EFFECTS OF BENEFICIATION AND SALTING AGENTS ON YIELD AND QUALITY OF ALUM FROM KANKARA KAOLIN

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BY

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DECEMBER 2008

DECLARATION

I declare that the work in this thesis entitled “Effects of beneficiation and salting agents on the yield and quality of alum from Kankara kaolin” has been performed by me in the Department of Chemical Engineering under the supervision of Drs. B.O. Aderemi and Y.B. Jibrin. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.

Edomwonyi-Otu, Lawrence

_____	_____	_____
Name of student	Signature	Date

CERTIFICATION

This research project entitled "EFFECTS OF BENEFICIATION AND SALTING AGENTS ON THE YIELD AND QUALITY OF ALUM FROM KANKARA KAOLIN" by Edomwonyi-Otu Lawrence meets the regulations governing the award of the degree of Master of Science of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

I dedicate this work to my wife Osarense Osarumwense Edomwonyi-Otu for giving her all and sharing in the pains and joyful moments of this work, and to my children John, David and James who suffered my absence during the course of this work.

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I am eternally grateful to the Lord Jesus Christ who initiated, funded and granted grace and mercy for this work to be successful. To Him be all the praise and glory forever more, amen.

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ABSTRACT

Alums are very important products because of their vast array of uses. In this investigation, about 91% kaolinite fraction was recovered from Kankara kaolin after beneficiation. The silica-alumina ratio of 2:1 obtained after calcination conformed to typical literature values. The raw clay yielded 72.91% alum (in terms of % wt of alumina extracted from the clay) while the fully beneficiated clay yielded 81.30% alum. Similarly, about 86% reduction in MgO content was achieved via beneficiation of the raw clay. When different salting agents (i.e sodium, potassium and ammonium sulfates and ethanol) were added to the dealumination filtrate, alum yields (in terms of % wt of alumina extracted from the clay) ranges between 60 to 81.30 % in contrast to the unsalted filtrate which gave a corresponding value of 37.63%. It was also observed that as the concentration of the potassium sulfate solution increased, alum yield also increased and the quality of the potassium alums was significantly constant. When dried at 250^0C for 6 hours, the soda, potassium and ammonium alums showed a loss in weight of about 47.00% corresponding to the occluded acid and crystallization water content. The use of the heat of hydration of sulfuric acid in water for the dealumination process gave 81.30% alum yield, while the use of additional heat from oil bath for up to 3 hours gave a marginal increment of only about 6% yield. It was on this basis that dealumination without external heating source is recommended.

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LIST OF ABBREVIATIONS, DEFINITIONS AND SYMBOLS

kg	-	Kilogram
(g)	-	Gram
ml	-	Milliliter
^{O}C	-	Degree Celsius
wt	-	Weight
%	-	Percent
S	-	Alum from soaked and sieved kaolin
B	-	Alum from fully beneficiated kaolin.
XRF	-	X-ray fluorescence
PTDF	-	Petroleum Technology Development Fund
RMRDC	-	Raw Materials Research and Development Council
SiO_2	-	Silicon (IV) Oxide (silica)
Al_2O_3	-	Aluminum Oxide (Alumina)
K_2O	-	Potassium Oxide
CaO	-	Calcium Oxide
MgO	-	Magnesium Oxide
Na_2O	-	Sodium Oxide
CuO	-	Copper Oxide
NiO	-	Nickel Oxide
Cr_2O_3	-	Chromium Oxide
SO_3	-	Sulfur (VI) Oxide

Fe_2O_3	-	Iron (III) Oxide
TiO	-	Titanium Oxide
NH_4OH	-	Ammonium Hydroxide
$(NH_4)_2SO_4$	-	Ammonium Sulfate
K_2SO_4	-	Potassium Sulfate
Na_2SO_4	-	Sodium Sulfate
C_2H_5OH	-	Ethanol
$Al_2(SO_4)_3$	-	Aluminum Sulfate

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CHAPTER ONE

1.0 INTRODUCTION

The word alum is derived from its Latin generic form "alumen", which was applied to several astringent substances, most of which contained aluminum sulfate (Kirk Othman, 1993). Examples of these are single salt alums: $Al_2(SO_4)_3.xH_2O$ and double salt alums: Potassium alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$; Ammonium alum $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$; Soda alum $Na_2SO_4.Al_2(SO_4)_3.24H_2O$: Ferric alum. $FeSO_4.Al_2(SO_4)_3.24H_2O$; and so on (Kirk Othmer,1993).

Alum is commonly used in food and pharmaceutical related industries as well as in water purification. It is also extensively used in the manufacture of vegetable glues, porcelain cements, natural deodorants, tanning, dyeing, fireproofing textiles and paper and in alumina production for catalytic and refractory applications (Kirk Othman, 1997, Wikipedia, 2008).

In ancient times, alum (potash alum) was mined from the mineral alunite. Scotland and Belgium are known to have some deposits of alunite eventhough of little significance in quantity (Wikipedia, 2008). The traditional and commercial source of alum is bauxite (45-65wt % alumina). However world bauxite deposits are vastly declining (Marstiller, 1978; Azom, 2004). In Nigeria particularly, there is no known commercial bauxite deposit. Nevertheless, respite is found in kaolin clay, (containing 33-39wt % alumina content) and is abundantly available (RMRDC, 2000). In the 1980s, attempts were made by some workers in the Northern States of Nigeria through the Super Phosphate Fertilizer Company (FSFC) in Kaduna and others to produce alum for water purification from local clay, but this suffered

from myriads of problems including high associated free silica content which was observed to cause blockage to the water piping system. Hence, the effort was discontinued (oral communication).

Happily, the research thrust received a new boost as from the middle 1990s when the Chemical Engineering Department of the Ahmadu Bello University in search for zeolitic catalyst from local raw materials obtained alum as a by-product from the spent acid recovery process (Aderemi, 2000). Subsequent investigations resulted to the development of the governing rate equation for dealumination of Kankara kaolin (Aderemi et al, 2000, 2001). Speculation was equally made at sourcing aluminum metal for the metallurgical industry from Kankara kaolin (Aderemi et al, 2002). The production of alum from Kankara kaolin clay, which met industrial requirements, has also been reported by Aderemi et al (2006). A preliminary investigation to produce alumina from Kankara kaolin was similarly reported by Abdul (2005).

A careful review of the above contributions, undoubtedly, is not without some unanswered questions and uncovered grounds if alum was to be the primary product. First, is the intensive kaolin beneficiation step routinely described in all the cited publications really necessary, in view of its considerable time and energy demand? Second, from the experience of the zeolite group under the PTDF Professorial Chair, a noble speculation has been made as to the possibility of capturing the heat released when acid is mixed with water for use during the dealumination process, in an attempt to reduce production cost (Boniface, 2007). However, experimental facts to validate this speculation are not available as at present.

Furthermore, the referenced works were mostly on synthesizing single alums, notwithstanding the use of ethanol as a salting agent by Abdul (2005). Use of other salting agents has not been reported for alum production from Kankara kaolin considering the fact that other types of alums have their peculiar applications (Wikipedia, 2008). Finally, a quantitative evaluation of purity level dependency on operating process conditions for alum production from Kankara kaolin is yet to be considered by the acknowledged investigators. Hence, these above spelt research gaps are the subject of this current investigation.

The heavy dependence on alum for diverse applications and in particular for water treatment process coupled with the abundant nature of kaolin within the country Nigeria and the long term benefit of job creation including its contribution to Gross Domestic Product (GDP) and consequent reduction on import dependence when these processes are fully developed are unarguable justifications for this work. The use of kaolin clay for the production of different types of alum, for the development of aluminum metal, and alumina based catalysts is a step in realizing the dream of indigenizing our technology currently being pursued by the Federal government through academic institutions.

1.1 Research Problem

- Alums do not exist freely in clays
- Effect of associated impurities such as quartz, feldspar, free silica, carbonaceous materials, metallic ions etc in the clay on yield and quality of alums need to be quantified.

- The need to develop different types of alum for different applications from our local clay is outstanding.
- The effect of beneficiation and salting agents on alum yield and quality from Kankara kaolin has not yet been reported.
- Increasing global energy cost demands a complete review of energy consumption pattern and management in every existing process

1.2 Research Justification

- Kaolin is abundant in Nigeria.
- There is heavy dependence on alum and its products.
- Extensive background knowledge on alum production from kaolin is available
- Acquisition of local technology
- Long term benefits include;
    - Job creation.
    - Contribution to GDP and reduction in import dependence

1.3 Research Objectives

- To compare the quality and yield of alum from each stage of the beneficiation process
- To synthesize different types of alum using different salting agents
- Compare the yield of alum from the different salting agents used.
- Test the effectiveness of the heat of acid dissolution in water on alum yield and quality.

1.4 Research Limitations

Some of the factors that limited this research are:

- Lack of funds.
- Erratic power supply.
- Dearth of relevant analytical equipment within a reasonable distance.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The word ‘alumen’ which was translated ‘alum’ occurs in *Pliny’s Natural History.* Pliny informs us that alumen was found naturally in the earth. He called it *salsugoterrea.* Different substances were distinguished by the name ‘alumen’, because they were all characterized by a certain degree of astringency, and were all employed in dyeing and medicine. The light-colored alumen is used in brilliant dyes, while the dark-colored ones are used only in dyeing black or very dark colors. There was another kind of alumen that the Greeks call schistos. It is formed in white treads upon the surface of certain stones. From the name schistos, and the mode of formation, there can be little doubt that this species was the salt which forms spontaneously on certain salty minerals, as alum slates and bituminous shale, and which consists chiefly of sulfates of iron and aluminum (Wikipedia, 2008).

