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ROAST-ALKALINE LEACHING OF SILICA FROM KAOLINITIC CLAY

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ABSTRACT

The main aim of this study is to extract silica from calcined kaolinitic clay treated with sodium hydroxide solution. Beneficiated kankara kaolinitic clay was calcined at 1000°C for 1 hour to activate the silica content in the clay. The silica was extracted from the clay in an alkaline medium using 5, 10, 20, 30, and 40% w/w NaOH and a contact time of 20minutes. Although the logarithmic function gave silica extraction efficiency of 99.6% ($R^2 = 0.996$) and solubility of 65%, with 40% w/w NaOH, the high solubility of alumina in this solution was a major drawback. Investigations on the effect of contact time on the solubility of silica in the alkaline solutions revealed 49% leaching of silica, decreased solubility of alumina and extraction efficiency of 84.9% ($R^2 = 0.849$) at 30mins in 25% NaOH optimized concentration. The amount of alumina leached by different concentrations of NaOH increased with increase in concentrations of NaOH but the solubility of the alumina in the alkaline solution was less than that of the silica at any specific contact time studied.

Keywords: kaolinitic clay, silica, leaching, extraction, alkali.

INTRODUCTION

The total annual production of high alumina cement is a very small fraction of the world production of Portland cement. However, this special cement possesses certain valuable properties. Concrete made with ordinary aggregates and high-alumina cement is slow setting but extremely rapid hardening and it has a high resistance to many aggressive agents such as chemical attack (Robson, 2002). When a refractory aggregate is used, the concrete is suitable for continual service at high temperatures. These main properties of rapid development of strength, chemical resistance, and refractory bond, are responsible for most of the attention paid to high alumina cement (Robson, 2002).

The material customarily used for the manufacture of ordinary high-alumina cement are calcium carbonate (nearly always in the form of limestone), and bauxite (of quality employed in the aluminum industry). Various suggestions and attempts (Vassan, 2001) have been made to substitute some other available materials for bauxite as source of the alumina required to form calcium aluminate. Kaolinite with high alumina content is the most likely candidate as a replacement for bauxite. Although cheap and widely distributed, it contains too much Silica to yield directly high-alumina cement. Their employment would necessitate a preliminary chemical treatment designed to separate Silica from the alumina (Vassan, 2001).

The extraction of silica from kaolin proceeds in series of processes that involve clay preparation (beneficiation), heat treatment (calcinations) and the use of sodium hydroxide as agent for extraction (Rayzman, *et al*., 2003; Santos *et al*., 2005; Smith, 2008). The reaction time in the removal of silica is crucial to the reaction yield. Therefore by varying both the concentration and the reaction time, this research work seeks to determine the best possible condition necessary for optimum yield of alumina (Keller, 1999) using NaOH.

The extraction of silica from clay by the use of alkali as leaching agent is dependent on calcination temperature, reaction time and may be the leaching agent. Investigating the effect of reaction time on the overall yield of silica extraction from kankara clay is necessarily expedient in the understanding of this method of extraction.

Kaoline which has about 36 - 39wt % of alumina and next to bauxite (45 - 65wt %), is cheap and in great abundance in Nigeria with about six million tones scattered all over the country (RMRDC, 2004). If the technology of thermally extracting silica from kaoline is well harnessed it could provide a boost to indigenous technology.

Pure Kaolin basically contains, Al_2O_3 (39.50%), SiO_2 (46.6%) and H_2O (13.90%).

After calcination, the percentages of alumina and silica become, Al_2O_3 (46.60%), SiO_2 (54.00%). Apart from these principal components, clay in as mined condition contains certain impurities, such as quartz, which is also widely distributed. At about 1300-1350^{0}C, quartz is inert and plays the part of non plastic filler (Budnikov, 1964). Another common impurity of clays is some forms of ferruginous compounds such as pyrite, mascasite (FeS_2), Siderite ($FeCO_3$) and iron oxides (Fe_2O_3). Fluxing agents such as CaO, MgO, Na_2O and K_2O are also found in clays in addition to calcite ($CaCO_3$), gypsum ($CaSO_4$), rutile (TiO_2) and organic matter of vegetable origin. Hence, the complete chemical analysis of clays would normally comprise the determination of loss on ignition, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, Na_2O, H_2O and other oxides (Budnikov, 1964).

