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Application of the Shrinking Core Models to Hydrochloric Acid Dissolution of Alumina from Clay

Henry Oghenero ORUGBA[1], Okechukwu Dominic ONUKWULI[2], Akinpelu Kamoru BABAYEMI[3], Jonah Chukwudi UMEZUEGBU[3]

[1]*Department of Chemical Engineering, Delta State University, Abraka Nigeria*
orugbahenry@yahoo.com

[2]*Department of Chemical Engineering, Nnamdi Azikiwe University, Awka Nigeria*
okechukwuod@yahoo.com

[3]*Department of Chemical Engineering, Odumegwu Ojukwu University, Uli, Nigeria*
akinbabs40@yahoo.com/umejonah@gmail.com

Corresponding Author: akinsbab40@yahoo.com

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Abstract: *The steady depletion of bauxite which is the major source of alumina from which aluminium is produced has prompted the need to seek for means of obtaining alumina from other materials like clays that are relatively high in alumina content. Acid leaching has been found to be a viable means of obtaining the ore from clays. In order to design alumina dissolution process from clays, the influence of process parameters as well as values of the relevant thermodynamic parameters on the yield of alumina must be determined. In this research, the local clay was characterized to ascertain its viability for alumina production. The influence of particle size of clay, stirring speed, leaching temperature, acid-to-clay weight ratio and acid concentration on the yield of alumina from the local clay were studied. In order to develop a kinetic model for the dissolution process, the different forms of the shrinking core model were tested with the experimental data. The characterization result revealed that the clay having 33.9% of alumina is a viable source of producing alumina. With the exception of particle size of clay, increasing all the parameters tested showed increase in the percentage of alumina leached from the clay. The results of the model testing showed that the liquid film diffusion-controlled model gave the best fits for the experimental data and based on the Arrhenius equation, the activation energy for the dissolution process was calculated to be 35.32 kJ/mol.*

Keywords: *Acid-dissolution, alumina, hydrochloric acid, thermodynamic data, clay.*

1. INTRODUCTION

In the world today, alumina is commercially important being used majorly in the production of aluminium metal and hence a very important ore in the mineral industry. The ore alumina has also been used as catalyst, abrasive and as adsorbent [1-3]. Alumina is widely distributed in nature and usually occurs in the purest natural form in corundum and bauxite. Of the two purest minerals from which alumina can be obtained, bauxite appeared to be the most important as it is found in much quantity in many regions of the world. Bauxites have been widely used in industry to produce alumina via the Bayer process [4]. In order to meet the increasing demand for alumina and to supplement the steady depletion of bauxite, researchers have been seeking for alternative raw materials from which alumina can be obtained. Also, some countries some countries of the world like Nigeria have no deposit of this bauxite and importing this ore is capital-intensive, hence efforts have been directed to source for other minerals from which it can be obtained. Clay has been identified as a rich source of many ores like alumina and iron and is mainly found in huge deposits in many countries. Many Nigerian clays have been found to be very rich in alumina and iron oxide [5-8].

Amongst the different processes employed by researchers in obtaining alumina from clays, acid leaching has been found to be very efficient as it has guaranteed the recovery of very high percentage of the ore from clay [7]. For example, in the leaching of Saudi local kaolin in hydrochloric acid, an approximate yield of 62.9% was obtained [9].Both minerals and organic acids have been used in dissolution of alumina from clays [9].Of the many acids used in the dissolution process, hydrochloric acid and tetra-oxosulphate (vi) acid have been commonly used as they produce better results compared to many others. In the dissolution process, the raw clays are usually subjected to thermal treatment called heat activation which helps to open up the pores of the clay in order to enhance the release of these metallic ions from the clay[10-12].

Although the kinetics of alumina and other ores dissolution from clays have been studied for different clays by different researchers over the years in order to obtain the relevant thermodynamic parameters for the leaching process, very little or nothing has been done on Ozoro clay. Udeigwei et al., (2015) [13] found the hydrochloric acid dissolution of alumina from a Nigerian local clay to follow the liquid-film diffusion-controlled model. Using tetra-oxosulphate (vi) acid, alumina has been synthesized from a Nigerian local clay by extracting alumina from meta-kaolin [14]. The leaching of alumina from Jordan clay using tetra-oxosulphate (vi) acid followed by hydrochloric acid dissolution has been studied and a very high purity of alumina was obtained [15]. In another work, the leaching of alumina from a Nigerian clay using hydrochloric acid has been studiedin order to obtain the thermodynamic parameters for the clay [8].

