APPLICATION OF THE SHRINKING CORE MODEL TO THE ANALYSIS OF ALUMINA LEACHING FROM UKPOR CLAY USING NITRIC ACID

By

Regina O. Ajemba* and Okechukwu D. Onukwuli

Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Anambra State, Nigeria

Abstract

In this research, the application of shrinking core model to the dissolution of Ukpor clay in nitric acid solution was investigated. Ukpor clay comprises various minerals that contains about 26.9 wt% of extractable alumina. The clay sample was grounded, calcined at different temperature range from 500 to 750 ^{0}C, and reacted with the acid solution in a batch reactor under controlled conditions. The dissolution was done using the sample calcined at 650 ^{0}C. Effects of the reaction process variables were monitored at different values. The variables considered include: reaction temperature, acid concentration, particle size, solid/liquid ratio, and stirring speed. The results showed that the dissolution rate varies directly with reaction temperature, acid concentration, and stirring speed, and inversely with solid/liquid ratio and particle size. The experimental data were analyzed using the shrinking core model and the analysis based on statistical and graphical method proved that the dissolution followed the product layer diffusion controlled equation of the model. The dissolution model can be expressed as$1 + 2(1 - X) - 3(1 - X)^{2/3} = 0.96 \times 10^2 C_{[HNO3]}^{0.52} (d_p)^{-1.73} (S/L)^{-0.66} (w)^{0.68} e^{(-30521/RT)}$. The activation energy of the process over the temperature range was calculated to be 30.521kJ/mol.

Keywords: Shrinking core model, dissolution, nitric acid, variables, clay, calcination

Introduction

Clay is a naturally occurring aluminium silicate composed primarily of fine-grained minerals. The clay mineral is composed essentially of silica, alumina or magnesia or both, and water, but iron substitutes for aluminium and magnesium in varying degrees, and appreciable quantities of potassium, sodium, and calcium are frequently present as well. These essential elements of the clay mineral can be leached out by treating the clay with mineral acid solution. Acid treatment of clay mineral is one of the most common chemical modifications of clays, used for both industrial and scientific purposes. Prior to acid treatment, the clay mineral is usually calcinated to increase its dissolubility in the acid solution (Brown and Hrishikesan, 1962). Calcination is a thermal treatment process applied to ores and other solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction.

Alumina is one of the major constituents of clay mineral it is one of the basic materials in high-tech fields, and it is used in space navigation, nuclear energy, metallurgy, electronics, medicine, etc, due to its excellent heat resistance, abrasion resistance, and corrosion resistance properties (Wang et al, 2010; Ying-mei, 2012). Due to the limited availability of bauxite in most countries of the world, many researchers have carried out various investigations in using non-bauxite raw materials in producing alumina (Numluk and Chaisena, 2012; Ying-Mei et al, 2009; Claude et al, 2005; Lai-shi et al, 2011; Al-Ajeel and Al-Sindy, 2006). Numluk and Chaisena, (2012) investigated the leaching of alumina from Lampang clay in sulphuric acid and ammonium sulphate solutions. They reported that an alumina dissolution efficiency of 95.1% was achieved under the following conditions: 200 mesh size, calcining at 750 ^{0}C for 30 min, leaching with 3M sulphuric acid, and using an acid to clay ratio of 80 wt% at 100 ^{0}C for 120 min.

Many researches have been carried out to clarify the kinetics and mechanisms of dissolutions of clay minerals in various acid solutions. Zafar and Ashraf, (2008), investigated the kinetics of low grade bauxite in sulphuric acid. They reported that the process kinetics followed chemical reaction control equation of the shrinking core model. Hulbert and Huff, (1970) reported that the kinetics of alumina removal from clay material could be modeled by the nucleation equation. Lai-shi et al, (2011) reported that extraction of alumina from coal fly ash is controlled by both internal diffusion and interface-chemical reaction at the early stage and later by interface-chemical reaction.

The purpose underlying this present work is to investigate the applicability of the shrinking core model in the analysis of the experimental data and the effects of the process variables on the dissolution rate.

Materials and Methods

The chemical composition and structural vibration conformation of the clay sample were determined using x-ray fluorescence spectrometer (XRF: Phillips) and Fourier transform infrared spectroscopy (FTIR; Shimadzu FT S8400 model), respectively. The aluminium ion content in the leach solution was analyzed with MS- Atomic Absorption Spectrophotometer (AAS)

The clay material was mined at Ukpor (N: 5° 54’ 27.5”; E: 6° 56’ 3.7”; A: 137m), Nigeria. The mined clay was washed and sun-dried for 24 hours then oven dried at 100 ^{0}C for 3 hours. The sample was then grinded with porcelain mortar and pestle, sieved into various sizes and calcined in a furnace in the temperature range of 500 to 750 ^{0}C. The duration of calcination was varied from 30 to 180 minutes.

