THERMODYNAMICS AND KINETICS STUDIES OF ALUMINA LEACHING FROM KARAWORO CLAY USING OXALIC ACID SOLUTIONS

Onukwuli, O. D. and Okafor, V. N.
Department Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, Uli.

ABSTRACT
The leaching kinetics and mechanisms of reaction of Karaworo clay in oxalic acid was studied. Calcination temperature, leaching temperature, acid concentration, particle size and solid-to-acid ratio was selected as process parameters. It was observed that the dissolution rate increased with a decrease in particle size and solid-to-acid ratio, but increased with an increase in leaching temperature and acid concentration. The experimental results indicate that for dissolution rate chemical reaction controlled in hydrogen ion [H+] medium with reaction order of (0.32), the reaction kinetics can be expressed as: $1-(1-X)1/3 = 1.7275x\ 104\ C_{(H2C2O4)}^{0.3113}\ d_p^{-0.4102}\ (S/L)^{-0.3104}\ (W)^{0.2709has}\ exp\ (-2621/T)\ t$. *The activation energy of the process was determined to be 21.791kJ/mol. The experimental data was tested by graphical and statistical methods and it was observed that the above model best fitted the data.*

Keywords: Karaworo Clay, Kinetics, Statistical Method, Shrinking Core Model, Oxalic Acid.

1.0 INTRODUCTION
Dissolution process is one of the most frequently used techniques in extractive metallurgy for the recovery of valuable materials using aqueous solutions. Reduced environmental pollution, low energy consumption and ability to treat low grade ores are amongst attracting features which motivates its application in hydrometallurgical routes. For the past few years, numerous works were conducted on the leaching of clay minerals in order to understand the controlling and optimizing effects of process parameters on the percentage yield (Baba, et al, 2007; Guillermo, et al, 2005; Girgin, et al, 2011). Brown et al, (1966) studied the production alumina from clay mined at Delaware, USA, by dissolving the clay mineral in nitric acid solution of known concentration. They found out that the dissolution is dependent on the calcinations temperature and time as well as the acid concentration. They recommended a calcinations temperature and time of 700^{o}C and one and half hours, respectively.

Hulbert, et al, (1970), studied the kinetics of alumina removal from calcined clay using sulphuric, hydrochloric, and nitric acids. They found out that the rate- controlling step for the leaching of aluminum ions from the calcined clay when employing nitric acid was diffusion of reaction products from the phase boundary. They also reported that about 85% of alumina was removed using 160% concentration of the acid as other process parameters were kept at constant values. Karaworo clay has not found any commercial application in the recent years, but, it is only used local potters in their pottery work. The high content of alumina in the clay necessitate this research work, as bauxite, which has remained the main raw source of alumina for aluminium industries in Nigeria, is depleting and there is need for substitute local raw material.

2.0 PROCEDURE

In this present research work, the kinetics and mechanism of alumina removal from calcined Karaworo clay dissolved in oxalic acid ($H_2C_2O_4$) have been investigated and the best dissolution conditions established.

Experimental Procedure: Clay sample was mined at Karaworo (N:7º 15'0"; E: 6º 5'0"; A: 315m) in Kogi State, Northern part of Nigeria. The raw clay material was sun-dried for three days and then crushed with pestle and mortar. The ground sample was sieved into different particle sizes ranging from 0.075 to 0.500 mm. The sized samples were calcined at different temperatures in a muffle furnace and then dissolved in oxalic acid solution. In the dissolution experiments, 100ml of the oxalic acid of predetermined concentration was poured into a 250 ml spherical glass reactor equipped with a mechanical stirrer. The reactor and its content were placed inside a thermostatically controlled heating plate . Heat was applied and at the attainment of the desired temperature, 2g of the sized clay samples was introduced into the reactor with constant stirring. At the completion of the period of reaction, the contents of the reactor were filtered using Whatman filter paper. The filtrate containing the aluminium oxalate was evaporated to dryness and the residue ignited at 1100ºC to form oxide from the oxalate salt and was weighed. The fraction of the alumina removed (x) was calculated by dividing the residue weight by the theoretical total alumina content of the calcined clay samples. The above experimental procedure was repeated to study the effect of the process parameters by varying their values as follows: acid concentration (1.6M); leaching temperature (30-90ºC); particle size (0.075-0.500mm); solid-to-liquid ratio (0.01- 0.06 gm/ml).

