AAS).

2.2 Calcinations experiment

To evaluate effects of calcinations temperature and time of calcinations, the samples were subjected to heat treatment in a muffle furnace and the temperatures considered where 400 ^{o}C, 500 ^{o}C, 600 ^{o}C, 700 ^{o}C, 800 ^{o}C and 900 ^{o}C at different periods of 30min, 60min, 120min and 180minutes making a total of 24 activated samples. The samples were all ground to the same particle size of 0.045mm and properly labeled. They were subjected to the same leaching conditions.

2.3 Leaching experiment

Leaching experiments were carried out using the calcined samples in a reflux system on a magnetic stirrer and temperature was measured with a thermometer. 12g of the calcined sample was added to already determine volume of the acid and heated while stirring continuously. After every 15min of leaching, 1ml of leaching solution was taken out of the round bottom flask by a pipette. The collected sample of leached liquor was cooled, filtered and used for alumina estimation using AAS. The dissolution fraction of the alumina in the slurry was calculated by:

$$X = \frac{amount\ of\ Al^{3+}\ in\ the\ solution}{total\ amount\ of\ Al^{3+}\ in\ original\ sample}\ x\ 100 \qquad (1)$$

Experiments were performed using the calcined sample to investigate the effects of the following variables on the leaching process: Particle size, (mm): 0.045, 0.105, 0.25 and 0.54; Acid concentration, (M): 0.5, 1.5, 2 and 3; Liquid-solid ratio, (cm^3/g): 4, 8, 10 and 16; Stirring speed, (rpm): 90, 360, 540 and 720 and Leaching temperature, (°C): 45, 65 and 85.

3. Results and discussions.

3.1 XRF Characterization of the clay sample

The XRF characterization was performed to know the chemical composition of the minerals that are present in the clay sample and the result is shown in Table 1.

Table 1: The XRF results of the raw clay sample.

Chemical composition	% composition	Chemical composition	% composition
Al_2O_3	34.50	TiO_2	3.50
SiO_2	40.20	Cr_2O_3	0.19
Fe_2O_3	12.00	V_2O_5	0.15
CaO	0.50	NiO	0.57
MnO	0.09	CuO	0.20
K_2O	4.12	Rh_2O_3	2.99
Ga_2O_3	0.19		

3.2 FTIR characterization

Fourier Transform Infra-red (FTIR) studies of the raw and activated materials helps in the identification of various forms and shown in Figures 1a and 1b respectively. The coupled vibrations are appreciable due to the availability of various constituents. Nevertheless, observed bands (in the range, 4000–500 cm^{-1}) have been tentatively assigned. In the IR studies of clay, the Si–O stretching vibrations were observed at 790·9 cm–1, 693·4 cm^{-1}, 538·8 cm^{-1} and 468·9 cm^{-1} showing the presence of quartz (Marel and Bentelspacher 1976). The appearance of ν (Si–O–Si) and δ (Si–O) bands also support the presence of quartz (Marel and Bentelspacher 1976), a strong band at 3696·7 cm^{-1}, 3622·5 cm^{-1} and 3450·4 cm^{-1} indicate the possibility of the hydroxyl linkage. However, a broad band at 3450·4 cm^{-1} and a band at 1633·4 cm^{-1} in the spectrum of clay suggest the possibility of water of hydration in the adsorbent.

The inter layer hydrogen bonding in clay is assigned by a characteristics band at 3622·5 cm^{-1}. Most of the bands such as 3696·7 cm^{-1}, 3622·5 cm^{-1}, 3450·4 cm^{-1}, 1033·3 cm^{-1}, 914·5 cm^{-1}, 790·9 cm^{-1}, 693·4 cm^{-1}, 538·8 cm^{-1}, 468·9 cm^{-1} show the presence of kaolinite. The vibrations observed at 914·5 cm^{-1} indicate the possibility of the presence of hematite. The presence of bands at 3696·7 cm^{-1}, 3622·5 cm^{-1}, 3450·4 cm^{-1}, 2369·8 cm^{-1}, 1633·4 cm^{-1}, 1033·3 cm^{-1}, 914·5 cm^{-1} and 790·9 cm^{-1} indicate the possibility of the presence of illite, whereas 3622·5 cm^{-1}, 1633·4 cm^{-1}, 1033·3 cm^{-1} are indicative of gypsum and 693·4 cm^{-1} shows the possibility of the presence of calcite. Thus the results of IR are quite helpful in the identification of various forms of minerals present in the used sorbents. IR spectra of these sorbents show adsorption band at 3622·5 cm^{-1} of clay corresponding to H2O vibrations, indicating the hydrous nature of these materials and the presence of hydroxyl linkage. However, owing to the mixing of various overtones and complexity of the spectrum of clay, distinct assignments of various other vibrations have not been made. For the activated sample, in the IR studies of clay, the Si–O stretching vibrations were observed at 774.45 showing the presence of kaolin (Marel and Bentelspacher 1976). The band of 857.39 and 3450.77 indicate the possibility of the hydroxyl linkage. The band of 1875.84 in the spectrum of clay suggests the possibility of water of hydration in the clay.

The bands such as 774.45 and 857.39 show the presence of kaolinite. The vibration observed at 669.32 indicates the possibility of the presence of Quartz, whereas 2353.23 is indicative of phenyl ring.