A number of methods have been proposed to reduce silica content of starting materials as first step prior to processing of clay materials to high alumna containing materials. The methods frequently employ a preliminary treatment of starting materials by heat treatment at elevated temperatures and subsequently leaching with caustic soda (NaOH) solution or soda (Na_2CO_3) solutions.

Neither of these known methods is applicable to clays having silica (SiO_2) content higher than 40%. Certain clays with much lower silica content have been heated to temperatures between 400^0Cand 700^0C and have been extracted, with concentrated solutions of alkali metal hydroxides, whose treatment results in preferential extraction of silica, leaving a residue richer in alumina and poorer in silica than the original material (Qiu, *et al*., 2004, Guillermo, 2008).

In the case of large group of clay materials, such as Kaolins as well as pyrophyllites and certain montmorillonites all of which have silica content above 40%, heating temperatures between 400^0C and 700^0C does not have any marked effect on the solubility of the Silica contained in the materials. Heat treatment below 800^0C converts only about 5 to 7.5% of the Silicate content into a soluble form (Guillermo, 2008).

When calcining alumina containing materials of various SiO_2 contents at higher temperatures (800-1100^0C) the ratio of soluble silica to soluble alumina is greatly improved (Guillermo, 2008). Silica solubility also increases with the temperature and therefore it is advantageous to conduct the leaching step at as high temperature as possible. However, to avoid the need for costly high pressure reactions, it is advantageous to leach at temperature at or below the boiling point of the leaching solution (Guillermo, 2008).

Leaching time is dependent upon several factors including the quantity of the Silica to be removed, the porosity of the body prior to leaching, concentration of the leaching solution and temperature of leaching (Jiang, *et al*., 2000; Chakraborty, 2003). Finally, control of calcination conditions influences several properties including the degree of the clay conversion to mullite and free Silica (Guillermo, 2008).

The aim of the present study is to extract silica from calcined Kaolinitic clay pretreated with sodium hydroxide solution.

MATERIALS AND METHODS

Clay beneficiation

The process involves the pre-treatment of raw kankara kaolin to remove impurities. The raw kankara kaolin was poured into plastic bucket and mixed with sufficient deionized water. The mixture was stirred and allowed a vintage of 24 hours. The fluid above the kaolin was decanted after this period of time. These steps were repeated until the decanted water was clear. The dried clay was crushed and sieved with a 75µm mesh size.

Calcination

The beneficiated kaolin clay was calcined at 1000˚C in a furnace for 1hour. This period and temperature are suitable for the conversion of silica content in clay to soluble form in appreciable amount and prevent recrystallization of kaolin from mullite.

Extraction of silica (SiO_2)

The knowledge of solubility of silica in alkali solution was employed to leach the calcined kaolin.

$$2NaOH_{(aq)} + SiO_{2(s)} \rightarrow Na_2SiO_{3(l)} + H_2O_{(l)}$$

The extraction agent used was sodium hydroxide prepared from its pellets and the extraction temperature used was 75˚C. In the extraction process, 25g Sample of calcined kaolin was weighed. 5% w/w NaOH solution was prepared with deionized water. A solution containing 20% excess NaOH solution was required to dissolve the silica content in the clay sample in a three neck open round bottom flask. The flask was placed in an electric water bath and stirred continuously using a mechanical stirrer. A thermometer was inserted in the first opening, a stirrer in the second opening and a cork at the third opening to prevent heat loss. The extraction was carried out for 20 minutes after which the silicate containing solution was filtered. The residue was dried in an oven at 65˚C for 4 hours. The dried sample was weighed.

