

**ALKALI TREATMENT OF CLAY TO PRODUCE ALUMINA FOR  
CEMENT PRODUCTION**

By

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**(2005/21813EH)**

**DEPARTMENT OF CHEMICAL ENGINEERING,  
SCHOOL OF ENGINEERING AND ENGINEERING TECHNOLOGY,  
FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA  
NIGERIA**

**October, 2010.**

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**A PROJECT SUBMITTED TO THE  
DEPARTMENT OF CHEMICAL ENGINEERING,  
FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA  
NIGERIA**

**IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF  
BACHELOR IN ENGINEERING (B.ENG) DEGREE IN CHEMICAL  
ENGINEERING**

**October, 2010.**

## DECLARATION

I declare that the work in the project report (thesis) entitled 'alkali treatment of clay to produce alumina for cement production' has been performed (carried out) by me under the supervision of Engr. A. Aboje. No part of this project report (thesis) was presented for other degree or diploma elsewhere at any institution to the best of my knowledge.

THEIN A.B. WUYAH  
Name of student

  
Signature

25-10-2010  
Date

**CERTIFICATION**

to certify that this project report (thesis) entitled 'ALKALI TREATMENT OF CLAY  
PRODUCE ALUMINA FOR CEMENT PRODUCTION' by Matthew A. B. Wuyah  
the requirements for the partial fulfillment of the award of Bachelor of Engineering (B.  
degree in chemical in Chemical Engineering. Federal University of Technology, Minna.

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25/11/10  
Date

External Examiner  
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Date

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My profound gratitude goes to my parents, for their unflinching support throughout the course of this study. I would also like to acknowledge Jummai Wuyah for her support. Not to forget all other relatives who assisted me in one way or the other during my entire programme.

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## ABSTRACT

In this work an attempt was made to remove silica from kaolin clay. The aim was to determine the suitability of kankara clay on industrial application using alumina rich clay for production of high alumina cement. An investigation of the alkali leaching of calcined kankara clay was made to study the effect of concentration on leaching of its silica content. Kankara clay was calcined at  $1000^{\circ}\text{C}$  for 1 hour to activate its silica content. It was then leached with sodium hydroxide solution at varying concentrations of 5 %, 10 %, 20 %, 30 % and 40 %. The chemical analysis of the leached residue revealed that silica could be sufficiently removed by alkali leaching. At 20 % NaOH concentration 30 % of silica content was leached without noticeable loss in alumina content; giving the best result in terms of alumina/ silica ratio of the residue of 1.15. A further investigation of the effect of time at constant alkali concentration of 25 % w/w was carried at varying time of 5, 10, 20, 30 and 40 minutes which gave 51 % leaching of silica at 30 minutes time interval without noticeable loss of alumina and giving a better alumina to silica ratio of 1.65.

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## Chapter One

### 1.0 INTRODUCTION

The total annual producer, of high-alumina cement is a very small fraction of the world production of cement. However, this is a special cement possessing certain valuable properties. Concrete made with ordinary aggregates and high-alumina cement is slow setting but extremely rapid hardening and it is also resistance to many aggressive agents. When a refractory aggregate is used, the concrete is suitable for continual service at high temperatures. These main properties; rapid development of strength, chemical resistances, refractory bond, are responsible for most of the attention paid to high-alumina cement (Marble institute of America, 2010).

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 suggestion and attempt have been made to substitute some other available material for bauxite as source of the alumina required to form calcium aluminate. Kaolinite with its high alumina content is the most likely candidate as a replacement for bauxite. Although cheap and widely distributed, it's contains too much silica to yield directly high-alumina cement. Their employment would necessitate a preliminary chemical treatment designed to separate silica from alumina.

The purpose of this research topic therefore; is to extract silica from calcined kankara kaolin by treatment with sodium hydroxide solution (NaOH).

In this report literature on clay and clay minerals were reviewed. Experimental procedure used was reported. The result obtained was presented and discussed. Finally, conclusion and recommendation were made (Usman, 2003).

### **1.1 Aims of Research**

The primary aim of this project is to extract silica from clay (a mixture of silica and alumina) in order to combine the alumina with calcium carbonate (limestone) in the production of high alumina cement.

It is also aimed at reducing the overall cost of production of cement as it is a suitable and cheaper substitute for bauxite.

### **1.2 Objective of Research**

The objective of this research work is to reduce the overall cost of production of cement as it is a suitable and cheaper substitute for bauxite.

### **1.3 Scope of Research**

The research is limited to clay beneficiation, Calcinations, Silica extraction, and Filtration.

### **1.4 Justification of Research**

Completion of the study will promote the following;

- Generation of employment opportunities
- An affordable price range for cement
- Investment opportunities in the cement industry.

## Chapter Two

### LITERATURE REVIEW

#### 2.1 Clays

Clays are in form of naturally occurring fine grained minerals, which developed plasticity when mixed with the right proportion of water. They are natural argillaceous matters formed by decomposition of feldspathic rock as result of weathering action of wind and rain and are of chemical formula  $m\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot p\text{H}_2\text{O}$

Clay's posses distinctive properties that make them useful technologically. The distinctive properties are:

##### 2.1.1 Plasticity

This signifies the property of the clay when melted that permits deformation by relative application of slight pressure and retention of deformed shape after removal of applied pressure. Clays are composed of extremely fine crystals or particles, often in colloidal in size and platy in size. The very fine particles yield large specific surface areas that are physically sorptive and chemically surface active.

The dominance of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}$  in the clays clearly defines them as hydrated alumino-silicates contaminated mainly by free silty quartz. Clays serves as substrates that selectively absorb catalyzed amino acids in the origin of life, and also they apparently catalyze petroleum formation in rocks. However, geologists, scientist and technologist view clay minerals in different perspective base on their professional applications.

The clay fraction is probably the most important component of surface deposits and soils, whether for its origin, as agricultural use, or as a factor in environmental processes whether physical, chemical or biological. Although clay minerals are usually considered the breakdown product of silicates, largely by hydrolysis, they maybe built up from hydrates of silica and

alumina. Its deposit contain usually non clay minerals as impurities, although these impurities maybe essential in determining the unique and specially desire properties of clay.

The deposit of clay contains both crystalline and amorphous mineral compounds

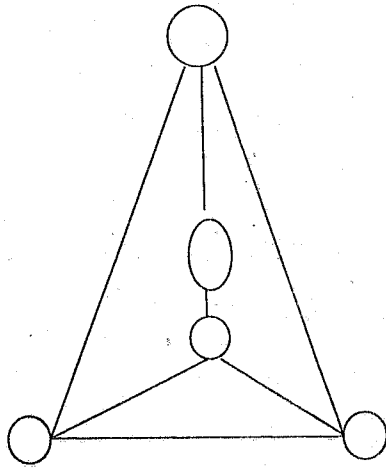
(clay- wikipedia,2010).

## 2.2 Structure of Clays

Clays differ very considerably among themselves in structure, workability, plasticity, particle size distribution and mineralogical composition.

Clays are crystalline in structure .The chemical analyses of clay show them to be composed essentially of silica, alumina and water, with appreciable amounts of iron alkalis and alkaline earth metals.