Leaching experiments were carried out using the calcined samples in a reflux system on a magnetic stirrer and temperature was noted using thermometer. 5 g of the calcined sample was added to already determined volume of the acid and heated while stirring continuously. At the end of the reaction, the slurry was filtered and the filtrate collected for Al^{3+} analysis using AAS. The dissolution fraction of the alumina in the slurry was calculated by

$$X = [\text{amount of } Al^{3+} \text{ in the solution/ total amount of } Al^{3+} \text{ in original sample}] \quad (1)$$

Experiments were performed using the calcined sample to investigate the effects of the following variables on the leaching process:

Acid concentration, (M): 2, 4, 6, 8, and 10
Leaching temperature, (°K): 333, 343, 353, 363, and 373

Particle size, (mm): 0.045, 0.075, 0.106, 0.212, and 0.408
Leaching period, (Minutes): 20, 40, 60, 80, 100, 120, and 150
Solid/liquid ratio, (g/ml): 0.02, 0.025, 0.03, 0.035, and 0.04
Stirring speed, (rpm): 90, 180, 360, 540, and 720

Results and Discussions

Characterization

The x-ray fluorescence analysis of the clay sample is presented in Table 1.

The table shows that Ukpor clay contains 26.9% extractable alumina and this confirms the feasibility of the leaching process of alumina.

Table 1: XRF analysis of Ukpor clay

Chemical constituent	Composition (%)	Chemical constituent	Composition (%)
Al_2O_3	26.9	Cr_2O_3	0.084
SiO_2	48.6	NiO	0.011
Fe_2O_3	20.13	CuO	0.064
CaO	0.08	ZnO	0.008
MnO	0.003	Rb_2O	1.15
SO_3	0.05	ZrO_2	0.12
P_2O_5	0.20	Rh_2O_3	0.032
Sc_2O_3	0.002	CdO	0.03
TiO_2	2.06	Re_2O_7	0.02
V_2O_5	0.14	PtO_2	0.03

The FTIR of the clay is shown in Fig. 1. The bands at 445, 577, 3355, and 3550 cm-1 are attributed to Si – O bending, while those at 783, 1046, and 1170 cm-1 are assigned to Si – O stretching. The bands at 643 and 957 cm-1 are assigned to Al – O – Si stretching, and the band at 3550 is assigned to Si – O- Al bending. Appearance of bands at 3260 and 3419 cm-1 are related to O – H stretching, while band at 1643 represents H – O – H bending (Preeti and Singh, 2007; Davarcioglu, 2011; Saikia et al, 2010; Madejova, 2003).

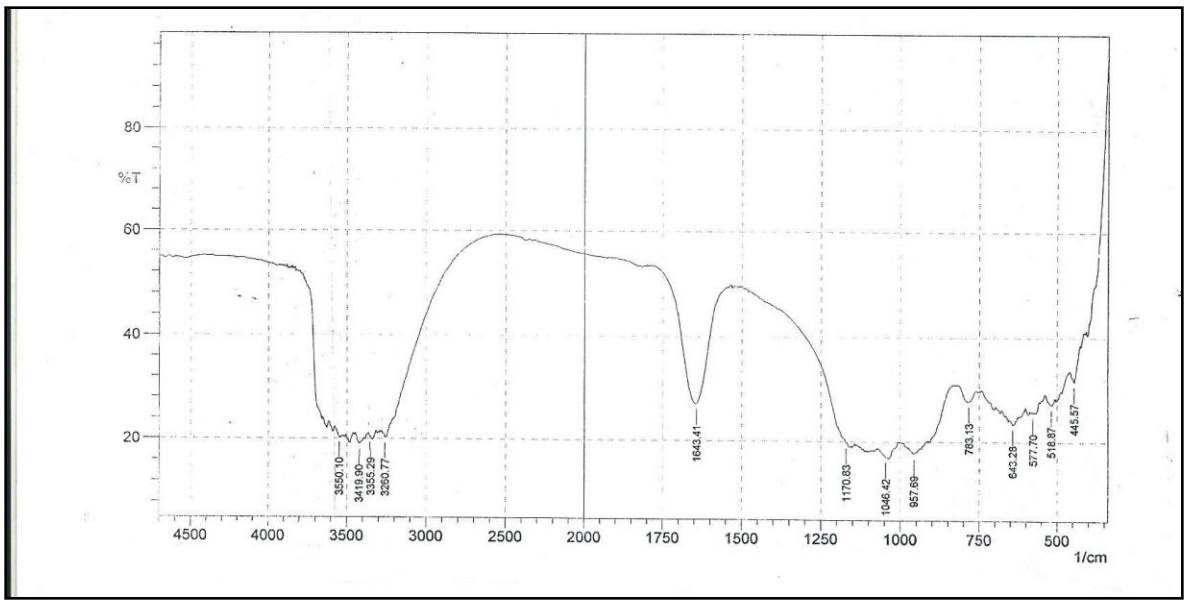

Figure 1: FTIR spectrum of Ukpor clay.