Though clays from different locations may have high percentages of alumina content in them, they have their peculiar thermodynamic parameters and respond differently to the different kinetic models when leached with different solvents. The aim of this research is to explore the viability of Ozoro clay and to establish the best kinetic model for its alumina dissolution using hydrochloric acid in order to obtain the relevant thermodynamic parameters guiding the leaching process.

2. MATERIALS AND METHODS

2.1 Material Preparation

In this research work, the local clay was obtained from Ozoro (6.24ºN, 5.55ºE) in Delta State Nigeria. In order to remove debris from the raw clay, the clay was soaked in water for two days and using the method of filtration, the debris were removed. The sieved clay was sun-dried for 24 hours and then oven-dried at 60ºC for 18 hours to aggregate the particles. The samples were subjected to heat activation in a muffle furnace (model LMF-3550/120V) for a period of 1hr at700 ºC being the best calcinations condition for the local clay [7]. The samples were all groundand sieved into different particle sizes and properly labeled.

2.2 Characterization

The local clay was characterized to determine its chemical composition. The morphology of the clay was determined with the Scanning Electron Microscope, SEM (Model S-3700N) while the alumina content from each leached sample was analyzed with MS- Atomic Absorption Spectrophotometer (AAS).

2.3 Leaching Experiment of the Kinetic Studies

In each leaching experiment, 30g of the activated clay was weighed into an already determined volume of the acid and heated in a round bottom flask. At intervals of 15 minutes, a pipette was used to withdraw 2ml of the leaching solution from the round bottom flask. The collected sample of leached liquor was allowed to cool on standing for 20 minutes and after which, it was filtered and used for iron estimation using the AAS. The dissolution percentage of the iron in the slurry was calculated according to Orugba*et al*. [7]. The influence of particle size, acid concentration, liquid-solid ration, stirring speed and leaching temperature on the yield of alumina from the local clay were studied.

3. RESULTS AND DISCUSSION

3.1 Results of Clay Characterization

1)XRF Analysis of Clay: The XRF analysis of the local clay is presented in Table 1 as follows:

Table1: The XRF results of the raw clay sample.

Chemical composition	% composition
Al_2O_3	33.90
SiO_2	41.80
Fe_2O_3	12.00
CaO	0.45
MnO	0.08
K_2O	5.15
Ga_2O_3	0.01
TiO2	2.00
Cr_2O_3	0.16
V_2O_5	0.10
NiO	0.21

CuO	0.17
Rh_2O_3	3.10

The XRF result of the local clay shown in Table 1 revealed that the clay is rich in silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) with the percentages of 41.8%, 33.90% and 12.00% respectively. This shows that the local clay is a viable source of alumina.

2) SEM Analysis of Clay: The result of SEM of the raw and heat-activated clay samples are presented in Figures 1 and 2 respectively as follows:

Figure 1: SEM result of the raw clay

Figure 2: SEM result of the heat-activated clay

The SEM results of the raw and the heat-activated clay revealed that the pores appeared to open more after the activation process. This implies that heat-activation of the local clay will enhance release of metal ions from the clay compared to the raw (non-activated clay).

3.2 Effects of Process Parameters on Alumina Dissolution

In order to study the reaction mechanism and kinetics of the dissolution processes of alumina from Ozoro clay using hydrochloric acid, the experiments were performed at various values of the process variables (particle size, acid concentration, liquid-solid ratio, temperature and stirring speed) as a function of time. The percentage of alumina dissolution from the clay was measured and plotted against time at different values of the process variables. Figures 3, 4, 5, 6 and 7 show the effects of particle size, acid concentration, liquid-solid ratio, stirring speed and temperature on alumina extraction from Ozoro clay with hydrochloric acid respectively.