Alum has played a major role in economic history. In the 1400’s, trade in alum was a significant economic factor in Rome. The use of alum in baking began in 1830 and it was identified as one of the first food “adulterants” in England in 1851 (Wikipedia 2008). A concise definition of some relevant terms and a brief literature survey of some of the reagents and processes involved in this work will be undertaken to enhance our understanding as we go through this work.

2.2 Definitions

2.2.1 Alum

The word **alum** is derived from the Latin word 'alumen', which was applied to several astringent substances, most of which contained aluminum sulfate. Unfortunately, the term is now used in several different senses and care must be taken to determine its meaning. Paper maker's alum refers to commercial aluminum sulfate. Common alum or ordinary alum usually refer to potash alum **(**$KAl(SO_4)_2.12H_2O/K_2SO_4.Al_2(SO_4)_3.24H_2O$**),** ammonia alum ($(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$) etc. The term is also applied to a whole series of crystallized double sulfates **[**$M(I)M'(II)(SO_4)_2.12H_2O$**]** having the same crystal structure as the common alums, in which sodium and other univalent metals may replace the potassium or ammonium, and other metals may replace the aluminum, even the sulfate radical may be replaced (e.g. by selenate). Examples of such salums are Cesium alum [$CsAl(SO_4)_2.12H_2O$]; iron alum [$KFe(SO_4)_2.12H_2O$**]**; Chrome alum [$KCr(SO_4)_2.12H_2O$**]**; and Chrome selenic alum [$KCr(SeO_4)_2.12H_2O$] (Kirk Othman, 1993).

2.2.2 **Astringents** are substances, such as alum, that are used medicinally or industrially to contract tissues and reduce mucus and other secretions. Solutions of mineral salts are usually astringent, and vegetable astringents contain tannic acid (Microsoft® Encarta, 2006)

2.2.3 **Dealumination** refers to the leaching of clay minerals (in this case kaolin) by the use of acids to obtain a solution that is rich in alum. The resulting mixture is then filtered to obtain the filtrate rich in alum and the residue rich in silica. A typical dealumination process for metakaolin (from Kankara Kaolin) is shown;

$$\underset{\text{Metakaolin}}{Al_2O_32SiO_2(s)} + \underset{\text{acid}}{3H_2SO_4(aq)} + 24H_2O \xrightarrow{100^oC} \underset{\text{alum}}{Al_2(SO_4)_3.27H_20(aq)} + \underset{\text{silica}}{2SiO_2(s)} \quad \ldots\ldots\ldots\ldots \quad 2.1$$

2.3 Chemistry of the Alums

Double sulfates with the general formula $A_2SO_4 \cdot B_2(SO_4)_3 \cdot 24H_2O$, are well known where A is a monovalent cation such as sodium, potassium, rubidium, caesium, or thallium(I), or a compound cation such as ammonium (NH_4^+), methylammonium($CH_3NH_3^+$), hydroxylammonium ($HONH_3^+$) or hydrazinium ($N_2H_5^+$), B being a trivalent metal ion, such as aluminium, chromium, titanium, manganese, vanadium, iron (III), cobalt(III), gallium, molybdenum, indium, ruthenium, rhodium or iridium (Wikipedia, 2008). The specific combinations of univalent cation, trivalent cation and anion depend on the sizes of the ions. For example, unlike the other alkali metals the small lithium ion does not form alums, and there is only one sodium alum.

Alums usually crystallizes in one of the three common classes of crystal structures, these classes are called α-, β- and γ-alums.

2.4 Types of alum and their properties

Table 2.1 Common types of alums and their properties
(Kirk Othmer, 1997; Perry and Green, 1997; Wikipedia, 2008)

	Single alum	**Soda alum**	**Ammonium alum**	**Potassium alum**
Formula	$Al_2(SO_4)_3.XH_2O$ (X=14-27)	$NaAl(SO_4)_2 \cdot 12H_2O$	$NH_4Al(SO_4)_2.12H_2O$	$KAl(SO_4)_2.12H_2O$
Mol wt	666	458.12	453.33	474.39
Mp (^{0}C)	770	61	94.5	92.5
Sp. Gr		1.675	1.645	1.757
Solubility (g/100g H_2O):				
0^OC	23.9-27.5	110.0	2.62	3.90
16^OC		51.0		
20^OC	36.4		15.90	11.40
100^OC	46.9-89.0		109.7	357.48
Crystal color	White/colorless	White	Colorless	White
Dehydration temp (^{0}C)	40 – 420	≤250	≤250	≤200
Decomposition temp (^{0}C)	770	Not available	280	200

2.4.1 **Chemistry of the synthesis of alum.**

After the filtration of the dealumination mixture, the filtrate contains water, sulfuric acid (from the excess acid used) and aluminum sulfate in addition to very minor impurities. The solution of the salting agent i.e potassium sulfate of predetermined concentration is added and then cooled. The formation of double salt alum is enhanced by lower temperature since the process is exothermic. Typical or representative reaction between aluminum sulfate and potassium sulfate in the presence of water (Wikipedia, 2008) is given in equation 2.2

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \ 2.2$$

To decrease the solubility of all the possible salts from this solution and precipitates the least soluble material, there is need to cool the solution:

$$K^+ (aq) + Al(H_2O)_6^{3+} (aq) + 2\ SO_4^{2-} (aq) + 6\ H_2O\ (l) \rightarrow KAl(SO_4)_2\ .\ 12H_2O\ (s) \ \ldots\ldots\ldots.. \quad 2.3$$

In the alum crystal, the aluminum ions are tightly coordinated to six water molecules while the potassium ions is coordinated loosely to six additional water molecules, accounting for the 12 waters of crystallization. The formula could more appropriately be written as

$$K^+(H_2O)_6\ Al(H_2O)_6^{3+}(SO_4^{2-})_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. \ 2.4$$

Alums are noted for the large crystals which they form from aqueous solutions. These crystals often have an **octahedral** shape.

This process of synthesis is similar to those of ammonium alum and soda alum where K^+ is replaced by the NH_4^+ or Na^+ respectively.

2.5 CRYSTALLIZATION

Crystallization is a unit operation through which a chemical compound, dissolved in a given solvent, will precipitate under certain conditions to allow successive separation between the

phases (Cheresources.com, 2008). When the salting agents are added to the dealumination filtrate during the production of double salt alums, precipitation of the crystals of the double salt alums occur (section 2.4.1 referred) which is further increased by cooling. Crystallization is therefore an aspect of precipitation, obtained through a variation of the solubility conditions of the solute in the solvent, as compared to precipitation due to chemical reaction (e.g. water freezing, removing sucrose from beet solutions, removing potassium chloride (KCl) from an aqueous solution). In chemical engineering crystallization occurs in a crystallizer (Wikipedia, 2008).

2.5.1 Crystallization dynamics

A **crystal** is formed following a well-defined pattern, or structure, dictated by forces acting at the molecular level. As a consequence, during its formation process the crystal is in an environment where the solute concentration reaches a certain critical value, before changing status. Solid formation, impossible below the solubility threshold at the given temperature and pressure conditions, may then take place at a concentration higher than the theoretical solubility level. The difference between the actual value of the solute concentration at the crystallization limit and the theoretical (static) solubility threshold is called supersaturation and is a fundamental factor in crystallization dynamics. Supersaturation is the driving force for both the initial nucleation step and the following crystal growth, both of which could not occur in saturated or undersaturated conditions (McCabe & Smith, 2000; Wikipedia, 2008). Fig 2.1 shows the stages in the process of crystallization.

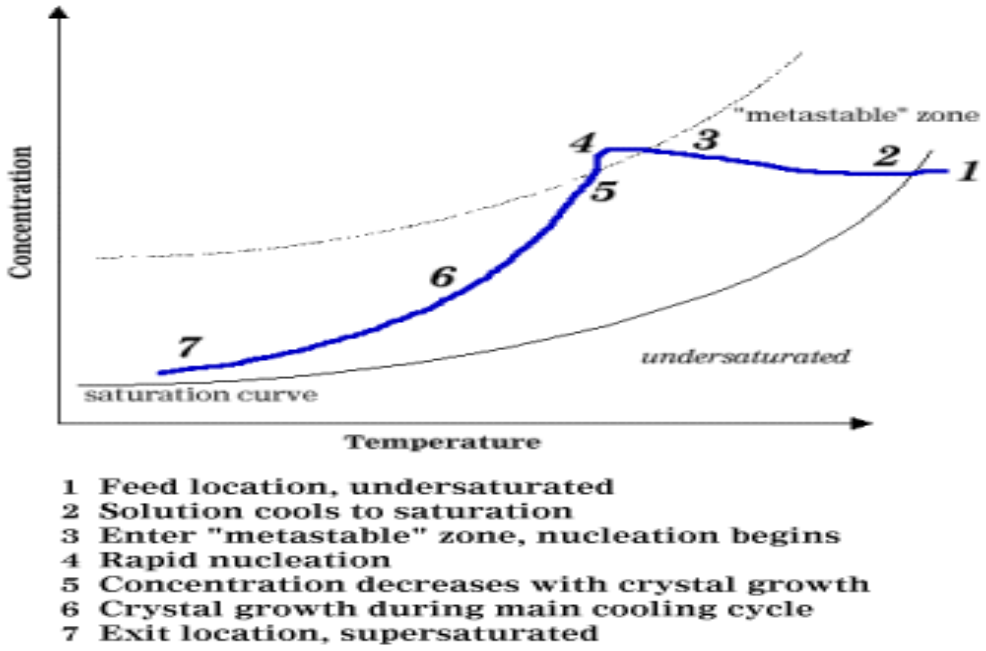


Fig 2.1 Progression of crystallization (Cheresources, 2008).