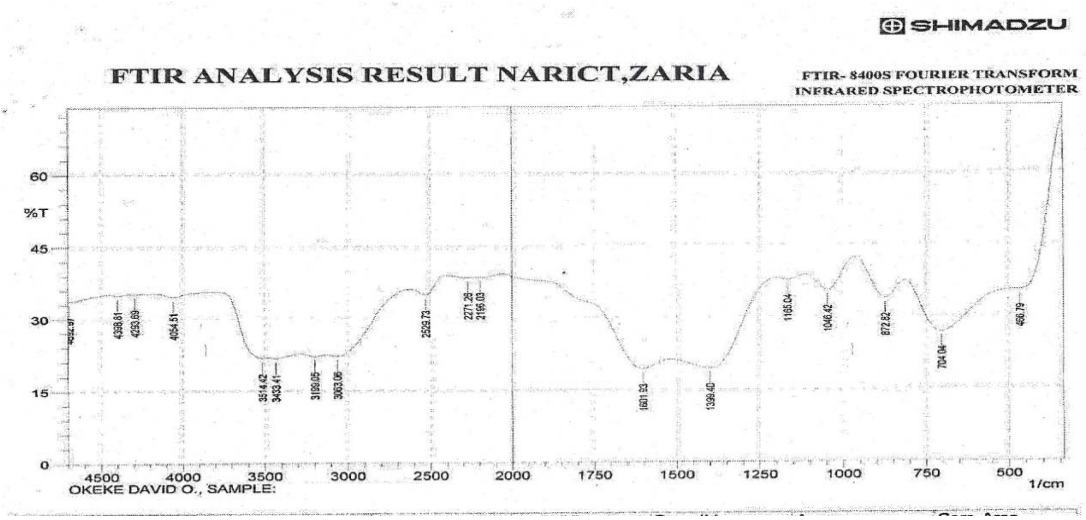

Fig 1a: FTIR result of the raw clay

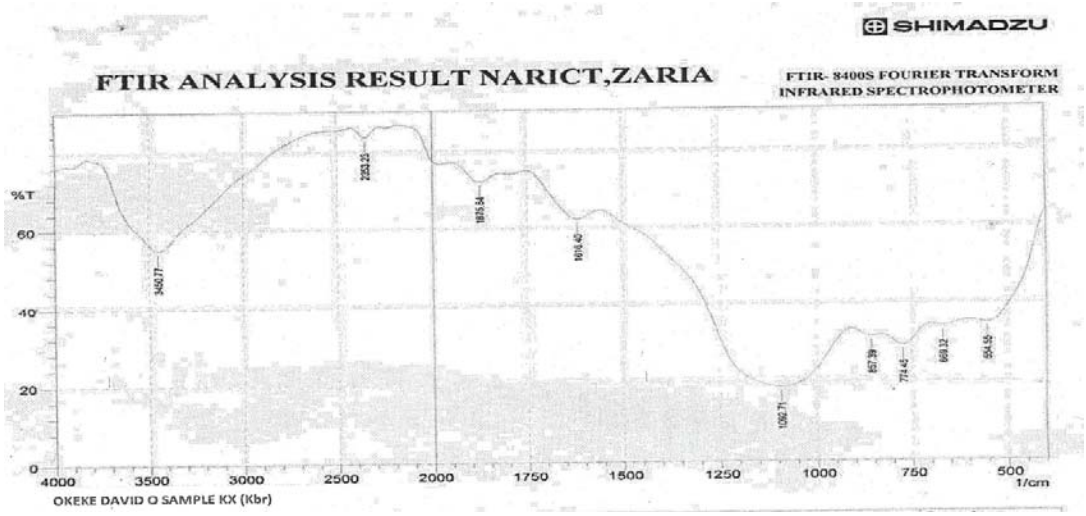

Fig 1b: FTIR result of the activated clay

3.3 SEM results for raw and activated clay samples

Morphology of the solid sample could be seen through the use of SEM as shown in Figures 2a and 2b. The result showed that the pores are more opened after the calcinations process.