Leaching studies

Effect of calcination temperature and duration

The effect of the calcination temperature and time of calcination is shown in Fig. 2. The figure indicates that below 500 ^{0}C temperature and above 700 ^{0}C temperature, the percentage of alumina dissolution in the acid solution is low. The dissolution rate increased in the temperature range of 550 to 650 ^{0}C. The highest dissolution percentage of 78.7 was reached at 650 ^{0}C. The figure also indicates that time is an important factor in calcination, the dissolution increased as time increased up to 80 min and starts to drop as time increased. So duration of 80 min was chosen as the best calcination time.

Effect of acid concentration on alumina removal

The effect of concentration of the nitric acid solution on the leaching process was studied by varying the concentration in the range of 2 to 10M. The experimental data are given in Table 2. The table shows that the dissolution rate is favoured as the acid concentration was increased from 2 to 6M and above 6M, the dissolution rate decreased, and this could be attributed to the destruction of the clay structure by excess acid.

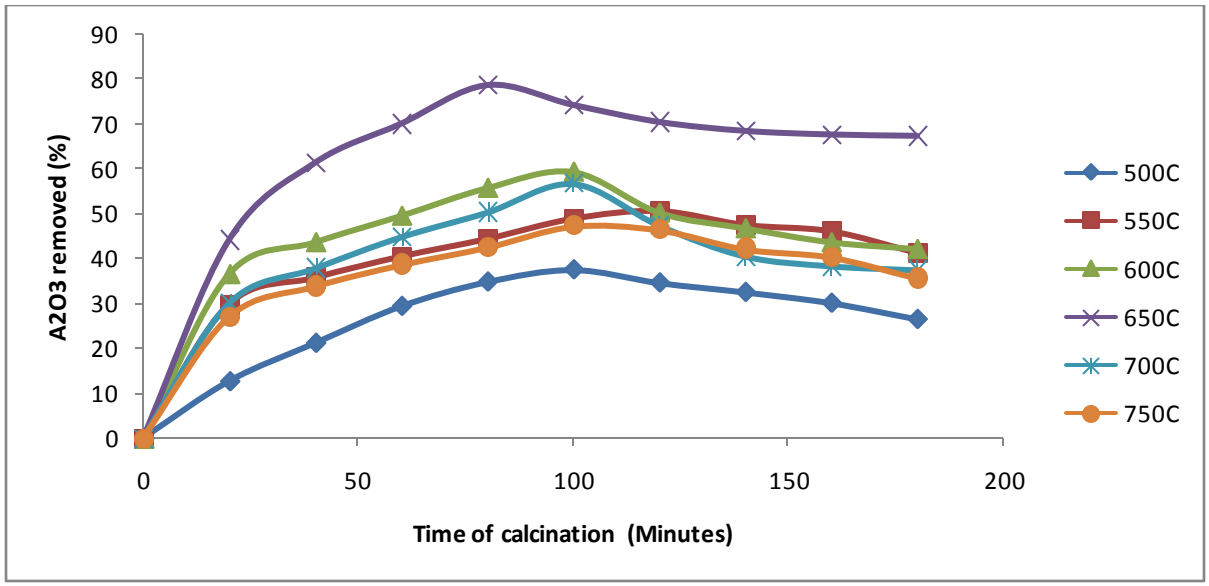

Figure 2: Effect of calcination temperature and duration on Al_2O_3 removal (4M HNO_3; 353 ^{0}K, temperature; 0.02 g/ml solid/liquid ratio; 540 rpm, stirring speed; and 60 minutes leaching time).

Table 2: Effect of acid concentration on alumina dissolution [calcination 650 ^{0}C for 80 min; leaching temperature 373 ^{0}K; solid/liquid ratio, 0.02g/ml; particle size, 0.045mm; and stirring speed, 540rpm]

Concentration of HNO_3 (M)	2	4	6	8	10
Time of leaching (min)	Alumina dissolution (%)				
0	0	0	0	0	0
20	15.8	21.5	30.9	25.5	18.1
40	23.5	30.7	44.6	37.2	26.7
60	30.6	36.7	56.3	45.6	32.4
80	34.9	40.4	67.1	53.4	37.6
100	37.3	44.1	75.4	59.8	41.5
120	38.8	46.6	80.6	63.7	43.8
150	39.1	47.8	82.7	64.9	44.6

Effect of leaching temperature on alumina dissolution

The leaching temperature effect on the dissolution rate was investigated by varying the temperature from 333 to 373 ^{0}K. The data are presented in Table 3. The data shows that the dissolution rate increases with an increase in the temperature. This is as a result of high kinetic energy available for the reacting molecules. The maximum dissolution found from the data is 83.7% Al_2O_3 at 373 ^{0}K for 150 minutes or two hours thirty minutes.