The lattices of most of the clay minerals are composed of two structural units. The first unit consists of closely packed six oxygen atoms or hydroxyls in the basal planes of an octahedral structure. Al, Fe or Mg atoms are embedded in the octahedral positions so that they are equidistant from six oxygen or hydroxyls in basal plane (Fig2.1)



**Fig 2.1: Silicon Dioxide; Each Silicon Atom is Surrounded Tetrahedrally by Oxygen.**

Fig 2.1 shows the unit that has the silica structure made of the tetrahedron in which the silicon atom is centrally placed equidistant from the four oxygen (or hydroxyl if

needed to balance the structure). The silica tetrahedral groups are arranged to form hexagonal network, which is repeated indefinitely to form a sheet composition  $\text{SiO}_4\text{O}_6(\text{OH})_4$ . The tetrahedrons are arranged so that the tops of them point in the same direction, and the basis of all tetrahedron are in the same plane, (clay-wikipedia, 2010).

### 2.3 Classification of Clay

Clays are classified mainly in two ways and are based on mineralogical constituents and the properties of the clays.

On mineralogical basis, clay minerals are divided into major groups in accordance with their crystallographic structure.

#### 2.3.1 Montmorillonite Minerals

They occur only in extremely small particles. The structural unit composed of layers made up of two silica ( $\text{SiO}_2$ ) tetrahedral sheets with a central gibbsite octahedral sheet by mutual sharing of the unsatisfied oxygen on the vertical side of the silica layers.

The theoretical chemical formula of this clay without taking lattice substitutions into consideration is  $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot n\text{H}_2\text{O}$  with theoretical composition of:  $\text{SiO}_2$ , 66.70 %;  $\text{Al}_2\text{O}_3$ , 28.30 %;  $\text{H}_2\text{O}$ , 5.0 %.

#### 2.3.2 Illite Minerals

The structural unit of illite minerals is similar to that for montmorillonite and has the same 2:1 crystal lattice structure. But in Illite about 20 % of the silicon ions ( $\text{Si}^{4+}$ ) in the silica layer are always replaced by aluminum ions ( $\text{Al}^{3+}$ ).

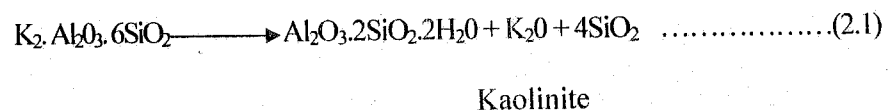
The structural formula of this clay is  $(\text{OH})_4\text{K}_2(\text{Si}_6\text{Al}_2)\text{Al}_4\text{O}_{20}$  and composition is:  $\text{K}_2\text{O}$ , 11.8 %;  $\text{SiO}_2$ , 45.2 %;  $\text{Al}_2\text{O}_3$ , 38.50 %;  $\text{H}_2\text{O}$ , 4.5 %.



### 2.3.3 Kaolinite Minerals

Kaolinite group, have the simplest clay mineral structure. These minerals have the chemical formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$  and include kaolinite, nacrite, dickite and livesite. When kaolinite are heated they begin to lose their OH structural water at about  $400^\circ\text{C}$  with the dehydration being complete at  $550\text{-}600^\circ\text{C}$ . The precise temperature for this OH water varies from kaolinite to kaolinite, and may be explained by variation in particle size. Kaolinite leaves a residue consisting of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  after losing its combine water.

Kaolins are the main residual clays form under acid condition at low temperature and pressures. The principal mineral that undergoes alteration is the feldspar component which losses its alkali and some of its silica and gains water of constitution, which the reaction maybe represented as



The alkali is usually removed as soluble salt however; the nature of the reaction is not yet understood, since several intermediate stages are thus formed between end products. In some granite (Cornish) the reaction proceeds through the agency of water containing free silica acids (such as hydrofluoric acid; hydroboric and carbonic acid) at high temperatures and pressures, the solution being forced up from below penetrating the granite through tissue and jointings. The breakdown of feldspar makes the granite mass become porous and more powdery and china-clay (Greenwood, 1997).

## 2.4 Chemical Analysis of Clay

Theoretically, pure kaolin contains basically oxides in the percentage as follows:  
 $\text{Al}_2\text{O}_3$ -39.50;  $\text{SiO}_2$ -46.6;  $\text{H}_2\text{O}$  -13.90.

After calcining, the percentages of oxides are  $\text{Al}_2\text{O}_3$ -46.60;  $\text{SiO}_2$ -54.00. Apart from these principal components clays in as mined condition contains certain impurities. The commonest of them is quartz, which is widely distributed. Up to 1300-1350 °C quartz is inert and plays the part of non plastic filler.

Another common impurity of clays is some form of ferruginous compounds. They include pyrite, mascasite ( $\text{FeS}_2$ ), siderite ( $\text{FeCO}_3$ ) and iron oxides.

Fluxing agents such as  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  are found in clays. Others are calcite ( $\text{CaCO}_3$ ), gypsum ( $\text{CaSO}_4$ ), rutile ( $\text{TiO}_2$ ) and organic matter of vegetable origin. Hence, the complete chemical analysis of clays would normally comprise the determination of the following oxides: loss on ignition;  $\text{SiO}_2$ ;  $\text{TiO}_2$ ;  $\text{Al}_2\text{O}_3$ ;  $\text{Fe}_2\text{O}_3$ ;  $\text{CaO}$ ;  $\text{Na}_2\text{O}$ ;  $\text{H}_2\text{O}$  and other oxides.

## 2.5 Industrial Application of Kaolin

Kaolin because of its desirable properties has a wide application industrially. It is white color, very fine particle size, non-abrasiveness and chemical inert in most uses. The individual particle is a thin, flat, pseudo-hexagonal plated, so thin that approximately 10,000,000 spread on a postage stamp would form a layer thinner than the thinness of human hair. The thin flat particle shape is a distinct advantage in many uses.

The largest consumer of white kaolin is the paper industry, which uses them to make paper products smoother, whiter and more printable. The kaolin is used both as a filler in the sheet to enhance opacity and receptivity to ink and as thin coating about (0.05 cm) on the surface of the sheet to make it smoother and whiter for printing. Other important properties

of kaolin to paper industries are softness and texture, ease of dispersion in the coating formulation and ability to produce a high gloss finish.

In ceramics the kaolin clays are used in white wares, sanitary ware, special refractory and porcelain insulators. In white wares and sanitary wares the kaolin provides a white body, gives easy moulding properties, additional strength, dimensional stability, and smooth surface to the finished product. Refractoriness, dimensional stability, and chemical inertness make the kaolin uniquely suitable for special refractory.

Kaolin clays are used as a functional filler manufacture of both natural and synthetic rubber. They add strength, resistance, rigidity and whiteness; they cost less than other fillers used in rubber. In paint and ink industries, Kaolins are used as extenders because of their chemical inertness, smooth flow properties, ease of dispersion, non abrasiveness, relatively low cost, and high pigment volume concentrations that can be attained.

Plastics kaolin are used to provide smooth surface, dimensional stability and better resistance in chemical attack, and to improve physical and electrical properties, to minimize water absorption, to reduce brittleness, and to lower cost. In insecticides the inertness, low abrasiveness, and food absorption and flow properties of kaolin make it carrying agent in dust and spray forms. Kaolin clay could be used as bleaching agent on palm oil and rubber seed oil. The use of bleaching (or decolorising) earths is common and enormous, in industries that use vegetable oils, petroleum and sugar products (Blatt *et al*, 1980).