3.0 RESULTS AND DISCUSSION

The chemical analysis of the raw and calcined (at 700Oc for one hour) Karaworo clay are given in Table 1. The calcined clay sample was used in the leaching experiments

Table 1: Chemical Analysis of the Raw and Calcined Clay Samples.

Composition (%)	SiO_3	Al2O3	FeO_3	CaO	MnO	SO_3	Rh_2O_3	TiO_2	LOI
Raw clay	52.000	16.600	19.530	0.160	0.290	0.160	1.100	0.450	8.090
Calcined (at 700º)	53.420	17.950	21.160	0.185	0.350	0.201	1.280	0.54	3.340

When the clay sample is added to the oxalic acid solution, the reaction taking place in the medium could be represented as follows:

$$Al_2O_{3(s)} + 3H_2C_2O_{4\,(aq)} \rightarrow 2Al[C_2O_4]_{3\,(aq)} + 3H_2O \qquad (1)$$

3.1 Dissolution of the Clay Samples

Effect of calcinations temperature: To investigate the effect of calcination temperature and time on the dissolution reaction, the calcined clay samples were dissolved in oxalic acid solution and the dissolution rate was measured by the percentage yield of alumina as a function of time as shown in Figure 1. The figure shows that the dissolution rate increased up to calcination temperature of 750ºC above which there was a decrease in the percentage yield of alumina. As can be seen from the figure, the increase in the percentage yield in the range from 700ºC to 750ºC is not significant and so 700ºC was chosen as the best calcination.

Effect of leaching temperature: To investigate the effect of leaching temperature and time on the dissolution reaction, the calcined clay samples were dissolved in 3M oxalic acid solution at different temperatures of 30, 40, 50, 60, 70, 80 and 90°C. The obtained results are presented in figure 1 and the figure shows that the dissolution rate of alumina are extremely increased by temperature and the best result was obtained at 100°C.

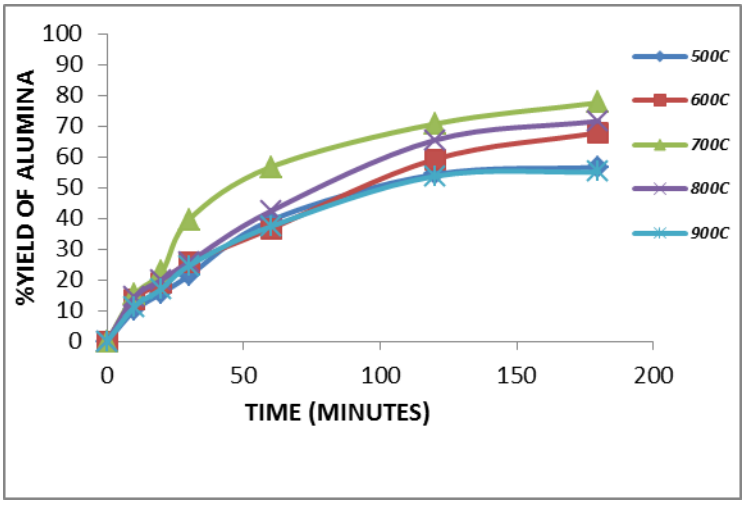

Figure 1: Effect of Calcination Temperature.