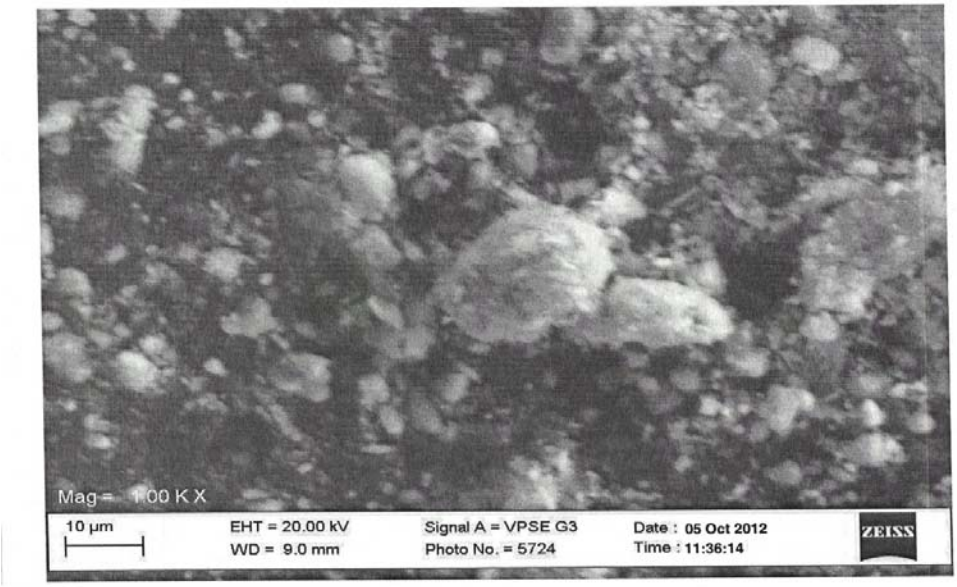

Fig 2a: Result of SEM for the raw clay sample

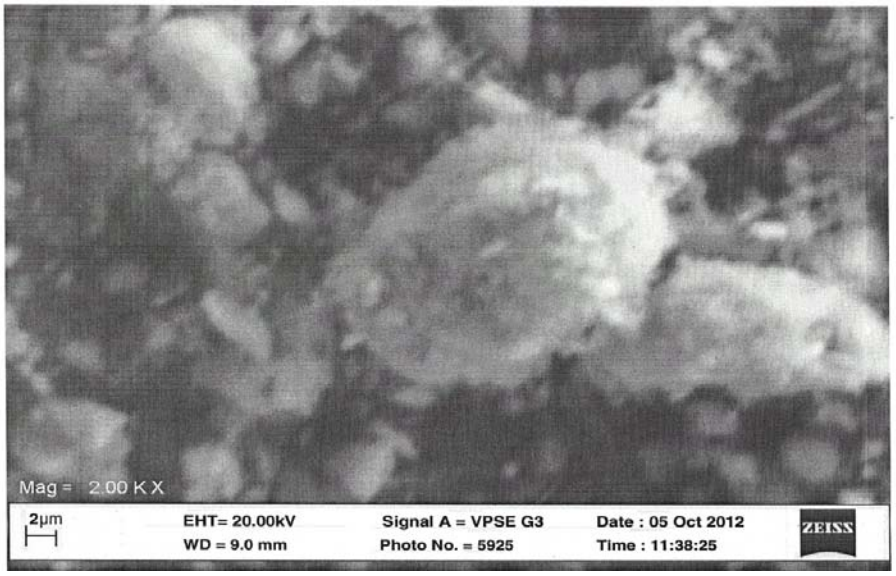

Fig 2b: Result of SEM for the activated clay sample

3.4 Effect of temperature and time on calcinations process

Experimental results of the effect of varying the calcinations time and temperature on the yield of alumina (Figure 3) revealed that below the temperature of 500 °C showed an inert zone for the extraction of alumina. A sharp increase in yield occurred in the temperature range of 600-700 °C, this was due to the chemically bonded water being removed to modify the crystalline structure of the clay, creating cracks in the clay particle to allow leach liquor reach the alumina embedded into particles. Higher temperatures above 800 °C revealed a general decrease in alumina yield which may be due to total dehydration and solid-phase transformation of alumina beyond 700 °C. Larger periods of calcinations at temperatures beyond 700 °C showed a decrease in alumina yield which may be due to the partial sintering of clay subject to larger periods of calcinations at higher temperatures. The highest yield was recorded at a temperature of 700 °C at a period of 1hr. These results are in agreement with previous researchers (Al-Zarhani, 1999; Ozdemir *et al.,* 2005; Tinget *et al.,* 1997).

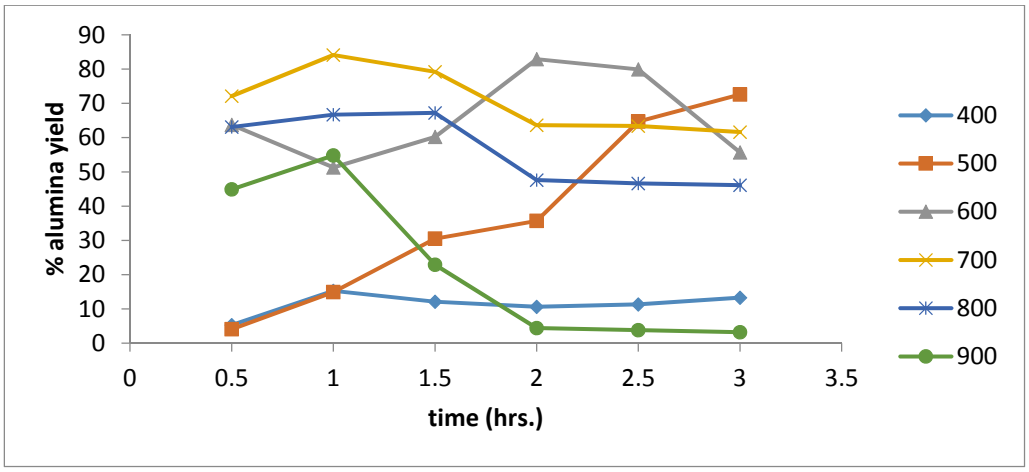

Fig.3: Effect of temperature and time of calcinations

3.5 Effects of dissolution parameters

The reaction mechanism and kinetics for the dissolution of alumina in hydrochloric acid was investigated by the variation of the fraction of alumina removed with time at different values of the process parameters. The process parameters (Figures 4; 5; 6; 7 and 8) considered were particle size; leaching temperature; acid concentration; liquid-solid weight ratio and stirring speed.

3.5.1 Effect of particle size

To study the effect of particle size on alumina yield, four different particle sizes of 0.054mm, 0.105mm, 0.25mm and 0.54mm were used at acid concentration of 3M, stirring speed of 540mm, liquid-solid ratio of 16 and leaching temperature of 85 °C. Experimental results of the effect of particle size on alumina yield (Figure 4) revealed that as particle size of clay decreased, the yield of alumina increased. This may be due to the fact that the smaller particle sizes have larger surface area to contact the solvent hence more alumina ions were exposed to the solvent. Highest yield was recorded with the particle size of 0.045mm while the particle size 0.54mm being the biggest produced very low alumina yield.

