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Kinetic Model for Ukpor Clay Dissolution in Hydrochlorlc Acid Solution

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Abstract

The dissolution kinetics of Ukpor clay in hydrochloric acid is studied. The study was done by varying the various process parameters viz; calcination temperature, reaction temperature, acid concentration, solid-to-liquid ratio, particle size, and stirring speed. The experimental results show that the dissolution reaction increases with increase in calcination temperature, reaction temperature, acid concentration, and stirring speed, while it decreases with increasing solid-to-liquid ratio and particle size. The experimental data were analyzed according to the kinetic models for heterogeneous reaction processes using graphical and statistical methods and it was found that the dissolution of Ukpor clay in hydrochloric acid solution is controlled by ash product layer diffusion. The kinetic equation is given by $1 + 2(1 - X) - 3(1 - X)^{2/3} = 1.40 \times 10^3 C_{[HCl]}^{0.37} (d_p)^{-0.89} (s/l)^{-0.63} (w)^{0.42} \exp(-4677/T)\, t$. The activation energy of the dissolution reaction was calculated to be 39.009kJ/mol. This study has shown that Ukpor clay can serve as an alternative raw material for the aluminium industry in Nigeria and the kinetic data can be used in the design of process equipments for large scale production.

Keywords: dissolution, alumina, kinetics, shrinking core, clay

INTRODUCTION

Alumina is produced from bauxite and the bauxite is not readily available to meet the industrial demand for its production. It is therefore necessary to look for the production of this important raw material through other available resources of raw materials that contain high alumina and low iron oxide. Clay is one of the numerous aluminous raw materials that is distributed on a large scale in Nigeria. Many of the clays contain as much as 25 – 40 % alumina which can be extracted for industrial use. 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 sulphuric acid. Hydrochloric acid is added during the crystallization step to form aluminium chloride which crystallizes readily. Much raw material must be handled in the process, because the clays and shales have lower alumina content than bauxite (Barclay et al, 1976; Al-Zahrani et al, 2004 and 2009). Other methods involve the treatment of clays with different mineral acids or the continuous electrolysis of aluminum chloride (Austin G., 1984; Yuksel et al, 2011; Zafar and Ashraf, 2008).

Hydrochloric acid is preferred over the other acids for leaching alumina from clays because of the ease of filtration of slurries, ease of iron removal and the insolubility of titanium dioxide, which is present in many types of clay (Peters et al, 1962; Tilley et al, 1927; Schoenborn et al, 1979). 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 (Peters et al, 1962).

Al-Zahrani and Abdul-Majid (2009) investigated the extraction of alumina from local clays by hydrochloric acid process. They observed that calcination of the clay samples before extraction increased the alumina removal. The optimum calcination conditions were 600 ^{0}C and 1 hour for calcination temperature and time, respectively, and the corresponding alumina extraction was about 63%. Ozdemir and Cetisli (2005) studied the extraction of alunite in sulphuric acid and hydrochloric acid in a batch reactor. The effects of reaction temperature, acid concentration, particle size, calcination temperature, calcination 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 works reported in the literature on the extraction of alumina from clay by hydrochloric acid treatment include the work of Ziegenbalg et al, 1983; Poppleton and Sawyer, 1977; Eisele et al, 1983; Shanks, et al, 1986; and Salih et al, 2006.

Hulbert and Huff (1970) studied the kinetics of alumina removal from calcined kaolin with nitric, sulphuric and hydrochloric acids. They concluded

that the extraction of alumina using the acids could be described by a nucleation rate equation and that under the conditions employed the rate of alumina leaching was fastest with hydrochloric acid, slower with sulphuric acid, and slowest with nitric acid. Alafara et al (2009) studied the dissolution kinetics and leaching of rutile ore in hydrochloric acid. They reported that the dissolution rates were greatly influenced by the hydrogen ion concentration, temperature, stirring speed and particle diameter. They concluded that the kinetic data showed that the dissolution mechanism followed diffusion controlled shrinking core model with the surface chemical reaction as the rate controlling step. Ranjita et al, (2010), studied the leaching kinetics for iron from partially laterised khondalite rocks by hydrochloric acid solution. They concluded that the best condition found for the leaching study was 3 M acid concentration at 80 ^{0}C temperature for 4 hours time period with apparent activation energy calculated from the first order reaction kinetics as 40.72kJ/mol.