Table 3: Effect of leaching temperature on alumina dissolution [calcined at 650 ^{0}C for 80 min; 6M HNO_3; 0.045 mm particle size; 0.02g/ml solid/liquid ratio; and 540rpm stirring speed].

Dissolution	Dissolution rate for Al_2O_3 (%)

time (min)	333K	343K	353K	363K	373K
0	0	0	0	0	0
20	20.6	25.9	31.2	36.4	40.6
40	24.8	31.8	39.4	45.4	51.1
60	28.4	35.7	42.8	52.7	58.2
80	32.7	39.6	48.3	57.2	66.3
100	35.9	44.3	52.2	63.8	71.9
120	39.6	46.9	55.7	68.5	77.5
150	42.5	49.4	58.6	70.1	83.7

Effect of particle size on alumina removal

Particle size was varied to study its effect on the dissolution rate. The samples were ground to different sizes ranging from 0.045 to 0.408mm. the experimental results shown in Table 3 revealed that the dissolution rate is inversely proportional to the particle size. This is attributed to larger specific surface area provided by the smaller particles for contact with the acid molecules.

Table 4: Effect of particle size on Al_2O_3 removal [calcined at 650 ^{0}K for 80 min; 6M HNO_3; 0.02g/ml solid/liquid ratio; 373 ^{0}K leaching temperature; and 540rpm stirring speed].

Dissolution time (min)	**Dissolution rate for Al_2O_3 (%)**				
	0.045mm	**0.075mm**	**0.106mm**	**0.212mm**	**0.408mm**
0	0	0	0	0	0
20	34.8	26.2	20.5	17.1	12.7
40	47.4	37.3	31.8	25.5	19.5
60	55.4	44.2	38.5	30.4	26.4
80	62.3	50.9	43.4	37.6	32.3
100	69.3	57.6	49.7	41.8	36.8
120	75.7	64.3	55.5	47.3	41.5
150	82.4	72.7	63.2	52.7	48.6

Effect of solid/liquid ratio on alumina removal

Experimental data in Table 5 shows that the dissolution rate of alumina is highly affected by the solid/liquid ratio. The rate of dissolution decreased appreciably as the solid/liquid ratio was increased from 0.02 to 0.045 g/ml. This could be attributed to the decrease in the fluid reactant per unit weight of the solid

Table 5: Effect of solid/liquid ratio on alumina dissolution [calcined at 650 0K for 80 min; 6M HNO3; 373 0K leaching temperature; 0.045mm particle size; and 540rpm stirring speed]

Dissolution time (min)	**Dissolution rate for Al_2O_3 (%)**				
	0.02g/ml	**0.025g/ml**	**0.03g/ml**	**0.03g/ml**	**0.045g/ml**
0	0	0	0	0	0
20	24.8	19.2	16.2	12.4	9.8
40	35.2	26.5	20.5	16.9	12.3

60	42.4	33.2	27.1	22.1	17.2
80	58.6	47.4	35.7	29.0	21.9
100	64.9	51.6	41.3	36.5	28.8
120	70.5	56.4	47.8	42.4	35.6
150	79.8	60.3	52.4	48.2	40.7

Effect of stirring speed on alumina removal

The effect of stirring speed on the dissolution rate of alumina was investigated in 6M HNO_3 solution with 0.045mm particle size fraction at 373 ^{0}K using stirring speed of 90 to 720 rpm for 150 min. The experimental results are summarized in Table 6. The results presented in Table 6 showed that the dissolution rate of alumina in HNO_3 increases as the stirring speed increases. The rate of increase from 540 to 720rpm was not high and so 540 rpm was chosen as the stirring speed for other experiments. Increase in stirring speed causes a decrease in the thickness of the film layer, therefore, causing an increase in the dissolution rate.

Table 6: Effect of stirring speed on alumina dissolution

Dissolution time (min)	**Dissolution rate for Al_2O_3 (%)**				
	90rpm	**180rpm**	**360rpm**	**540rpm**	**720rpm**
0	0	0	0	0	0
20	23.9	27.3	33.7	38.5	39.7
40	27.6	30.6	39.6	46.7	48.1
60	31.7	36.2	43.5	51.6	52.3
80	35.6	39.5	50.4	58.2	59.0
100	40.4	42.7	55.8	64.4	65.7
120	43.7	48.1	56.4	70.8	71.5
150	46.5	50.7	62.9	79.9	81.1

Dissolution kinetics using shrinking core model (SCM)

In order to establish the reaction kinetics and rate controlling step for the dissolution of alumina in HNO_3, the experimental data were analyzed using the shrinking core model (SCM). The fluid-solid heterogeneous reaction can be represented in the form as:

$$A\ (aq) + bB\ (s) \longrightarrow Products \qquad (2)$$

From the shrinking core model, the reaction is considered to take place first at the outer surface of the particle (Levenspiel, 1972). The region of the reaction goes into the solid and the reacting particle shrinks during the reaction. The reactions occurring in the fluid-solid heterogeneous system generally have the following steps:

- Diffusion of fluid reactant through the main body of the fluid layer to the surface of the solid.

