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Extraction of Alumina from Local Clays Using Hydrochloric Acid

[1]Eze, J.U., [2]Anyakwo, C.N., [3]Osoka, E.C.[4]Nnodum, A.N., [5]Onuoha, C., [6]Anusi, M.O.,
[1,2,4,5]Department of Material and Metallurgical Engineering, Federal University of Technology, Owerri
[3,6]Department of Chemical Engineering, Federal University of Technology, Owerri

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Abstract
The present work investigates the extraction of alumina from different local clay samples; Ihiala clay (sample A), Nsu clay (sample B), and Umuhu clay (sample C), which contain 27.83%, 29.93%, and 28.31% of Al_2O_3 respectively and are extremely abundant in the Eastern part of Nigeria. The clay samples were crushed, ground and sieved using 100 mesh standard tyler screens and were further calcined at a temperature of 700^0C, held for 1hr and then leached with 5ml of concentrated hydrochloric acid at different leaching temperatures (25^0C,50^0C,75^0C, 100^0C) and time (10,30,60,80,100 and 120mins). A relatively large increase in percentage extraction of Al_2O_3 was also observed with increasing leaching temperature in the range of 25^0C to 100^0C. The effects of the leaching time and temperatures were investigated using response surface methodology. A pure-quadratic model fit well to experimental data for the three clay samples. The surface plot revealed a linear relationship with temperature, which had more effect of percentage alumina extracted, and a quadratic relationship with time. An estimated optimum extraction condition for the three clay samples would be a leaching time of 76minutes and temperature of 100^OC. The optimization also indicated that increasing temperature will increase percentage of alumina extracted. Leaching these local clay samples under these conditions resulted in about 81%, 79% and 79% alumina extraction for samples A, B and C respectively. The highest percent concentration was achieved with the Ihiala clay (sample A). The research therefore shows that Eastern Nigerian local clays are very suitable raw materials for the production of aluminium and other alumina based products. It is hoped that this work will help to encourage the use of our local clays as raw materials in the aluminium industries in the nearest future.

Keywords: Alumina, Extraction, Kinetics, Local clay, Leaching

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INTRODUCTION

The most generally known raw material for the manufacture of alumina, which is bauxite, is found in Nigeria in very limited amounts. Alumina (aluminium oxide) is a chemical compound of aluminium and oxygen with the chemical formula Al_2O_3. It is the most commonly occurring of several aluminium oxides, and specifically identified as aluminium (III) oxide. It may also be called aloxide, aloxite, or alundum depending on the particular form or application (www.slideshare.net). It commonly occurs in its crystalline polymorphic phase α-Al_2O_3, in which it comprises the mineral corundum, varieties of which form the precious gemstones, ruby and sapphire. Al_2O_3 is significant in its use to produce aluminium metal as an abrasive owing to its hardness, and as a refractory material owing to its high melting point (www.researchgate.net)

Aluminium is produced by an electrolytic reduction process of alumina using the "Hall- Heroult process", which involves the smelting of alumina into metallic aluminium and this takes place in a steel vat called a "reduction pot". The process was invented independently by an American chemist, Charles Martin Hall and the Frenchman, Paul Heroult in 1886 (Russel and Allen,1997). Another process of alumina production is the "Bayer Process" which was invented by an Australian Chemist named "Carl Josef Bayer" in 1887. He tried to develop a method for supplying alumina to the textile making industry for use as "mordant", a substance that combines with dye to give colour to a material. The process gained its importance when combined with the Hall-Heroult process. When both processes combined, bauxite ores are processed into alumina which is then converted to aluminium. Today, the Bayer process is still the same and is used to manufacture nearly all the world's alumina supplies for Aluminium production (Habashi,1995). Bauxite deposits in Nigeria can be found in Plateau state, Rivers state and Ekiti state and they are present in little quantities. A greater percentage of the bauxite gotten from these areas are used for the extraction of alumina mostly used in aluminium production while fewer percentages goes for the manufacture of abrasives, papers, fillers, glass, composite fibres, catalysis, water purification materials, health and medical facilities, laundry detergents, cement, soda cans, spark plugs, foil containers, cookware coatings, toothpaste, etc.(Hudson et al.,1997). As a result, there is need to increase the production of alumina locally. One of the numerous aluminous raw materials found in large scale in Nigeria that contains a high percentage of aluminium oxide and low percentage of impurities is the "kaolinitic clays" (Ajemba and Onukwuli, 2012). Kaolinitic clays are layered silicate clay minerals which form from the chemical weathering of feldspar or other aluminum silicate minerals. It is usually white, but sometimes has red color impurities due to iron oxide. Kaolinitic clays have a low shrink–swell capacity and a low cation-exchange capacity, making it perfect for many industrial applications.