MATERIALS AND METHODS

Calcination

The clay samples were mined and separated from the dirt that contaminated them. The mined clays were wet and they were sun-dried for three days after which the dried samples were ground with mortar and sieved with 75µm sieve size. The sieved samples were then calcined in a furnace with a temperature range of 100^{0}C to 1200^{0}C. The calcination temperature was chosen in the range of 450^{0}C to 900^{0}C for all the samples. The calcination time was also varied between 0.5 to 4 hours. The calcined samples were then dissolved in the prepared hydrochloric acid solutions to determine the optimum calcination temperature and period. The determined optimum calcination temperature and time were used in the subsequent dissolution reactions for all the samples.

Dissolution Experiment

The calcined samples were then ground and sieved into various particle sizes and labeled accordingly. For each experiment, 10 g of the sized fractions was weighed out and reacted with already determined volume of the acid in a 250 ml bottomed flask. The flask and its contents were heated to a fixed temperature of 70^{0}C while on a magnetic stirring plate and stirring was continued throughout the reaction duration. After the reaction time was completed, the suspension was immediately filtered to separate un-dissolved materials, washed three times with distilled water. The resulting solutions were diluted and analyzed for aluminum ion using MS Atomic Absorption Spectrophotometer. The filtrate containing aluminium salt was then injected with hydrochloric acid gas to precipitate the aluminium salt ($AlCl_3.6H_2O$). The salt was separated, dried and ignited at 1000^{0}C to form alumina (Al_2O_3). The residue was also collected, washed to neutrality with distilled water, air dried and oven dried at 60^{0}C and then reweighed. The difference in weight was noted for determining the fraction of the alumina ore that dissolved. The above procedure was repeated for different values of the process parameters investigated and the values are as recorded in Table 1.

Table 1: The ranges of parameters used for the experiment

Parameter	Values				
Concentration (mol/l)	0.8	1.5	3.0	4.8*	6.5
Temperature (^{0}C)	50	60	70	80	90*
Particle size (mm)	0.045*	0.075	0.106	0.212	0.408
Solid/liquid ratio (g/ml)	2/100*	2.5/100	3/100	3.5/100	4/100
Stirring rate (rpm)	90	180	360	540*	720

*The process parameter value that was held constant while the effect of other parameters was being investigated.

RESULTS AND DISCUSSIONS

Effect of Calcination

It was observed that the heat treatment of the clay samples in the temperature range of 450 – 900^{0}C is necessary because it increased the dissolubility of the alumina in the acid solution. The process of calcination is thought to increase clay reactivity by affecting dehydration and transformation of the clay to amorphous form (Connor, 1988; Phillips and Wills, 1982). Figure 1 shows that clays calcined at high temperature of 750^{0}C yielded more alumina than those at lower temperatures. This is in agreement with the work of Al-Ajeel and Al-Sindy (2006) that investigated the aluminium recovery from Iraqi kaolinitic clay in hydrochloric acid and recommended a calcination temperature of 720^{0}C.

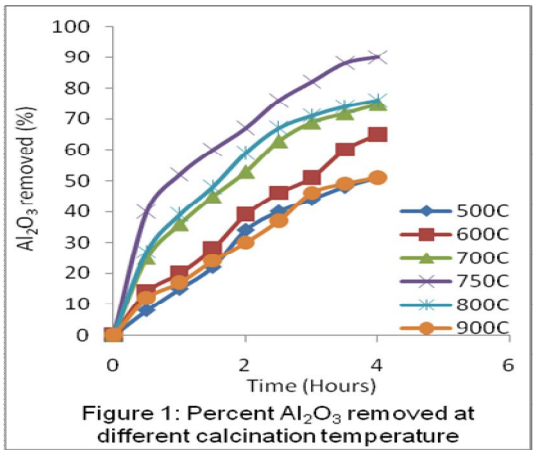

Figure 1: Percent Al_2O_3 removed at different calcination temperature

Effect of dissolution parameters

The reaction mechanism and kinetics of Ukpor clay in hydrochloric acid was studied by the variation of the fraction of alumina removed with time at different values of the process parameters. The process parameters studied include: temperature, acid concentration, particle size, solid/liquid ratio, and

stirring speed. The experimental data are shown in Figures 2, 3, 4, 5 and 6 for the different parameters.

Effect of Dissolution Temperature

Figure 2 shows that the dissolution rate increases with increase in temperature up to the highest temperature range employed (80^0C). The extraction was observed to reach 95% at 80^0C. This shows that the reaction is endothermic. At high temperature collision of the particles and the liquid molecules is enhanced.