The above procedure (extraction and filtration) was repeated for 10%, 20%, 30%, and 40% w/w NaOH solutions and at varying reaction times of 5, 10, 20, 30, and 40 minutes at 25% w/w optimized concentration of NaOH, in order to study the effect of time on the solubility of the silica in NaOH solutions.

X-Ray fluorescence

Calcined kaolin, ten samples of silica and alumina clay extracted at varying concentrations and time were analyzed using XRF Mini Pal 4 Machine (PW 4030 X-ray Spectrometer) at the National Geo-science Research Laboratories (NGRL) Kaduna, Nigeria.

The Mini Pal 4 version used is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in solids, powders or liquids.

The sample for analysis was weighed and pulverized in agate mortar and a binder (PVC dissolved in toluene) was added to the sample. It was carefully mixed and pressed in a hydraulic press into a pellet. The pellet was loaded in the sample chamber of the spectrometer and maximum voltage of 30kv and a maximum current of 1mA was applied to produce the X-ray to excite the sample for a preset time of 10mins. The spectrum from the sample was analyzed to determine the concentration of the elements in the sample.

RESULTS AND DISCUSSIONS

Table-1 shows the percentage oxide composition of the kaolinitic clay calcined at 1000˚C. The calcined clay sample was 36.2% alumina in association with 56.0% silica.

Table-1. Percentage oxide composition of Kankara kaolinitic clay calcined at 1000˚C.

Oxide	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**Ag_2O**
% weight	36.2	56.0	3.19	0.418	0.389	0.023	1.65	1.62

The effects of concentration of NaOH and soaking time of clay on the solubility of alumina and silica at 75˚C for 1 hour are shown in Tables 2 and 3, respectively.

Table-2. X-ray fluorescence of calcined alkali-treated clay at varying NaOH concentrations.

% NaOH used	**% SiO_2 leached**	**% Al_2O_3 leached**
5.0	23	24
10.0	36	25
20.0	49	40
30.0	57	46
40.0	65	52

Table-3. X-ray fluorescence of calcined alkali-treated clay using 25% w/wNaOH concentration at varying time of leaching.

Time (mins)	**% SiO_2 leached**	**% Al_2O_3 leached**
5	38	27
10	39	28
20	40	35
30	49	37
40	48	38

Different mathematical functions were tested to describe the relationship between the amounts of silica leached from the calcined kaolin and NaOH concentrations as shown in Figures 1 to 5. The exponential function gave an accuracy of 87.2% with regression coefficient (R^2) of 0.872 (Figure-1). Linear, polynomial and power functions gave accuracies of 95.1% (R^2 = 0.951) (Figure-2), 98.9% (R^2 = 0.989) (Figure-4) and 98.8% (R^2 = 0.988) (5) respectively. All these values gave a good description of the trend observed, but the best function that describes the trend of the solubility of silica in the NaOH solutions is the logarithmic function, which has an accuracy of 99.6% (R^2 = 0.996) (Figure-3).

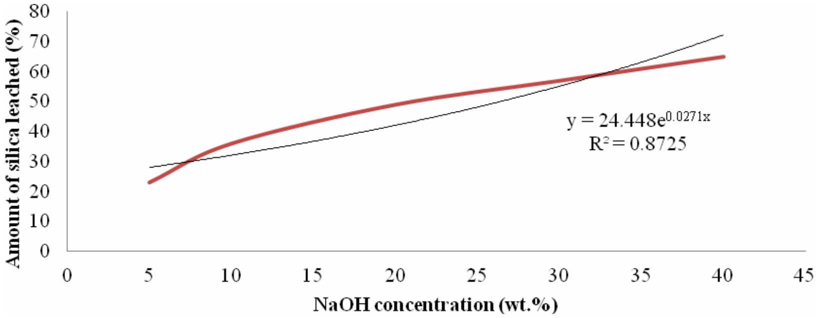

Figure-1. Exponential fitting of data points.