Kaolonite clays are therefore a suitable replacement for bauxite from which highly pure alumina can be obtained (Udochukwu et al., 2019). Several research works have been done on the acid extraction processes for production of alumina from Kaolinitic clays using nitric acids, hydrochloric acids, sulphuric acid, etc but investigations show that hydrochloric acid has more advantages over other acids for leaching alumina. It is usually added during crystallization to form aluminium chloride which readily crystallizes. It is preferred because of its ease of slurry filtration, iron removal, and insolubility of titanium oxide which is present in most clay. The major disadvantage connected with the use of hydrochloric acid is the severe corrosion problems. However, the development of corrosion resistant rubbers and plastics has almost completely solved the problem, such that corrosion is a less prohibitive factor (Peters et al.,1962).

Udeigwe et al (2015) studied the kinetics of hydrochloric acid leaching of alumina from Agbaja clay. The research was targeted at the modification of local clays by heat treatment and investigation of kinetic models. The effects of temperature and time on the calcination processes, particle size, concentration of acid, acid clay weight ratio, stirring speed and leaching temperature were studied and the results show that all process parameters increased the yield of alumina except particle size. Other works reported on the extraction of alumina from clay by hydrochloric acid treatment include the works of Ajemba and Onukwuli (2012), Ebere et al. (2018), Yilan et al. (2019), Udochukwu et al. (2019), Ziegenbalg et al. (1983), Poppleton and Sawyer (1977), and Shanks et al.(1995).

This paper investigates the production of alumina from selected local clays abundant in the eastern part of Nigeria, rather than the much limited bauxite, through leaching using hydrochloric. The effects leaching time and temperature on the process will be studied and optimum conditions recommended.

MATERIALS AND METHODOLOGY

Materials

The clay samples were mined at Ihiala in Ihiala Local Government Area, Anambra State, Nsu in Mbano Local government Area Imo State, and Umuhu in Orsu Local Government Area, Imo State. This is due to the high availability of clay around those areas. The concentrated hydrochloric acid, filter papers and distilled water were gotten from the chemical market at Ama Jk, Ekeonunwa-Owerri. The analysis were carried out at Soil Science Department, Federal University of Technology, Owerri (FUTO), in conjunction with the Agronomy Department, University of Ibadan.

Table1: Chemical composition of the local clays

COMPOUNDS	IHIALA CLAY (%)	NSU CLAY (%)	UMUHU CLAY (%)
SiO_2	48.57	45.64	46.93
Al_2O_3	27.83	29.93	28.31
TiO_2	1.35	1.07	1.02
SO_3	0.43	0.36	0.33
CaO	0.083	0.005	0.003
MgO	0.176	0.036	0.012
K_2O	0.009	0.026	0.022
Na_2O	3.013	3.028	3.019
MnO_2	0.002	0.002	0.003
Fe_2O_3	3.125	3.166	3.278
P_2O_5	0.049	0.169	0.056
LOI	15.35	16.38	17.92

Methods

The average sizes of the diameter of the raw local clay samples were about 2 to 3 inches. The raw clay samples were crushed and ground manually using mortar and pestle. The ground clay was placed on a sieve and mechanically vibrated for about 5mins. The oversize was further ground followed by sieving on the same sieve. These procedures were repeated till the entire clay sample passed the sieve.

The chemical compositions of the different clays were determined at the Soil Science department, FUTO in conjunction with the Agronomy department, University of Ibadan using the XRF characterization method. The results are given in Table 1 above.