## 2.6 Review of Some Nigerian Clays

Recent national search for local sources of industrial raw materials will of course benefit from detailed documentation of known kaolin deposit in Nigeria. The Nigerian clay deposits are basically of two types; the basement derived or residual clay and sedimentary or detrital clay.

The former is product of chemical weathering of pre-Cambrian basement complex rocks formed in-situ (Prettijohn, 1957) while the latter originates as products of chemical weathering of varieties of parent rocks-igneous, metamorphic, and sedimentary; which were transported by various agencies such as water, wind, and among others. Most Nigerian detrital clay deposit (usually kaolinitic) were probably laid down as sedimentary muds in ancient marine and brackish water environment.

Nigeria has large deposits of kaolin clays which have not been properly harnessed in its industrial scale, such as Ubulu-Uku, Awo-Omama and Buan in Southern Nigerian, Ado-Ekiti, Ile\_Ife, Igarra in south-western Nigeria, Sokoto, Katsina, plateau, Nassarawa in Northern Nigeria.

From the work carried out and published by Journal on mining and geology Vol.28 no.2 1992, it has shown that, the Ubulu\_Uku, Awo-Omama and Bruan clay deposits are kaolinite location and geology of the investigated kaolin deposit are briefly stated below.

#### **2.6.1 The Ubulu-Uku kaolin body**

This lies within the Ogwashi-Asaba formation which is characterized by variable sequence of clay, sand and thick seams of lignite of either Oligocene. The deposit outcrops near Amoma Village which is about 9 km southwest of Ubulu-Uku town in Bendel state, it has an estimated reserve of more than  $15.5 \times 10^6$  metric tonnes (G.C.U. report). The kaolins observed, are brownish-red ferricretic layer from which Fe is leached by percolating into the upper horizons of kaolin body as a result of which the contact zone of the kaolin body and ferricretic layer is invariably purplish, mottled in colour, lies below a 20-30 cm thick.

### **2.6.2 The Awo-Omama body**

This kaolin deposit is now being worked for the manufacture of ceramics wares. It outcrops along the western wall of the Njiagba river Valley near Awo-Omama village in Orly local government area of Imo State .Exposures of this deposit are also known to occur along the Onitsha-Owerri, as well as the vicinity of Onitsha town. The exposure of Awo-Omama kaolin at the quarry site show that kaolin is predominantly grey to creamy white in color at -the lower levels and grades upward through one half to one meter thick purplish and mottled transitional zone into a reddish brown sandy over burden of variable thickness. The estimated thickness of the deposit, based on geoelectrical vertical sounding (VES) varied from 30 m to 90 m with estimated reserve of  $6.86 \times 10^6$  metric tones (G.C.U, report 1986).

### **2.6.3 The Buan Body**

The Buan clay deposit is situated in mangrove swamps of the Niger Delta about 68 km southeast of Port Harcourt. The clay occurs immediately north of the coastal sands and is over lain by a sandy slightly muddy lateritic layer of variable thickness. The estimated reserve is 39.318 MT. The area in which the deposit occur is subjected to flooding by saline water at high tide thereby making accessibility and yield operations difficult. However, the deposit has earlier been exploited for use in local pottery industry which once existed in the area, (clay-wikipedia, 2010).

### **2.6.4 Kankara clay**

Kankara clay is found in Kankara village. Kankara village is head quarter of kankara local government area, Katsina state, Nigeria.

Then deposit is estimated at 900000 tones, the quality of deposition is as shown below in table compared to other kaolin source and theoretical composition of kaolinite.

**Table 2.1: Kaolin composition**

Composition	Theoretical Composition	Kankara unrefined	American Refined	Jos Refined
Silica (SiO <sub>2</sub> )	46.50	43.30	44.52	46.94
Alumina (Al <sub>2</sub> O <sub>3</sub> )	39.50	36.70	39.27	37.49
Loss on Ignition	-	11.10	11.63	11.44
Moisture and Combined H <sub>2</sub> O		8.75	13.88	13.0
Free Moisture		1.25	6.28	0.86

(www.perseus.com, 2010)

### 2.7 Clay Mineral Bonding and Ion Interaction

The cohesive energy in kaolinite is primarily electrostatic augmented by van der waals attraction and a certain degree of hydrogen bonding between the hydroxyl groups of one layer and the oxygen atoms of the adjoining layer. In the absence of the interlayer cations, only surface hydration energy is apparently insufficient to overcome the rather large cohesive energy. Neither are those organic compounds intercalated which are commonly adsorbed between the layer of montmorillonites. Hence, the kaolinite were generally

considered to be non expandable until in the early sixties it was discovered that certain compounds were able to expand kaolinite crystals. These comprise such salt as potassium acetate which are intercalated as the total salt, hence the intercalation process is referred to as intercalation. Other intercalating compounds are strong hydrogen bonding compound such as urea, hydrazine, dimethyl sulfoxide e.tc.

The cation exchange capacity of 1-10 msq per 100 g. It has been suggested that the exchangeable ions are located on the broken edges of the kaolinite plates, where they would compensate charge deficiencies owing to broken bonds. However, as will be discussed later, it is not likely that the broken edges have cation exchange site. It is more reasonable to assume that, as in montmorillonite and in illites; the exchangeable cations are located on the flat layer surface compensate a negative layer charge which is due to a small degree of isomorphous substitution. Since, the basal spacing of kaolinite does not leave room for interlayer cation, all the charge compensating cations must be absorbed on the exterior surface of the stack layer representing particle.

A recent study of cation and anion adsorption equilibria on a well-purified kaolinite has shown that at least for the particular kaolinite studied, the theory of equivalence of cation exchange capacity and isomorphous substitution did not apply. The negative surface charge appears to vary with electrolyte concentration in a manner to be expected for a surface of constant potential rather than of constant charge (Prettijohn, 1957).

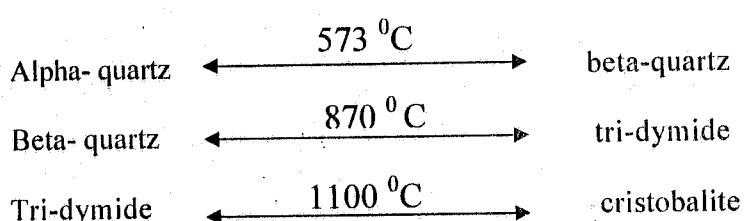
## **2.8 Major Constituent of Kaolin**

We discuss briefly the major constituent of kaolin clay i.e silica and alumina in this section.

### 2.8.1 Silicon Dioxide (SiO<sub>2</sub>)

Silicon dioxide occurs in a number of different crystalline forms, but each contains silicon atoms bonded tetrahedrally to four oxygen atoms by means of single Si-O bonds. Silicon dioxide is thus unlike carbon dioxide in its structure and the reluctance of silicon to form multiple bond (this time with oxygen atom) is noted.

The three crystalline forms of silicons dioxide are quartz tridymide and cristobalite, each of which has a high temperature and low temperature modification.



The naturally occurring is alpha- quartz that transform rapidly to beta-quartz at 573 °C. Quartz is the most thermodynamically stable of the three forms, but there is no tendency for the other two forms to transform themselves into quartz, since the migration of atoms solids is a process requiring very high activation energy.