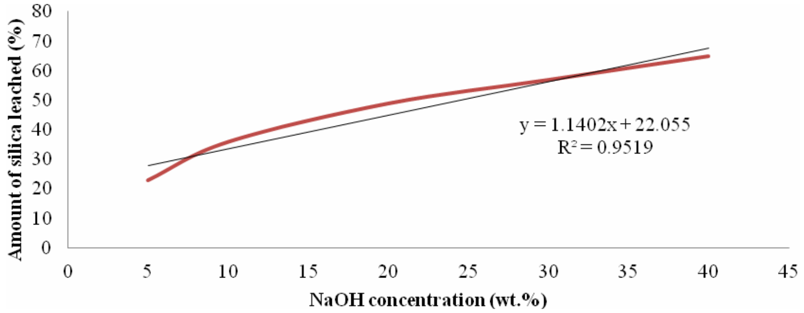

Figure-2. Linear fitting of data points.

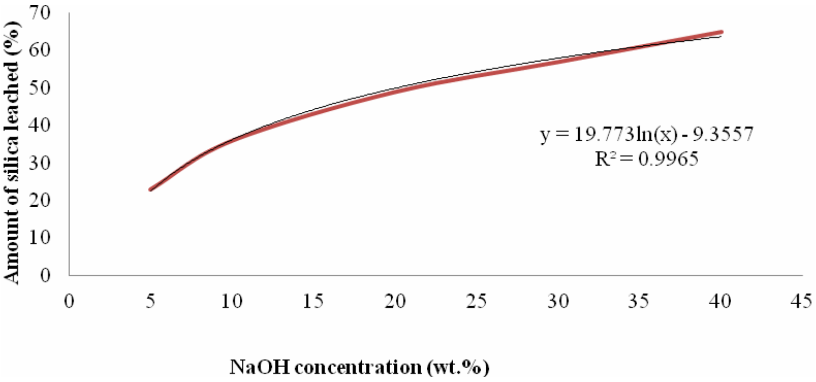

Figure-3. Logarithmic fitting of data points.

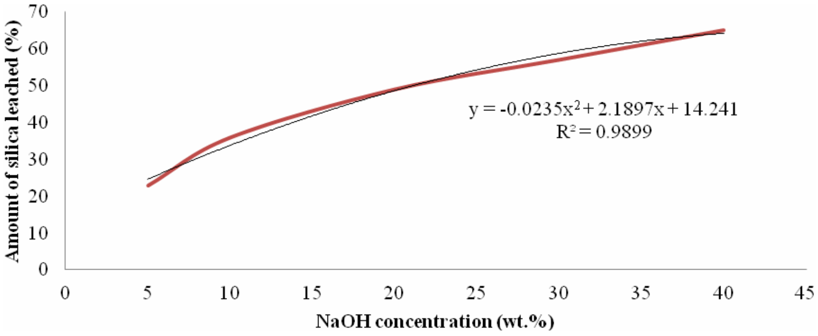

Figure-4. Polynomial fitting of data points.

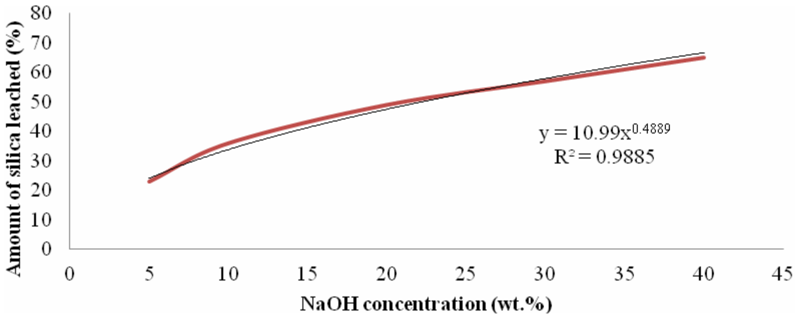

Figure-5. Power fitting of data point.

It can be deduced that the model equation that best describes the solubility of silica from the calcined kaolin in various solutions of NaOH is described by the curve in Figure-3 with regression coefficient of 0.996 and a gradient of 19.77.