- Reaction of the fluid reactant with the solid on the surface of the solid.
- Diffusion of the products through the film layer back to the bulk of the fluid.

The slowest of these steps is considered the rate determining step. The rate may be described by film diffusion, chemical reaction, or product layer diffusion models. The rate equations can be written as follows:

$$X = \frac{3bk_gC_A}{\rho_B R_o}\, t = k_f t \qquad (The\ film\ diffusion\ equation) \qquad (3)$$

$$1 - (1-X)^{1/3} = \frac{bk_sC_A}{\rho_B R_o}\, t = k_r t \qquad (Chemical\ reaction\ control) \qquad (4)$$

$$1 + 2(1-X) - 3(1-X)^{2/3} = \frac{6bD_eC_A}{\rho_B R_o}\, t = k_d t \qquad (Product\ layer\ diffusion) \qquad (5)$$

The analysis of the experimental data using the above equations showed that the dissolution of Ukpor clay in nitric acid solution is controlled by the product layer diffusion (Equ.5) step. This was proved through the graphical and statistical methods applied in the calculation. The graphs are shown in Figures 3 – 7, while the values of the rate constants and regression coefficients are shown in Table 7.

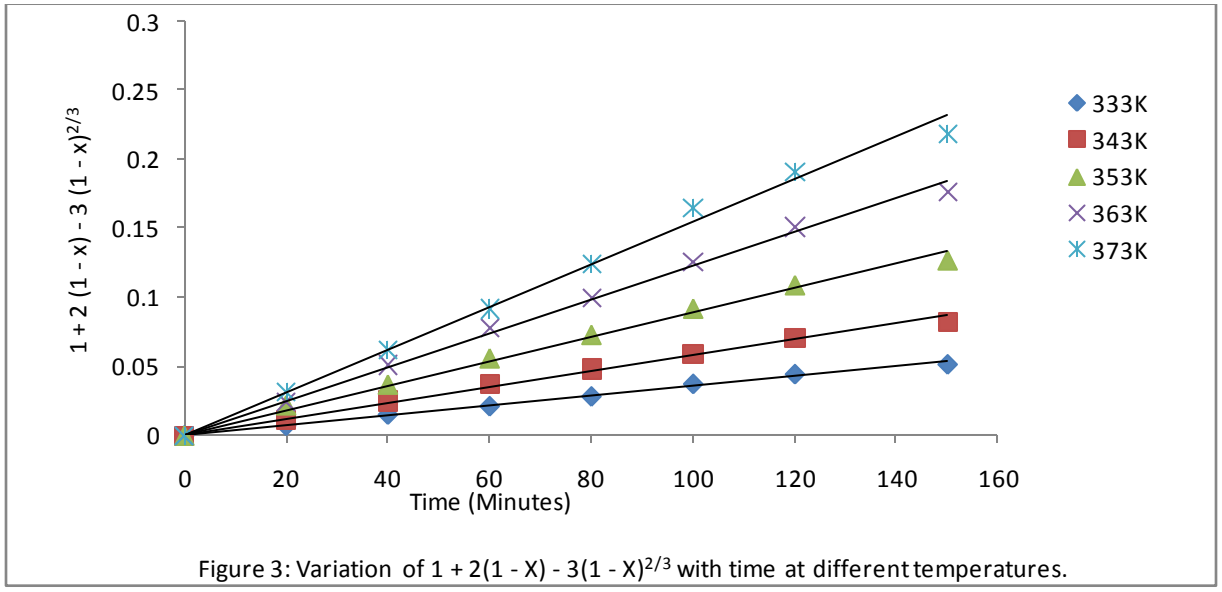

Figure 3: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different temperatures.