The four most common methods of reaching supersaturation in industrial processes are:

1. Cooling (with some exceptions).

2. Solvent Evaporation.

3. Drowning method.

4. Chemical Reaction.

Drowning method is described as the addition of a non-solvent to the solution which decreases the solubility of the solid. A chemical reaction can be used to alter the dissolved solid to decrease its solubility in the solvent, thus working toward supersaturation. Each method of achieving supersaturation has its own benefits. For cooling and evaporative crystallization, supersaturation can be generated near a heat transfer surface and usually at moderate rates. Drowning or reactive crystallization allows for localized, rapid

crystallization where the mixing mechanism can exert significant influence on the product characteristics (Cheresources, 2008). Fig 2.2 shows the variation of the solubility of several salts (in water) with temperature and also the amount of salt precipitates that are obtainable at such temperature. Those salts whose solubility increases with temperature are easily crystallized out of solution by cooling.

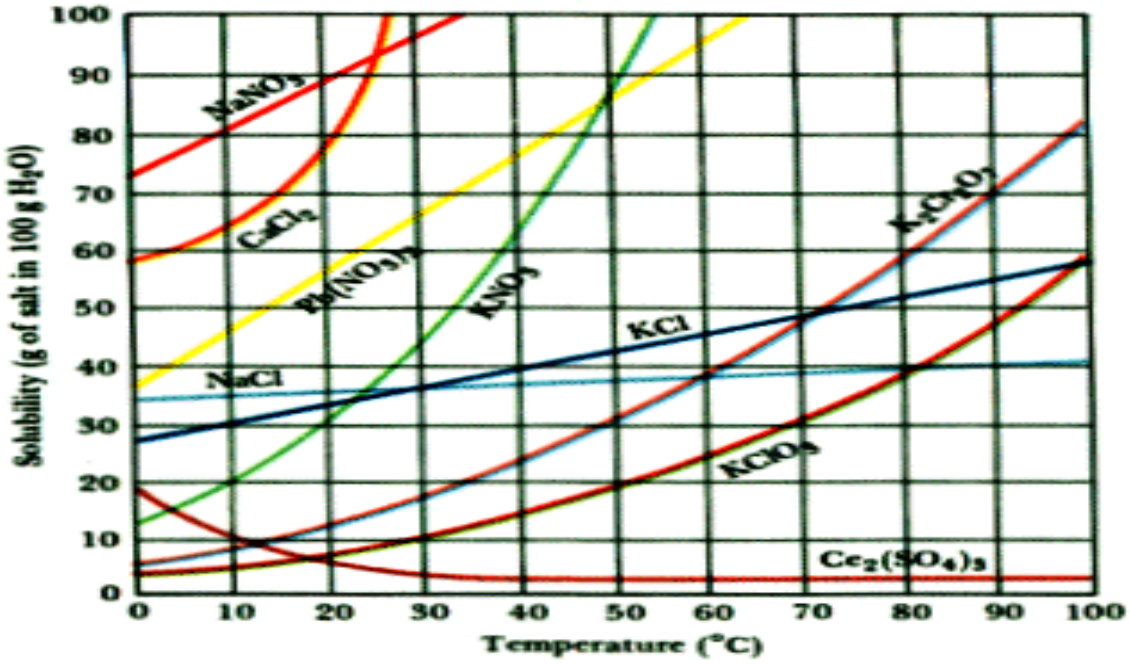


Fig 2.2 Solubility of some salts (Cheresources, 2008).

In the production of alum (aluminum sulfate) from Kankara kaolin, the cooling method (using a refrigerator) of reaching supersaturation has hitherto been used in crystallizing the alum out of the mother liquor (Aderemi, 2001, 2002). Clear acidified aluminum sulfate solutions can be easily super cooled to 10^{o}C or less below super-saturation point without incurring immediate nucleation. But once nucleation starts, the cooling effect of the crystallizing salt leads to accelerated crystallization rate and the supersaturated solution sets

rapidly into a mushy immobile mass. On gentle agitation clear supersaturated solutions show the onset of nucleation by the appearance of silky curling streamer of microscopic nuclei (Kirk Othmer, 1997). This behavior is due to orientation effects of hydraulic currents on the thin plate like crystals. Without agitation, nucleation in a clear acidified solution (in glass tubes) can sometimes yield extended crystalline membranes of such thinness as to exhibit colors due to optical interference (MacZura et al, 1978)

Kinetics studies on aluminum sulfate crystal growth, a necessary part of the recovery of spent excess acid from Kankara kaolin dealumination process show that the crystal growth rate mimics a first-order reversible reaction model on using alum as "seed".

$$-r_{Al}^{3+} = 6.825 \times 10^{-13}\, e^{3444.5/T}\, C_{Al}^{3+} - 2.201 \times 10^{-9}\, e^{-1393.3/T}\, C_{alum} \quad \ldots\ldots\ldots\ldots \quad 2.5$$

With an equilibrium constant of $Kc \geq 10^4$ (Aderemi, 2002).

It was also quantitatively shown that 85% purification level was attained at 2^oC within the first 6 minutes of the reaction time in the presence of alum seed (Aderemi, 2002). Experience in the production of this alum from Kankara kaolin shows that the poorly formed crystals poses a great difficulty when the crystals are to be separated from the mother liquor in which it was formed, this results because of the presence of occluded acid. The use of salting agents as seed is known to greatly reduce this difficulty because it aids the crystal separation from the mother liquor (Kirk Othmer, 1997).The production of double sulfate alums requires both the reactive and cooling mechanism to obtain an appropriate yield of the alums from the mother liquor. The salting agent first reacts with the solute and the resulting compound is crystallized out of solution by cooling.

2.5.2 Steps in crystallization

1. Primary nucleation is the first step in crystallization. Simply defined, it's the growth of a new crystal. Primary nucleation is the initial formation of a crystal where there are no other crystals present or where, if there are crystals present in the system, they do not have any influence on the process.
2. The second chief mechanism in crystallization is called secondary nucleation. In this phase of crystallization, crystal growth is initiated with contact. The contact can be between the solution and other crystals, a mixer blade, a pipe, a vessel wall, etc. This phase of crystallization occurs at lower supersaturation (than primary nucleation) where crystal growth is optimal.

2.6 KAOLINITE

Kaolinite is amongst the clay minerals found in soils sediments, sedimentary rocks and hydrothermal deposits (Eberl, 1997). The clay minerals are essentially hydrous aluminum silicates with magnesium or iron proxying wholly or partly for the aluminum in some minerals and with alkalis or alkaline earth metals present as essential constituents in some of them. Some clay is composed of a single clay mineral while others contain a mixture. In addition to the clay minerals some clay contains varying amounts of so-called non-clay minerals of which quartz, feldspar, calcite, pyrites and mica are major examples. Also, many clay materials contain organic matter and soluble salts which may have been entrained in the clay at the time of accumulation or may have developed as a consequence of weathering or alteration processes e.g. the oxidation of pyrites to give sulfates. It is necessary to wash out the soluble salts before other attributes of the clay are studied.

Common water-soluble salts found in clays are: chlorides, sulfates and carbonates of alkali earths, aluminum and iron (Ahmed, 1986).

2.6.1 **Kaolin**

Kaolin is a corruption of the Chinese "kauling" which means "high ridge", the name of a hill near Jauchau Fu, China, where the material was obtained centuries ago (Grim,1953).

Kaolin is the rock mass which is composed essentially of a clay material that is low in iron and usually white, near white or colored depending on the associated impurities from the source. The kaolin-forming clays are hydrous alumino.-silicates of approximate composition $2H_2O.Al_2O_3.2SiO_2$ and it is believed that other bases if present represent impurities or adsorbed materials. Kaolinite is the mineral that characterizes most kaolin. Kaolin is now known to have globe-wide occurrence (Aderemi et al, 2001; Wikipedia, 2008).

2.6.2 **Kaolinite structure**

The structure of Kaolinite was first suggested in general outlines by Pauling in 1930 and was worked out in some detail by Gruner and later revised by other workers (Grim, 1953). The structure is composed of a single silica tetrahedral sheet joined to a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer. Apical oxygen atoms from the tetrahedral sheet replace hydroxyl ions (OH-) on the octahedral sheet and thereby articulate the sheets to form a 1:1 layer. Thus, kaolinite minerals are composed of structurally asymmetric layers with oxygen planes exposed on one side of a layer and hydroxyls on the other (Eberl, 1997). In the layer common to the octahedral and tetrahedral groups, two-

thirds of the atoms are shared by the silicon and aluminum and then they become O instead of OH. Only two thirds of the possible positions for aluminum are filled and there are three possible planes of regular population of the octahedral layer with aluminums. Two aluminum atoms are separated by an OH above and below making a hexagonal distribution in a single plane in the centre of the octahedral sheet. The OH are placed such that each OH is directly below the perforation of the hexagonal net of oxygens in the tetrahedral sheet (Figure 2.3 referred).

The charge distribution in the layers is thus:

Specie	**Charge**
$6O^{2-}$	12^{-}
$4Si^{4+}$	16^{+}
$4O^{2-} + 2(OH)^{-}$	10^{-} (layer common to tetrahedral sheets)
$4Al^{3+}$	12^{+}
$6(OH)^{-}$	6^{-}

The charges within the structural unit are seen to balance (sum up to zero). The structural formula is $(OH)_8Si_4Al_4O_{10}$, and the theoretical composition expressed in oxides is: SiO_2 46.54wt%, Al_2O_3 39.50wt%; H_2O 13.96wt%. Analysis of many kaolinite samples (Table 2.2 referred) indicates very little substitution within the lattice except in few cases where evidence suggests a very small amount of substitution of iron and/or titanium for aluminum in the relatively poorly crystalline variety.