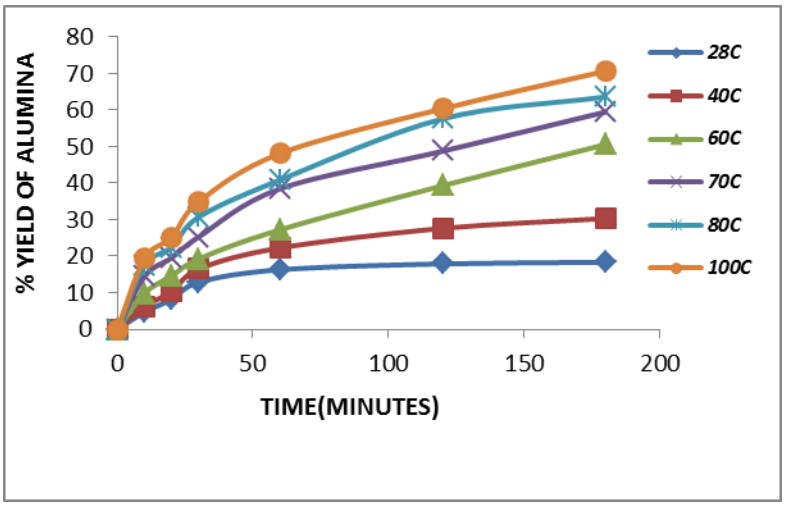

Figure 2: Effect of Leaching Temperature (calcined at 700°C for 1hr; concentration 3M; particle size 0.075mm; solid –to –liquid ratio 0.01gm/ml).

Effect of oxalic acid concentration: The effect of oxalic acid concentration was examined by varying the concentrations of the acid solution from 1, 2, 3, 4, 5, and 6 M. The experimental data are presented in Figure 2. The figure shows that as the concentration increases, the percentage yield increases and the optimum oxalic acid concentration with in the experimental conditions was determined to be 3M.

Effect of particle size: The clay samples of different particle sizes ranging from 0.075 to 0.500 mm were dissolved in the solution of oxalic acid. It was observed that the dissolution rate increased with decreasing particle size and experimental data is shown in Figure 3.

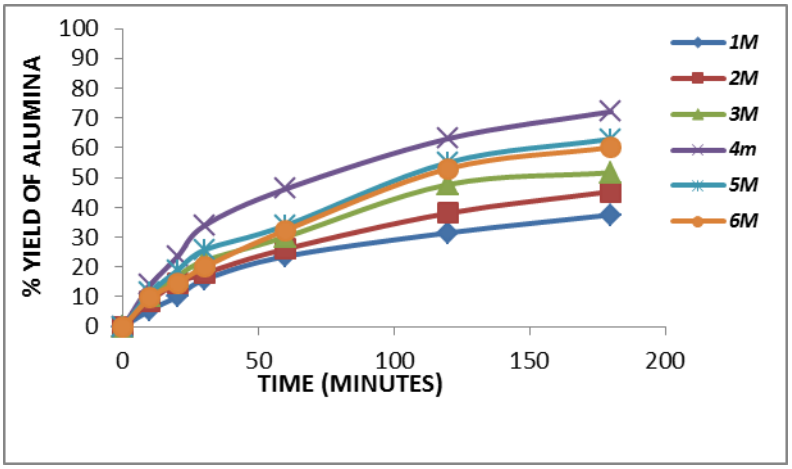

Figure 3: Effect of oxalic acid concentration (calcined at 700°C for 1hr; leaching temperature 100°C concentration 3M; particle size 0.075mm; solid –to –liquid ratio 0.01gm/ml)