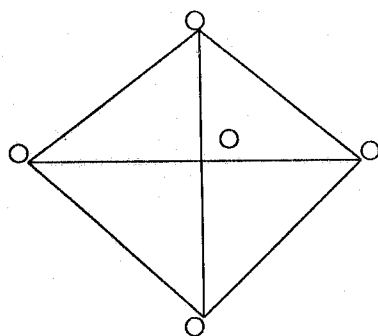


Fig 2.2: Diagrammatic sketch showing a single Silica tetrahedron.

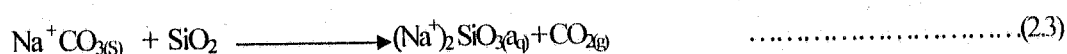
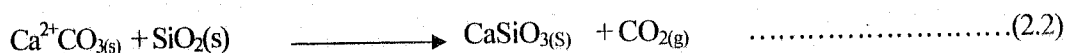


In quartz and tridymite spiral structures isomers (right and left handed spirals). Since all the three forms of silicon dioxide have covalent bonds extended in three dimensions they are giant molecules and high melting solids.

When molten silica is allowed to cool, the substance called silica glass is obtained. It consists of randomly oriented chains, sheets and three dimensional networks of SiO<sub>4</sub> groups.

Slow cooling of molten silica or heating any form of solid silica to softening temperature gives an amorphous material which is glassy in appearance and indeed a glass in the general sense, that is a material with no long range order but rather disordered array of polymeric chain sheet or three dimensional units.

Soda glass, a mixture of calcium and sodium silicates, is manufactured by fusing the carbonates with white sand at temperature of about 1500 °C. The non-volatile silicon dioxide reacts thus



Silica is relatively unreactive towards Cl<sub>2</sub>, H<sub>2</sub>, acids and most metal at ordinary or slightly elevated temperature but it is attacked by fluorine aqueous HF, alkali hydroxide and fused carbonates, (Bagbany *et al*, 1954).

### 2.8.2 Alumina (Al<sub>2</sub>O<sub>3</sub>)

Stoichiometrically, there is only one oxide of aluminum namely alumina (Al<sub>2</sub>O<sub>3</sub>). However, this simplicity is compensated by the occurrence of various polymorphs, hydrated species. The formation of which depends on the conditions of preparation.

There are two forms of anhydrous alumina. Namely alpha- Al<sub>2</sub>O<sub>3</sub> and beta- Al<sub>2</sub>O<sub>3</sub>.

Alpha-alumina present in impure form in corundum, sapphire, ruby e.t.c has hexagonally closed packed array and aluminum ions are distributed symmetrically

among the octahedral interstices. Each aluminum ion is surrounded by six oxygen ions and each oxygen by four aluminum ions. This gives a hard dense structure which is insoluble in acids.

Alpha-  $\text{Al}_2\text{O}_3$  is stable at high temperature and indefinitely metastable at low temperatures. It occurs in nature as the mineral corundum and maybe prepared by heating gamma-  $\text{Al}_2\text{O}_3$  or anhydrous oxide above  $1000^\circ\text{C}$ .

Gamma-  $\text{Al}_2\text{O}_3$  is obtained by dehydration of hydrous oxide at low temperature of about  $450^\circ\text{C}$ . The Gamma-form has a badly organized micro - crystalline spinel structure and hence has a smaller particle size with greater absorbtive power.

It is less dense and readily soluble in acids and readily takes up water. Aluminum oxide, together with silica as a refractory material for furnace linings. The oxidation of almagated aluminum gives aluminum oxide in surface form (activated alumina)

The alumina rich source commonly use are:

#### **2.8.2.1 Bauxite**

This is an ore of metal which contain high percentage of alumina about 50-60 % alumina content.

#### **2.8.2.2 Clay**

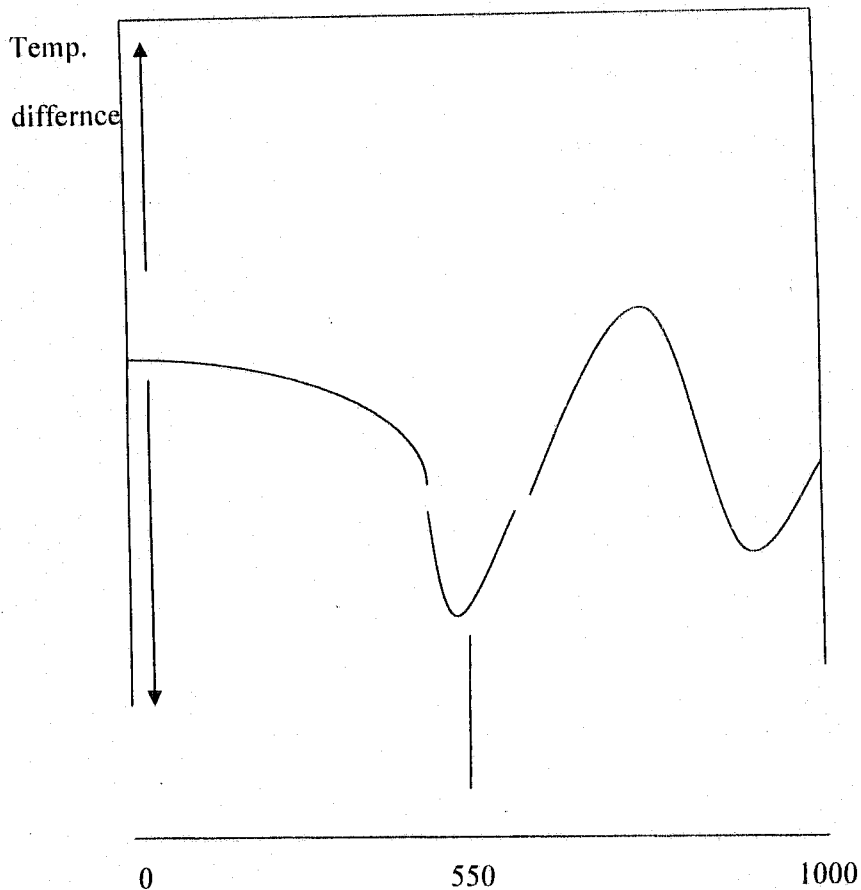
These are clays which have kaolinite minerals (i.e. have alumina content of 38-41 %) depending upon the type of clay used.

#### **2.8.2.3 Hydrated alumina**

Which being a synthetic product is least in impurities.

## 2.9 Effects of Calcination and Thermal Treatment on Kaolin

It is well known that the reactivity and phase transitions occurs in kaolin as it undergoes thermal transition. Typical thermal analysis curve for kaolinite is shown in fig 2.3. below



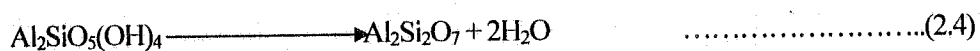
**Fig 2.3: An idealize DTA Curve for Kaolin**

From the curve it can be seen mat a small endothermic peak occurs with kaolinite at about 110 °C as a result of the evolution of absorbed water. At about 520 °C the main endothermic peak commences, the tip of the peak being at about 600 °C, corresponding to the decomposition of the mineral, and elimination of the hydroxyl groups as water. A further peak, which is exothermic, occurs at about 1000 °C, and is associated with a re-crystallization process. According to Worrall, this has been variously attributed to the formation of mullite, of alumina and of silicon spinal.

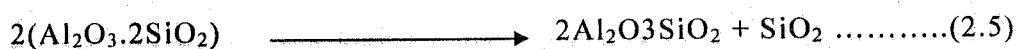
The main differences of found between well crystallized kaolinite and disordered kaolinite the initial peak due to absorb water is often larger than for well crystallized kaolinite. This main endothermic peak is some what lower usually at about 600 °C and the exothermic peak is higher and broader.