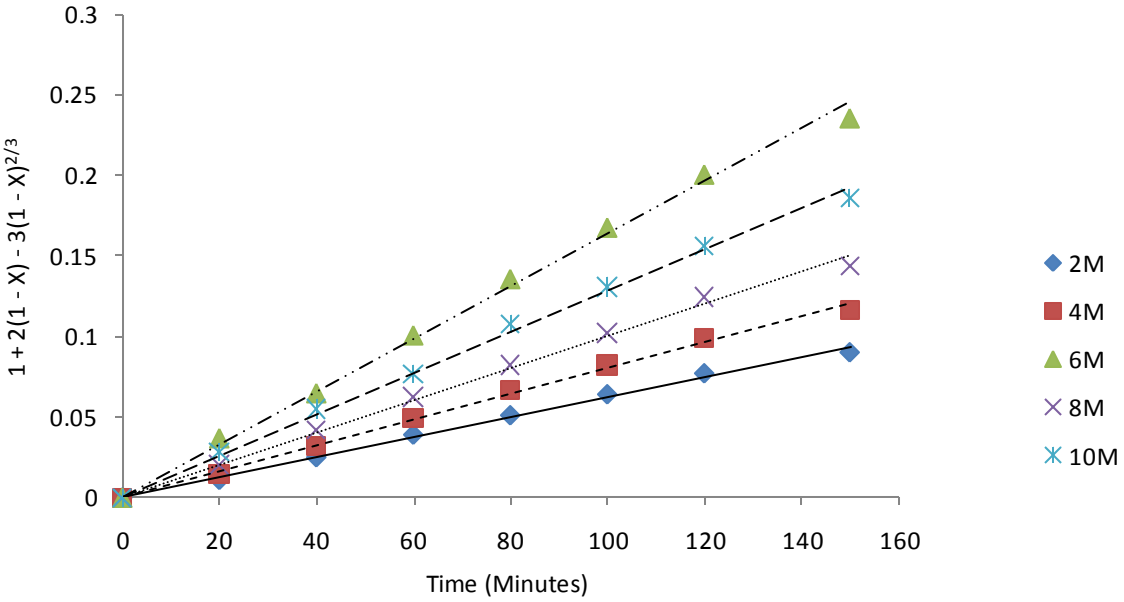

Figure 4: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different acid concentration.

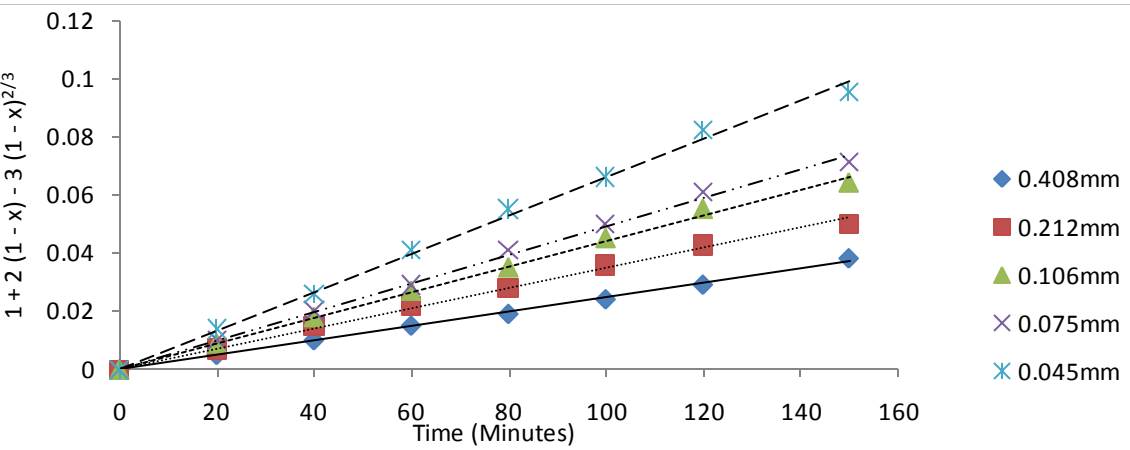

Figure 5: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different particle size.

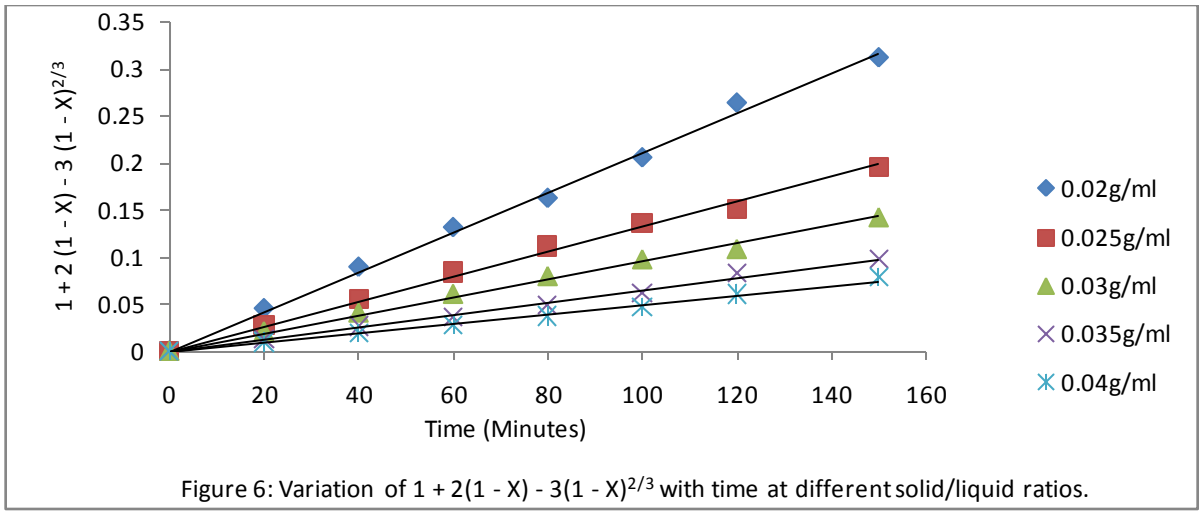

Figure 6: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different solid/liquid ratios.

