Slaking Of Nkalagu Quicklime for the Production of Agricultural Lime

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ABSTRACT

This work presents slaking of quicklime from Nkalagu limestone for the production of agricultural lime (slaked lime). It entails improving the quality of limestone (through calcination and slaking processes) for acidic soil amelioration. X-ray fluorescence spectroscopy was used for characterization of the uncalcined and calcined limestone samples. Calcination of the limestone was employed to produce quicklime, and slaked lime was was subsequently produced from the quicklime through slaking process. Effects of slaking factors on the reactivity of the slaked lime were determined. Central composite design of design expert software was used to optimize the reactivity of the slaked lime. Then, activation energy and pH of the lime were obtained. Characteristics of the quicklime showed that the calcination improved the quality of the sample. Quadratic model explained the relationship between reactivity and considered slaking factors of quicklime/water ratio, particle size and time. The optima reactivity values of the Nkalagu slaked lime was obtained as 57.1 ^{o}C, while the activation energy and pH of the slaked lime are 79.48 kJ/mol and 11.8 respectively. The qualities of the sample in terms of constituents, reactivity, activation energy and pH showed that Nkalagu slaked lime can be used for agricultural purpose (amelioration of acidic soil).

KEYWORDS: Slaked lime, limestone, slaking, soil amelioration

I.   INTRODUCTION

Erosion, leaching, flooding and continuous cropping practice leads to high soil acidity. And research has shown that high soil acidity limits the availability of land for fruitful agricultural purposes. Poor productivity arising from acidic soil is a major challenge that needs to be addressed. Acidic soil has been known not to support agriculture and the fertility of such soil can be restored by applying agricultural lime. But apart from using limestone for the production of cement, productions of other useful materials such as slaked lime have been neglected. Fertilizer (though available) has its limitations which include high cost and toxicity (Ryant et al, 2016). Even when it has been established that slaked lime enhances soil productivity (increases the pH value), its production from limestone has been neglected. Thus, there is need to produce slaked lime from limestone for agricultural purpose.

Lime is the material produced from the heating of limestone and its subsequent slaking with water. According to Moreira and Fageria (2010), liming is one of the most efficient and prevailing practices to correct soil acidity. Shaaban et al (2013) also stated that combined applications of organic and inorganic amendments are known to play a significant role in improvement of soil properties. Soil acidity adversely affects soil fertility and as such agricultural productivity. Acidic soil is caused by erosion and flood, the removal of Ca^{2+} and Mg^{2+} in the soil and replacing it with H^{+} is called Acidification. The production of quick lime (agricultural lime from the calcinations of limestone is cost effective and eco-friendly). According to Penuel et al (2015), sourcing of raw materials from the abundant natural endowment of Nigeria for industrial use has not generated significant success due to lack of technical information on the integrity of these natural endowment. Unfortunately, agricultural production in Nigeria is on the low side and one way to improve agriculture is improving the soil fertility. However, Ca^{2+} and Mg^{2+}, are eluded by erosion or flood there by making the soil to be acidic. One way of restoring the soil fertility is by adding slaked lime, to ameliorate the soil acidity. An agricultural liming material is a material containing calcium (Ca) and magnesium (Mg) compounds capable of neutralizing soil acidity. These materials include limestone (both calcite and dolomite), burnt lime, slaked lime and various by-products. Liming materials are carbonate, oxides or hydroxides of Ca and Mg.

From the review of previous related works, peripheral data on the processing of Nigerian limestone have been reported. There are no adequate information on the effects of process variables on slaking of quicklime for optimum production of agricultural lime. There is need to carryout comprehensive characterization and processing of the limestone samples for the production agricultural lime.

II.   MATERIALS AND METHOD

2.1 Limestone Preparation and Classification

The limestone samples were collected from the blasted areas Nkalagu, Ebonyi State, Nigeria. Method used by Suleiman et al (2013) was adopted in the sample preparation and classification. There were separately washed to remove impurities such as clay and sand associated with the limestone crystals. They were gradually sun dried at ambient atmospheric condition. 3000g of each sample was crushed with mortar and pestle on a hard surface. Crushed samples were classified and re-classified with the aid of the automatic vibrating sieves.