Calcination Experiment

To evaluate the effects of calcination temperature and time on calcination, the ground clay samples sieved through the 100mesh sieve were subjected to heat treatment in a muffle furnane at 700^0C for 1hr. This was done at different times of 10, 30, 60, 80 and 120 mins, making a total of 72 activated samples which were properly labelled and subjected to the same leaching conditions. This has been reported in some previous works to be the recommended conditions for activation of local kaolinitic clays (Al-Zahrani et al., 2003)

Leaching Experiments

The leaching experiment was carried out at the Soil Science Department, FUTO. 5grams of the calcined clay samples passing through 100 mesh sieve were leached using 5M hydrochloric acid for different periods of time, (10, 30, 60, 80 and 120 mins) and at different leaching temperatures (25^0C,

50^0C, 75^0C, and 100^0C) which were measured using a constant temperature water bath at a fixed stirring rate of 160cycles/min and using boiling under reflux. At the end of the leaching, the slurry obtained was filtered using filter papers to separate un-dissolved materials and washed three times with 10ml of distilled water. The solutions gotten were further diluted and analyzed for aluminium ion. This was done at the Agronomy department of the University of Ibadan using the MS-Atomic Absorption Spectrophotometer (Thermo Elements, 2000).

The dissolution fraction of alumina in the slurry was calculated by

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

Mathematical Methodology

The data of percentage Al_2O_3 extracted as response with leaching temperature and time as factors will be used for statistical study and optimization. The statistical study will be done based on a full factorial experimental design for the two factors at the respective levels studied using the statistical toolbox of MATLAB software for statistical modelling, response surface study and optimization. The study will be done for each data using leaching time (x_1) and leaching temperature (x_2) as factors, with percentage Al_2O_3 extracted (y) as response. These will be fit to four response surface models:

Linear: $y = a + bx_1 + cx_2$ (2)

Interaction: $y = a + bx_1 + cx_2 + dx_1x_2$ (3)

Pure-quadratic: $y = a + bx_1 + cx_2 + dx_1^2 + ex_2^2$ (4)

Quadratic: $y = a + bx_1 + cx_2 + dx_1x_2 + ex_1^2 + fx_2^2$ (5)

The model that best fits, based on the adjusted R-squared, will be considered the statistical model that best describes the parameter and will be used for optimization to determine optimum conditions (leaching time and temperature) for the Al_2O_3 extraction.

The value of the R-squared will be used as a measure of model accuracy and values greater than or equal to 0.90 will be considered acceptable. The p-value of the F-statistics will be used as a measure of model adequacy and a value less than or equal to 0.05 will be acceptable using 95% confidence interval. The significance of the main effects will be determined using Analysis of variance (ANOVA) which will be judged in a similar way to the F-statistics, using the p-value, while the statistical significance of each element in the model will be determined using the t-statistics value or its associated p-value.

The interaction between the factors will be determined using the surface plots, especially its contour lines, and the optimization toolbox of MATLAB used for the optimization of selected model parameter based on the model.

RESULTS AND DISCUSSION

Effect of Extraction Time and Leaching Temperature (Ihiala Clay)

The effects of leaching time and temperature on the yield of alumina extracted from Ihiala clay samples are shown in fig. 1 below. The figure shows that there is no further increase in percentage of alumina extracted from the clay samples after the first one hour, for all the leaching temperatures. It also shows a relatively large increase in the percentage extraction of aluminium oxide with increase in leaching temperature from 25^0C to 100^0C.

The experimental data was fit to linear, interaction, pure-quadratic and quadratic statistical models with adjusted r-squared values of 0.9170, 0.9133, 0.9771 and 0.9763 respectively. The pure-quadratic model with the highest adjusted r-squared was hence selected for the study. The numerical fit results are shown in table 2.

The model gave a very accurate fit to the experimental data with R^2 value of 0.9811, which means that the model explains more than 98% of the observed variability in the experimental data. The f-statistics analysis with a p-value of 4.4409e-16, which is less than 0.05, indicates that the model is adequate, since it is significant. All the variables in the model are significant as can be observed from the p-value of the t-statistics, which are all less than 0.05. Thus the model is acceptable for the study.

Figure 2 is the plot of the interaction of leaching time and temperature. It can be observed from figure 2 that percentage of alumina extracted increases linearly with increase in temperature, but has a quadratic relationship with time. The colour variation along the two axis shows that temperature has more significant effect on percentage alumina extracted, than time, and this in agreement with the result of analysis of variance from table 3 which shows that has a lower p-value and thus more significant. The surface plot gives an approximate value of the optimum leaching time as 76 minutes and temperature of 100^OC. A more accurate value was obtained by optimization using MATLAB as leaching time of 77.4530 minutes and temperature of 100 ^{O}C. The optimization results also indicate that more alumina can be extracted at temperatures above 100^OC. These results are in agreement with previous researchers (Al-Zarhani, 1999; Ozdemir et al., 2005; Tingent et al., 1997).