The equation with its intercept at -9.355 is given as:

$Y = 19.77 \ln(x) - 9.355$

Where

y = Amount of silica leached (%)

x = concentration of NaOH (w/w %)

Figure-3 shows a rapid increase in the percentage amount of silica leached between 5% and 10% NaOH concentrations, beyond this, a gradual and steady increase in the amount of silica leached from the calcined kaolin was observed thus indicating that silica became more soluble as the concentration of the NaOH solution increases. 40% w/w NaOH concentration gave the highest solubility of silica in the alkaline medium at 65%.The high solubility of alumina in this solution was however a major drawback.

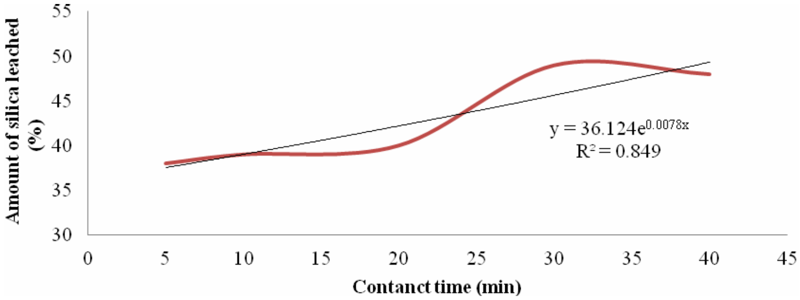

Figure-6. Exponential fitting of plotted point.

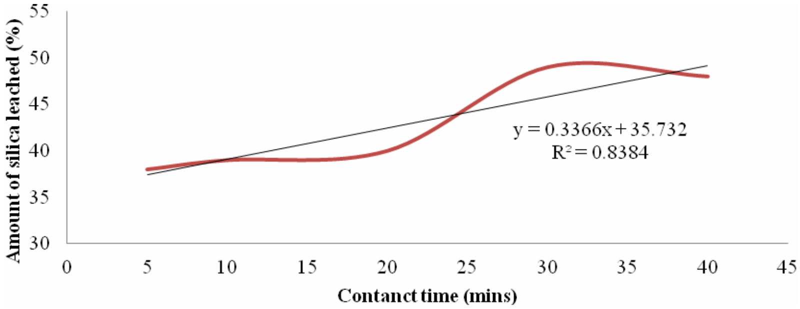

Figure-7. Linear fitting of plotted point.

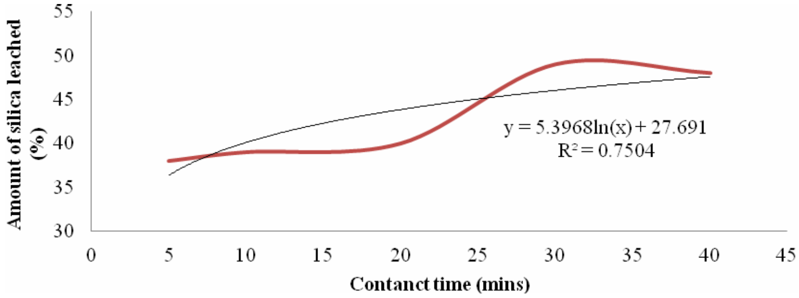

Figure-8. Logarithmic fitting of plotted point.

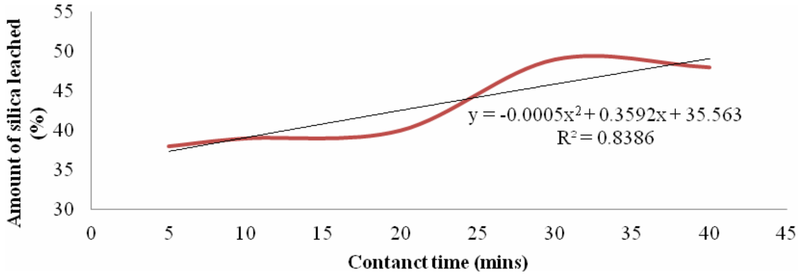

Figure-9. Polynomial fitting of plotted point.