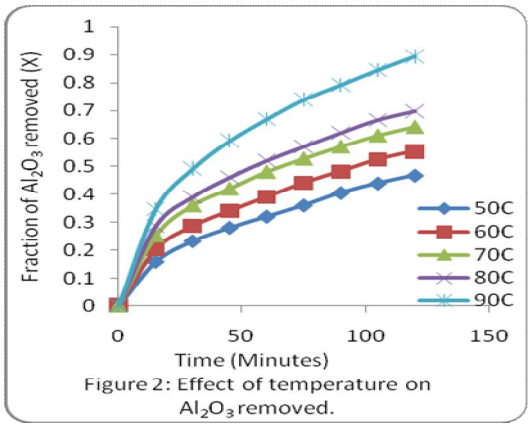

Figure 2: Effect of temperature on Al_2O_3 removed.

Effect of Acid Concentration

The effect of acid concentration was studied by varying the concentrations from 0.8 to 6.5 M. it was observed that the fraction of alumina removed increased with increase in acid concentration up to 4.8 M and above this the fraction removed decreased.

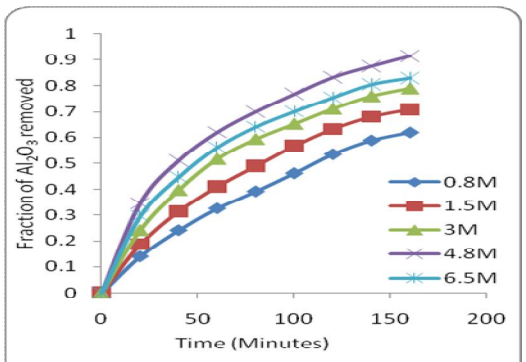

Figure 3: Effect of acid concentration on Al_2O_3 removed.

Effect of Particle Size

The particle size effect on the dissolution rate of the clay sample in the acid solution was studied by varying the size of the samples from 0.045 – 0.408 mm. it was observed that the dissolution rate decreased as the particle size increased. Smaller particle sizes create higher surface area for contact with the liquid thereby increasing the rate of dissolution of the clay particles in the liquid medium.

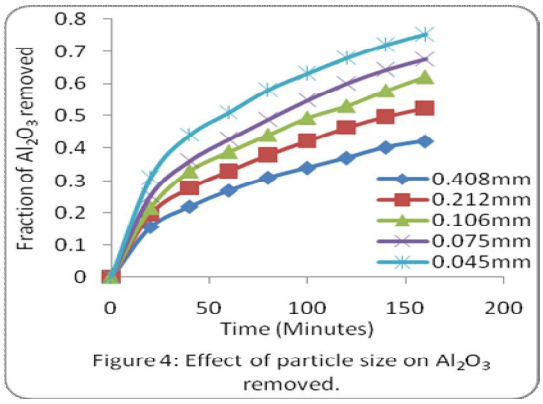

Figure 4: Effect of particle size on Al_2O_3 removed.

Effect of Solid-to-Liquid Ratio

The results of the effect of solid-to-liquid ratio on clay calcined at 750^0C for two hours and extracted at 80^0C using 6.8 M of HCl are shown in Figure 5. The data shows that the dissolution rate increases as the solid-to-liquid ratio decreases.

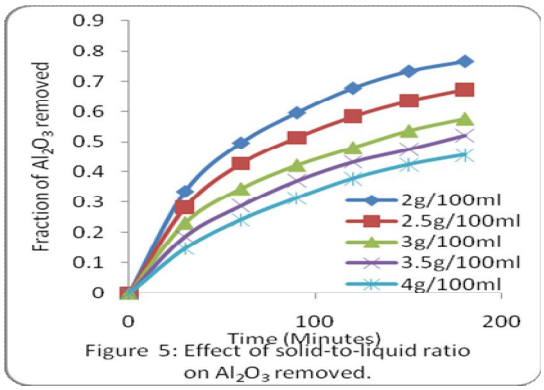

Figure 5: Effect of solid-to-liquid ratio on Al_2O_3 removed.

Effect of Stirring Speed

The effect of stirring speed on the dissolution rate of Ukpor clay in hydrochloric acid solution was investigated at different stirring rates from 90 to 720 rpm. It was found out that as the stirring speed increases, the dissolution rate increased up to 540 rpm as shown in Figure 6. The dissolution rate was observed to decrease beyond 540 rpm. Therefore, the stirring rate was kept at 540 rpm to investigate the effect of other parameters on the dissolution.