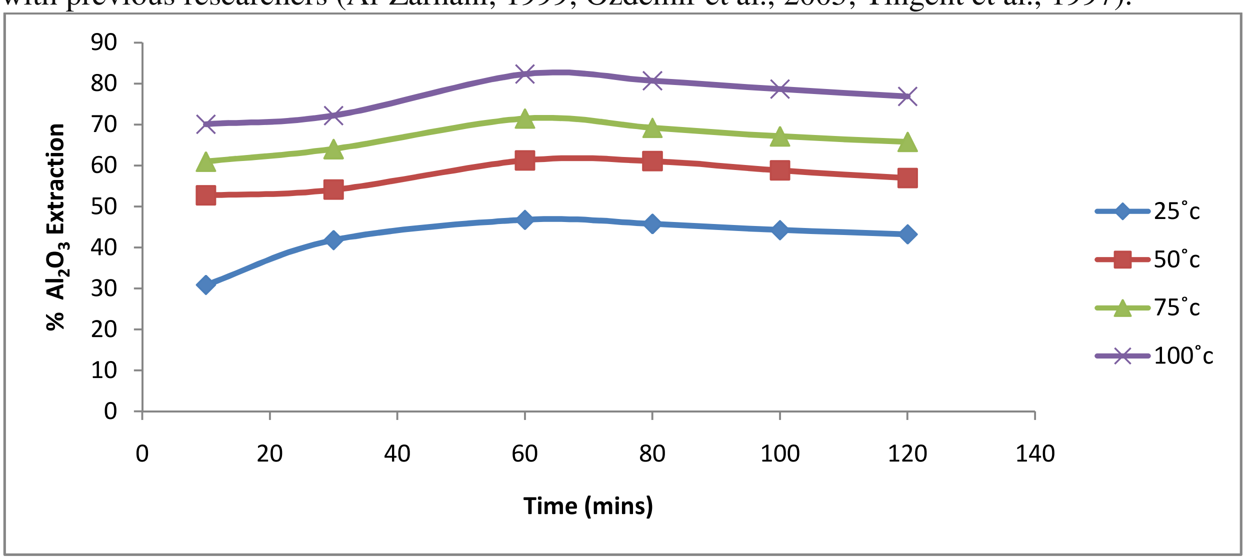

Fig 1: Effect of leaching time and temperature on alumina extraction from Ihiala clay (sample A)

Table 2: Model coefficients and numerical fit results from Response surface study (Ihiala clay)

Variable	Coefficients	Se	t-stat	p-val	F-variables	values
Constant	15.2858	2.6417	5.7863	1.4173e-5	Sse	81.436
Time	0.3811	0.046815	8.1407	1.2925e-7	Dfe	19
Temperature	0.7021	0.085861	8.1774	1.2083e-7	Dfr	4
Time^2	-0.0025	0.000353	-6.9612	1.2393e-6	Ssr	4225.8
Temperature^2	-0.0020	0.000676	-2.9559	0.008115	F	246.48
	R^2=0.9811	Adj-R^2=0.9771			p-val	4.4409e-16