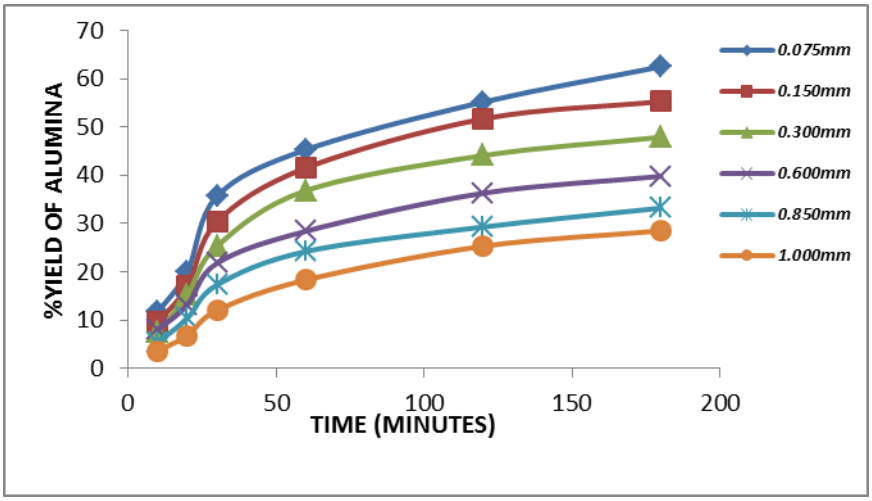

Figure 4: Effect of Particle Size (calcined at 700°C for 1hr; leaching temperature 100°C concentration 3M; solid–to–liquid ratio 0.01gm/ml).

Effect of solid to liquid ratio: The effect of of solid to liquid ratio on the dissolution rate of the clay sample was investigated using different ratios ranging from 0.01 to 0.06mg/ml. The experimental data show that dissolution rate increases with decreasing solid to liquid ratio as shown in Figure 5. The best ratio was chosen to be 0.01mg/ml.

Dissolution kinetics: In order to establish the kinetic parameters and rate –controlling step for the dissolution of alumina in oxalic acid solution, the experimental data plotted inFigures 2, 3, 4, and 5, that represent the dissolution of Karaworo cloy using oxalic acid, were fitted to the shrinking core kinetic model. According to the shrinking core model, reaction rate of a heterogeneous process may be controlled by one of the following steps:

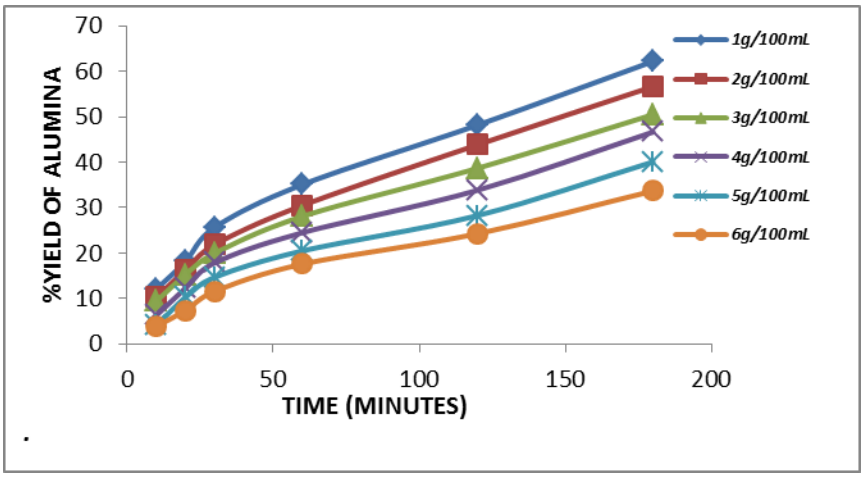

Figure 5: Effect of solid-to-acid ratio (calcined at 700°C for 1hr; leaching temperature 100°C; concentration 3M; particle size 0.075mm;)

Film diffusion control:

$$X = 6bDC_A/p_BR_e^2t = k_1t \quad (2)$$

Surface chemical reactions control:

$$1 - (1-X) - 3(1 - X)^{1/3} = 6bDC_A/P_BR_o^2t = k_2t \quad (3)$$

Product layer diffusion control:

$$1 + 2(1-X) - 3(1-x)^{2/3} = 6bDC_A/p_BR_o^2\, t = k_3t \quad (4)$$

Where p_B is the molar density of solid reactant (mol/m^3), R_o is the radius of a sphere (m), b is the stoichiometric coefficient of the solid, D is the effective diffusion coefficient (m^2/s) and C_A is the concentration of A in the bulk solution (mol/m^3).

It was found out that the experimental data fitted very well to the chemical reaction control of a spherical particle of the shrinking core model. The plots of the fitted equations for the process parameters are shown in Figures 6, 7, 8, and 9, for temperature, acid concentration, particle size, and solid to liquid ratio respectively.