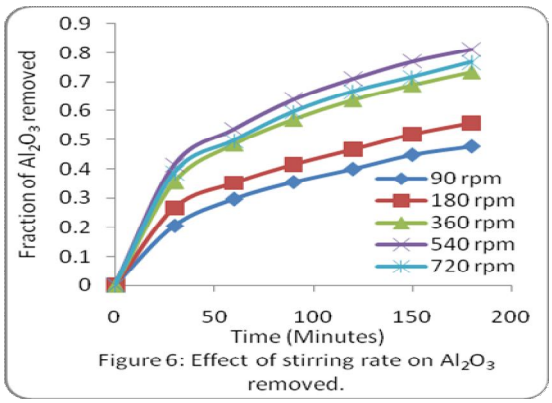

Figure 6: Effect of stirring rate on Al_2O_3 removed.

Dissolution Kinetics

For a liquid-solid reaction system, the reaction rate is generally controlled by one of the following steps: diffusion through the liquid film, diffusion through the ash/product layer or the chemical reaction at the surface of the shrinking core of the solid particle (Levenspiel, 1972). The rate of the process would be controlled by the slowest of these sequential steps.

The integrated rate equations can be given as follows:

$X = 3bk_cC_A/\rho_BR = k_ft$ (film diffusion) (1)

$1 + 2(1 – X) – 3(1 – X)^{2/3} = (2M_BDC_A/\rho_BbR^2)\ t = k_dt$ (ash diffusion) (2)

$1 – (1 – X)^{1/3} = (k_cM_BC_A/\rho_BbR)t = k_rt$ (chemical reaction) (3)

Where X is the fraction reacted, k_c is the kinetic constant, M_B is the molecular weight of the solid, C_A is the concentration of the dissolved lixiviant A in the bulk of the solution, b is the stoichiometric coefficient of the reagent in the leaching reaction, R is the initial radius of the solid particle, t is the reaction time, D is the diffusion coefficient in the porous product layer, ρ_B is the density of the solid particle, k_f, k_d, and k_r are the rate constants, respectively, which are calculated from Eqs. (1), (2), and (3).

In addition to the heterogeneous models, pseudo-homogeneous models can also be used to derive the rate equations for the heterogeneous reactions. In pseudo-homogeneous model, the rate equation is written as,

$-\ln(1 – X) = Kt$ (first-order pseudo-homogeneous model) (4)

In addition to these models, the Avremi model can be used and it is written as,

$-\ln(1 – X) = k_At^m$ (Avremi model) (5)

The reaction kinetics data between calcined Ukpor clay and hydrochloric acid solutions were analyzed statistically and graphically using the Avremi model, the first-order homogeneous model, and the shrinking core models. It was observed that the experimental data did not fit the Avremi and the first-order homogeneous models when plotted, as expected, straight lines passing through the origin were not obtained and low regression coefficient values were calculated as shown in Table 2. When the data were analyzed using the shrinking core models, it was observed that the data fitted very well to the diffusion of the ash/product layer control as shown in Figures 7, 8, 9, 10 and 11 for the different process parameters, temperature, acid concentration, solid-to-liquid ratio, particle size, and stirring speed, respectively. Therefore, the dissolution process was found to follow the shrinking core model and can be represented as follows.

$1 + 2(1 – X) – 3(1 – X)^{2/3} = k_dt$ (6)

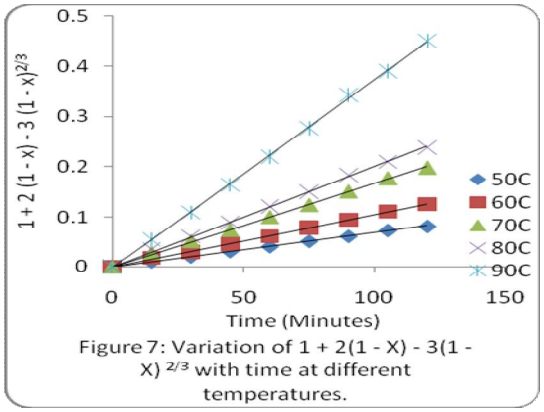

Figure 7: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different temperatures.

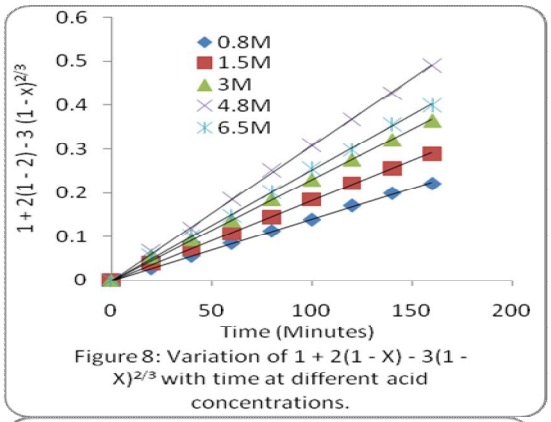

Figure 8: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different acid concentrations.