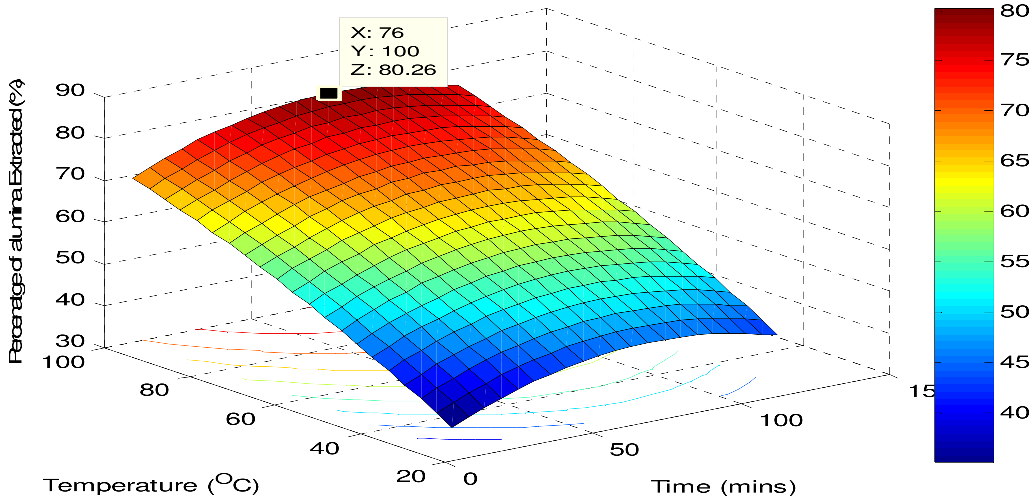

Figure 2: Surface plot of interaction of time and temperature for Ihiala clay

Table 3: Table of Analysis of variance for Ihiala clay

Source	Sum Sq.	D.f.	Mean Sq.	F	Prob>F
Time	374.67	5	74.93	27.43	4.82423e-7
Temperature	3891.57	3	1297.19	474.83	4.44089e-15
Error	40.98	15	2.73		
Total	4307.22	23			

Effect of Extraction Time and Leaching Temperature (Nsu Clay)

The effects of leaching time and temperature on the yield of alumina extracted from Nsu clay samples are shown in fig. 3 below. The figure shows that there is no further increase in percentage of alumina extracted from the clay samples after the first one hour, for all the leaching temperatures. It also shows a relatively large increase in the percentage extraction of aluminium oxide with increase in leaching temperature from 25^0C to 100^0C.

The experimental data was fit to linear, interaction, pure-quadratic and quadratic statistical models with adjusted r-squared values of 0.9367, 0.9337, 0.9864 and 0.9859 respectively. The pure-quadratic model with the highest adjusted r-squared was hence selected for the study. The numerical fit results are shown in table 4.

The model gave a very accurate fit to the experimental data with R^2 value of 0.9888, which means that the model explains nearly 99% of the observed variability in the experimental data. The f-statistics analysis with a p-value of 0, which is less than 0.05, indicates that the model is adequate, since it is significant. All the variables in the model are significant except the temperature squared, as can be observed from the p-value of the t-statistics, which are less than 0.05. Thus the model is acceptable for the study.

Figure 4 is the plot of the interaction of leaching time and temperature. It can be observed from figure 4 that percentage of alumina extracted increases linearly with increase in temperature, but has a quadratic relationship with time. The colour variation along the two axis shows that temperature has more significant effect on percentage alumina extracted, than time, though the analysis of variance from table 5 shows that both are equally significant. The surface plot gives an approximate value of the optimum leaching time as 76 minutes and temperature of 100^{O}C. A more accurate value was obtained by optimization using MATLAB as leaching time of 77.3520 minutes and temperature of 100 ^{O}C. The optimization results also indicate that more alumina can be extracted at temperatures above 100^{O}C. These results are in agreement with previous researchers (Al-Zarhani, 1999; Ozdemir et al., 2005; Tingent et al., 1997).