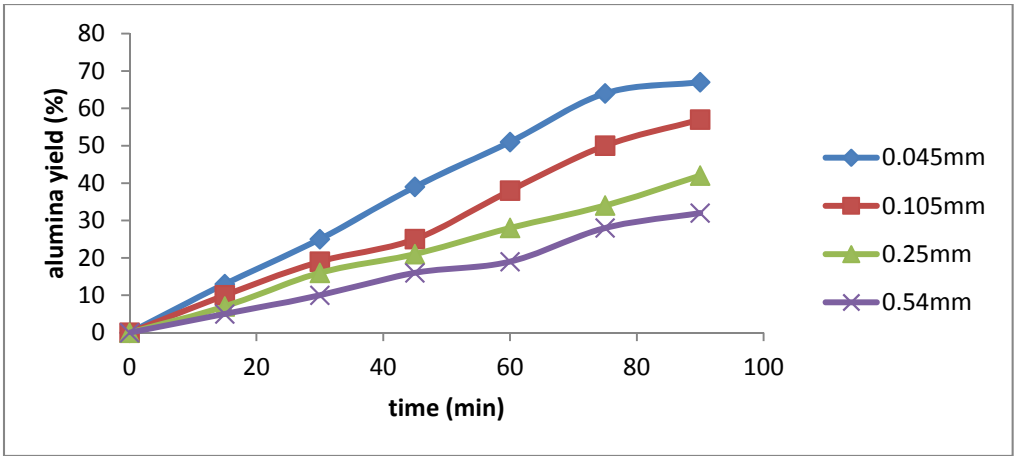

Fig 4: Effect of particle size and time on alumina yiel

3.5.2 Effect of acid concentration on alumina yield.
The particle size that gave the highest yield was used to study the effect of concentration on alumina yield at the liquid-solid ratio of 16; stirring speed of 540rpm and at 85 ºC. Acid concentration was varied from 0.5M to 3M. Experimental result of effect of acid concentration on alumina yield (Figure 5) revealed that as acid concentration increased, the fraction of alumina extracted from the clay also increased. Maximum yield of alumina was recorded at the highest concentration of 3M and the least yield at 0.5M concentration.

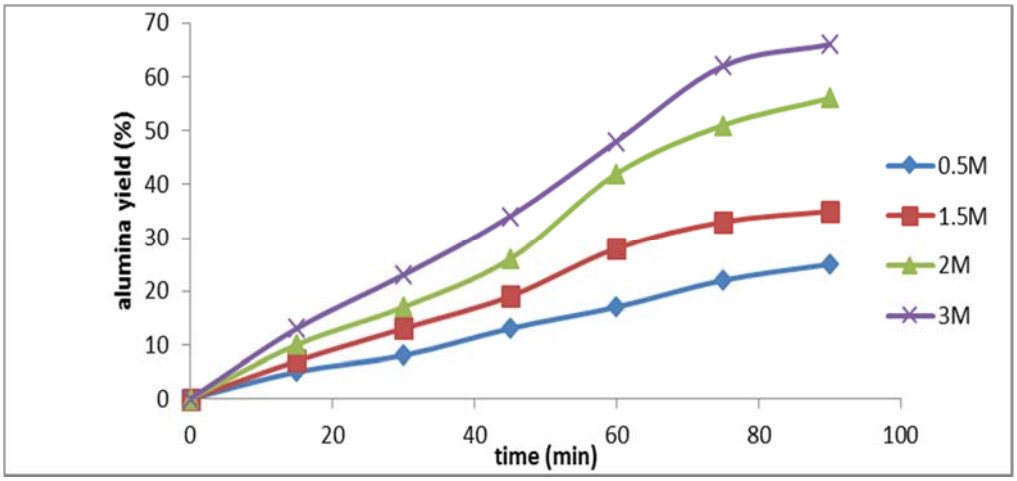

Fig 5: Effect of acid Conc. and time on alumina yield.

3.5.3 Effect of acid-clay weight ratio
The optimum particle size and acid concentration were used at stirring speed of 540rpm and at 85 ºC. The four levels of liquid-solid ratio considered were 4, 8, 10 and 16. Experimental result of effect of acid-clay weight ratio on alumina yield (Figure 6) revealed that as the acid-clay weight ratio increased, the fraction of alumina extracted increased since the clay samples have more leaching solvent to contact with, which resulted to more efficient dissolution.

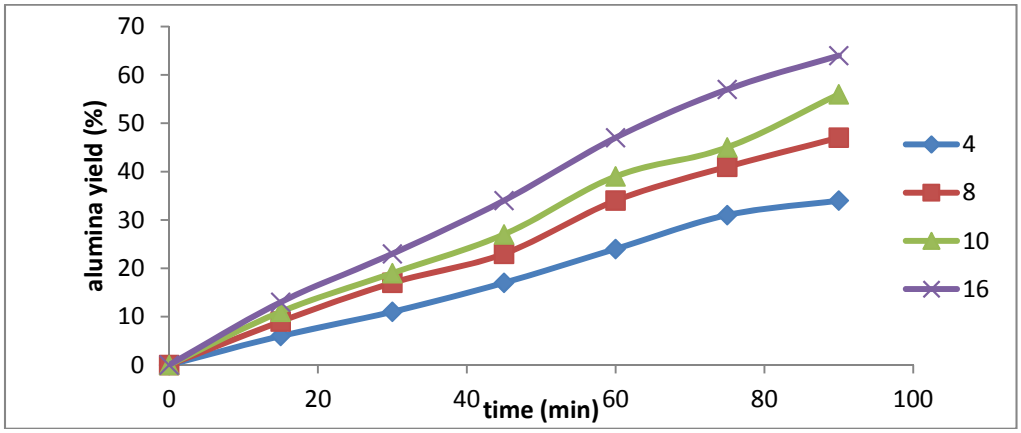

Fig 6: Effect of acid-clay weight ratio on alumina yield.

3.5.4 Effect of stirring speed on alumina yield

Different stirring speeds were investigated to determine effect of stirring speed on alumina yield. Experimental result of effect of stirring speed on alumina yield (Figure 7) revealed that alumina yield increased with stirring speed. A very low stirring speed of 90rpm had very low yield while the highest yield was recorded at 720rpm.