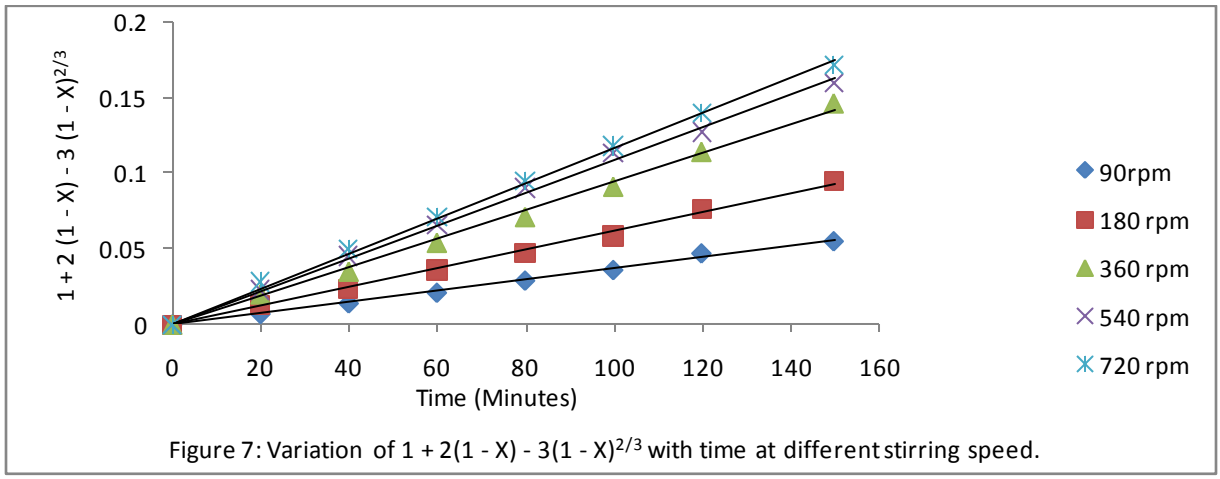

Figure 7: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different stirring speed.

The activation energy of the dissolution reaction was calculated from the Arrhenius equation

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

The values of k_o and E_a were calculated from the intercept and slope of the plot of ln k against T^{-1} (not shown).

To understand the combined effect of the process variables on the dissolution kinetics of Ukpor clay in nitric acid, a semi empirical kinetic model is proposed as follows:

$$1 + 2(1 - X) - 3(1 - X)^{2/3} = k_o C_{[HNO3]}^{\ a} (d_p)^b (S/L)^c (w)^d e^{(-Ea/RT)} \quad (7)$$

The reaction orders with respect to the acid concentration, particle size, solid/liquid ratio, and stirring speed were calculated from the slopes of the plots of the natural logarithm of the apparent rate constant

calculated from Figures 3 – 7 versus the natural logarithm of the variables, acid concentration, particle size, solid/liquid ratio, and stirring speed, respectively. The constants were calculated to be a = 0.52; b = -1.73; c = -0.66; d = 0.68; $k_o = 0.96 \times 10^2$; $E_a = 30.521$. Substituting these values into Eq. (6) gives

$$1 + 2(1 - X) - 3(1 - X)^{2/3} = 0.96 \times 10^2 \, C_{[HNO3]}^{0.52} \, (d_p)^{-1.73} \, (S/L)^{-0.66} \, (w)^{0.68} \, e^{(-30521/RT)} \quad (8)$$

Table 7: Values of the rate constants and regression coefficients

Process variables	Film Diffusion control $X = k_f t$		Chemical reaction control $1 - (1 - X)^{1/3} = k_r t$		Product layer diffusion control $1+ 2(1 - X) -3(1 - X)^{2/3} = k_d t$	
	k_f (min^{-1})	R^2	k_r(min^{-1})	R^2	k_d (min^{-1})	R^2
Temperature (K)						
333	0.3470	0.6210	0.00142	0.8569	0.00035	0.9955
343	0.4171	0.5031	0.00180	0.8439	0.00057	0.9934
353	0.4979	0.4570	0.00226	0.7820	0.00089	0.9937
363	0.6010	0.5025	0.00271	0.8260	0.00123	0.9956
373	0.6910	0.5783	0.00310	0.8449	0.00155	0.9925
Concentration (M)						
2	0.3365	0.5818	0.00142	0.8675	0.00062	0.9963
4	0.4114	0.5721	0.00164	0.8473	0.00081	0.9967
6	0.6921	0.7503	0.00242	0.8433	0.00164	0.9962
8	0.5495	0.7058	0.00212	0.8412	0.00129	0.9954
10	0.3816	0.6631	0.00184	0.8119	0.00100	0.9965
Particle size (mm)						
0.045	0.6668	0.6855	0.00160	0.7766	0.00066	0.9959
0.075	0.5623	0.8049	0.00136	0.7524	0.00049	0.9965
0.106	0.4851	0.8343	0.00121	0.8189	0.00044	0.9971
0.212	0.4067	0.8558	0.00105	0.8118	0.00035	0.9952
0.408	0.3591	0.9306	0.00085	0.7762	0.00025	0.9979
Solid/liquid ratio (g/ml)						
0.02	0.6122	0.8859	0.00209	0.7020	0.00211	0.9968