2.6.3 **Kaolinite Dehydration, Rehydration and Thermal Metamorphoses**

Dehydration curves are plots of weight loss on heating versus the temperature of heating. These show the dehydration effect of heat and that for a fixed time of heating, the weight

loss is directly proportional to the temperature. Dehydration includes the removals of loosely associated water and bonded (OH) water.

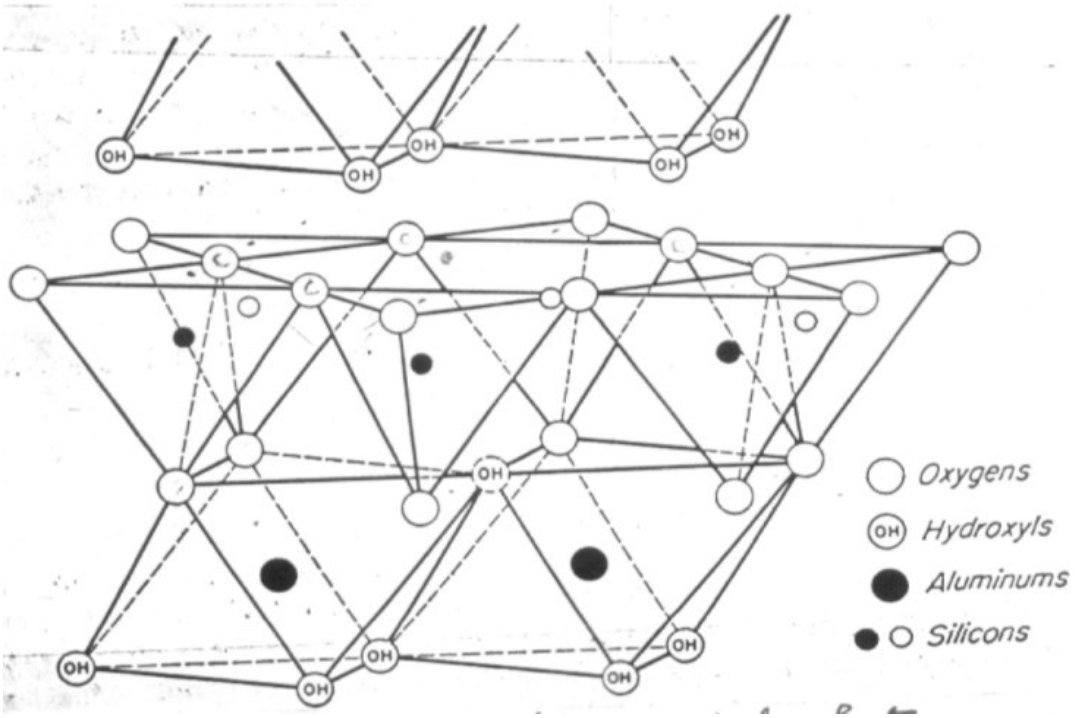


Figure 2.3: The Structure of the Kaolinite Layer (Eberl, 1997)

Differential thermal analyses by means of suitable apparatus, give the temperature at which thermal reactions occur in material when it is heated continuously to and at an elevated temperature and also the general character of such reactions (Grim, 1953; Ahmed and Onaji, 1987). These analyses for clay minerals show endothermic reactions due to dehydration and loss of crystal structure and exothermic reactions due to formation of new phases at elevated temperatures. Dehydration curves for kaolinite show that most of the dehydration takes place between 400^{o}C and 525^{o}C (Figure 2.4 referred). The precise temperature for the loss of the OH lattice water varies and may be explained by variations in particle size since the dehydration temperature is known to decrease with decrease in particle size (Figure 2.5 referred).

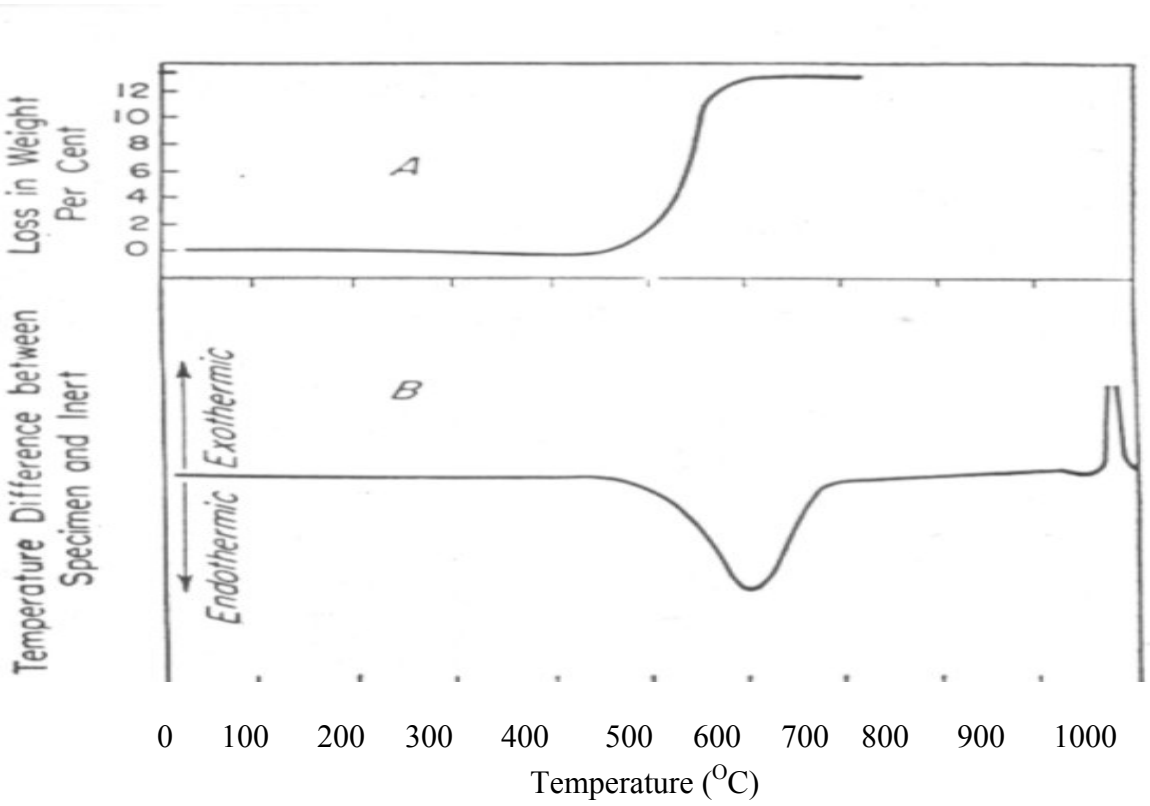


Figure 2.4: Idealized Dehydration and Differential Thermal Curves for Kaolinite (Grim, 1953)

Also, the more crystalline the material the more difficulty in losing the OH lattice water. A small amount of this water (2-3%) is retained at 525°C and dehydration is essentially complete at about 750°C to 800°C. (Grim, 1953; Wikipedia, 2008; Wiley, 2008).

De Keyser (1939) has stated that kaolinite can be dehydrated completely at temperatures as low as 350°C with heating times of as long as 200 hours. Generally very long times are needed to remove the OH lattice water at low temperatures where the water removal is just beginning. Differential thermal curves of kaolinite (Grim, 1953) show an intense sharp endothermic reaction corresponding to loss of OH water beginning at about 400°C and showing a peak at 600°C for well crystallized kaolinite and about 570°C for poorly crystallized kaolinite.

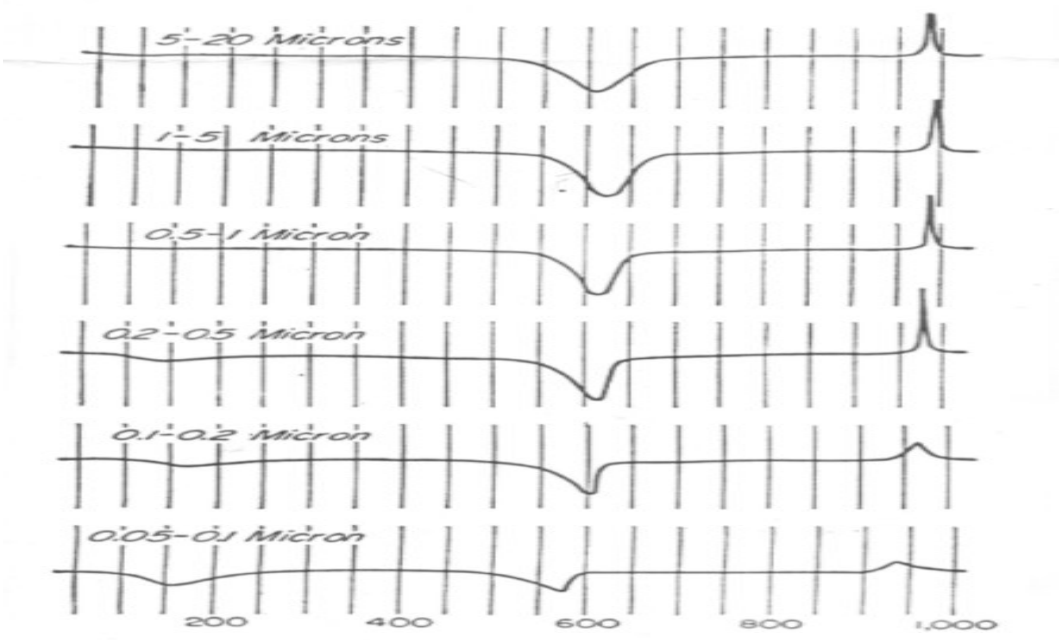


Figure 2.5: Variation of Differential Thermal Curves with Particle Size for Kaolinite (Grim, 1953)

Heating further, the differential thermal curves show an exothermic reaction peak between 900 and 1000°C. Spinel is formed between 925 and 950°C, while mullite and cristobalite are formed at 1050°C (Wikipedia, 2008; Wiley, 2008).