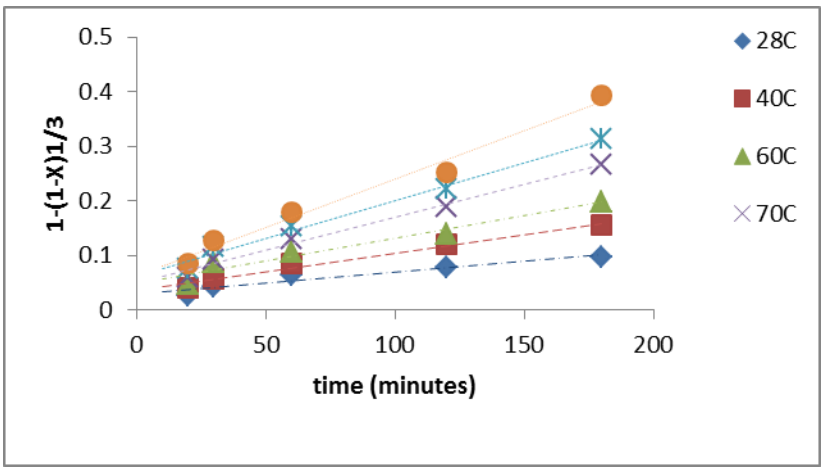

Figure 6: Plot of $1 – (1 –X)^{1/3}$ versus Time at Different Temperature.

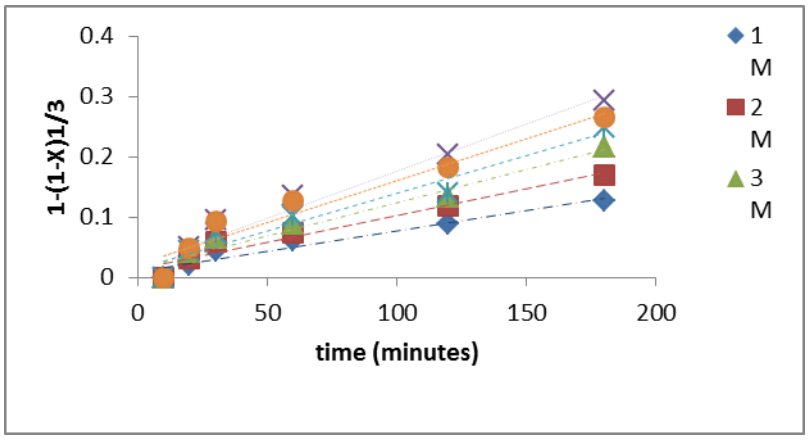

Figure 7: Plot of $1 – (1 –X)^{1/3}$ versus Time at Different Acid Concentrations.

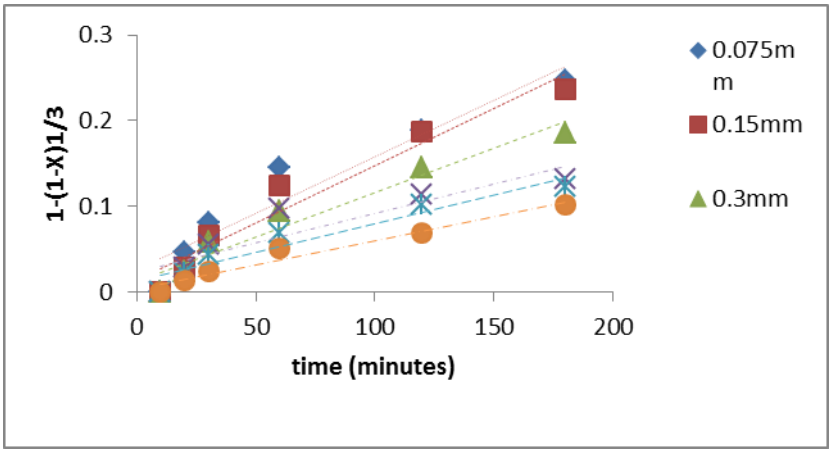

Figure 8: Plot of $1 – (1 –X)^{1/3}$ versus Time at Different Particle Size.