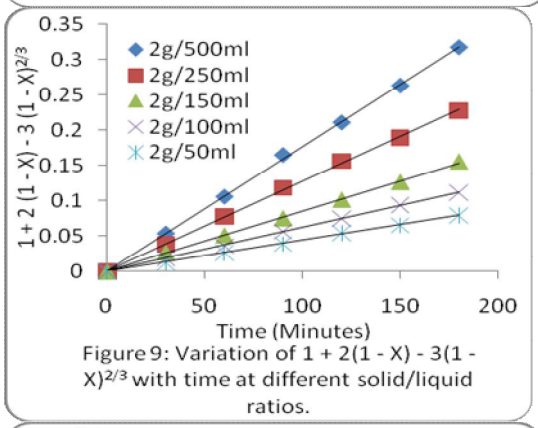

Figure 9: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different solid/liquid ratios.

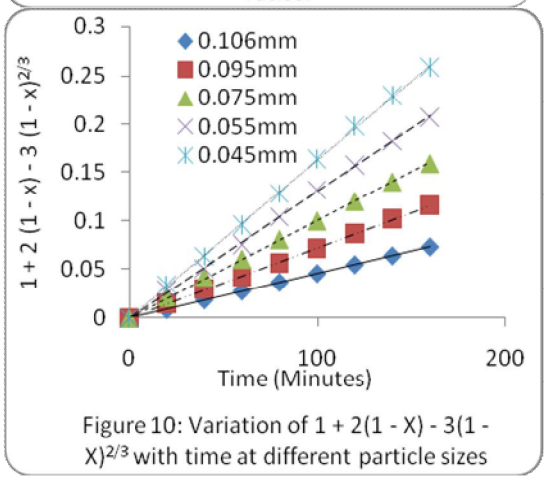

Figure 10: Variation of $1 + 2(1 - X) - 3(1 - X)^{2/3}$ with time at different particle sizes

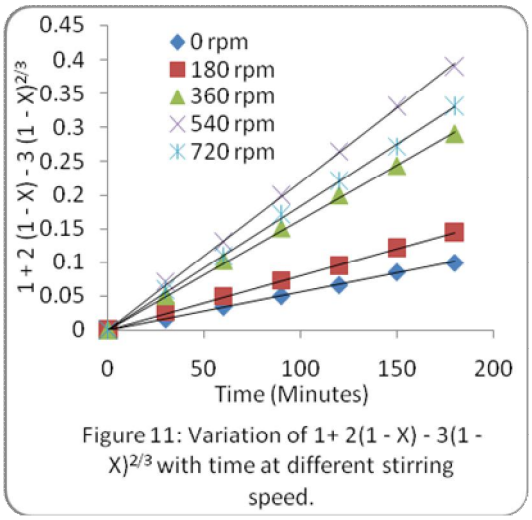

Figure 11: Variation of 1+ 2(1 - X) - 3(1 - X)$^{2/3}$ with time at different stirring speed.

The relationship between the overall reaction rate constant and temperature according to the Arrhenius equation was employed in calculating the activation energy. The plot of the Arrhenius equation is shown in Figure 12 and the slope of the figure was used to calculate the activation energy to be 39.009kJ/mol. This value is high for a diffusion controlled process, but recent studies showed that diffusion controlled reactions could have unusually high activation energy. For instance, the activation energy for the diffusion controlled dissolution of Nigerian cassiterite ore in hydrochloric acid was reported to be 50.05kJ/mol (Alafara, 2009) and that for diffusion controlled hydrochloric acid leaching of iron from bauxite varied from 62kJ/mol to 79kJ/mol for different particle size fractions (Paspaliaris, et al, 1987); while that for diffusion control through the product layer using hydrochloric and nitric acids were determined to be 40.8 and 38.3kJ/mol, respectively, for dissolution of sepiolite (Ozdemir et al, 2005).