Worall explained that during fining it is generally believed that absorbed water was first removed at just over 100 °C. At temperatures up to 300 °C, the water of plasticity is driven off and clay becomes rigid but not strong. At temperatures between 300 °C and 400 °C the organic matters present in the clay burn away and may result in an unfavourable packing of particles.

The kaolinite clay minerals decompose at about 460 °C by losing its hydroxyl groups combine with water. The dehydration is represented by the chemical equation shown below. The dehydration is completed at about 800 °C.

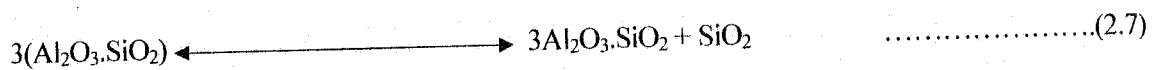
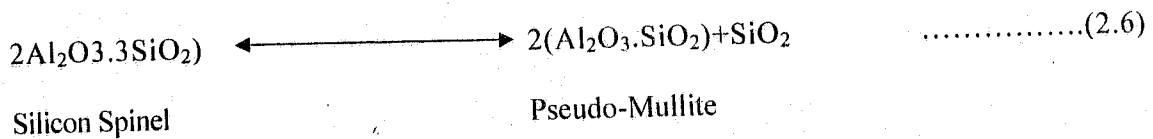


The product is known as metakaolin. However, organic matter are oxidized during heating and this occurs at about 550-900 °C. Decomposition reaction takes place, in which the carbonate or hydrated compounds decomposed to form oxides and gaseous products such as carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). At still higher temperatures the metakaolin undergoes further reactions to form crystalline compound, and products being cristobalite (free silica) and mullite (3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>). The relative percentage of silica and Alumina being 22-28 % and less than or equal to 70 % respectively. Brindly and hunter first proposed the entire process and this is represented by the following chemical equations



Metakaolin

Silicon Spinel



### 2.10 Beneficiation of Clay

The upgrading or removal of ore constituents that may be or not be considered as impurities is referred to as beneficiation. It is often necessary for ores to undergo such processes, example, if alumina is considered impurities in clay or if you want to extract alumina from clay, the alumina content is then concentrated by removing the other constituents like silica, feldspar, mica, sand and stones. Clay beneficiation takes different forms. Formerly, it was used for only processes involving grinding mills and screens. But today, beneficiation has been developed to a level where different types of equipment ranging from milling machines, air classifier, cyclones and hydro separators are used. Beneficiation, however, depends upon the types of ores and end product that will be used. The beneficiation of clay can take the form of selective mining, wet process and dry process (Haruna, 1986).

#### 2.10.1 Selective Mining

This is the method employed to choose the best quality ores among the available alternatives. Chemical analysis of these ores is often employed to ensure that qualitative and acceptable ores are mined. This type of mining can be employed to ascertain the expense of the deposit and variation in composition. Its limitation is that, it only ensures the choice of ore of best quality such that further beneficiation might still be necessary.

### 2.10.2 Dry process

Dry beneficiation process involves crushing, drying, grinding and sieving of clay minerals at industrial scale. Granular rocky clay minerals are first crushed and grinded to desired size (5 cm) in the Raymond ring-roll mill with an internal whizzer classifier. Oversized / impurities are being eliminated by automatic throw out devices, gases are often introduced to mill to pulverize the clay particles to the desired size. Oversize impurities such as quartz, feldspar, mica, sand and stones are easily removed by dry process.

### 2.10.3 Wet process

In the up grading of quality, the wet process beneficiation is found to be more effective than dry process. The wet process deagglomerates all clay particles in water. This is first done by mastication of clay lumps in a plug mill followed by dispersion process. At industrial scale, the process is achieved using equipment such as bowls, cone classifiers, hydroseparators, thickness continuous centrifuges, cyclone and vacuum filter.

## 2.11 Solubility of Amorphous Silica in Water

Fig 2.3 shows the relationship between pH and the solubility of amorphous silica (Krauskopf, 1959) and alumina (Correns, 1949) in distilled water. (Keller, 1958) relate the separation of silica and alumina by differential solubility influenced by pH. Above pH 10, both silica and alumina are relatively insoluble although silica still remains dissolved in low concentration.

Referring to Fig 2.3 when the hydrolysis of aluminum silicate recurs at pH 11, both silica and alumina are relatively soluble and mobile and can be removed, even to along

distances if the pH remains at 11. Aluminum is present predominantly as  $AlO_2$  as has been noted. As the solution becomes acidic, at pH 8 for example, aluminium precipitates as  $AlO_2$  will be precipitated, probably as gibbsite or possibly as metastable boehmite  $AlO(OH)$ , or diaspore,  $HAIO_2$ , and the silica remain in the solution sufficiently dilute ([www.undp.org.ng](http://www.undp.org.ng)).

## 2.12 Removal of Silica From Clay

In the decomposition of substance containing alumina, use is frequently made of the so called "lime soda" process in which silica present in starting material is intended to be converted by sintering with lime into calcium silicate, while the alumina is converted by soda ( $Na_2CO_3$ ) into soluble aluminate which is frequently recovered by leaching out the sintered product and processing the resulting solution to obtain alumina hydrate ( $Al_2O_3 \cdot H_2O$ ,  $Al_2O_3 \cdot 2H_2O$ ,  $Al_2O_3 \cdot 3H_2O$ ). A great number of methods have been proposed in the art for reducing the silicic acid content of starting material prior to using them as a first step of preparing suitable materials in the decomposition of alumina containing materials. These methods frequently employed a preliminary treatment of starting materials by heat treatment at elevated temperatures and subsequent leaching with caustic soda ( $NaOH$ ) solution or soda ( $NaCO_3$ ) solutions. Neither of these known methods is applicable to clays having silicic acid ( $SiO_2$ ) content higher than 40 %. Thus, certain clays preferably much lower silica content, have been heated to temperatures between  $400^\circ C$  and  $700^\circ C$  and have been extracted, with boiling concentrated solutions of alkali metal hydroxides, which treatment results in preferential extraction of silica, leaving a residue richer in alumina and poorer in silica than the original material.

In the case of large group of clay materials,, such as kaolins as well as pyrophyllites and certain montmorillonites all of which materials have silica content above

40 %, heating temperatures between 400 °C and 700 °C does not have any marked effect on the solubility of the silicic acid contained in these materials. SiO<sub>2</sub> is present in these materials in compounds which are difficultly soluble or completely insoluble in alkali solutions (sodium hydroxide or carbonate). Heat treatment below 800 °C converts only about 5 to 7.5 % of this silicate content into a soluble form.

Furthermore, about 2 to 40 % of the alumina contained in the heated material are made soluble, so that the ratio of soluble SiO<sub>2</sub> to soluble Al<sub>2</sub>O<sub>3</sub> in the material treated at temperatures below 800 °C is about 2:1, which is unduly high in view of the fact that it is desired to dissolve a maximum amount of silicic acid, but restrict the dissolution of alumina to a minimum or, preferably suppress the same completely.

Silica or silicic acid or SiO<sub>2</sub> content, this is to be understood as meaning that silicon is present bound to oxygen in these material in an amount which, in conventional qualitative chemical analysis, would be calculated as percent of SiO<sub>2</sub>.