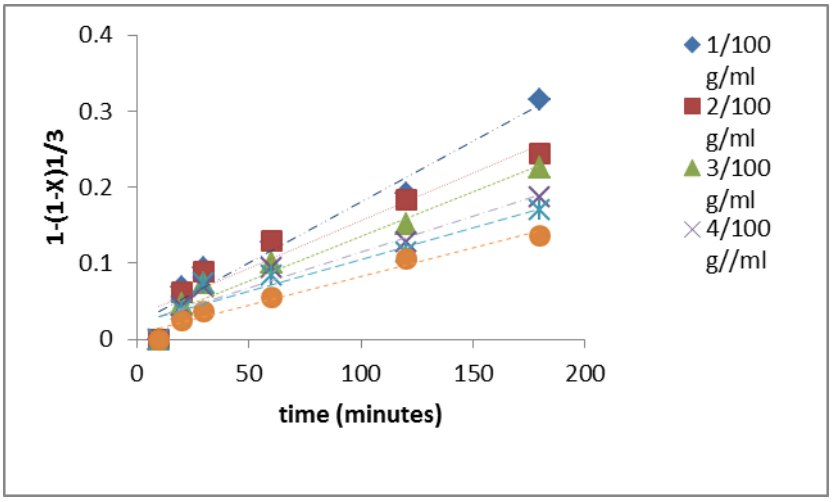

Figure 9: Plot of $1 – (1 –X)^{1/3}$ versus Time at Different Clay/Acid Ratios.