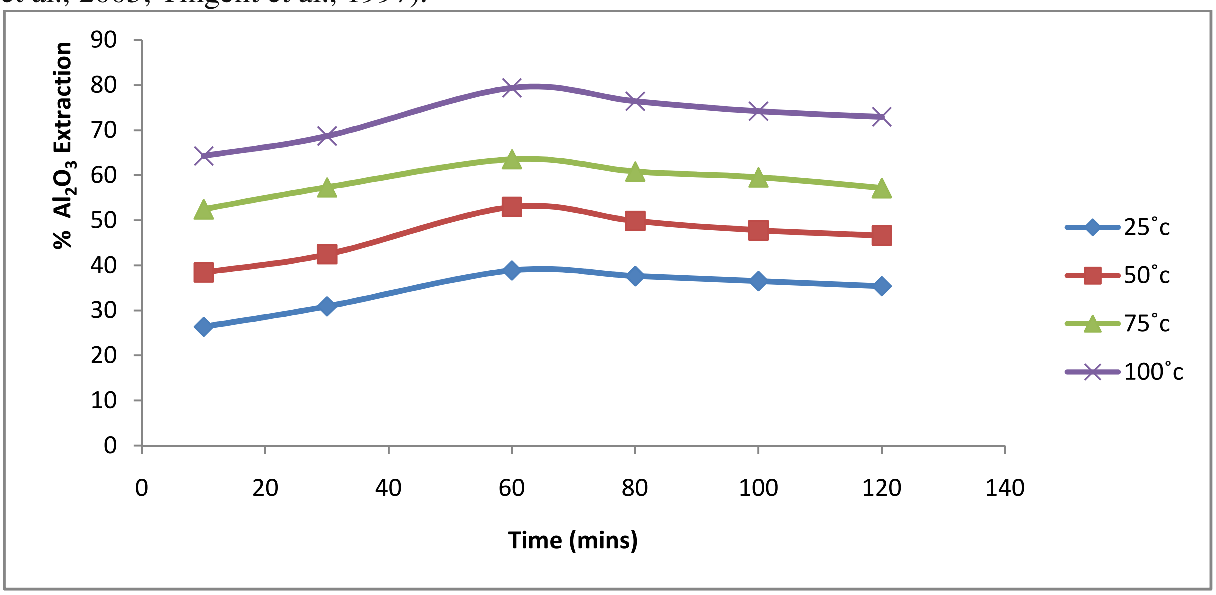

Fig 3: Effect of leaching time and temperature on alumina extraction from Nsu clay (sample B)

Table 4: Model coefficients and numerical fit results from Response surface study (Nsu clay)

Variable	Coefficients	Se	t-stat	p-val	F-variables	values
Constant	11.9603	2.2627	5.2859	4.2149e-5	Sse	59.742
Time	0.4111	0.040098	10.254	3.5108e-9	Dfe	19
Temperature	0.4063	0.073541	5.5251	2.4947e-5	Dfr	4
Time^2	-0.0027	0.0003027	-8.7795	4.1011e-8	Ssr	5273
Temperature^2	8.2133e-4	0.0005791	1.4182	0.17232	F	419.26
	R^2=0.9888	Adj-R^2=0.9864			p-val	0

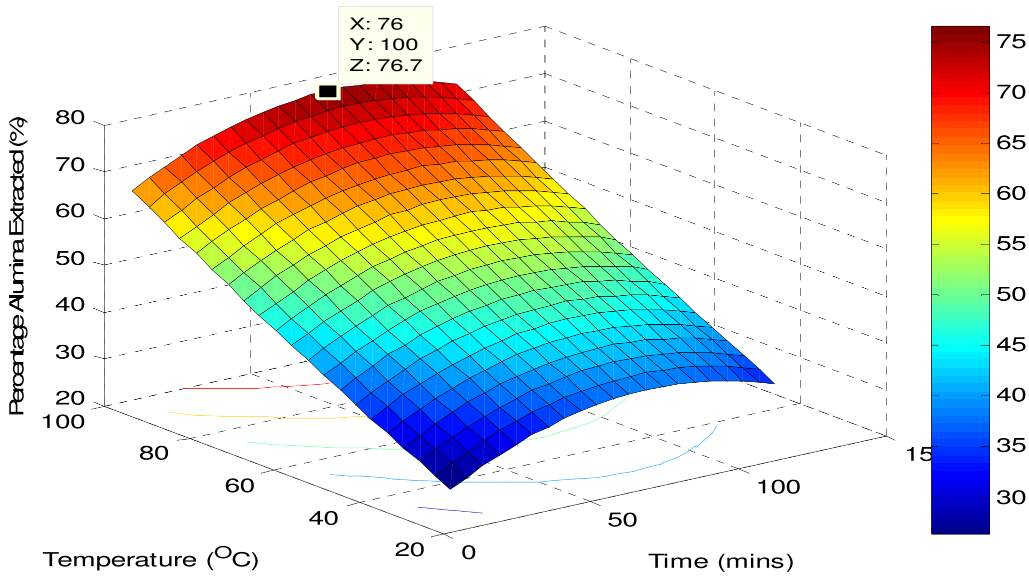

Figure 4: Surface plot of interaction of time and temperature for Nsu clay

Table 5: Table of Analysis of variance for Nsu clay

Source	Sum Sq.	D.f.	Mean Sq.	F	Prob>F
Time	450.83	5	90.17	80.21	0
Temperature	4865.07	3	1621.69	1442.69	0
Error	16.86	15	1.12		
Total	5332.76	23			

Effect of Extraction Time and Leaching Temperature (Umuhu Clay)

The effects of leaching time and temperature on the yield of alumina extracted from Umuhu clay samples are shown in fig. 5 below. The figure shows that there is no further increase in percentage of alumina extracted from the clay samples after the first one hour, for all the leaching temperatures. It also shows a relatively large increase in the percentage extraction of aluminium oxide with increase in leaching temperature from 25^0C to 100^0C.