2.2 Determination of Chemical Composition

X-ray Fluorescence spectroscopy (supreme 8000, oxford instrument) was used to determine the chemical compositions of the uncalcined and calcined limestone. The sample cups were assembled using oxford instruments Poly-M XRF sample film. The powdered samples were pressed in the cups using a set of dies and a press machine. Then, the cups containing the samples were placed on the auto–sampler using individual and removable secondary safety windows. After placing the samples on the instrument tray and entering their identification and position at the integrated keypad, measurement was started by pressing the start button. The samples were irradiated with high energy x-rays from the controlled x-ray tube. After the first few seconds of measurements, live results were displayed; allowing a rapid assessment of product quality to be made. The results were continually updated till the end of the measurements. XRF peaks with varying intensities were created and were present in the spectrum – a graphical representation of x-ray intensity as a function of peaks.

2.3 Samples Calcination

10g of the limestone sample (90μm particle size) was weighed into pre-weighed empty crucibles plates. The pre-weighed crucible plate with the limestone was set to laboratory furnace and heated at temperature 1000 ^{0}C. The sample was removed at time of 3 hours. After heating the calcined sample, it was allowed to cool for 15 minutes. The calcined samples were transferred to desiccators. The weight of the quicklime produced was measured.

2.4 Slaking of the Quicklime

Method used by Daud et al (2015) was adopted in the slaking of the quicklime. The hydrated lime (calcium hydroxide, $Ca(OH)_2$) was prepared by digesting calcium oxide (CaO) in distilled water. After being dissolved, chemical reaction occurred spontaneously between CaO and distilled water (exothermic reaction). During the hydration process, the temperature value rises were measured and recorded. The reactivity measurement continues till the reaction was complete. The slaking process was carried out using one-factor at-a-time and response surface methodology. Central composite design (CCD) tool of Design Expert Software 11 was used to design the experiment. Quicklime/water ratio, particle size and time were the considered slaking variables, while reactivity was considered as the response.

2.5 Determination of activation energy (E) of the calculation process

The activation energy of the calcination process was determined using Arrhenius equation (Octave, 2003; Onukwuli and Omotioma, 2016):

$$K = K_o e^{-E/RT} \tag{1}$$

Where K is the rate constant, K_o is the pre-exponential (frequency) factor, T is the absolute temperature, R is the universal gas constant (8.314kJ/kmol.K), and Ea is the activation energy. Considering different temperatures of the calcination processes, the linear form of the Arrhenius equation was used to obtain the activation energy:

$$Ln(K_2/ K_1) = (E_a/(2.303*R)) * (1/T_1 -1/T_2) \tag{2}$$

Thus,

$$E_a = (Ln(K_2/ K_1))*(2.303*R)*((T_1 T_2)/(T_2-T_1)) \tag{3}$$

Where K_1 and K_2 are the rate constants at T_1 and T_2 respectively, R is the universal gas constant (8.314kJ/kmol.K), and Ea is the activation energy

2.6 Determination of the pH of the Slaked Lime

The pH values of the samples were obtained using a pH meter.

III.   RESULTS AND DISCUSSION

3.1 Characteristics of the Limestone

3.1.1 Chemical Compositions of the Limestone

The graphical analysis of the Nkalagu limestone is shown in Figure 1. The limestone contains CaO (67.8%), SiO_2 (18.2%), Al_2SO_3 (6.9%), Fe_2O_3 (3.9%), and traces of Mn_2O_3, SrO, K_2O, Cl, P_2O_5, Cr_2O_3, ZnO, SO_3, MgO and TiO_2. The percentage compositions of the limestones can be improved through calcination