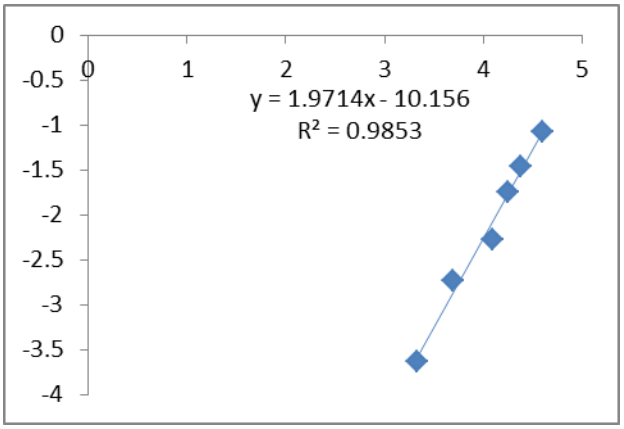

Figure 10: Plot of lnk versus T^{-1}

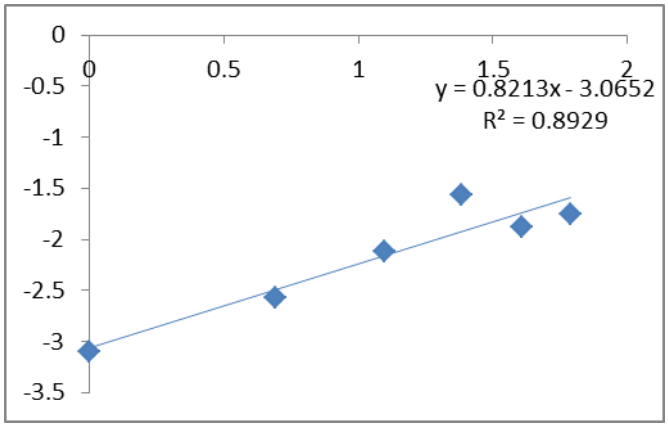

Figure 11: Plot of lnk versus $\ln[H_2C_2O_4]$

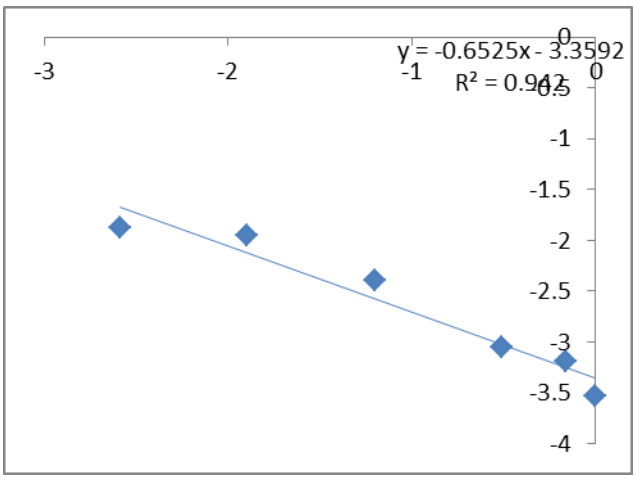

Figure 12: Plot of lnk versus ln[Particle size]

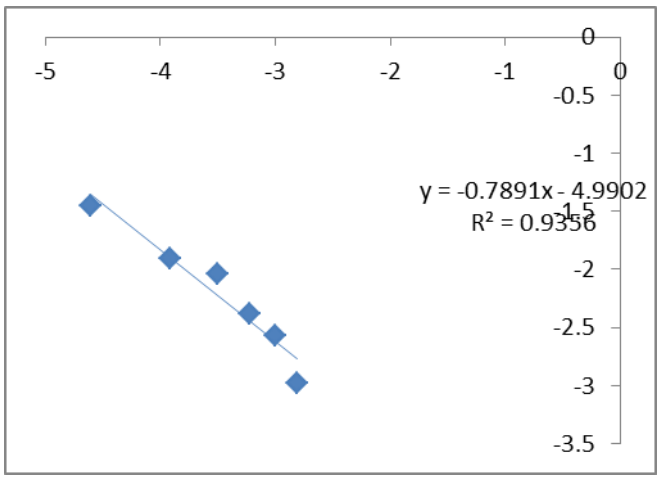

Figure 13: Plot of lnk versus ln[S/L]

The apparent reaction rate constant is calculated from the slopes of Figure 6, were plotted against the reciprocal of the temperature according to the Arrhenius equation to determine the activation energy of the process. The plot of the data is shown in Figure 10. The activation energy was determined to be 21.791kJ/mol, with a correlation coefficient of 0.9850, which is in close agreement with the value calculated by Gahrke et al (2005) of 18.642kJ/mol for Serbian montmorillonite using oxalic acid.

The apparent reaction rate constants calculated from the slopes of Figures 6, 7, 8, and 9, for acid concentration, particle size, and solid-to-liquid ratio respectively, were plotted against the natural logarithm of the respective parameter values to determine their effect on the kinetics of the dissolution of Karaworo clay in oxalic acid. The plots are shown in Figures 10, 11, 12, and 13, for acid concentration, particle size and solid/liquid ratio, respectively.

A semi-empirical model is also developed for the process as follows:

$$1 - (1-X)^{1/3} = k_o\, C_{[H2C2O4]}^{a}\, (dp)^{b}\, (S/L)^{c} \exp(-E_a/RT)t \qquad (5)$$

The variables a, b, and c, are determined from the slopes of Figures 10, 11, 12, and 13, respectively, they are calculated to be 0.3113, -0.4102, and -0.3104. Substituting these values in Equation (5), the dissolution of Karaworo clay in oxalic acid could be described by the following equation:

$$1 - (1- X)^{1/3} = 1.7275 \times 10^{4}\, C_{[H2C2O4]}^{\ 0.3113}\, (dp)^{-0.4102}\, (S/L)^{-0.3104} \exp(-26.355/T) \qquad (6)$$

The apparent reaction rate constants of the tested models are presented in Table 2. The comparison of analyzed data based on the linear regression coefficient (R^2) values (Table 2.) for different kinetic model equations showed the orders followed are surface chemical reaction of a spherical layer diffusion of a spherical particle. Hence, the surface chemical reaction of a spherical particle kinetic equation (Eq (2)), in general, has best agreed to present kinetic reactions.