Due to rather involved chemical reactions constituting a thermic cleavage and recrystallization of treated materials, calculation of same at temperature above 800 °C and up to 1100 °C leads to the conversion of much higher proportion to the total SiO<sub>2</sub> content into soluble form. When calcining alumina containing materials of various SiO<sub>2</sub> contents at higher temperature (800-1100 °C) the ratio of soluble silica to soluble alumina is greatly improved i.e a considerably higher rate of increase in the silicic acid solubility is accompanied by a considerably lower rate of increase in the solubility of alumina.

Free silica is removed from calcined bodies by leaching with strong alkali solution. The solubility of silica increase sharply when the pH of the leaching solution reaches about 11, and the solubility continues to increase with increasing pH.



Silica solubility also increases with the temperature therefore it is advantageous to conduct the leaching step at as high a 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.

Good results have been obtained using leaching temperature of about 80 °C.

Leaching time is dependent upon several factors including

1. The quantity of the silica to be removed
2. The porosity of the body prior to leaching
3. Concentration of the leaching solution and
4. Temperature of leaching

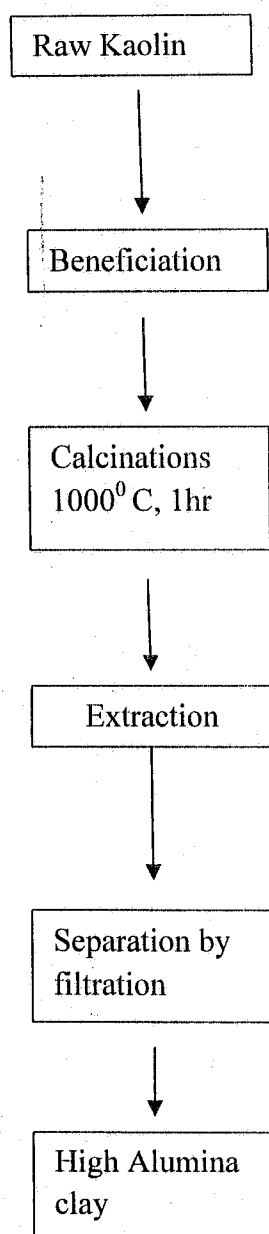
Finally, control of calcinations condition influences several properties including the degree of clay conversion to mullite and free silica (Keller, 1958) .

## Chapter Three

### 3.0 METHODOLOGY

#### 3.1 Experimental Procedure

The sequence of procedure adopted is shown in fig 3.1 below



**Fig 3.1: Flow Process Diagram For The Removal Of Silica From Kaolin Clay By Alkali Leaching**

### 3.2 Clay Beneficiation

The process involves the pretreatment of raw kankara kaolin design to remove impurities.

This process involves

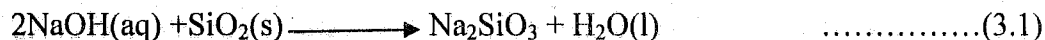
- I. Pouring the raw kankara kaolin into plastic and mixing it with sufficient water
- II. The mixing was stirred and allowed a vintage of 24 hours
- III. The fluid above the kaolin was decanted after this period of time
- IV. Steps one to three where repeated until the decanted water was clear?
- V. The dried clay was then crushed and sieved

### 3.3 Calcinations

The beneficiated kaolin clay was calcined at 1000 °C for one hour. This period and temperature is suitable for the conversion of silica content in clay to soluble form in appreciable amount and prevent recrystallization of kaolin to mullite.

### 3.4 Extraction of Silica (SiO<sub>2</sub>)

In the extraction of silica, knowledge of solubility of silica in alkali solution was employed to leach the calcined kaolin.



The extracting agent used was sodium hydroxide prepared from its pellets. While the extraction is as follows

- I. 25 g sample of calcined kaolin was weighed.

- II. Preliminary calculation was carried out to determine the mass NaOH require to dissolve completely the silica in the sample.
- III. 5 % w/w NaOH solution with calculated amount of distilled water was made. So, that a solution containing 20 % excess NaOH solution required to dissolve silica content in the clay sample in a three opening round bottom flask.
- IV. The content of the flask was placed on a heating mantle and stirred continuously. A thermometer was inserted in one of the openings, another with a cork to prevent heat loss and a stirrer in the third opening.
- V. The extraction was carried out for a period of 20 minute. After which the silicate containing solution was filtered.

### 3.5 Filtration

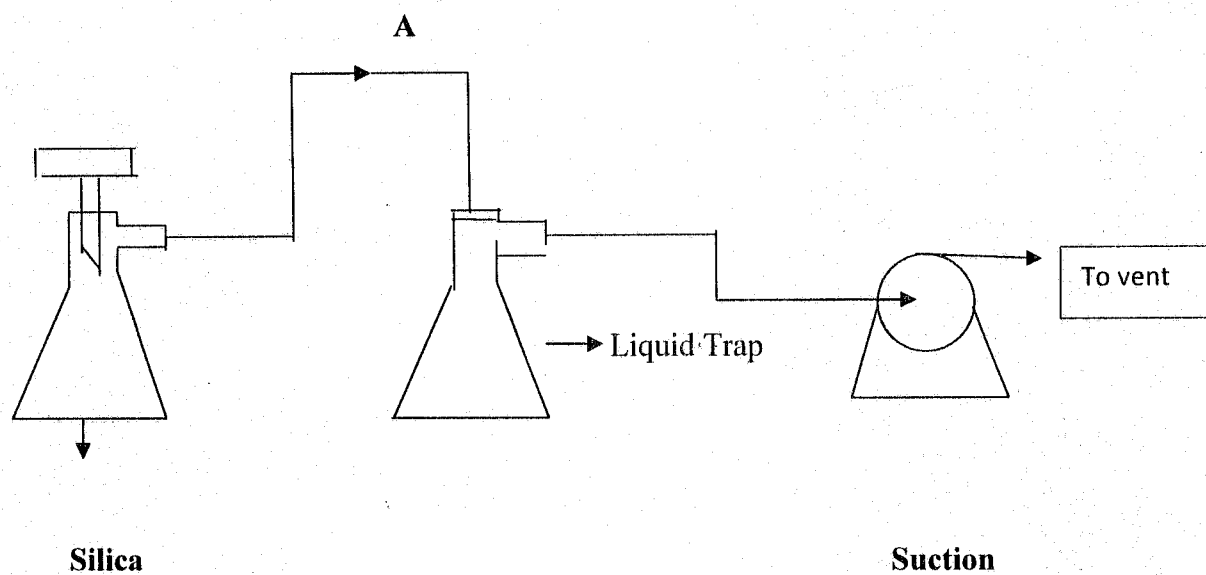
A funnel was placed on the filtration flask and a filtered paper inserted into the funnel.

While the silicate containing solution was connected to an air suction pump, which was started to enabled quick filtration process.

After filtration the residue was dried in the oven at temperature of about 450 °C for about one hour. The dried sample was weighed

The above procedure (extraction and filtration) was then repeated for NaOH Concentrations of 10 %, 20 % .....40 % w/w concentrations.

The procedure (extraction and filtration) was then repeated at 25 % w/w concentration using varying reaction time of 5, 10, 20, 30 and 40 minutes in order to study the effect of time on solubility.