process (Okonkwo and Adefila, 2013; Kilic, 2014). The chemical compositions of each sample will determine the level of its reactivity (Kilic, 2014; Ofulume et al, 2018).
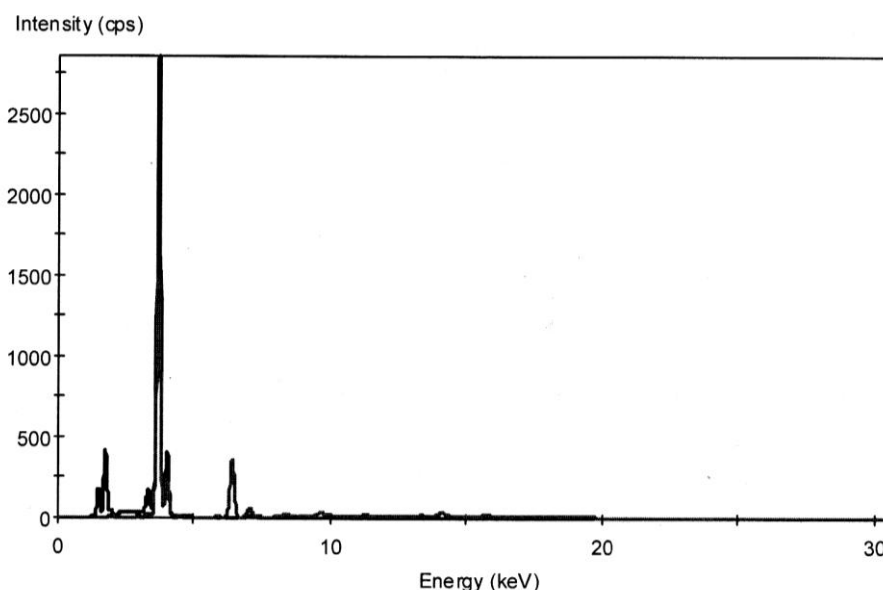

Figure 1: Chemical Compositions of the Limestone

3.1.2 Size Analysis of the Limestone

Size analysis (surface area data, pore volume data and pore size data) of the Nkalagu limestone sample is presented in Table 1. Density Functional Theory (DFT) cumulative surface area of Nkalagu limestone is 1.162 $\times 10^2 m^2$/g. The DFT helped to distinguish between different pore structures and morphologies. It accounted for the effects of microporocity, and predicted the pore sizes (Landers et al, 2013). Other methods of the size analysis such as BET and Langmuir methods grossly estimated the surface area, while DFT method gave reliable surface area and pore volume measurements. This observation is in agreement with the finding of previous work (Occelli et al, 2003). The parameters from the DFT methods are vital because of its rigorous theoretical basis that covers the whole region of micro- and mesopores and provides an opportunity of customization to different adsorbates, materials and pore morphologies (Landers et al, 2013). The DFT is adequate for the characterization of micro- and mesoporous materials of various origins. It introduces the surface roughness as additional structural parameter characterizing the pore wall heterogeneity.

Table 1: Size Analysis of Nkalagu Limestone

Analysis	Surface Area Data
Single point BET	2.848X$10^2 m^2$/g
MultiPoint BET	3.894 X$10^2 m^2$/g
Langmuir surface area	1.009 X$10^3 m^2$/g
BJH method cumulative adsorption surface area	4.865 X$10^2 m^2$/g
DH method cumulative adsorption surface area	5.184 X$10^2 m^2$/g
t-method external surface area	3.894 X$10^2 m^2$/g
DR method micropore area	4.822 X$10^2 m^2$/g
DFT cumulative surface area	1.162 X$10^2 m^2$/g
	Pore Volume Data
BJH method cumulative adsorption surface area	2.342 X$10^1 cc$/g
DH method cumulative adsorption surface area	2.398 X$10^1 cc$/g
DR method micropore volume	1.714 X$10^1 cc$/g

HK method micropore volume	$8.317 \times 10^2 cc$/g
SF method micropore volume	$2.633 \times 10^2 cc$/g
DFT method cumulative pore volume	$1.281 \times 10^1 cc$/g
	Pore Size Data
BJH method adsorption pore diameter (Mode Dv (d))	2.121nm
DH method adsorption pore diameter (Mode Dv (d))	2.121nm
DR method micropore pore width	5.644nm
DA method pore diameter (Mode)	2.740nm
HK method pore diameter (Mode)	3.675×10^1nm
SF method pore diameter (Mode)	4.523×10^1nm
DFT pore Diameter (Mode)	2.647nm