To investigate the effect of the process parameters, temperature, acid concentration, particle size, solid/liquid ratio, and stirring speed on the dissolution kinetics of Ukpor clay in hydrochloric acid, a semi-empirical model is postulated as follows:

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

The constants a, b, c, and d, are calculated from the plots of the relationship between the natural logarithm of the apparent rate constant (calculated from Figures 8 to 11) and the natural logarithm of the process parameters, acid concentration, particle size, solid/liquid ratio, and stirring speed; while k_o and E_a were calculated from the Arrhenius plot. The plots are shown in Figures 12, 13, 14, 15, and 16 for temperature, acid concentration, particle size, solid/liquid ratio, and particle size, respectively. The values of *a*, *b*, *c*, *d*, E_a, and k_o are; 0.37, -0.89, -0.63, 0.42, 39.009, and 1.40 x 10^3, respectively. Inserting these values into Eq. (7) gives

$$1 + 2(1 - X) - 3(1 - X)^{2/3} = 1.40 \times 10^3 C_{[HCl]}^{\ 0.37} (d_p)^{-0.89} (S/L)^{-0.63} (w)^{0.42} \exp^{(-39.009/RT)} \quad (8)$$

It can then be concluded that the dissolution kinetics of Ukpor clay in hydrochloric acid can be described by Eq. (8).

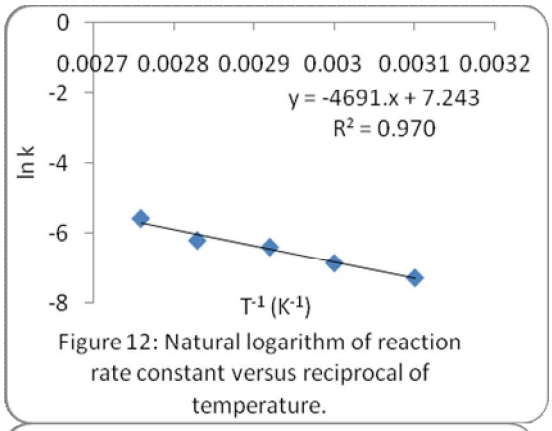

Figure 12: Natural logarithm of reaction rate constant versus reciprocal of temperature.

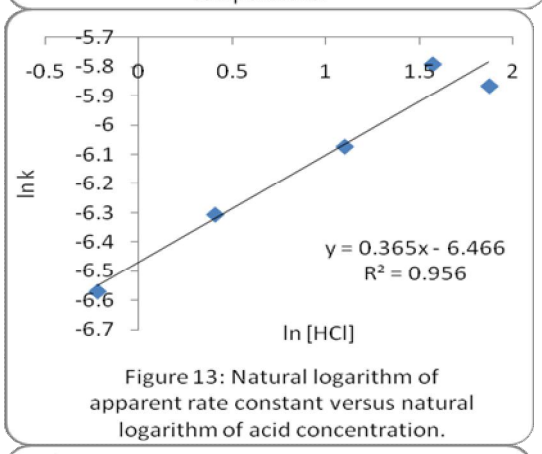

Figure 13: Natural logarithm of apparent rate constant versus natural logarithm of acid concentration.

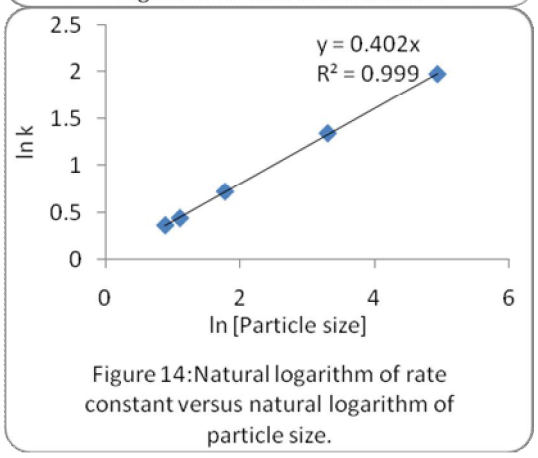

Figure 14:Natural logarithm of rate constant versus natural logarithm of particle size.

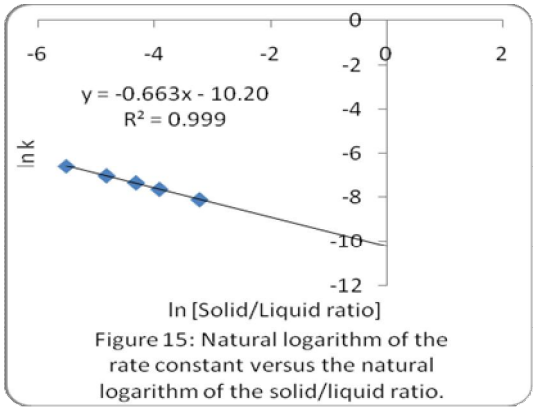

Figure 15: Natural logarithm of the rate constant versus the natural logarithm of the solid/liquid ratio.