**Fig 3.2: Filtration Set-up**

## Chapter Four

### 4.0 RESULTS AND DISCUSSIONS

#### 4.1 Experimental Results

The result of analysis of experiment carried out is tabulated below.

**Table 4.1: Percentage Composition of Kankara Clay (raw) Using Chemical Analysis**

Component	Weight %
Loss on ignition	12.00
Silica (SiO <sub>2</sub> )	47.12
Alumina(Al <sub>2</sub> O <sub>3</sub> )	38.35
Ferric Oxide(Fe <sub>2</sub> O <sub>3</sub> )	0.41
Others Composition	2.12

**Table 4.2: Result of chemical analysis of calcined alkali treated clay at varying alkali concentrations**

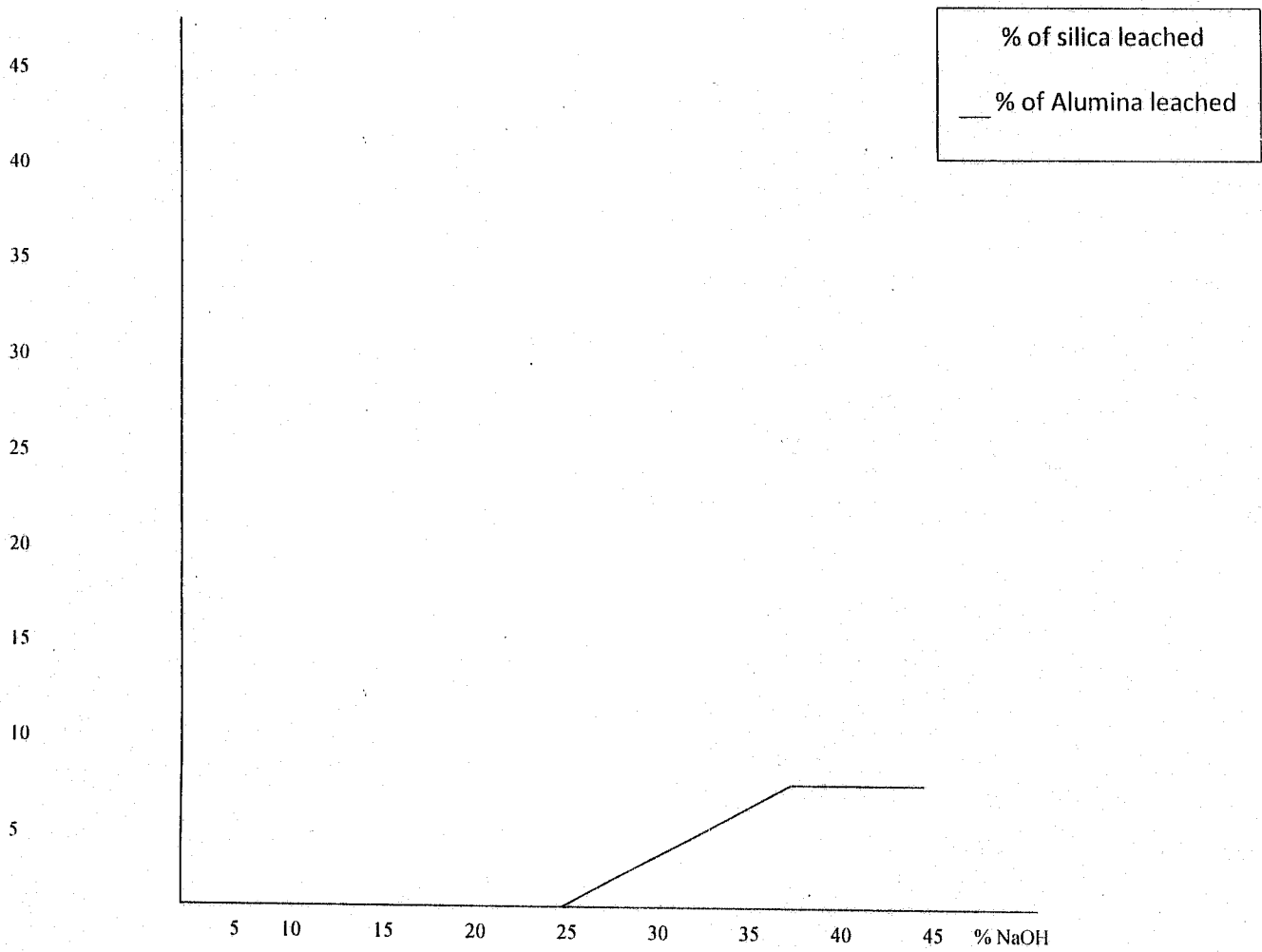
NaOH	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	Other Composition %	%SiO <sub>2</sub> Leached	% Al <sub>2</sub> O <sub>3</sub> Leached	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> Ration left in clay
0	53.0	45.2	1.8	5.0	0.0	0.85
0	47.1	50.9	2.0	25.0	0.0	1.08
0	45.4	52.6	2.0	30.0	0.0	1.15
0	46.0	51.8	2.2	31.0	6.0	1.13
0	46.0	51.8	2.2	31.0	6.0	1.13

**Table 4.3: Result of Chemical Analysis of Calcined Alkali Treated Clay At Concentration of 25 % W/W NaOH Concentration At Varying Time of Leaching.**

Time (in)	%SiO <sub>2</sub> Leached	% Al <sub>2</sub> O <sub>3</sub> Leached	% Composition Al <sub>2</sub> O <sub>3</sub> left	% Composition SiO <sub>2</sub> left	% Other Composition	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>
0.0	0.0	0.0	43.96	54.33	1.71	0.81
12.0	0.0	0.0	47.02	51.13	1.85	1.09
36.0	0.0	0.0	54.64	43.21	2.15	1.26
51.0	0.0	0.0	60.79	36.81	2.40	1.65
55.0	9.0	9.0	60.44	36.94	2.60	1.63