0.025	0.4788	0.8699	0.00138	0.3721	0.00132	0.9956
0.03	0.3965	0.9218	0.00126	0.4610	0.00096	0.9953
0.035	0.3487	0.9671	0.00109	0.5345	0.00064	0.9939
0.04	0.2840	0.9813	0.00096	0.6617	0.00049	0.9922
Stirring speed (rpm)						
90	0.3835	0.5799	0.00079	0.8421	0.00037	0.9959
180	0.4202	0.5219	0.00103	0.8181	0.00061	0.9960
360	0.5209	0.4880	0.00129	0.8363	0.00094	0.9960
540	0.6335	0.6170	0.00146	0.8396	0.00108	0.9971
720	0.6433	0.5994	0.00176	0.8370	0.00117	0.9977

Conclusion

- The optimum conditions for the dissolution of alumina in nitric acid include: activation temperature of 650 0C; activation duration of 80 min; leaching temperature of 373K; acid concentration of 6M; particle size of 0.045mm; solid/liquid ratio of 0.02g/ml; and stirring speed of 540rpm. Under these conditions the dissolution rate is 81.7%.
- The shrinking core model fits the experimental data obtained in this work and it was used successfully to analyze the kinetics of the process. The analysis showed that the dissolution of Ukpor clay in nitric acid is controlled by the product layer diffusion equation of the model with the activation energy calculated to be 30.521kJ/mol.
- This work also proves the possibility of producing alumina in industrial scale using Ukpor clay as the basic raw material.

References

AbdulWahab A. A., Suad I. A., (2006). Alumina recovery from Iraqi kaolinitic clay by hydrochloric acid route. Iraqi Bulletin of Geology and Mining, 2 (1), 67 – 76.

Ajemba R. O., (2012). Characterization, dissolution, and adsorptive applications of clays from Ukpor, Udi, and Nteje. PhD thesis, Nnamdi Azikiwe University, Awka, Nigeria.

Al-Zahrani A. A., Abdul-Majid M. H., (2009). Extraction of alumina from local clay by hydrochloric acid process. JKAU: Eng. Sci., 20 (2), 29 – 41.

Bhaskar J. S., Gopalakrishnarao P., (2010). Fourier transforms infrared spectroscopic characterization of Kaolinite from Assam and Meghalaya, Northeastern India. J. Mod. Phys., 1, 206 – 210.

Brown W. H., Hrishikesan K. G., (1966). Process for the production of alumina. United States Patent Online, No. 3, 240, 562.

Buhan D, (2011). Spectral characterization of non-clay minerals found in the clays (Central Anatolian-Turkey). International Journal of the Physical Sciences, 6 (3), 511 – 522.

Hulbert S. F., Huff D. E., (1970). Kinetics of alumina removal from calcined kaolin with nitric, sulphuric, and hydrochloric acids. Clay Minerals, 8, 337 – 345.

Levenspiel O., (1972). Chemical Reaction Engineering, 2nd edition, Wiley, New York.

Li Lai-shi, Wu Yu-sheng, Liu Ying-ying, Zhai Yu-chun, (2011). Extraction of alumina from coal fly ash with sulphuric acid leaching method. The Chinese Journal of Process Engineering, 11 (2), 254 – 258.

Madejova J, (2003). FTIR techniques in clay mineral studies. Vib. Spectrosc. 31, 1 – 10.

Numluk P., Chaisena A., (2012). Sulphuric acid and ammonium sulphate leaching of alumina from Lampang clay. E-Journal of Chemistry, 9 (3), 1364 – 1372.

Preeti S., Singh B., (2007). Instrumental characterization of clay by XRF, XRD, and FTIR. Bull. Mater. Sci., 30 (3), 235 – 238.

Xu Ying-Mei, He De-Min, Wang Dong-Mei, Lian Yu-Huan, Guan Jun, Zhang Qiu-Min, (2009). Influence of calcination temperature on leaching rate of aluminium and iron impurities in oil shale ash. Oil Shale, 26 (2), 163 – 168.

Y.-M. Xu, D.-M. He, J.-W. Shi, J. Guan, Q.-M. Zhang, (2012). Preparation of alumina from retorting residue of oil shale. Oil Shale, 29 (1), 36 – 50.

Zafar I. Z., Ashraf M., (2008). Reaction kinetic model for dissolution of low grade bauxite rock in sulphuric acid. J. Chem. Soc. Pak., 30 (1), 49 – 54.