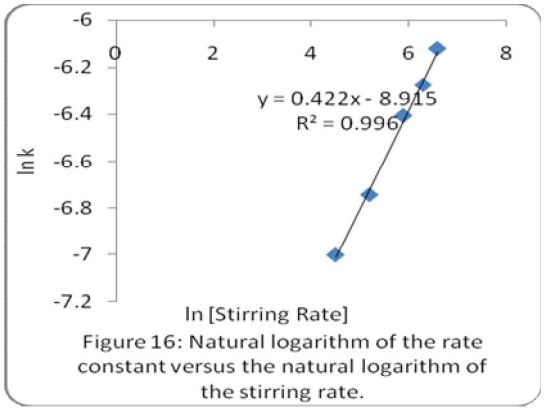

Figure 16: Natural logarithm of the rate constant versus the natural logarithm of the stirring rate.

Table 2: Values of the rate constants and the regression coefficients for the tested models

Process parameter	Models									
	Film diffusion		Chemical reaction		Product layer diffusion		Avremi		Pseudo first-order	
	k_f	R^2	k_r	R^2	k_d	R^2	k_A	R^2	k	R^2
Temperature (^{0}C)										
50	4.366	0.7876	1.700	0.8621	0.691	0.9988	0.367	0.9789	1.678	0.7564
60	5.268	0.7040	2.146	0.8269	1.054	0.9989	0.473	0.9767	1.985	0.7694
70	6.373	0.6553	2.731	0.8153	1.668	0.9989	0.582	0.9795	2.547	0.7712
80	6.895	0.6303	3.045	0.8151	2.010	0.9990	0.764	0.9856	3.065	0.7749
90	8.696	0.6173	4.365	0.8846	3.724	0.9991	0.947	0.9965	3.642	0.7886
Acid concentration (mol/dm^3)										
0.8	5.000	0.6686	2.179	0.8326	1.404	0.9990	0.115	0.9236	2.324	0.6584
1.5	5.515	0.6244	2.507	0.8234	1.825	0.9989	0.321	0.9475	2.865	0.6617
3.0	6.113	0.5990	2.895	0.8358	2.302	0.9988	0.386	0.9512	3.854	0.6658
4.8	6.752	0.5682	3.506	0.8734	3.068	0.9988	0.442	0.9546	4.052	0.6873
6.5	6.277	0.5911	3.078	0.8563	2.522	0.9987	0.486	0.9675	4.763	0.7143
Solid-to-liquid ratio (g/ml)										
2/100	2.869	0.7184	1.116	0.7990	0.445	0.9991	1.135	0.9648	2.567	0.6821
2.5/100	3.305	0.6589	1.326	0.7698	0.624	0.9990	1.437	0.9562	3.678	0.6873
3/100	3.733	0.6714	1.544	0.7975	0.849	0.9988	1.562	0.9256	4.116	0.6934
3.5/100	4.511	0.4832	1.980	0.6643	1.274	0.9987	1.785	0.9023	4.854	0.7053
4/100	5.140	0.4244	2.397	0.6547	1.766	0.9986	2.046	0.8967	5.621	0.7467
Particle size (mm)										
0.408	3.066	0.6712	1.178	0.7613	0.459	0.9994	1.643	0.9175	1.754	0.6986
0.212	3.787	0.6531	1.517	0.7736	0.725	0.9994	1.853	0.9326	2.532	0.7164
0.106	4.328	0.6418	1.795	0.7795	1.002	0.9991	2.245	0.9492	3.174	0.7375
0.075	4.833	0.6192	2.077	0.7838	1.302	0.9990	2.785	0.9538	3.652	0.7543
0.045	5.637	0.5133	2.574	0.7162	1.631	0.9990	3.057	0.9675	4.056	0.7653
Stirring speed (rpm)										
90	3.135	0.7683	1.242	0.8473	0.556	0.9992	1.085	0.9089	1.476	0.7432
180	3.676	0.7202	1.514	0.8313	0.801	0.9990	1.743	0.9123	2.153	0.7698
360	4.919	0.6836	2.259	0.8527	1.632	0.9989	2.375	0.9175	2.746	0.7743
540	5.480	0.6575	2.683	0.8703	2.197	0.9989	2.873	0.9327	3.532	0.7853
720	5.136	0.6700	2.417	0.8596	1.837	0.9988	3.176	0.9456	4.114	0.8165

CONCLUSIONS

In this work, the reaction kinetic model of the dissolution of clay from Ukpor in hydrochloric acid was investigated and from the experimental conditions employed, it can be concluded that:

- Ukpor clay is a viable source of alumina for the aluminium industry and can be produced in large scale.
- Calcination of the clay sample renders the alumina soluble within the temperature range of 500 to 750^{0}C.
- The dissolution rate increases with increase in temperature, acid concentration (up to 4.8M), stirring speed, and decrease in particle size and solid-to-liquid ratio.
- The dissolution process can be described by the shrinking core kinetic model with the product layer diffusion as the limiting step.