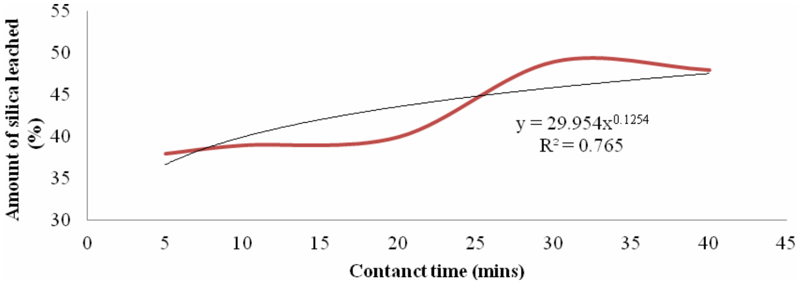

Figure-10. Power fitting of plotted point.

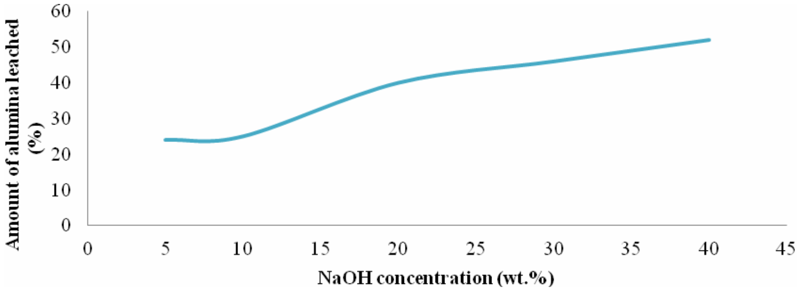

Figure-11. Alumina leached varying concentration.

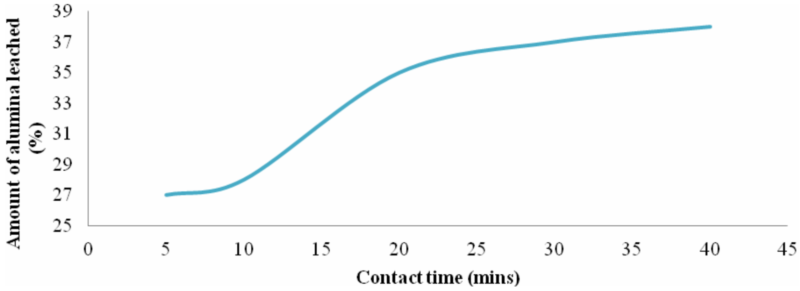

Figure-12. Alumina leached varying contact time.

Figures 6 to 10 show the variation of the amount of silica leached from the calcined kaolin at varying times of 5mins, 10mins, 20mins, 30mins, and 40mins respectively, using 25% w/w NaOH. From Figure-6, there was a rapid increase in the percentage amount of silica leached at 25mins, with an optimum height at 30mins time interval. Therefore, the highest solubility amount of silica leached was 49%. Figure-11 shows the amount of alumina leached as the concentration of NaOH was varied between 5% and 10% and no substantial difference was observed. But as the concentration of NaOH increases, the amount of alumina leached also increases. This agrees with the fact that alumina is an amphoteric oxide, which is behaving like an acid in the presence of a strong base like NaOH. But the solubility of the alumina was found to be less than that of silica. Figure-12 shows a rapid increase in the amount of alumina leached between 10mins to 20mins, and beyond this contact time, the amount of alumina leached was almost constant.

CONCLUSIONS

From the results obtained, it can be concluded that alkali leaching of Kankara Kaolinitic clay is a function of concentration of the extracting agent, NaOH. It can also be inferred that the suitable concentration for extraction is 40% w/w NaOH solution which gave the highest solubility of silica leached as 65%. The amount of alumina leached by different concentrations of NaOH increased with increase in concentrations of NaOH but the solubility of the alumina in the alkaline solution was less than that of the silica at any specific contact time studied.

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