3.2 Characteristics of the Quicklime
3.2.1 Chemical Compositions of the Quicklime
　　　　The chemical compositions of the quicklime samples were obtained through the XRF analysis. The graphical analyses of Nkalagu qucklime is shown in Figure 2. The concentration by weight of CaO was enhanced. The percentage CaO increased from 67.8% to 92.0%).
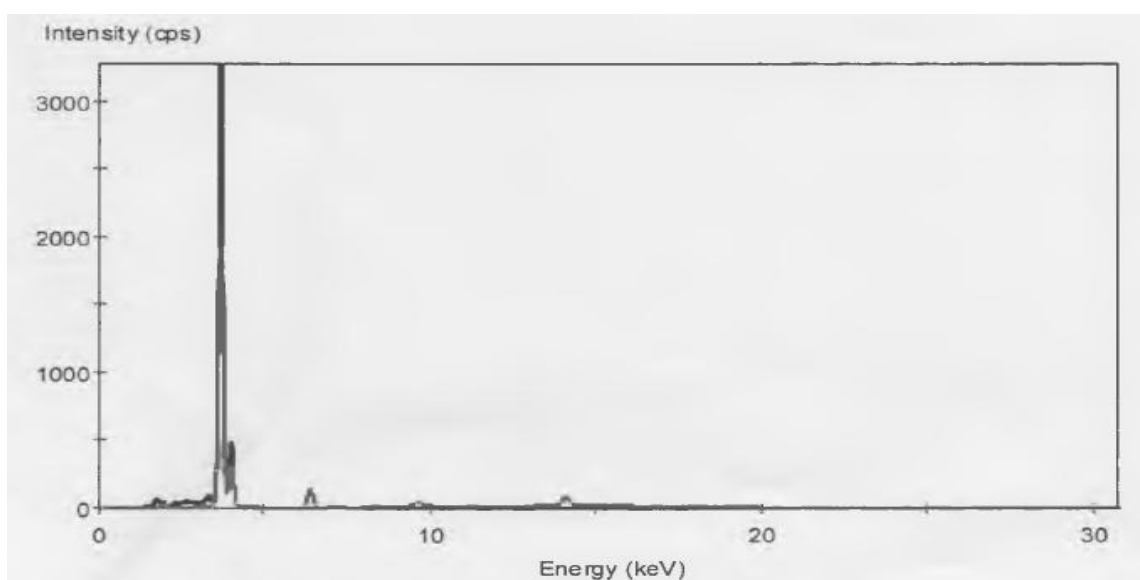

Figure 2: Chemical Compositions of the Quicklime

3.2.2 Size Analysis of the Quicklime
　　　　Size analyses (surface area data, pore volume data and pore size data) of the Nkalagu quickime is presented in Table 2. DFT cumulative surface area of the quicklime is $1.060 \times 10^2 m^2$/g. Other methods of the size analysis such as BET and Langmuir methods grossly estimated the surface area, while DFT method yields reliable surface area and pore volume measurements. This observation is in agreement with the finding of previous work (Occelli et al, 2003).

Table 2: Size Analysis of the Quicklime

Analysis	Surface Area Data
Single point BET	$2.573 \times 10^2 m^2$/g
MultiPoint BET	$3.328 \times 10^2 m^2$/g
Langmuir surface area	$7.770 \times 10^3 m^2$/g
BJH method cumulative adsorption surface area	$4.412 \times 10^2 m^2$/g