The experimental data was fit to linear, interaction, pure-quadratic and quadratic statistical models with adjusted r-squared values of 0.9108, 0.9063, 0.9809 and 0.9798 respectively. The pure-quadratic model with the highest adjusted r-squared was hence selected for the study. The numerical fit results are shown in table 6.

The model gave a very accurate fit to the experimental data with R^2 value of 0.9842, which means that the model explains more than 98% of the observed variability in the experimental data. The f-statistics analysis with a p-value of 1.1102e-16, which is less than 0.05, indicates that the model is adequate, since it is significant. All the variables in the model are significant, as can be observed from the p-value of the t-statistics, which are all less than 0.05. Thus the model is acceptable for the study.

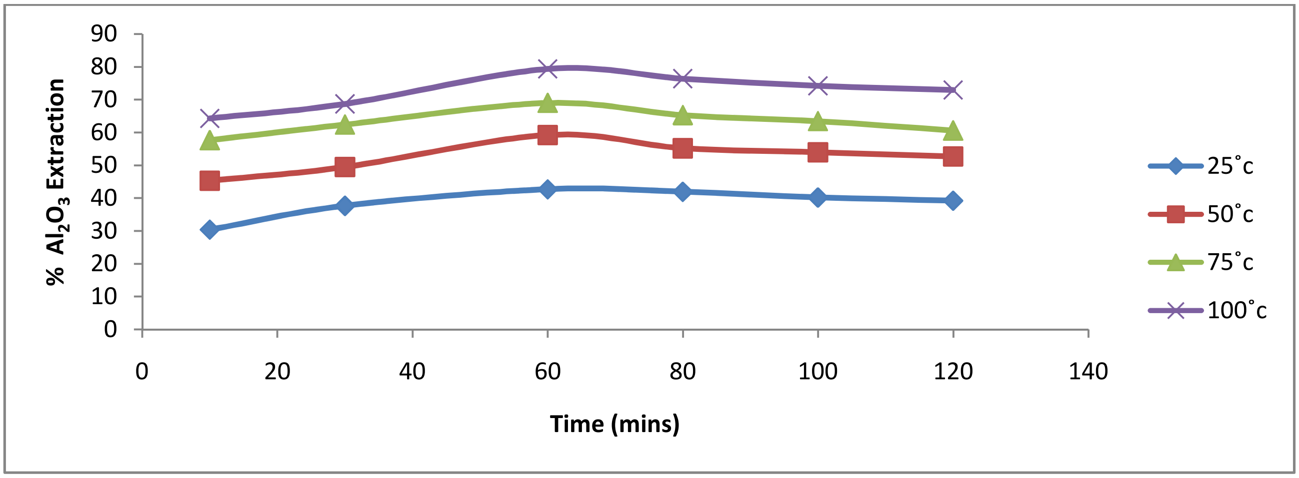

Fig 5: Effect of leaching time and temp on alumina extraction from Umuhu clay (sample C)

Table 6: Model coefficients and numerical fit results from Response surface study (Umuhu clay)

Variable	Coefficients	Se	t-stat	p-val	F-variables	values
Constant	11.9890	2.4017	4.9914	8.1039e-5	Sse	67.322
Time	0.4072	0.0426	9.5668	1.0688e-8	Dfe	19
Temperature	0.6680	0.0781	8.5562	6.0893e-8	Dfr	4
Time^2	-0.0027	3.2143e-4	-8.4143	7.8536e-9	Ssr	4189.7
Temperature^2	-0.0017	6.1477e-4	-2.8433	0.0104	F	295.61
	R^2=0.9842	Adj-R^2=0.9809			p-val	1.1102e-16