The thermal transition reactions for kaolin are represented as:

1. $2\,Al_2Si_2O_5(OH)_4 \xrightarrow{500\text{-}900^oC} 2Al_2Si_2O_7 + 4H_2O$ …… 2.6
   kaolin → metakaolin

2. $2Al_2Si_2O_7 \xrightarrow{925\text{-}950^oC} Si_3Al_4O_{12} + SiO_2$ …….. 2.7
   metakaolin → spinel

3. $3Si_3Al_4O_{12} \xrightarrow{1050^oC} 2Si_2Al_6O_{13} + 5SiO_2$ …… 2.8
   spinel → mullite + Cristobalite

2.6.4. **Other Properties of Kaolinite**

1. **Swelling:** Kaolinite does not swell in water. Many kaolinites can however be made to swell by using intercalation compounds such as hydrazine, urea and ammonium acetate. Intercalation is done either by mixing kaolinite directly with a liquid melt or concentrated aqueous solution or by mixing it with a solution containing an entraining agent or by displacement of a previously formed intercalation complex.
2. **Cation Exchange Capacity:** Kaolinite has low cation exchange capacity (5-15 meq/100g). Its cation exchange capacity arises due to occluded impurities or from broken bonds on crystal edges. This explains the source of impurities often found in Kaolinite ores.
3. **Plasticity:** It has good plasticity with an Atterberg plasticity index of 57.0 for beneficiated Kankara kaolin clay (Ahmed and Onaji, 1987).
4. **Particle Size:** The particles of kaolinite are very small indeed (colloidal in size, 1-2 microns) and platy in shape. This gives it high specific surface area for sorption and reaction enhancement (Eberl, 1997)
5. **Color**: It ranges in color from creamy to whitish but it is white when fired.
6. **Refraction Temperature**: Kaolinite mineral refracts at 1710^{o}C i.e. it becomes vitreous, hard and permanently non-plastic.

2.6.5 **Formation of kaolinite**

Kaolinite formation is favored by the presence of dilute acidic solutions such as those present in soils undergoing intense leaching (Eberl, 1997, Google books, 2008). These conditions are mainly found in wet tropical environments where kaolinite is a major component of lateritic soils. Kaolinite can also form in hydrothermal environments e.g. the void spaces of sand stones during burial digenesis, around hot springs and as a by-product of the alteration of smectite to illite. Feldspar component of granitic masses are kaolinized by loss of alkali content and some silica and gain of water of constitution. Though the reaction is not yet fully understood, it may be represented by equation 2.9.

$$\underset{\text{Feldspar}}{K_2O.Al_2O_3.6SiO_2} \xrightarrow{2\,H_2O} \underset{\text{kaolinite}}{Al_2O_3.2SiO_2.2H_2O} + K_2O + 4SiO_2 \quad \ldots\ldots\ldots\ldots \quad 2.9$$

Some of this potassium salt are washed away by water, while some of the silica are retained as free silica and in more complex forms like mica, thereby serving as impurities in the ore.

2.6.6 **Chemical Analysis of Kaolin**

Kaolins are difficult to detect because of their small particle size (Grim, 1953).

Complete identification may be accomplished by Atomic Absorption Spectrophotometry (AAS), X-ray Diffraction (XRD) and X-ray Fluorescence (XRF). Table 2.1 compares some Nigerian kaolins with samples from other countries

Table 2.2: Comparative Analytical Data of Nigerian Kaolin with Samples from other Countries (RMRDC, 2000)

S/No.	Parameters	Refined American	Refined English	Unrefined Katsina	Refined Jos
1.	Appearance	Off-white	Off-white	Off-white with brown patches; powdery	Slightly white
2.	Moisture and combined water, %	18.88	13.96	8.75	13.0
3.	Free moisture, %	6.28	6.49	1.25	0.86
4.	Loss on ignition %	11.63	11.99	11.10	11.44
5.	pH of 10% aqueous slurry	6.8	7.3	5.4	7.5
6.	Alumina (Al_2O_3), %	39.27	39.20	36.70	37.49
7.	Iron (Fe_2O_3), %	0.19	0.30	0.21	0.46
8.	Silica (SiO_2), %	44.52	46.14	43.30	46.94
9.	Purity, % kaolin	92.49	92.32	86.43	88.29
10.	Titania (TiO_2),%	2.14	Nil	Nil	0.40

2.7 Kankara kaolin

Kankara kaolin is the name given to the kaolin brand with a huge deposit in Kankara, Katsina state of Nigeria. Though kaolin is present in other parts of Nigeria, the deposit in Kankara, Katsina State has been under serious investigation by the Chemical Engineering department of the Ahmadu Bello University, Zaria for more than two decades. From available statistics with the Raw Material Research and Development Council (1995), the Kankara deposit holds the largest reserve within the country as shown in table 2.3.

Table 2.3 Kaolin deposits in Nigeria (RMRDC, 1995).

LOCATION OF DEPOSIT	STATE	RESERVE CLASSIFICATION	RESERVES (million tones)
Ozubulu	Enugu	Probable	1.0
Darazo	Bauchi	Proven	10.0
Major Porter	Plateau	Proven	7.0
Nahuta	Plateau	Proven	1.0
Jagalwa	Bauchi	Probable	8.0
Kankara	Katsina	Probable	20.0
Abeokuta	Ogun	Proven	10.0
Ifon	Ondo	Probable	1.0
Okitipupa	Ondo	Probable	1.0
Ado – Awaye	Oyo	n.a.	n.a.
Tede	Oyo	n.a.	n.a.
Sokoto	Sokoto	n.a.	n.a.

Properties of Kankara kaolin

This deposit has a grit context averaging 32-50%. The plasticity index approximates 13%. The linear and volume drying shrinkage ranges from 9% to 12% and 18% to 30% respectively. The color is off-white with pink or brown patches.

Table 2.4 XRF Analyses for Raw Kankara Kaolin, beneficiated Kankara kaolin and Metakaolin (Abdul, 2005).

Parameter, wt%	Raw Kaolin	Beneficiated Kaolin	Metakaolin
AI_2O_3	35.77	32.46	39.57
SiO_2	39.01	39.29	41.68
Fe_2O_3	0.21	bd	0.09
Na_20	bd	bd	bd
K_2O	0.53	0.27	0.43
CaO	0.98	1.10	1.27
MgO	1.02	1.07	1.13

bd = below detection limit

Because of the need to seek for alternative sources of alumina, owing to the lean deposit of bauxite in Nigeria, the Department of Chemical Engineering of the Ahmadu Bello University, Zaria, has been involved in intense research on Kankara kaolin. Though the kaolinite is lean in alumina content (36-39wt %) when compared to bauxite (45-65wt %), it was picked for these investigations largely due to its local and global abundance (Eberl, 1997; Aderemi et al, 2001). This is in addition to its being next to bauxite in alumina content and purity among the clay family (Aderemi et al, 2001). The works of Aderemi and Oludipe, Ahmed and Onaji, the PTDF Professorial Chair zeolite research group and others have yielded a pool of evidences that our kaolin deposits in Nigeria is a rich alternative source for obtaining industrial grade alum and alumina. Recently, Abdul (2005) produced alum (15.98 wt % alumina) and alumina (98.58 wt %) from Kankara kaolin. The chemical composition of the alumina is given in table 2.5.

Table 2.5: Chemical Composition of Alumina Samples Produced at 800°C with different Calcination Times using +212-355 μm Particles (Abdul 2005).

Time (min)	Al_2O_3 wt%	Fe_2O_3 wt%	K_2O wt%	MgO wt%	CaO wt%	Na_2O wt%	SiO_2 wt%
20	37.20	0.21	0.90	0.89	0.29	0.56	bd
40	50.75	0.26	1.24	0.97	0.30	0.50	bd
80	55.05	0.29	1. 26	0.96	0.37	0.46	bd
100	60.40	0.31	1.30	1.01	0.39	0.45	bd
180	98.58	0.57	1.48	1.40	0.65	0.34	bd

bd = below detection

2.8 Beneficiation of the clay material

The clay material, if obtained directly from the mines usually requires some purification (beneficiation) treatment to separate the various impurities present.

One method most frequently used is that of sedimentation which aims at separation of minerals on a morphological and gravity basis. It is broadly defined as the separation of a suspension into a supernatant fluid and rather dense slurry containing a higher concentration of solid. It is most commonly defined as the gravitational settling of solids in liquids (Kirk Othmer, 1997). The use of sedimentation in the industry fall into the following categories: solid-liquid separation (2); solid-solid separation (3); and other operations such as mass transfer, washing, etc. In solid-liquid separation, the solids are removed from the liquids either because the solids or the liquids are valuable, or because these have to be separated before disposal. If the primary purpose is to produce the solid in highly concentrated slurry, the process is called thickening. If the purpose is to clarify the liquid, the process is called clarification. In solid-solid separation, the solids are separated in fractions according to size, density, shape or other particulate properties. Sedimentation is also used for size

separation (qv), i.e. classification of solids. One of the simplest ways to remove the coarse or dense solids from a feed suspension is by sedimentation. Successive decantation in a batch system produces closely controlled size fractions of the product. Generally, however, particle classification by sedimentation does not give sharp separation.