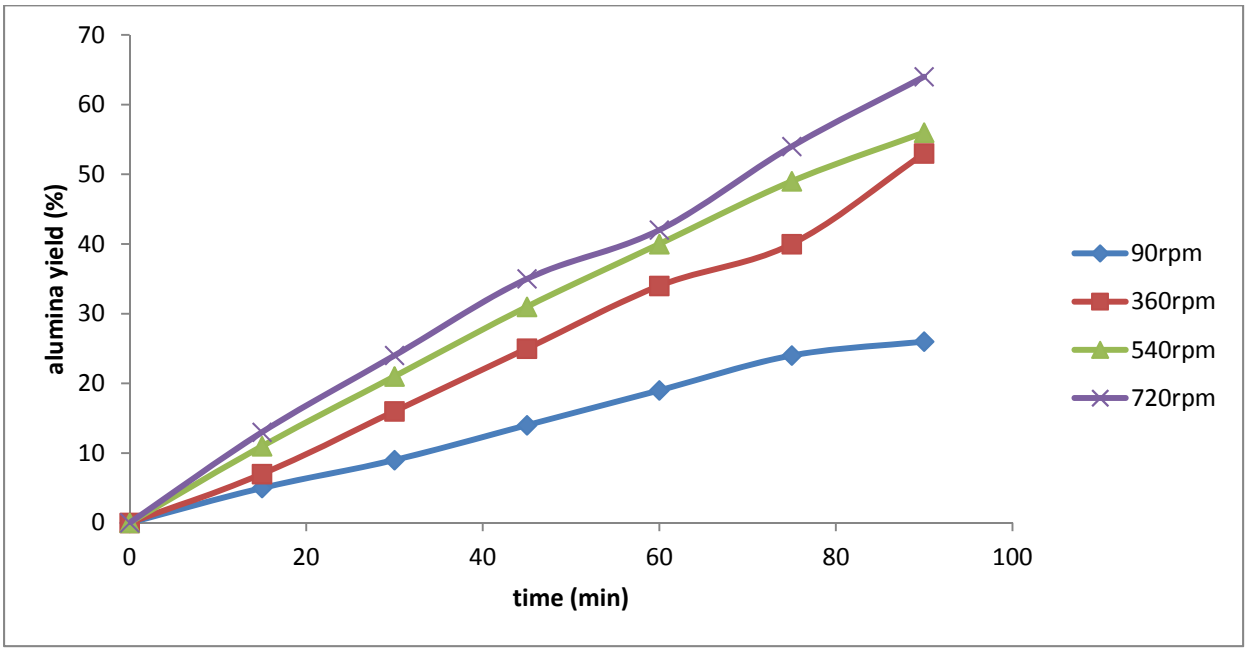

Fig 7: Effect of stirring speed and time on alumina yield.

3.5.5 Effect of leaching temperature on alumina yield

The effect of temperature on alumina yield was studied. Experimental result on the effect of leaching temperature on alumina yield (Figure 8) showed that as temperature increased, the rate of dissolution of alumina increased since higher temperatures increased kinetic energy of the reacting particles for more collisions to take place which directly resulted to increased alumina yield.

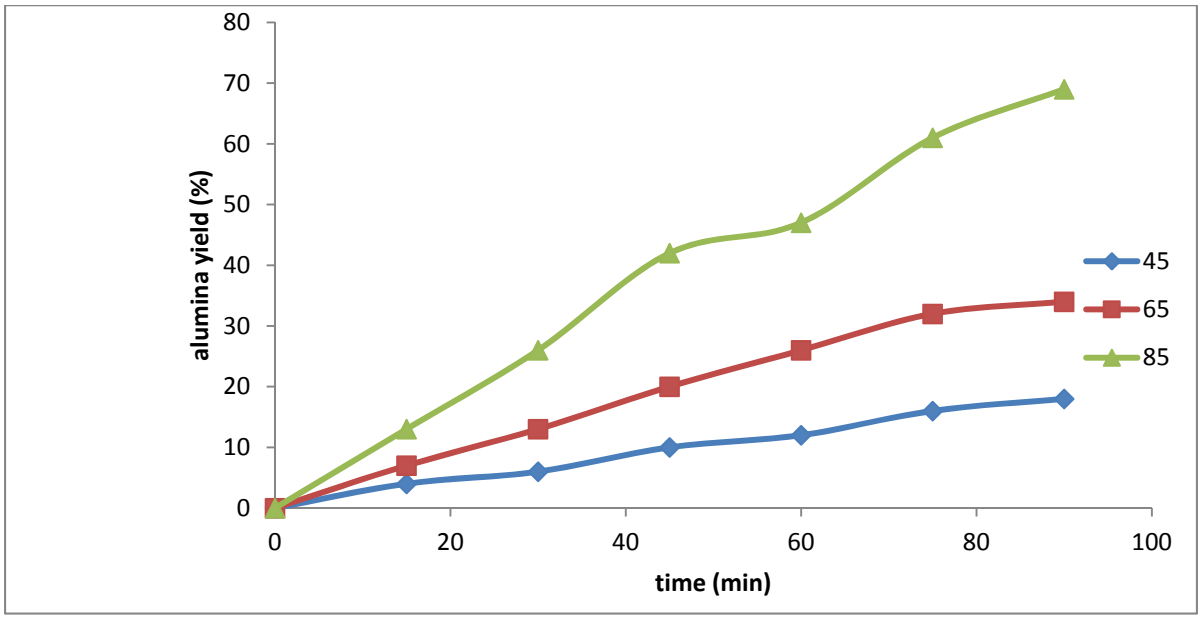

Fig 8: Effect of leaching temperature and time on alumina yield.