DH method cumulative adsorption surface area	4.716 X$10^2 m^2$/g
t-method external surface area	3.328 X$10^2 m^2$/g
DR method micropore area	4.143 X$10^2 m^2$/g
DFT cumulative surface area	1.060 X$10^2 m^2$/g
	Pore Volume Data
BJH method cumulative adsorption surface area	2.123 X$10^{-1} cc$/g
DH method cumulative adsorption surface area	2.180 X$10^{-1} cc$/g
DR method micropore volume	1.472 X$10^{-1} cc$/g
HK method micropore volume	7.530 X$10^{-2} cc$/g
SF method micropore volume	2.579 X$10^{-2} cc$/g
DFT method cumulative pore volume	1.218 X$10^{-1} cc$/g
	Pore Size Data
BJH method adsorption pore diameter (Mode Dv (d))	2.433nm
DH method adsorption pore diameter (Mode Dv (d))	2.433nm
DR method micropore pore width	5.349nm
DA method pore diameter (Mode)	2.680nm
HK method pore diameter (Mode)	3.675X10^{-1}nm
SF method pore diameter (Mode)	4.523x10^{-1}nm
DFT pore Diameter (Mode)	2.847nm

3.3 RSM Results of the Slaking Process

Experimental results of the response surface methodology are presented in Table 3. It showed the interactive effects of quicklime/water ratio, particle size and time on the reactivity of the slaked lime. Maximum reactivity of 57.6% was obtained at the midpoints of the considered factors. This is an indication that the relationship is in quadratic form.

Table 3: RSM Results of the Slaking of Nkalagu Quicklime

Std	Run	Factor 1 A: Quicklime/Water Ratio g/ml	Factor 2 B: Particle Size μm	Factor 3 C: Time min.	Response 1 Reactivity °C
14	1	0.25	90	20	48.5
16	2	0.25	90	16	57.6
13	3	0.25	90	12	44.2
1	4	0.2	80	12	24.3
12	5	0.25	100	16	45.5
4	6	0.3	100	12	34.1
3	7	0.2	100	12	13.6
2	8	0.3	80	12	29.5
15	9	0.25	90	16	57.6
20	10	0.25	90	16	57.6
8	11	0.3	100	20	31.4
10	12	0.3	90	16	48.7
9	13	0.2	90	16	40.4
18	14	0.25	90	16	57.6
5	15	0.2	80	20	30.8
6	16	0.3	80	20	33.2
7	17	0.2	100	20	19.5
17	18	0.25	90	16	57.6
19	19	0.25	90	16	57.6
11	20	0.25	80	16	50.3

3.3.1 Analysis of variance

In Table 4, the model F-value of 385.26 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The predicted R² of 0.9653 is in reasonable agreement with the Adjusted R² of 0.9945; the difference is less than 0.2. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 58.051 indicates an adequate signal. This model can be used to navigate the design space.

Table 4: ANOVA of Reactivity the Nkalagu Slaked Lime

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3784.92	9	420.55	385.26	< 0.0001	significant
A-Quicklime/Water Ratio	233.29	1	233.29	213.72	< 0.0001	
B-Particle Size	57.60	1	57.60	52.77	< 0.0001	
C-Time	31.33	1	31.33	28.70	0.0003	
AB	76.88	1	76.88	70.43	< 0.0001	
AC	16.24	1	16.24	14.88	0.0032	
BC	6.13	1	6.13	5.61	0.0394	
A²	382.62	1	382.62	350.51	< 0.0001	
B²	196.15	1	196.15	179.69	< 0.0001	
C²	274.75	1	274.75	251.70	< 0.0001	
Residual	10.92	10	1.09			
Lack of Fit	10.92	5	2.18			
Pure Error	0.0000	5	0.0000			
Cor Total	3795.83	19				
Std. Dev.	1.04		R²			0.9971
Mean	41.98		Adjusted R²			0.9945
C.V. %	2.49		Predicted R²			0.9653
			Adeq Precision			58.0505

3.3.2 Mathematical model of the reactivity of the slaked lime

The mathematical model of the reactivity of, Nkalagu slaked lime (in terms of significant terms) is presented in Equations (4). The model can make adequate predictions about the response for given levels of each factor, and it is useful for identifying the relative impact of the factors by comparing the factor coefficients. As revealed by the analysis of variance, each model adequately described the relationship between the reactivity and the factors of quicklime/water ratio, particle size and time. Thus, the reactivity is a function of quicklime/water ratio, particle size and time. The positive signs in the model signified synergistic effect, while the negative signs signified antagonistic effect (Omotioma and Onukwuli, 2017). As such, there is a synergistic effect on the interaction of quicklime/water ratio and particle size in all the models. On the hand, the negative sign of the coefficients of AC indicates antagonistic effect of the interaction of quicklime/water ratio and time for the reactivity model. The highest power of at least one of the variables is two, which showed that the mathematical model is a quadratic equation.