The variation of Figure 3 shows that the fraction of alumina removed increased with reduced particle size and the highest yield of 70% was obtained with the smallest particle size of 0.045mm. Figure 4 revealed that increasing the concentration of hydrochloric acid increases the rate of alumina yield and the highest yield of 69% was recorded at the highest concentration of 3M that was used. Figure 5 shows that increasing liquid-solid ratio increases alumina yield from the clay and the highest yield of 67% was obtained with the highest acid-clay ratio of 16cm^3/gm. This may be due to the fact that sufficient solvent is present to reach the solute for sufficient dissolution. Figure 6 shows that increasing stirring speed increases alumina yield from the clay because as speed increases, the particles are being made to contact the solvent to enhance dissolution rate. Figure 7 shows that increasing leaching temperature increases dissolution rate of alumina in hydrochloric acid since more energy is given to the reacting molecules for reaction.

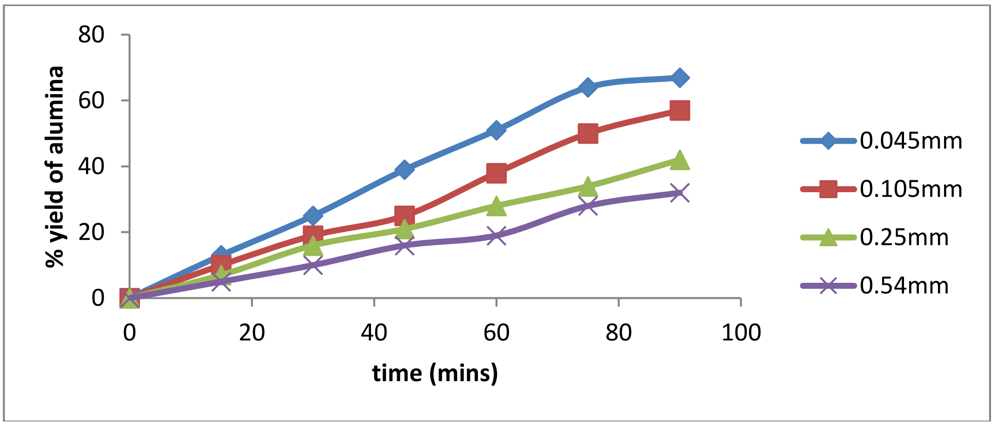

Figure 3: Effect of particle size of clay on alumina yield with HCl

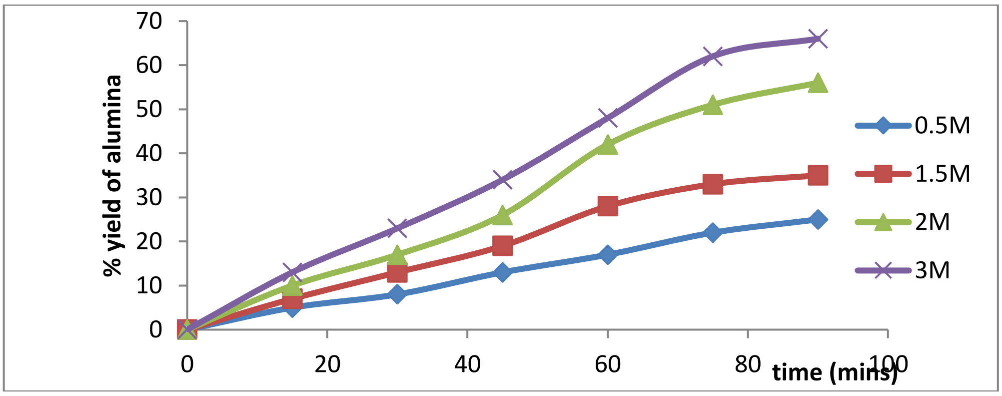

Figure 4: Effect of HCl concentration on alumina yield

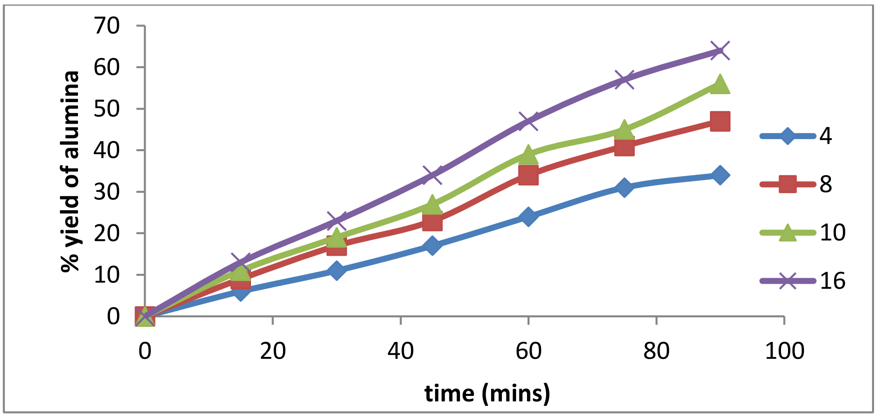

Figure 5: Effect of solid-liquid ratio on alumina yield with HCl

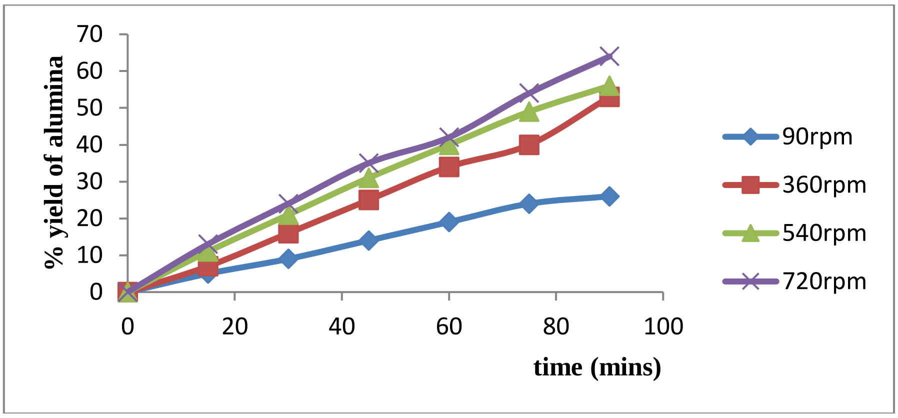

Figure 6: Effect of stirring speed on alumina yield with HCl

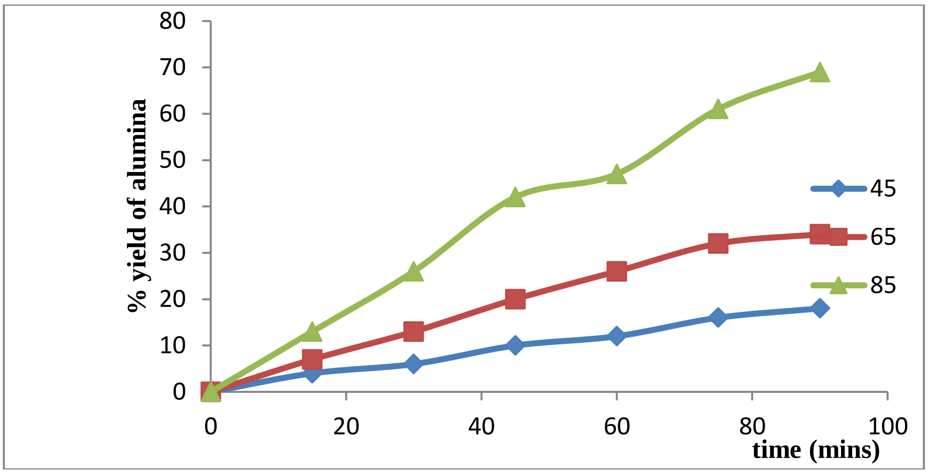

Figure 7: Effect of leaching temperature on alumina yield with HCl

3.3 Testing for the Reaction Mechanism using the different forms of the Shrinking Core Model

The different forms of the shrinking core model (Equations 1-6) were applied to fit the experimental data in order to identify the reaction mechanism for comparative analysis of the leaching kinetics of alumina from the clay with hydrochloric acid.