Another method of purifying clay material is by combining sedimentation with sieving. Sieving, which also separates materials on a size basis is sometimes preferred to the sedimentation technique because it is much faster to accomplish. Sieving is achieved by soaking clay in water, blunging and sieving through the appropriate sieve. The choice of sieve size is guided by the knowledge of the particle size distribution of the clay (Ahmed, 1986).

Another method also used for purifying clay (for alum/alumina production) is by calcination. This method helps in removing some components which would otherwise not dissolve in the solvent (in this case water) but will decompose under the influence of high temperatures (this includes some carbonates, chlorides, oxides and other organic compounds present in the clay). This further concentrates the wanted. Clay is reported to loose between 12-15wtpercent when heated to above 500^0C in furnaces (Ahmed, 1986; Ahmed and Onaji, 1987).

2.9 Alum Production

The commercial grade alum (0.5% iron max) is usually produced by digesting finely ground bauxite in sulfuric acid near the boiling point of the solution (Acquah et al,, 1978). The acid strength used varies between 20% - 50% depending on the nature of the product and limitations on intermediate purification steps. Aderemi and Oludipe (2000) observed

that an acid concentration of 60% gave about 93.16% to 94.44% dealumination yield for Kankara kaolin. The clear supernatant solution is often concentrated to about 61.50 Bé and allowed to solidify to blocks or sold in liquid form. The finished dry product may have the following analysis: insoluble 0.08%; Al_2O_3 17.15%; Fe_2O_3, O.45%; SO_3, 39.66%; water of composition 42.66%. Liquid alum is usually limited to 8% Al_2O_3 content to avoid crystallization of the product in transit. The iron free grade is obtained by using pure alumina hydrate from the Bayer process instead of bauxite. (MacZura et al, 1978; Chemical Land 21, 2004). The different types of alums are synthesized by the addition of the respective metallic sulfates to the supernatant solution obtained (sometimes by filtering), followed by cooling. The choice of cooling which was employed in this work is informed by the fact that the supernatant solution contains some acid which is the result of using excess acid during the dealumination step. This acid-water solution is separated from the crystals when cooled and can further be separated by filtration. The spent acid can be re-concentrated and reused (Aderemi, 2002).

CHAPTER 3

METHODOLOGY

3.1 Materials

The major materials used in this work are:

(i) Kankara kaolin from Kankara, Katsina State

(ii) 96wt% Sulfuric acid ,Johnson Solomon Ltd England, General Purpose Reagent

(iii) Absolute ethanol (99wt%),BDH, Analar grade

(iv) Potassium sulfate, Johnson Solomon Ltd England, Analar grade

(v) Sodium sulfate, Johnson Solomon Ltd England, Analar grade

(vi) Ammonium sulfate, Johnson Solomon Ltd England, Analar grade

(vii) Ammonia solution (20 wt%), BDH, Analar grade

(viii) Distilled water

3.2 Apparatus

This section details the glass/ceramic ware and other equipment used in this work.

(i) Beakers (Pyrex), 1000ml and 500ml

(ii) Conical flasks (500ml), Pyrex

(iii) Measuring cylinders (1000ml, 500ml, 10ml), Pyrex

(iv) Crucibles (Haldenwanger, Germany)

(v) Laboratory mortar and pestle

(vi) Sieves (50, 355μm)

(vii) Spatula

(viii) Plastic spoons

(ix) Buchnel flask (1 litre)

(x) Sinta glass filter (Quickfit TM)

(xi) Plastic bucket (Eleganza)

(xii) Glass rod stirrer

(xiii) Thermometer (-10^{o}C to 360^{o}C)

(xiv) Desiccators (Dry seal type, Jencons)

(xv) Sample bottles (glass and plastic)

(xvi) Petri dishes, Pyrex

(xvii) Stainless steel thongs

Table 3.1: List of other equipment used in this work and their specifications

S/No	Name	Model	Manufacturer
1	Weighing Scale (0-100kg Range)	1455T 18	WEDA,Holland
2	Centrifuge	Sorval GLC-2	Dupont USA
3	Oven	TM OV-420 (0-260^{o}C)	Gallenkamp England
4	Analytical Balance	AB 204 (0 – 180g)	MettlerToledo, Switzer land
5	Immersion Heater	002-4082/194014379011	Haake, Germany
6	High Vacuum Pump	ES-100	Edwards, England
7	Magnetic Stirrer Regulated Hot Plate	8/SS-670	Gallenkamp, England
8	Refrigerator	C1202	Thermocool, England
9	Deionizer	ZEROLIT	
10	Muffle Furnace (0-1100K)		Vecstar, England
11	Exposed Element Furnace (0-1400^{0}C)	TIKIR 11/12	Heraeus, Holland
12	X-ray Fluorescence Machine	PW1660,XRA	PANalytical,England
13	Distilled water machine	A4000	Aquatron

3.3 Procedure

Below is the sequence of procedure that was followed in the course of this work;

3.3.1 **Beneficiation of Kankara clay.**

9.0kg of raw Kankara kaolin clay (procured from Kankara village, in Katsina state) was weighed on a scale and crushed using a mortal and pestle. It was then soaked in water (in a plastic bucket) and properly stirred to break up the small lumps and the solution was allowed to stand for three (3) days. During the three days it was periodically stirred and fresh water added after removing the previous day's water by decantation. This is to remove the soluble impurities in the clay. Samples (raw, day1, day2 and day3) of the clay were taken on a daily basis before fresh water was added. The 50 micron sieve was then used to sieve the kaolin suspension twice to get rid of the intermediate coarse particles on the third day. A sample from the ≤50μm clay fraction (sample S) was also taken before the commencement of the following secondary decantation steps: The slurry (≤50μm clay fraction) thus obtained was allowed to stand for about ten minutes and then decanted leaving about ten percent (10%) of the sediment in the bucket (Ahmed, 2008). This decantation procedure was repeated five times until almost no free-silica was visible. The ten percent was rewashed with fresh water (and subjected to the decantation procedure also) to recover some of the kaolin that would otherwise have been discarded. This is to ensure a high recovery of the pure kaolin present in the raw. The suspension thus obtained was then dewatered by pressure to thick clay mass. This was then gradually dried overnight at 120^{o}C (Aderemi et al, 2001) to remove free water. The product from this stage is hereafter referred to as fully beneficiated kaolin (sample B). The partially beneficiated samples taken at the different stages of beneficiation and the raw kaolin were also dried to 120^{0}C alongside the fully beneficiated kaolin.

3.3.2 **Milling and sieving of dried kaolin samples**

The dried lumps of the samples were then crushed in a jaw crusher and then ball milled into fine powder. This powder was then sieved using a 212 μm sieve.

3.3.3 **Calcination**

The sieved dry kaolin powder samples were then placed into crucibles and calcined in a muffle furnace at 750^{o}C for two (2) hours (Murat et al, 1989) to yield the more reactive metakaolin.

3.3.4 **Dealumination of metakaolin using sulfuric acid**

Investigation into the effectiveness of the heat of mixing of the sulfuric acid in water in the dealumination of metakaolin was carried out. In a typical run, 50g of the metakaolin was measured into the conical flask and a calculated amount of distilled water that will bring the acid concentration to 60 wt % (Aderemi, 2000) was added and stirred. A calculated quantity of 96wt% sulfuric acid (5 folds stoichiometric requirement) was measured and then added to the metakaolin suspension in the conical flask and the reaction left for about 30 minutes, after which additional distilled water was then added to quench the reaction. The reaction mixture was then filtered through the sinta glass filter. In another set of batches, external heat was applied to the dealumination reaction using the oil bath at 100^{0}C for 1, 2 and 3 hours (Aderemi and Oludipe, 2000; Aderemi et al, 2001). The samples earlier marked raw, day1, day2, day3, S, and B were also dealuminated using the heat of mixing method. In yet another set of runs, 20g, 50g, 80g, 100g, and 500g metakaolin were dealuminated in other to test the effect of scale up on the yield of alum from Kankara kaolin. In a mini optimization

attempt, 2, 3 and 5 folds stoichiometric acid requirement were separately used for the dealumination of 100g metakaolin to see how this will affect the yield of alum.

3.3.5 **Crystallization of alum**

Prior to crystallization, the filtrate was diluted with predetermined quantity of distilled water (detailed calculation is shown in the appendix) to enhance the ease of separation of the excess acid from the alum by taking advantage of the freezing point depression of sulfuric acid solutions on dilution (Weast, 1968).The filtrates was then cooled at temperature of 0^0C for about 4 hours (Aderemi et al, 2001; Abdul, 2005). In another round of runs, solutions of the different salting agents (ammonium, potassium and sodium sulfates, 1.4ml ethanol/ml filtrate and 20wt% ammonia) were prepared and added separately to the dealumination filtrates in separate beakers, prior to the cooling stage. Yet in another set of runs, direct crystals of the salts (ammonium and potassium sulfate) were added separately to the filtrates.

3.3.6 **Drying of the alum**

After the crystals have formed, they were then separated from the mother liquor using a sinta glass filter on a bucknel flask attached to a high vacuum pump. The alum crystals were then dehydrated by heating at 250^0C for 6 hours in an oven to ease handling and analysis by the XRF machine. Two sets of commercial alums procured from Sokoto central market were similarly dried.