- The activation energy of the dissolution energy was calculated to be 39.009kJ/mol.

This study was faced with unresolved challenges. The unavailability of x-ray diffractometer limited the characterization of the alumina produced and the mineral characterization of the Ukpor clay that was used as the basic raw material.

REFERENCES

Al-Jeel A. A., Al-Sindy S. I., 2006. Alumina recovery from Iraqi kaolinitic clay by hydrochloric acid route. Iraqi Bulletin of Geology and Mining, 2 (1), 67 – 76.

Alafara A. B., Folahan A. A., Emmanuel E. T., Rafiu B. B., 2009. Dissolution kinetics and leaching of rutile ore in hydrochloric acid. Journal of Minerals and Materials Characterization and Engineering, 8 (10), 787 – 801.

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

Al-Zahrani A., Abdel-Majid M. H., 2004. Production of liquid alum coagulant from local Saudi clays. JKAU: Eng. Sci., 15 (1), 3 – 17.

Austin G., 1984. Shreve's Chemical Process Industries, 5th. Ed., McGraw-Hill, New York, 244 – 250 and 355 – 359.

Barclay A., Peters D., 1976. New sources of alumina. Min. Cong. J., 62 (6), 29 – 33.

Connor D. J., (1988). Alumina extraction from non bauxitic materials: aluminium. Verlag Gmbh, Dusseldorf, 370.

Eisele J. A., Bauer D. J., Shanks D. E., 1983. Bench-scale studies to recover alumina from clay by a hydrochloric acid process. Industrial & Engineering Chemistry, Product Research and Development, 22 (1), 105 – 110.

Hulbert S. F., Huff D. E., 1970. Kinetics of alumina removal from calcined kaolin with nitric, sulphuric, and hydrochloric acids. Clay Minerals, 8, 337 – 340.

Levenspiel O., 1972. Chemical Reaction Engineering. John Wiley and Sons, New York.

Ozdemir M., Cetisli H., 2005. Extraction kinetics of alunite in sulphuric acid and hydrochloric acid. Hydrometallurgy, 76 (3 – 4), 217 – 224.

Paspaliaris, Y., Tsolakis, Y. 1987. Reaction kinetics for the leaching of iron oxide in diasporic bauxite from the Paranassus-Giona zone (Greece) by hydrochloric acid. Hydrometallurgy, 19, 259 – 266.

Peters F. A., Johnson P. W., Kirby R. C., 1962. Methods for producing alumina from clay, an evaluation of five hydrochloric acid processes. U. S. Bureau of Mines R. I. No. 6133.

Phillips C. V., Wills K. J., (1982). A laboratory study of the extraction of alumina of smelter grade from China clay micaceous residues by a nitric acid route. Hydrometallurgy, 9, 15 – 28.

Poppleton H. O., Sawyer D. L., 1977. Hydrochloric acid leaching of calcined kaolin to produce alumina. Instruments and Experimental Techniques. 2, 103 – 114.

Ranjita S., Bhima R., 2010. Leaching kinetics for iron from partially laterised khondalite rocks by hydrochloric acid solution. Proceedings of the XI International Seminar on Mineral Processing Technology, 839 – 847.

Salih A., Murat E., Ali A., Gokhan U., Alper O., 2006. Dissolution kinetics of celestite ($SrSO_4$) in HCl solution with $BaCl_2$. Hydrometallurgy, 84, 239 – 246.

Schoenborn N., Hofman H., 1979. Reaction of selected clays with hydrochloric acid. Freiberger Forschungshefte A, A616, 39 – 50.

Shanks D. E., Thompson D. C., Dan G. L., Eisele J. A., 1986. Options in the hydrochloric acid process for the production of alumina from clay. Metallurgical Soc. Of AIME, 2, 25 – 33.

Tilley G. S., Millar R. W., Ralston O. C., 1927. Acid process for the extraction of alumina. U. S. Bureau of Mines Bull. No. 267.

Yuksel A., Salih B., Elvan M. 2011. Leaching kinetics of ulexite in oxalic acid. Physicochem. Probl. Miner. Process. 47, 139 – 148.

Zafar 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.

Ziegenbalg S., Discher G., 1983. Extraction of alumina from clay by hydrochloric acid process. Freiberger Forschungshefte (Reihe) A, 7 – 25.