$$Reactivity = + 57.10 + 4.83A - 2.40B + 1.77C + 3.10AB - 1.43AC - 0.8750BC - 11.80A^2 - 8.45B^2 - 10.00C^2$$
$$(4)$$

3.3.3 Graphical analyses

Graph of predicted versus actual reactivity is presented in Figure 3. It showed a linear graph, with the points clustered along the line of best fit. This is an indication that the generated model can predict the experimental data. The 3-D surface plots showed the relationship between the factors and response of the designed experiment (Figures 4 - 6). The 3-D graphs revealed the optimum reactivity of 57.1^0C with the corresponding quicklime/water ratio of 0.25 g/ml, particle size 90 μm and time of 16 minutes.
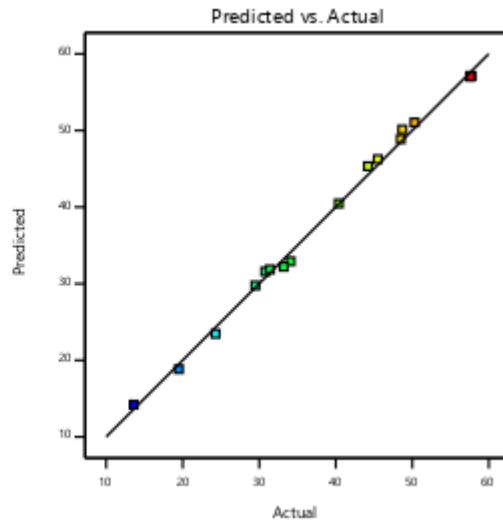
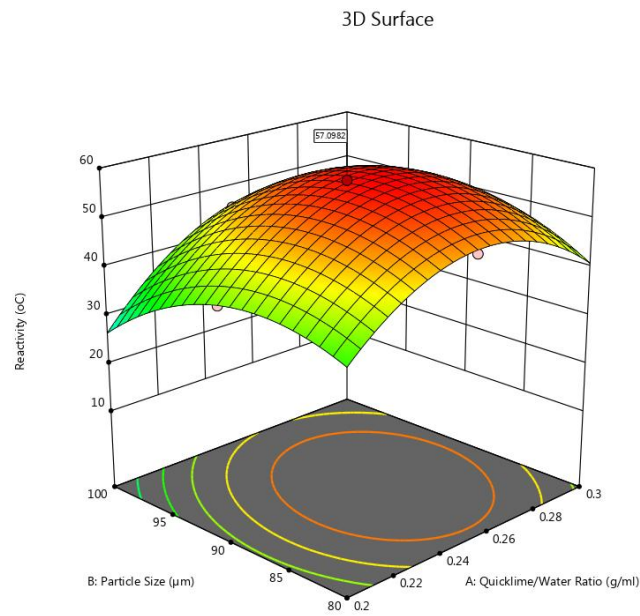**Figure 3:** Predicted versus Actual Reactivity of Nkalagu Slaked Lime