$Chemicalreactioncontrolledprocess\ 1-(1-X)1/3 = kt$ (1)

$Liquidfilmdiffusioncontrolledmodel\ 1-(1-X)2/3 = kt$ (2)

$Productlayerdiffusioncontrolledprocess\ 1+2(1-X)-3(1-X)2/3 = kt$ (3)

$AvremiModel{-}\ln(1-X) = KAtm(4)$

$First - orderpseudo - homogeneousmodel{-}\ln(1-X) = kt$ (5)

$GinstlingandBrounshteinmodel\ 1-2/3(X)-(1-X)2/3 = kt$ (6)

When the experimental data of Figures 3, 4, 5, 6 and 7 were tested with Equations 1-6 to determine the equation that best describes the reaction kinetics alumina dissolution from the local clay, the liquid film diffusion controlledmodel gave the best fits. The fitted plots are shown in figures 8, 9, 10, 11 and 12 for each of the parameters as follows:

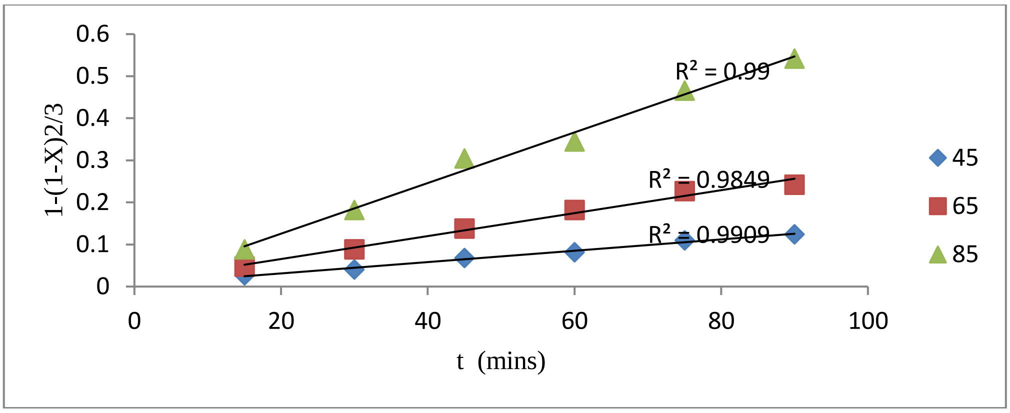

Figure 8: Plot of 1-(1-X)^2/3 against time at different temperatures with HCl for alumina yield

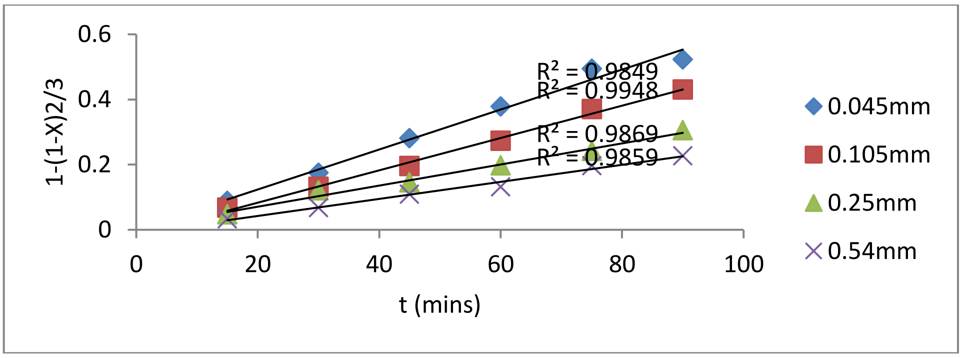

Figure 9: Plot of 1-(1-X)^2/3 against time at different particle sizes with HCl for alumina yield

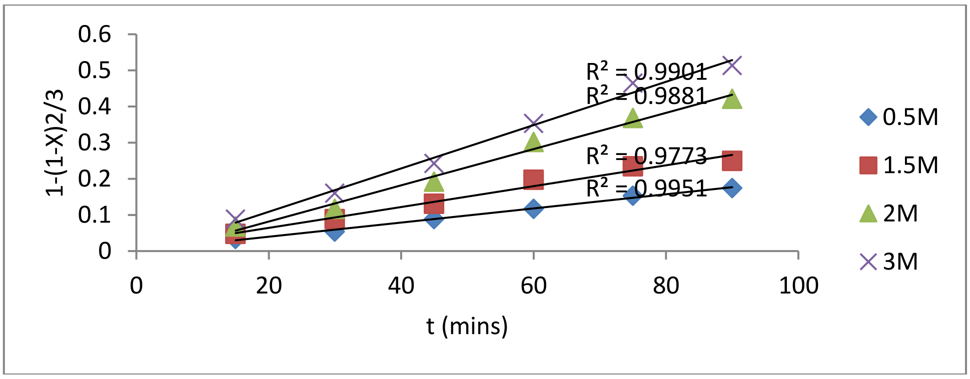

Figure 10: Plot of 1-(1-X)^2/3 against time at HCl concentration for alumina yield