3.3.7 **Characterization of the dried alum**

The dried alums were thereafter analyzed using an Energy Dispersive X-ray Fluorescence (ED-XRF) machine to determine their elemental composition. This was used for the determination of the quality of the alums.

CHAPTER 4

4.0 RESULTS AND DISCUSSION

The results of this work (beneficiation, calcination and dealumination of Kankara kaolin; crystallization, drying and analysis of the produced alums) are presented and discussed in this chapter.

4.1 Beneficiation of Kankara Kaolin

After two successive beneficiation batches carried out, an average of 0.91kg of dried beneficiated kaolin was obtained per kg of raw Kankara kaolin, owing to the rigorous sieving and decantation procedures. This implies a high recovery rate for kaolin from its raw state and it is in agreement with Ahmed (1986) who showed that Kankara kaolin contains about 83wt% and 90wt% kaolinite in the raw and beneficiated samples respectively with the remaining mineralogical composition being montmorillonite, mica, quartz, carbonaceous and soluble components.

4.2 Calcination of dry beneficiated Kankara kaolin

Thermo gravimetric analysis of the produced metakaolin indicated that on the average 0.8585kg metakaolin was obtained per kg of beneficiated Kankara kaolin clay calcined at 750^{o}C for 2 hours. This shows 14.147% calcinations loss, which is in good agreement with stoichiometric expectation of 13.95% for pure kaolinite (Grim, 1953, Flores and Neves, 1997) and indicates a high conversion to metakaolin which is necessary for high dealumination rates.

Table 4.1 shows the elemental composition of the raw kaolin, beneficiated kaolin and metakaolin from Kankara kaolin.

Table 4.1 Elemental composition of raw and beneficiated kaolin and metakaolin

SAMPLES	**SiO_2**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**MgO**	**K_2O**	**Na_2O**	**TiO_2**	**$\frac{SiO_2}{Al_2O_3}$**
Raw Kankara kaolin	45.10	33.41	0.343	0.555	1.49	0.693	0.016	0.100	2.295
Beneficiated kaolin	47.48	36.80	0.325	0.562	1.27	0.544	0.050	0.066	2.179
Metakaolin (750^0C/2hr)	49.40	41.56	0.289	0.483	1.12	0.427	0.038	0.067	2.0203

*ND = Not detectable

It was observed that the alumina content increases steadily with beneficiation, which suggests that, the goal of the beneficiation process which is aimed at increasing the ratio of alumina to silica was achieved. Though the silica content is also seen to increase numerically, this was not in the same proportion with the alumina. This also implies that the materials removed during the beneficiation process are high in silica content, basically, montmorillonite, mica and quartz as reported by Ahmed (1986), and free silica which is known to be present in clays. The ratio of the silica to alumina was observed to attain the literature value of 2 to 1 for metakaolin (Wikipedia, 2008), thus indicating full conversion of Kankara Kaolin to metakaolin at 750^0C (Grim, 1953; Wikipedia, 2008). The oxide impurities are observed to reduce less significantly as expected from the raw kaolin to the beneficiated kaolin suggesting that the water used may have contained some of these impurities too.

4.3 **Dealumination of metakaolin**

It was observed that during the dealumination process using the heat of acid dissolution in water that an average of 16.7051g of alumina per 50g of metakaolin (which contains 20.55g of alumina) was recovered from the dealumination filtrate. This represents 81.29wt% alumina recovered which compares favorably with the 85wt% reported by Aderemi (2002) using additional external heat source for 3 hours at 100^0C. Fig 4.1 shows the comparative alum yield obtained with and without external heat in addition to the heat of dissolution of acid in water. It can be observed that the difference between the yields of alum obtained using only the heat of hydration/dissolution and that employing additional heat for three hours via oil bath at 100^0C is only about 6.07% which might not justify the extra energy cost considering the current global drive for reduction in production cost. This is a noble innovation, which justify the earlier speculation made by Boniface (2007). This energy saving route was therefore followed throughout this work in the dealumination processes.

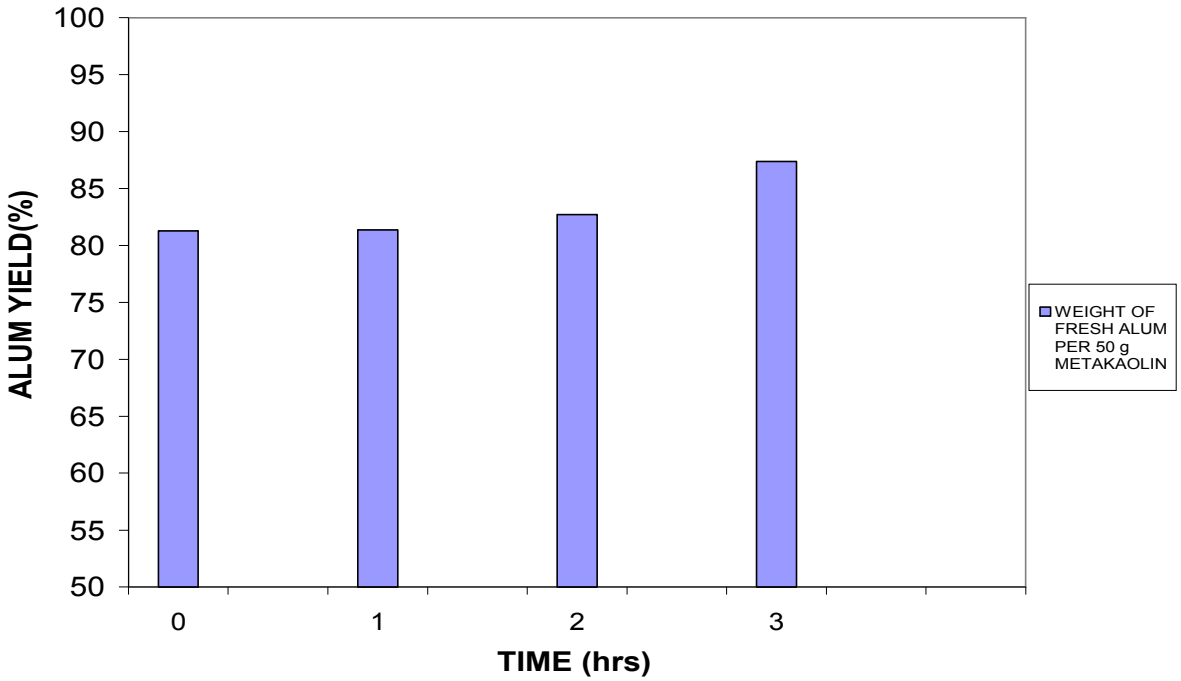


Fig 4.1 Variation of ammonium alum yield with heat source.

4.4 Effect of beneficiation on the yield of alum

Fig 4.2 shows the variation of the yield of alum per 50g of metakaolin as against the extent of beneficiation. It was observed that the yield of alum is relatively constant for the first two days of soaking and plunging and rose slightly on the third day signifying probably slight increase in the surface area due to pulverization effect. Following the same reasoning, further increment was attained after sieving through 50µm sieve (point S on fig 4.2 referred). Expectedly, point B on figure 4.2 gave the highest yield possible in this setup. This is because the fully beneficiated clay has the highest alumina concentration and purity as corroborated by table 4.1 and figure 4.3 respectively (fig 4.3 shows that the kaolin obtained after the rigorous beneficiation has a coefficient of uniformity of 9.3).

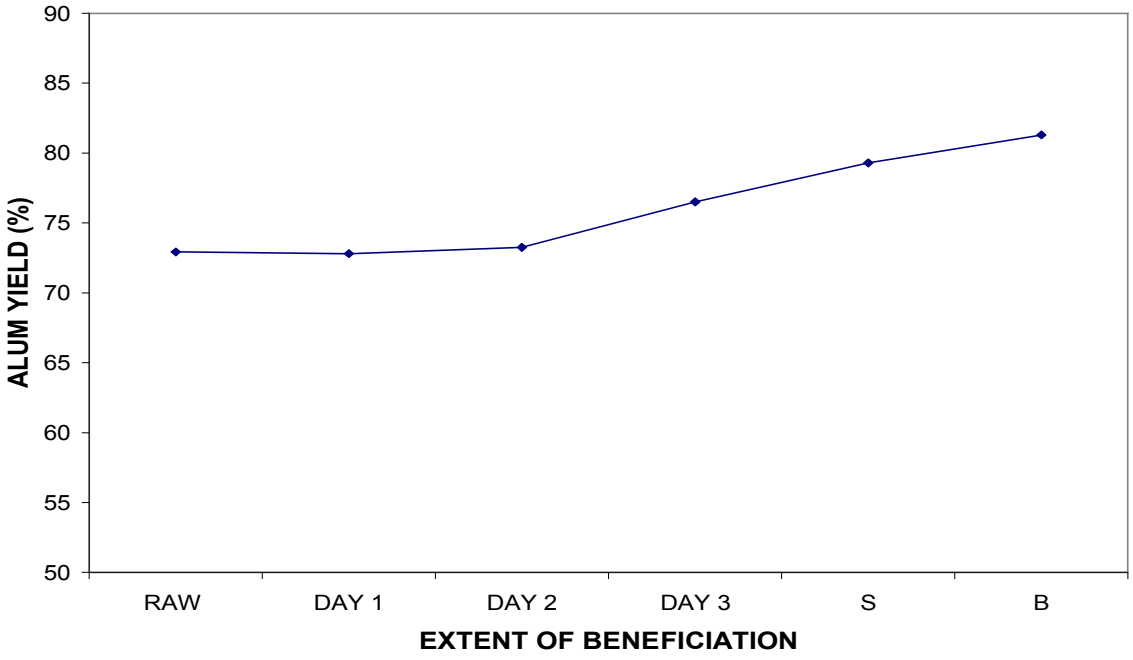


Fig 4.2 Variation of alum yield with extent of beneficiation of Kankara kaolin

Where S = sieved through 50µm sieve after 3 days of soaking; B = rigorously beneficiated kaolin; RAW = raw calcined kaolin; DAY1, DAY2, DAY3 = clays soaked in water for 1, 2, 3 days respectively before calcination

It therefore implies that the yield of alum per mass of metakaolin is a function of the pulverization level and purity of the kaolin. From these results, it can be deduced that the use to which the alum will be put will determine the extent of beneficiation demand. For general purpose and for most industrial uses, the rigorous beneficiation may be unprofitable due to the present low cost of kaolin, which may make the 72% alum yield obtained from the raw calcined clay adequate. But for processes that demand high grade especially low concentrations of MgO, the described rigorous beneficiation step may be inevitable though at additional cost chargeable to the product.