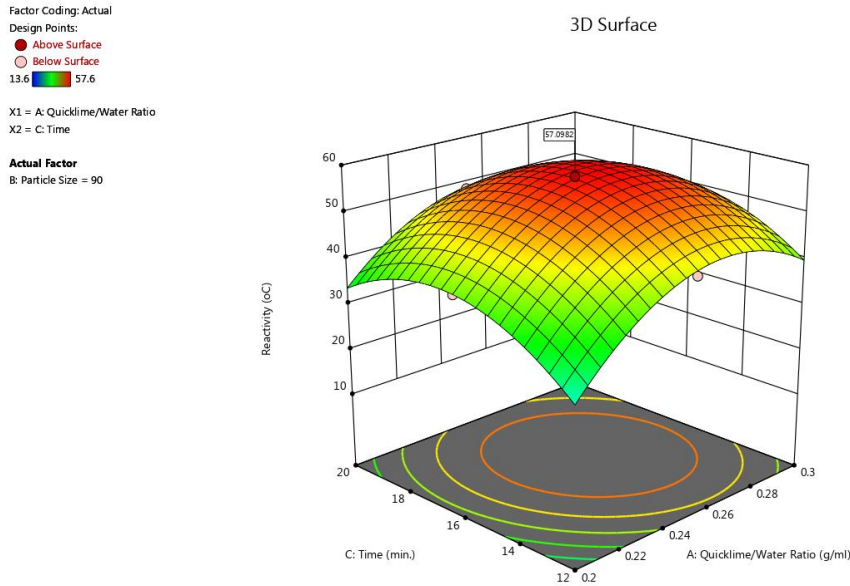**Figure 4:** Reactivity versus Quiklime/Water Ratio and Particle Size for the Nkalagu Quicklime

Figure 5: Reactivity versus Quiklime/Water Ratio and Time for the Nkalagu Quicklime
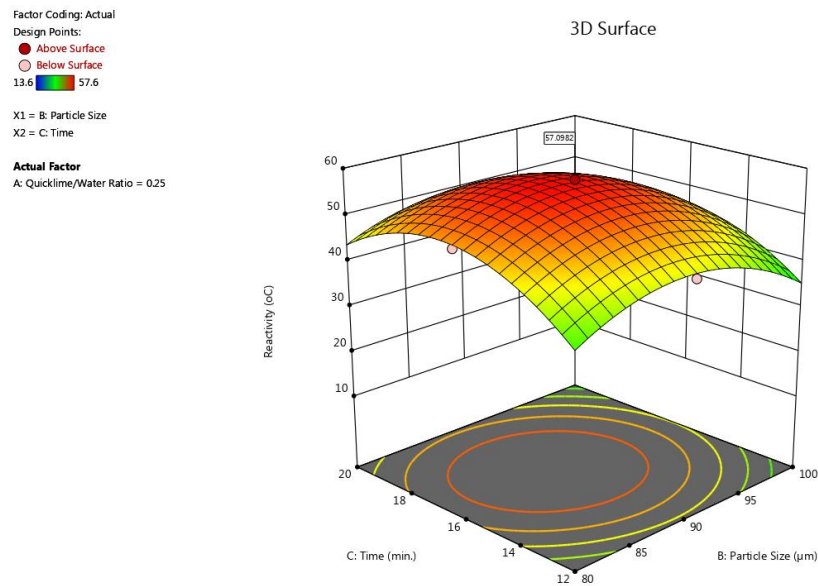

Figure 6: Reactivity versus Particle Size and Time for the Nkalagu Quicklime

3.4 Validation of the Results of the Slaking Process

Data for the validation of the results are presented in Table 5. The experimental results were validated by the determination of percentage deviation of experimental reactivity from the predicted reactivity. Recorded percentage deviation is less than 5%, an indication that RSM is adequate for the optimization of the slaking process. It is also an affirmation that the generated models can adequately describe the slaking process (Onukwuli and Omotioma, 2016).

Table 5: Validation of the Results of the Slaking Process

Quicklime Sample	Quicklime/ Water Ratio (g/ml)	Particle Size (μm)	Time (min.)	Experimental Reactivity (^{o}C)	Predicted Reactivity (^{o}C)	Percentage Deviation (%)
Nkalagu	0.25	90.0	16.0	58.3	57.1	2.06