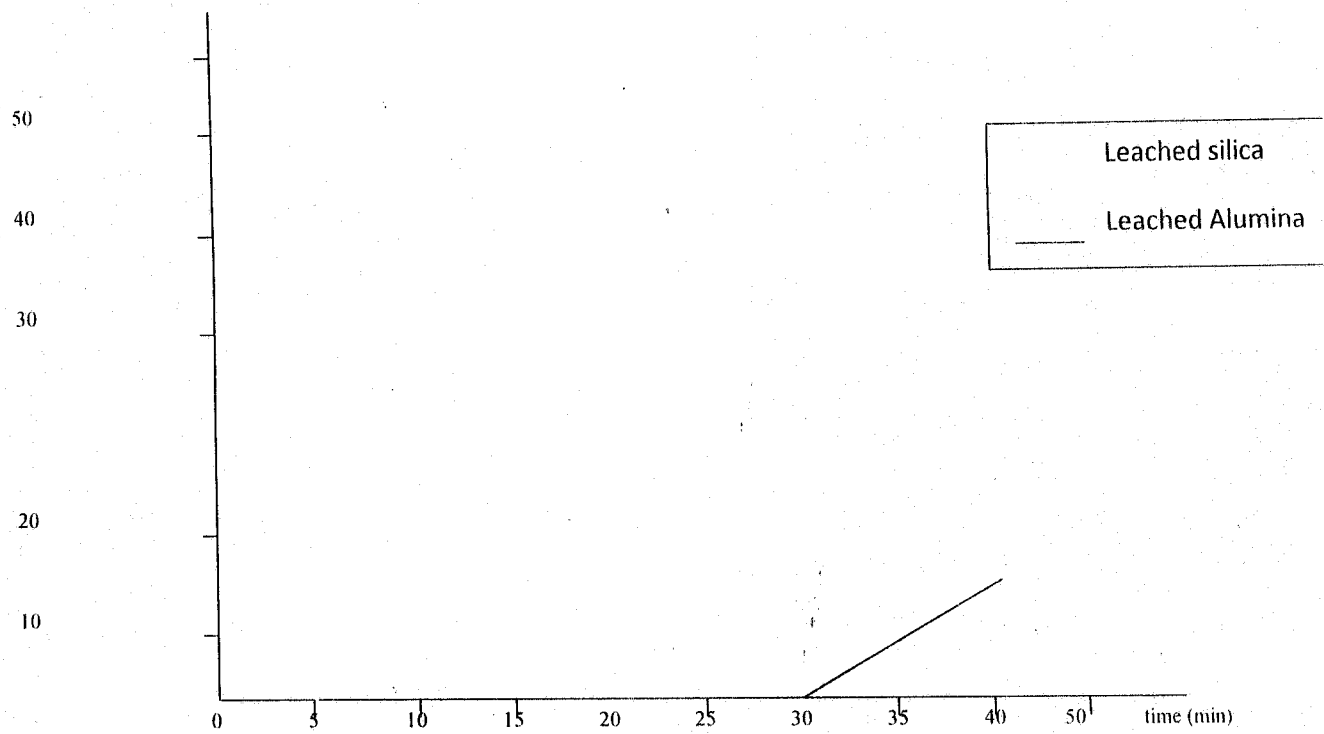


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**Fig 4.1: Amount of Silica Soluble in Sodium Hydroxide**

silica leach



**Fig 4.2: Amount of Silica Leached as a Function of Time**

## 4.2 Discussion of Results

Table 3.1 shows the dissolve component of silica and alumina in calcined Kankara Clay calcined at 1000 °C for 1 hr as a function of sodium hydroxide concentration. The result is also depicted graphically in fig 3.1. The result shows that silica solubility in extracting agent (NaOH) increases with concentration and attains a fairly constant maximum value at 20 % concentration and above. From the result; at high concentration of 30 % and 40 % NaOH solution the loss alumina in the solution becomes noticeable; of about 6 %. A maximum leaching of about 32 % of SiO<sub>2</sub> was attained at 40 % NaOH solution with 6 % loss in Alumina. At 20 % concentration of NaOH; 30 % of silica content was soluble without noticeable loss in alumina given the best result in terms of alumina to silica ratio of about 1.15 maximum value.

Table 3.3 shows the effect of time on the solubility of silica in NaOH solution at 25 % w/w concentration at varying time interval. It can also be deduced from the result that solubility increases with time; however at 40 minute time interval an appreciable amount of alumina 9 % was dissolved; suggesting that an increase in time might lead to the dissolution of alumina into the solution. The optimum ratio of Alumina to silica was attained at 30 minute time interval a value of 1.65. Fig 3.2 depicts this information graphically.

Since, the amount of silica dissolve is strongly dependent on calcination condition it is my opinion that a close study of this variables (time of calcinations and temperature of calcinations) is essential to obtain better result. However, this will depend on the availability of furnace that attains this desired temperature at required time. Also, such an experiment will require carrying out large number of analysis as the work progress; the presence therefore of an easily accessible electronic analysis machine cannot be over emphasized.

## Chapter Five

### 5.0 CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

From the result obtained in the conduct of this work, it is concluded that alkali leaching of kankara clay is a function of concentration of the extracting agent NaOH.

From the results, it could be inferred that the suitable concentration of extraction is 20 %w/w NaOH at which 30 % of the silica were extracted without appreciable loss of alumina.

A further investigation was conducted to achieve better result of 51 % leaching of silica without noticeable loss of alumina and giving an alumina to silica ratio of 1.65 at 30 minute time interval.

From the foregoing it is concluded that more than 50 % of silica content of the clay is leached at 25 % w/w of alkali concentration and 30 minute time interval

#### 5.2 Recommendations

From the experiences gathered from the conduct of this work, the following recommendations are made.

1. Electronic analysis equipment such as X -ray fluorescence, X -ray diffract meter, atomic absorption spectra should be acquired in the department and used in further analysis in order to obtain accurate result; and also make the work less tedious.

2. A furnace; which could attain the desire temperature (800-11000 °C) at reasonable time (1-2 hrs) should be acquired as unduly long period of calcinations leads re- crystallization of activated clay. This will allow for further study of calcinations temperature.
3. Alternative source of provided in case of power interruption from main power source.

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## APPENDIX A

### Preliminary Calculations

Calculation to determine the quantity of NaOH required to remove completely all the silica content in calcined kaolin.

Basis; 25 g sample of calcined kaolin.

Amount of silica in 100 g sample of calcined kaolin = 54.12 g

1 g sample of calcined clay contains 54.12/100 g of silica.

25 g sample of calcined clay will contain  $25 \times 54.12/100 = 13.53$  g of silica

stoichiometry of the reaction



Mole ratio of NaOH: SiO<sub>2</sub> = 2:1

Weight of one mole of NaOH = 40 g

Weight of one mole of SiO<sub>2</sub> = 60 g

From stoichiometry of the reaction

80 g of NaOH will react with 120 g of silica

Therefore, amount of NaOH required to react with all the silica content in 25 g sample i.e 13.53 g of silica =  $120/80 \times 13.53 = 20.3$  g of NaOH.

But 20 % excess weight of NaOH was used.



Therefore, actual weight of NaOH used =

$$1.2 \times \text{amount required} = 1.2 \times 20.3 = 24.4 \text{ g}$$

## APPENDIX B

### The classical schemes of analysis

The overall principle of analysis involves chemically separating a clay sample dissolved in aqueous solution into individual elemental components that could be determined gravimetrically.

The procedure is explained as follows:

- a) Dissolution of clay: The finely divided rock powder (1 g) is fused with anhydrous sodium carbonate (3-5 g) in a platinum crucible at temperatures increasing from 700-1200 °C. After, drops of ethanol must be added to reduce manganese, present as alkali manganate to manganous (ii) salts.
  
- b) Determination of silica (SiO<sub>2</sub>): The silica mixture from above is dissolved in hydrochloric acid and then evaporated to dryness until all hydrochloric acid fumes have been expelled. During this process silicic acid in solution is dehydrated to silica:



The residue after evaporation is attacked with hydrochloric acid solution. Soluble chloride salts are taken up into solution, leaving a gelatinous precipitate of SiO<sub>2</sub>. This is filtered off and washed. However, the filtrate and washings still contain some dissolved silica. This is recovered by acidifying the filtrate with hydrochloric acid and evaporating to dryness a second time. The soluble chlorides are re-dissolved and the small silica residue filtered off and combined with the original residue. The soluble chloride filtrate is reserved for next group separation. Corrections

are applied for the silica content of the filter papers ashed during ignitions and the silica reagent blank.

c) Separation of mixed oxides (the  $R_2O_3$  group). The mixed oxides are recovered from combine filtrates and washing from (b) Above by adding ammonia to a hot solution acidified with hydrochloric acid until it becomes just alkaline (pH= 7). The hydroxide precipitate it then filtered from the slightly alkaline solution