3.6 Kinetics studies

In order to identify the reaction mechanism for comparative analysis of the leaching kinetics of alumina from the clay with HCl, the shrinking core model was used to fit the experimental data. The forms of the shrinking core model as proposed and modified by different authors were presented in the following equations:

Chemical reaction controlled process

$$1 - (1 - X)^{1/3} = kt \qquad (2)$$

Liquid film diffusion controlled model

$$1 - (1 - X)^{2/3} = kt \qquad (3)$$

Product layer diffusion controlled process

$$1 + 2(1 - X) - 3(1 - X)^{2/3} = kt \qquad (4)$$

Avremi Model

$$-ln(1 - X) = KAt^{m} \qquad (5)$$

First-order pseudo-homogeneous model

$$-ln(1 - X) = kt \qquad (6)$$

Ginstling and Brounshtein model

$$1 - 2/3(X) - (1 - X)^{2/3} = kt \qquad (7)$$

Jander

$$[1-3(1-X)^{1/3}]^2 = kt \qquad (8)$$

Holt, Cutter and Wadsworth

$$(1-X)\ln(1-X) + X = kt \qquad (9)$$

Experimental data obtained from the study of alumina yield on variation of each of the five process parameters (Figures 4; 5; 6; 7 and 8) were tested with equations (2) through (7) to determine the equation that best describes the reaction kinetics of Agbaja clay dissolution in HCl. The liquid film diffusion controlled process gave the best fits.

The relationship between the overall rate constants K calculated from (Figure 12) at different temperatures may be expressed according to the Arrhenius equation as follows.

$$K = A\,exp\,(-E/RT) \qquad (8)$$

Where K is the overall rate constant in m^2/min, A is the frequency factor in min^{-1}, E is the apparent activation energy in $Jmol^{-1}$, R is the universal gas constant ($8.314 JK^{-1}mol^{-1}$) and T is the reaction temperature in Kelvin. The reaction rate constants for different temperatures were calculated from the slope (Figure 9) and the plot of lnK against T^{-1} is shown in (Figure 18).

The activation energy for the process was calculated from the plot in (Figure 18) to be 35.32 KJ/Mol.

The liquid film diffusion model had the best fit. This showed that the leaching of alumina from Ozoro clay with HCl followed the liquid film diffusion model.

The reaction order for each process parameter (Figures 14; 15; 16; 17 and 18) was determined from the plot of the natural logarithm of the apparent rate constants against the natural logarithm of each process variable according to the following equation:

$$ln\,(-r) = lnk + n\,lnCA \qquad (9)$$

A semi-empirical model was developed from the analysis given above as follows

$$1 - \frac{(1-x)2}{3} = ACa[HCl](dp)b\left(\frac{L}{S}\right)c(sp)dexp\left(-\frac{Ea}{RT}\right) \qquad (10)$$

The variables a, b, c, d were determined from the slopes of the plots as 0.6402, -0.362, 0.497 and 0.453 respectively. The value of A was obtained as 0.001204 and E was 35.32. Substituting these values in the equation, the dissolution of alumina in Ozoro clay in HCl could be described by the following equation

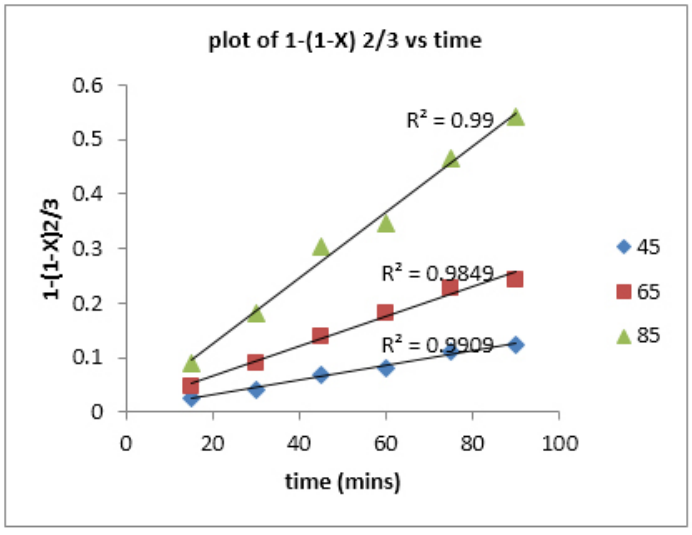

Fig 9: Plot of 1-(1-X)^2/3 Vs time at different temperatures with HCl for alumina yield

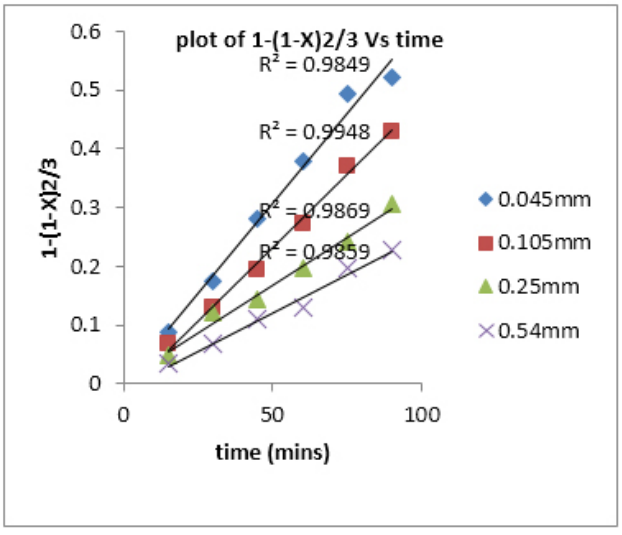

Fig 10: Plot of 1-(1-X)^2/3 Vs time at different particle sizes with HCl for alumina yield