Figure 6 is the plot of the interaction of leaching time and temperature. It can be observed from figure 6 that percentage of alumina extracted increases linearly with increase in temperature, but has a quadratic relationship with time. The colour variation along the two axis shows that temperature has more significant effect on percentage alumina extracted, than time, and this observation is endorsed by the analysis of variance which has a lower p-value for temperature than time from table 7. The surface plot gives an approximate value of the optimum leaching time as 76 minutes and temperature of 100^{O}C. A more accurate value was obtained by optimization using MATLAB as leaching time of 75.3035minutes and temperature of 100 ^{O}C. The optimization results also indicate that more alumina can be extracted at temperatures above 100^{O}C. These results are in agreement with previous researchers (Al-Zarhani, 1999; Ozdemir et al., 2005; Tingent et al., 1997).

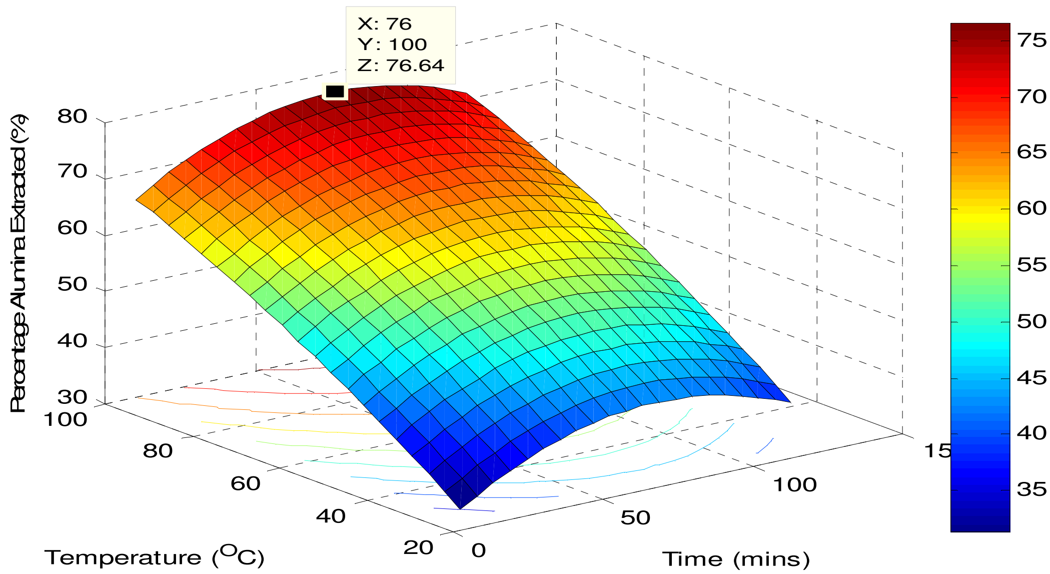

Figure 6: Surface plot of interaction of time and temperature for Umuhu clay

Table 7: Table of Analysis of variance for Nsu clay

Source	Sum Sq.	D.f.	Mean Sq.	F	Prob>F
Time	411.95	5	82.39	46.59	1.30586e-8
Temperature	3818.56	3	1272.85	719.84	2.22045e-16
Error	26.52	15	1.77		
Total	4257.03	23			

CONCLUSION

Approximately 81%, 79%, and 79% of alumina respectively present in the three local clays (Ihiala, Nsu and Umuhu) were extracted by calcination, followed by a leaching step using hydrochloric acid. The extraction procedure recommended is a first step calcination at 700^{0}C for about one hour which is followed by a leaching process of the calcined clays after grinding and size reduction to a 100 Standard Tyler screen. Leaching was carried out using 5M solution of Hydrochloric acid at 100 ^{0}C under reflux for an hour using 5:1 liquid to solid weight ratio. The results showed a pure-quadratic model can effectively be used to study the process as a function of leaching time and temperature, since it explains more than 98% of variability observed in experimental data for all cases, with the percentage alumina extracted increasing linearly with temperature, which is the more significant variable. An approximate optimum condition for extraction for all clays is 76 minutes at 100^{O}C, though there was indication that increased temperatures will increase percentage of alumina extracted. Possible location of alumina extraction plants in Ihiala in Anambra State, Nsu and Umuhu in Imo State, in Nigeria, will prove to be a feasible entrepreneurial venture.

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