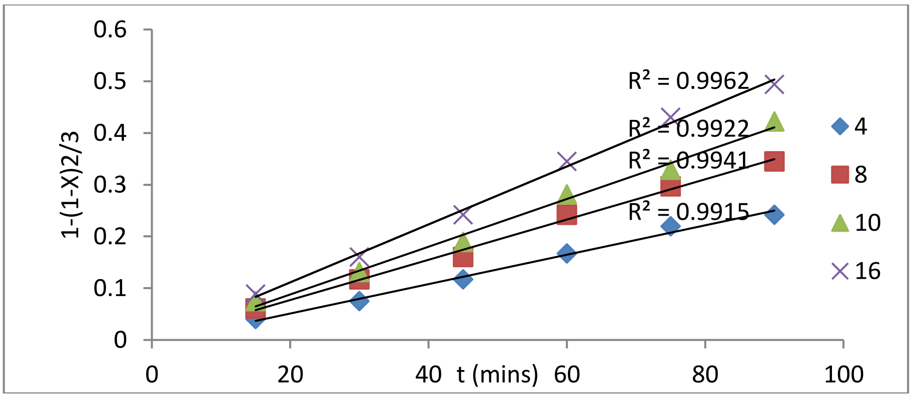

Figure 11: Plot of 1-(1-X)^2/3 against time at different liquid-solid ratio with HCl for alumina yield

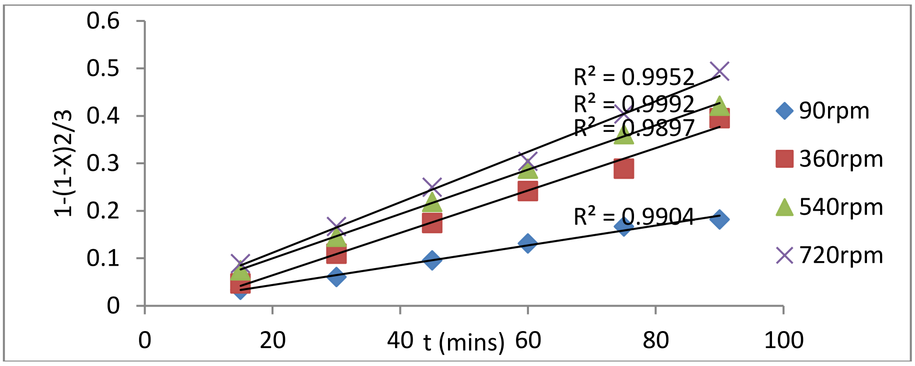

Figure 12: Plot of 1-(1-X)^2/3 against time at different stirring speed with HCl for alumina yield

The reaction order 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:

$$ln\,(-r) = \;lnk\; + n\,lnCA \qquad (7)$$

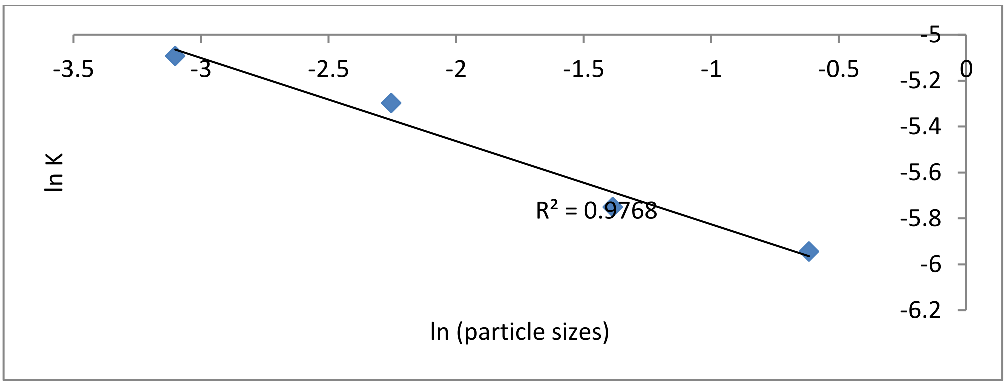

Figure 13: Plot of ln K against ln (particle size) with HCl

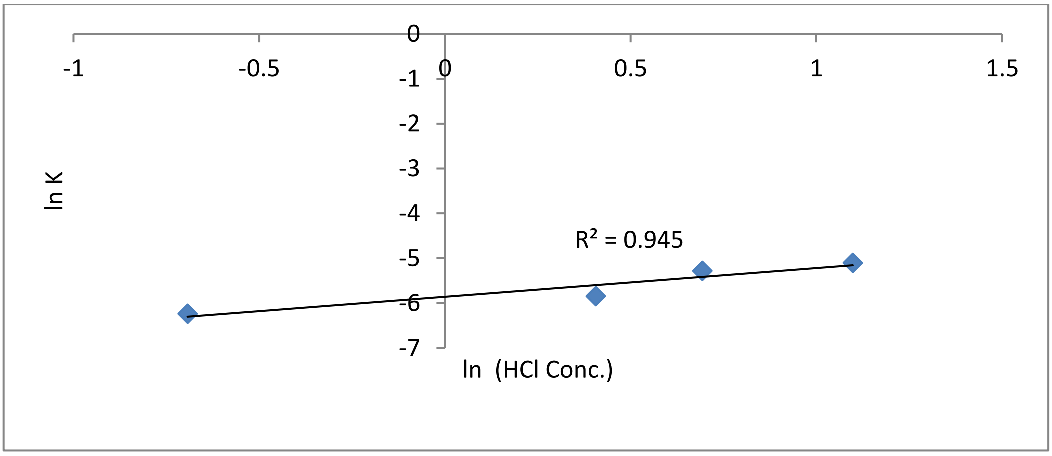

Figure 14: Plot of ln K against ln (conc. of HCl)