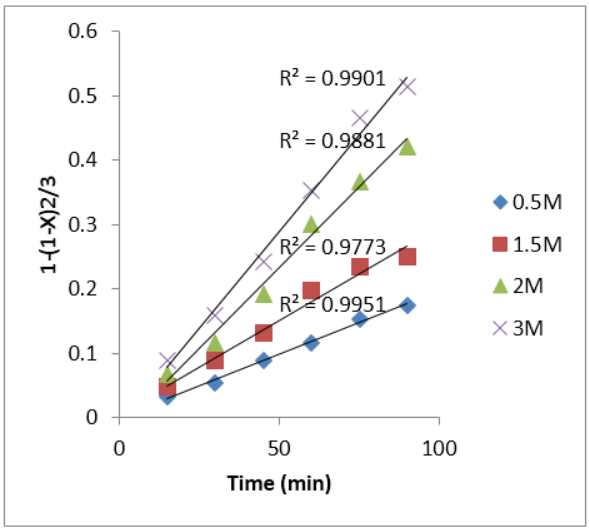

Fig 11: Plot of 1-(1-X)^2/3 Vs time at HCl concentration for alumina yield

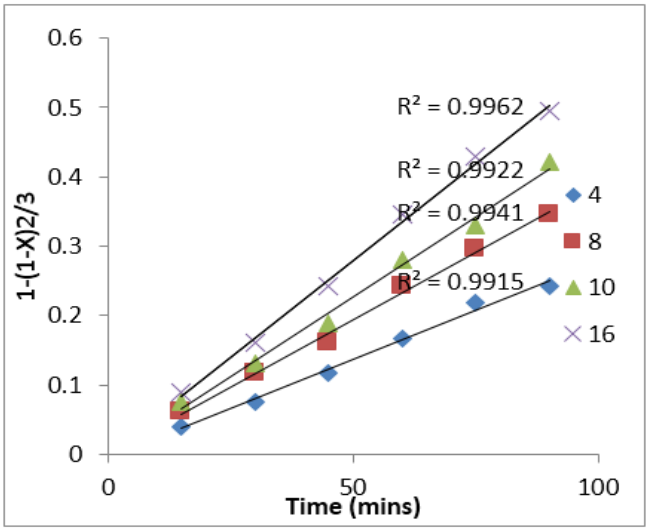

Fig 12: Plot of 1-(1-X)^2/3 Vs time at different liquid-solid ratio with HCl for alumina yield

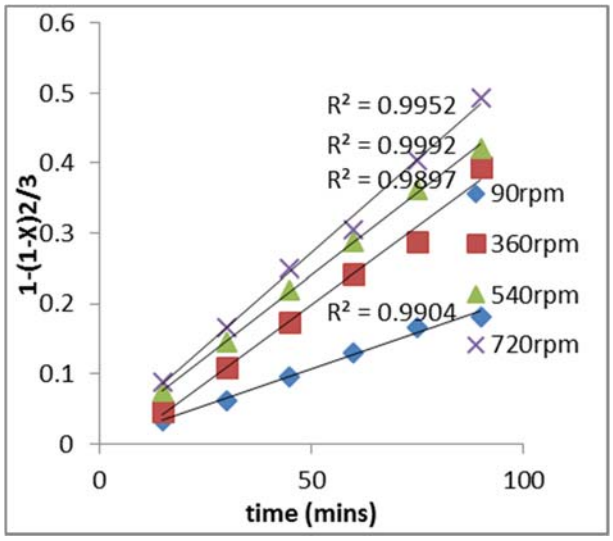

Fig 13: Plot of 1-(1-X)^2/3 Vs time at different stirring speed with HCl for alumina yield

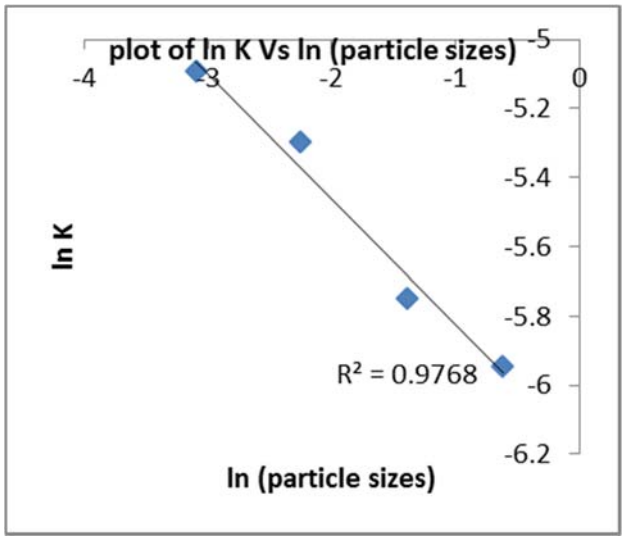

Fig 14: Plot of ln K Vs ln (particle size) with HCl

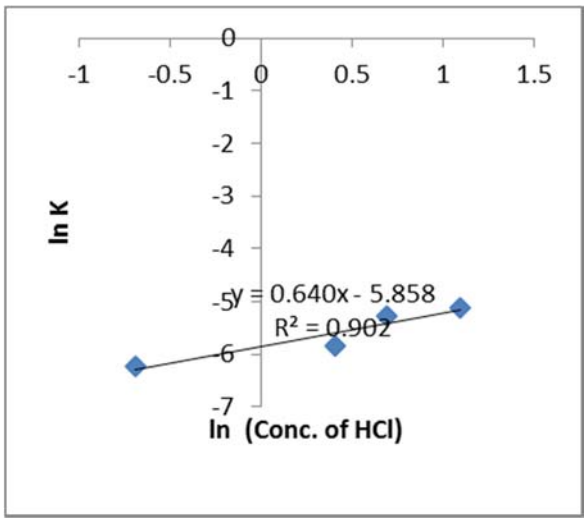

Fig 15: Plot of ln K Vs ln (conc. of HCl)