3.4 Rate of the Reactivity of the Slaked Lime

The rate of the reactivity of Nkalagu slaked lime is shown in Figure 7. The graph showed the relationship between reactivity and time at various temperatures. In the reactivity versus time, linear graphs were obtained. The straight line graphs were confirmed by linear equations obtained using Trend line Function of Microsoft Excel. The coefficient of determination R^2 is close to 1 in all the cases. More so, rate constants were revealed in all the Equations. The rate constant was useful for the determination of the activation energy using Arrhenius Equation (Octave, 2003; Mu'azu et al, 2011, Onukwuli and Omotioma, 2016).
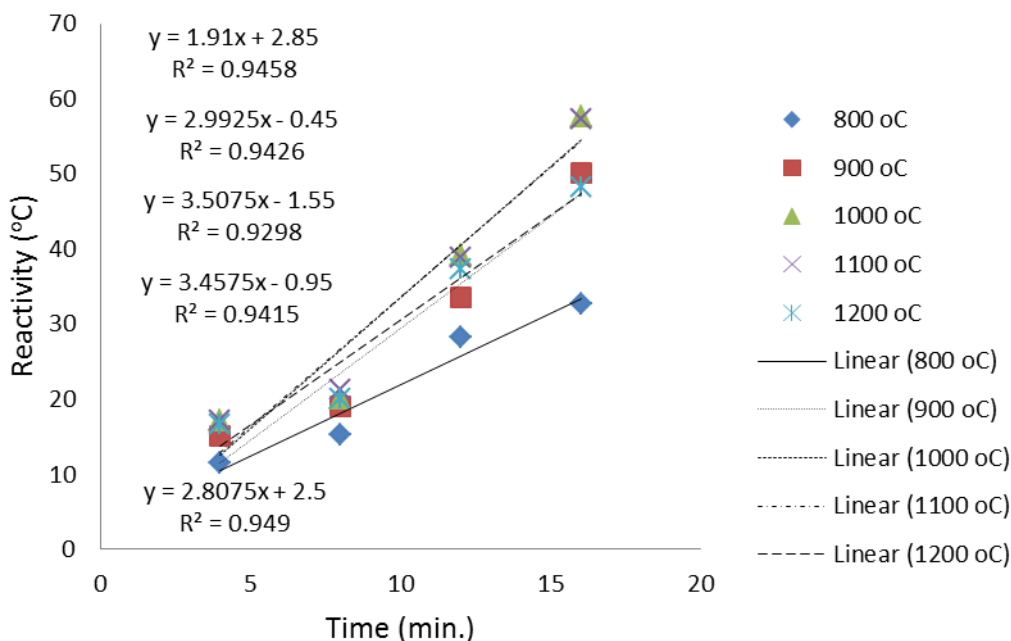

Figure 7: Reactivity versus Time for the Nkalagu Slaked Lime

3.6 Activation energy of the slaked lime

Table 6 presents 79.48 kJ/mol as the activation energy of the slaked lime sample. It was obtained using Arrhenius law and it activation energy of the slaked lime sample. The reaction temperature has a direct effect on the rate of reactivity. This observation corroborates with the assertion of Mu'azu et al (2011).

Table 6: Activation energy of the slaked lime

slaked lime Sample	Activation Energy, E_a (kJ/mol)
Nkalagu	79.48

3.5 pH Values of the Slaked Lime

The pH value of the slaked lime sample is presented in Table 7. The data revealed that Nkalagu slaked lime has pH of 11.8, which indicates that it is an alkaline sample. According to Moreira and Fageria (2010), liming is one of the most efficient and prevailing practices to correct soil acidity and improve agricultural yield. So, the obtained high pH values showed that Nkalagu slaked lime for the amelioration of soil acidity, and subsequent improvement of agricultural output.

Table 7: pH Value of the Slaked Lime

slaked lime Sample	pH Value of the Slaked Lime
Nkalagu	11.8

IV.   CONCLUSION

From the analyses of the experimental results, the following conclusions can be drawn:

The XRF and size analyses revealed the mineralogical pore size and structural characteristics of the Nkalagu. The quicklime was successfully produced through the calcination. Characteristics of the quicklimes showed that the calcination improved the quality of the samples in terms of chemical, mineralogical, morphological and pore size and structural properties. The percentage CaO increased from 67.8% to 92.0%).

Quadratic model adequately described the relationship between reactivity and the considered factors of the slaking process. Optimum reactivity was obtained as 57.1^0C at quicklime/water ratio of 0.25 g/ml, particle size 90 μm and time of 16 minutes. The obtained high pH value showed that Nkalagu slaked lime is suitable for the amelioration of soil acidity, and subsequent improvement of agricultural output.

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