Table 2: Values of Rate Constants and their Correlation Coefficients at different variables (parameters) (for alumina dissolution from Karaworo clay using $H_2C_2O_4$.).

Temp (^{0}C)	Apparent rate constant (x 10^{-3} min^{-1})					Correlation coefficient (R^2)				
	K1	K2	K3	K4	K5	R2	R2	R2	R2	R2
28	0.050	0.238	0.034	0.106	0.734	0.977	0.871	0.978	0.916	0.8753
40	0.129	0.387	0.088	0.204	1.208	0.985	0.919	0.984	0.966	0.9247
60	0.279	0.587	0.193	0.370	1.875	0.988	0.900	0.988	0.962	0.9093
70	0.454	0.718	0.319	0.535	2.350	0.957	0.870	0.956	0.942	0.8844
80	0.311	0.562	0.216	0.385	1.815	0.920	0.745	0.924	0.855	0.7613
100	0.951	1.104	0.685	1.017	3.871	0.945	0.842	0.948	0.924	0.8631
Concentration (M)										
1	0.1750	0.454	0.120	0.256	1.429	0.9863	0.8839	0.9870	0.9474	0.8916
2	0.2510	0.551	0.173	0.339	1.752	0.9871	0.8805	0.9882	0.9500	0.8900
3	9.4470	0.717	0.313	0.528	2.343	0.8689	0.7558	0.8725	0.8334	0.7690
4	0.5730	0.823	0.405	0.944	2.725	0.9751	0.8470	0.9778	0.8694	0.8656
5	0.6340	0.859	0.451	0.994	2.869	0.9598	0.8146	0.9636	0.8399	0.8363
6	0.4260	0.717	0.298	0.807	2.333	09972	0.9209	0.9976	0.9360	0.9325
Particle size (mm)										
0.075	0.2930	0.554	0.243	0.370	1.782	0.9521	0.7886	0.9549	0.8925	0.8034
0.15	0.3400	0.613	0.237	0.421	1.980	0.9851	0.8513	0.9865	0.9347	0.8657
0.3	0.4650	0.744	0.326	0.549	2.434	0.9919	0.8913	0.9925	0.9685	0.9056
0.6	0.4310	0.721	0.302	0.518	2.347	0.9788	0.8639	0.9809	0.9453	0.8777
0.85	0.4350	0.721	0.305	0.521	2.350	0.9621	0.8435	0.9643	0.9276	0.8579
1.0	0.0710	0.279	0.048	0.132	0.862	0.9213	0.9143	0.9200	0.9375	0.9171
Clay/Acid Ratio										
1/100	0.5550	0.783	0.393	0.627	2.597	0.9683	0.8087	0.9718	0.9242	0.8305
2/100	0.4890	0.723	0.345	0.562	2.384	0.8822	0.7223	0.8870	0.8316	0.7414
3/100	0.4340	0.679	0.305	0.509	2.226	0.9755	0.8218	0.9772	0.9321	0.8410
4/100	0.3940	0.643	0.276	0.469	2.099	0.9633	0.8104	0.9648	0.9186	0.8286
5/100	0.3760	0.633	0.263	0.453	2.057	0.9791	0.8259	0.9809	0.9325	0.8432
6/100	0.2260	0.544	0.156	0.319	1.721	0.8689	0.9678	0.8656	0.9332	0.9655

CONCLUSION:

In the course of the study of dissolution of iron oxide and alumina using oxalic acid, the following conclusions were made: The leaching rate was positively affected by leaching temperature, and concentration, while particle size and solid-to-liquid had negative effect. The leaching of alumina in (oxalic acid $H_2C_2O_4$) was enhanced by calcinations of the raw clay sample. The rate of alumina

leaching followed the chemical reaction controlled mechanism, $1 - (1-X)^{1/3} = 1.7275 \times 10^4 C_{[H2C2O4]}^{0.3113} (dp)^{-0.4102} (S/L)^{-0.3104} \exp(-26.355/T)$,with an apparent activation energy of 21.79kJ/mol.

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