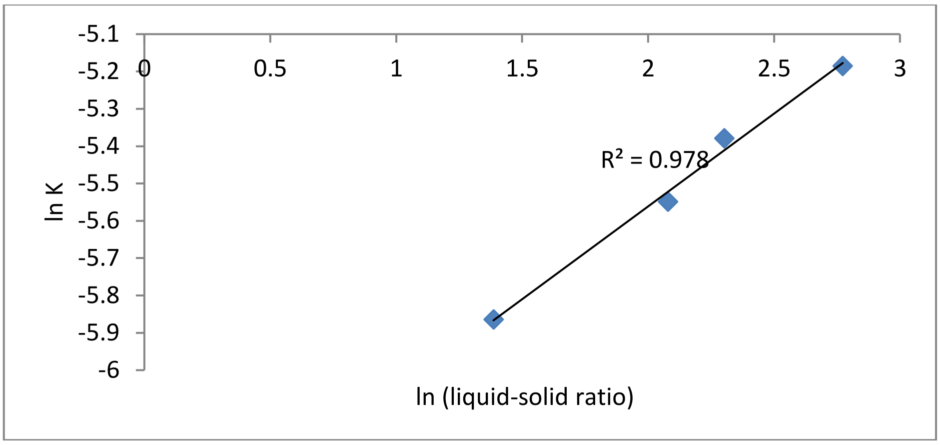

Figure 15: Plot of ln K against ln(liquid-solid ratio) with HCl

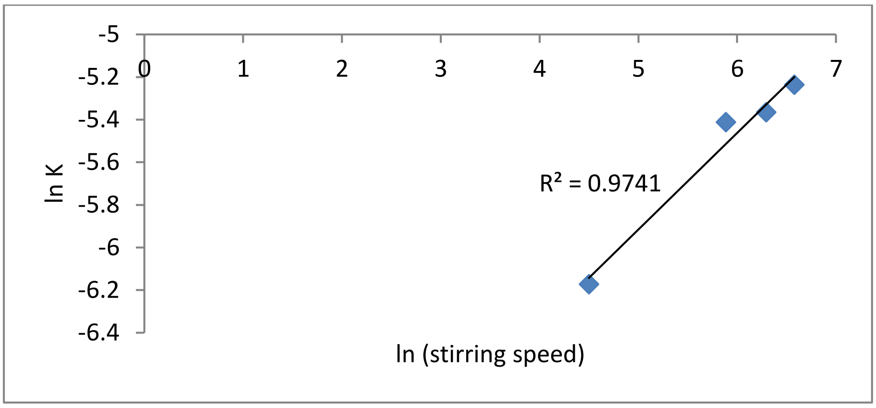

Figure 16: Plot of ln K against ln (stirring speed) with HCl

The relationship between the overall rate constants K calculated from Figure 7 at different temperatures may be expressed according to the Arrhenius equation as follows.

$$K = A\,exp\left(-\frac{E}{RT}\right) \quad (7)$$

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 ($8.314JK^{-1}mol^{-1}$) and T is the reaction temperature in Kelvin. The reaction rate constants for different temperatures were calculated from the slope of the plot of lnK against T^{-1} is shown in Figure 17.

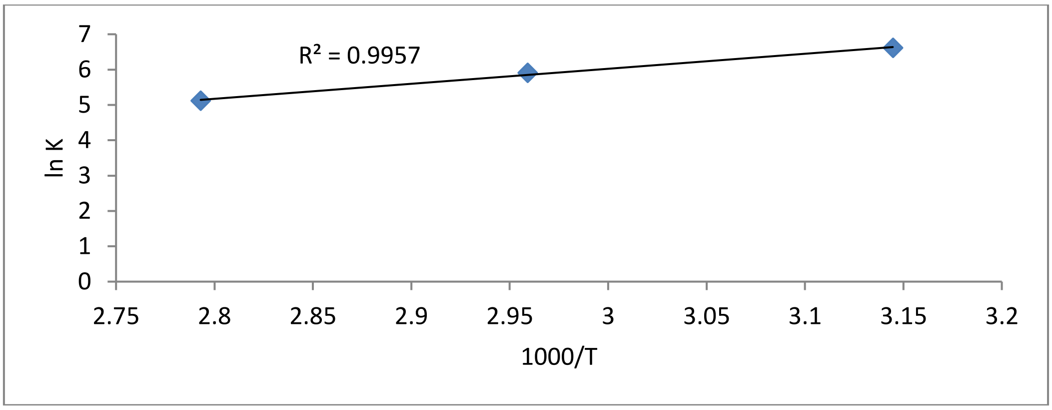

Figure 17: Plot of ln K against 1000/T using HCl

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

$$1-(1-x)^{2/3} = AC^{a}_{[HCl]}dp^{b}\left(l/_{s}\right)^{c}(sp)^{d}exp\left(-Ea/_{RT}\right) \quad (8)$$

The variables a,b,c,d were determined from the slopes of the plots of Figures 13-17 as 0.6402, -0.362, 0.497 and 0.453 respectively. The values of A and E were obtained from Figure 17 as 0.001204 35.32 respectively. Substituting these values in the equation, the dissolution of alumina in Ozoro clay in HCl could be described by the following equation

$1-(1-x)^{2/3} = 0.001204C^{0.6402}_{[HCl]}\,(d_p)^{-0.362}\,(l/s)^{0.497}(sp)^{0.453}exp\,(-35.32/RT)t.$

4. CONCLUSION

A study of alumina dissolution from a Nigerian local clay using hydrochloric acid has been studied. The yield of alumina from the clay was studied by varying particle size, leaching temperature, acid-clay weight ratio, stirring speed and acid concentration. The influence of each process variable on the yield of alumina from the clay was determined and a kinetic model was developed to obtain the relevant thermodynamic parameters for the dissolution process. The activation energy of the hydrochloric acid dissolution of alumina from the local clay was obtained to be 35.32 kJ/mol.

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NOMENCLATURE

x= fraction extracted
K= rate constant
t= time
X= fraction of alumina extracted
C= acid concentration
D= diameter of particle
L= liquid-solid ratio
S= stirring speed
E_a = activation energy
A= collision frequency
R= universal gas constant
t= time
a= reaction order for acid concentration variation
b= reaction order for particle size variation
c= reaction order for liquid-solid ratio variation
d= reaction order for stirring speed variation