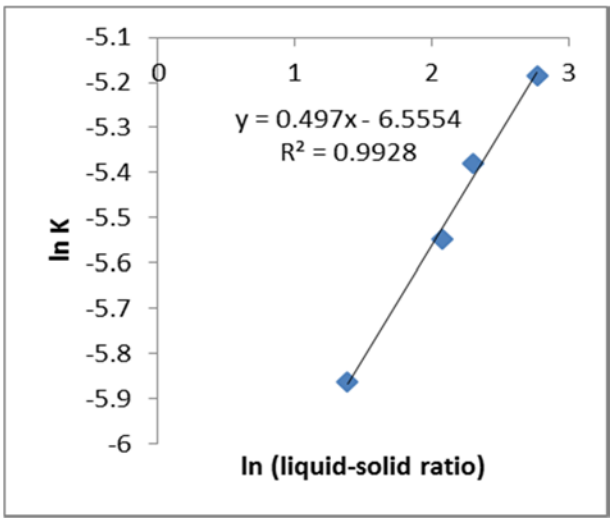

Fig 16: Plot of ln K Vs ln (liquid-solid ratio) with HCl

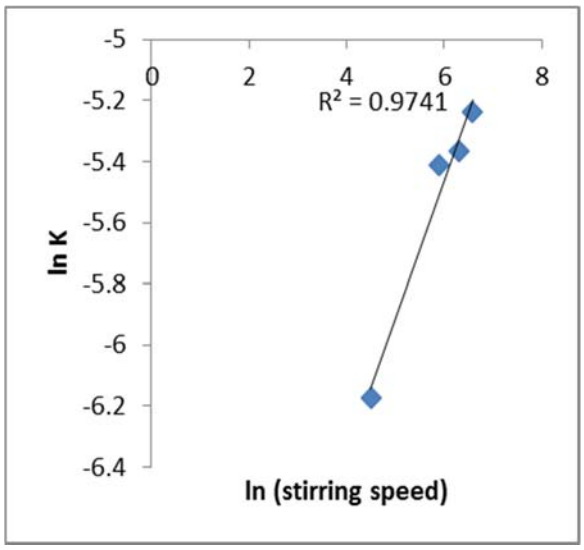

Fig 17: Plot of ln K Vs ln (stirring speed) with HCl

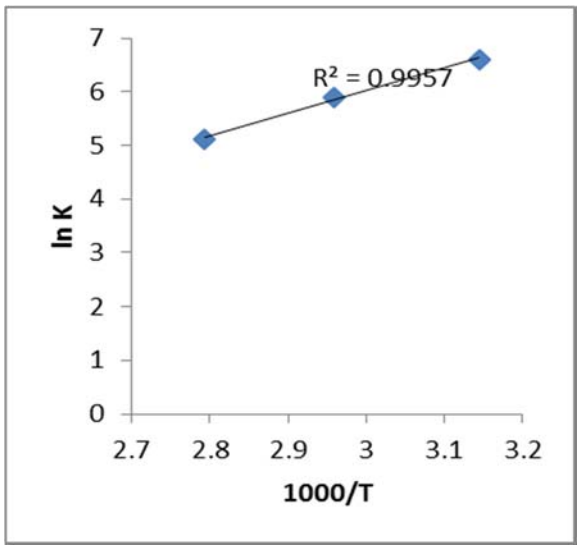

Fig 18: Plot of ln K vs 1000/T using HCl

4. Conclusion

From this study, it could be concluded that Agbaja clay is a potential source for alumina. The optimum calcinations conditions were found to be 700 ^{o}C for a period of 1hr and dissolution rate was found to increase with all the process parameters except particle size. The dissolution process followed the liquid film diffusion controlled model and the activation energy was found to be 34KJ/Mol.

5. Reference

1. Ajemba RA, Onukwuli OD. Process Optimization of Sulphuric Acid Leaching of Alumina from Nteje Clay using Central Composite Rotatable Design. International Journal of Multidisciplinary sciences and engineering. 2012; 3(5):116-121.
2. Ajemba RA, Onukwuli OD. Kinetic Model for Ukpor Clay Dissolution in Hydrochloric Acid Solution. Journal of Emerging Trends in Engineering and Applied Sciences. 2012; 3(3):448-454.
3. Alafara AB, Folahan AA, Emmanuel ET, Rafiu BB. Dissolution kinetics and Leaching of Rutile ore in Hydrochloric Acid. Journal of Minerals and Materials Characterization and Engineering. 2009; 8(10); 787–801.
4. Al-Zahrani AA, Abdul-Majid MH. Extraction of alumina from local clays by Hydrochloric Acid Process. JKAU: Eng Sci. 2009; 20(2):29–41.
5. Eisele JA, Bauer DJ, Shanks DE. Bench-scale Studies to Recover Alumina from Clay by a Hydrochloric Acid Process. Industrial & Engineering Chemistry, Product Research and Development. 1983; 22(1):105–110.
6. Levenspiel O. Chemical Reaction Engineering. John Wiley and Sons, New York, 1972.
7. Marel H, Bentelspacher H. Atlas of infrared spectroscopy of clay minerals and their admixtures. Elsevier Science Publishers. 1976, 234-245.
8. Ogbemudia J, Felix O, Uzoma N. Characterization of Ugbegun Clay Deposit for its Potential. International Journal of chemistry research, 2010, 1(2).
9. Ozdemir M, Cetisli H. Extraction kinetics of Alunite in Sulphuric Acid and Hydrochloric Acid. Hydrometallurgy. 2005; 76(3–4):217–224.
10. Peters FA, Johnson PW, Kirby RC. Methods for Producing Alumina from Clay, an Evaluation of Five Hydrochloric Acid Processes. U. S. Bureau of Mines R. I. No. 6133, 1962.
11. Poppleton HO, Sawyer DL. Hydrochloric Acid Leaching of Calcined Kaolin to Produce Alumina. Instruments and Experimental Techniques. 1977; 2:103–114.
12. Ziegenbalg S, Discher G. Extraction of Alumina from Clay by Hydrochloric Acid Process. Freiberger Forschungshefte (Reihe) A. 1983, 7–25.