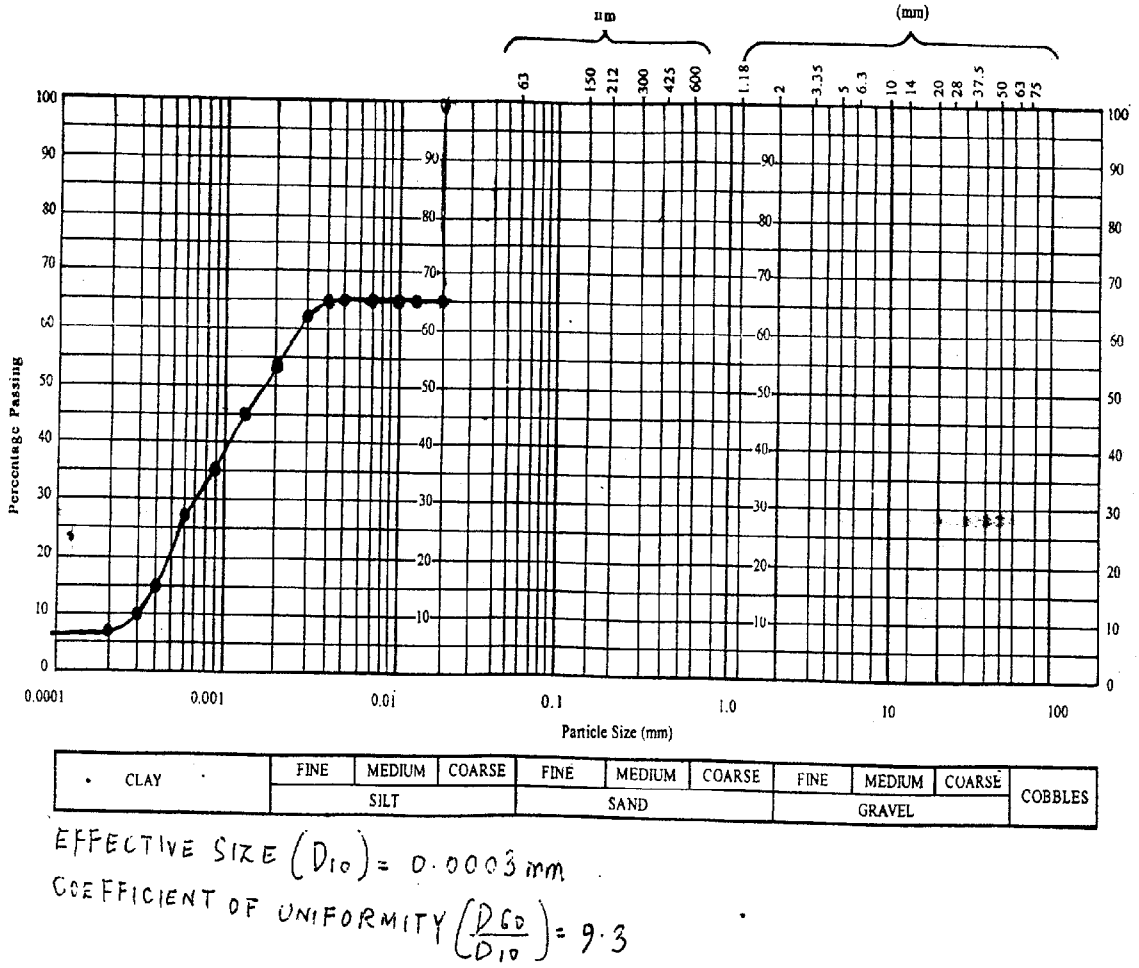


Fig 4.3: Particle size analysis for beneficiated Kankara kaolin

4.5 **Effect of beneficiation on alum quality**

Table 4.2 shows the result of beneficiation on the quality of alum from Kankara kaolin. The amount of impurities present as oxides is a reflection of the quality of the alum. The major constituent oxides are shown. It is interesting to note that silica (SiO_2), which was the major setback in the attempt by the pioneer workers to make alum for water purification from kaolin in Nigeria, is below detection or altogether absent in this investigation (table 4.2 referred), indicating the superior quality of the alums developed in this work and its suitability for water treatment processes for public consumption (Acquah et al, 1978; Harrison, 2004). This success, we believe was a result of stringent carefulness in the filtration step maintained in this work, which is the reason we use sinta glass filter instead of filter paper grades that was used by previous workers. It was observed also, that the major oxide that was affected by the beneficiation process is magnesium oxide (MgO), with about 85.97% reduction. This tremendous reduction in the MgO content is observed between the alum from the raw kaolin and that from the sieved kaolin. The presence of MgO derives from magnesium sulfate ($MgSO_4$) and magnesium carbonate ($MgCO_3$) and are known to increase the hardness of water were the alum to be used for water treatment. This is undesirable for public consumption (Harrison, 2004).

Table 4.2: Variation of alum quality with extent of beneficiation.

	OXIDES IN WT %									
Time(Days)	**SiO_2**	**SO_3**	**K_2O**	**CaO**	**Fe_2O_3**	**MgO**	**CuO**	**Na_2O**	**Cr_2O_3**	**NiO**
Raw kaolin	ND*	74.5 7	ND	0.17	0.13	1.96	0.049	0.095	0.008	001
DAY 1	ND	71.92	0.04	0.20	0.14	1.21	0.060	0.055	0.01	0.015
DAY 2	ND	67.40	0.01	0.20	0.195	1.68	0.045	0.08	0.01	0.01
DAY3	ND	70.50	0.04	0.24	0.165	1.68	0.045	0.11	0.015	0.013
S	ND	70.61	ND	0.24	0.25	0.29	0.105	0.085	ND	0.01
B	ND	69.61	ND	0.19	0.125	0.275	0.06	0.13	0.01	0.02

ND*= Not detectable S=alum from sieved kaolin, B=alum from fully beneficiated kaolin

The other oxides are not observed to change much and are insignificant in quantity. Potassium oxide (K_2O) is observed to be significantly low and/or below detection in all the alums probably owing to its high solubility index, which explains why it remained in the mother liquor. This result reveals that these alums can serve as a precursor to refractory purpose alumina. The produced alum from the fully beneficiated kaolin sample meets the requirements for portable water treatment purposes (≤0.5% Fe. Acquah et al, 1978, Alibaba.com, 2008), while all others including the alum from the raw clay can conveniently serve in any process in which MgO is not an impediment (Richardson, 1992: Steven et al, 2008; Haznan et al, 2008). It is obvious that the soaking time did effect a significant reduction of the magnesium oxide (MgO) in the clay, rather it was evidently removed during the sieving of the kaolin (sample S in table 4.2 referred), this observation may not be unconnected with the fact that most magnesium compounds are insoluble in water at room temperature (Perry and Green, 1997; Wikipedia, 2008).

4.6 **Sample alum versus commercial alum**

Table 4.3 shows the elemental composition of alums produced from Kankara kaolin in the course of this investigation in comparison with two commercial alums obtained from the Sokoto central market. Silica and potassium oxides are observed to be below detection level while the sulfite (SO_3) contents are almost the same for all the alums. The calcium content of commercial alum 2 is twenty times that in sample alum, while the MgO content of commercial alum 1 is ten times that in sample alum. Also, the ferric content of commercial alum 2 is about six times that in the sample alum. Hence, it appears that the alum produced from the raw clay in the course of this investigation appears purer than the two commercial

alum samples. It can therefore be clearly stated that to get the same quality of alum as that available in the market today, one needs not bother about the rigorous beneficiation process.

Table 4.3 Comparison of the quality of sample alums and commercial alums

ALUMS	Al_2O_3	SiO_2	SO_3	K_2O	CaO	Fe_2O_3	MgO	CuO	Na_2O	Cr_2O_3	NiO
Sample alum	19.00	ND	70.01	ND	0.20	0.13	0.275	0.06	0.13	0.01	0.02
Commercial alum 1	19.60	ND	69.60	ND	0.25	0.11	2.86	0.05	0.13	0.017	0.007
Commercial alum 2	23.02	ND	71.70	ND	3.68	0.85	0.41	0.06	0.21	0.02	ND
Alum from raw kaolin	18.02	ND	73.10	ND	0.16	0.12	1.96	0.05	0.10	0.016	0.01

4.7 **Effect of salting agent on alum yield**

Fig 4.4 shows the variation in alum yield observed when different salting agents were used for crystallizing alum out of solution of the dealumination filtrate. It can be observed that the highest yield was obtained when sodium sulfate solution was used. This may not be unconnected to the fact that the alum obtained after the addition of sodium sulfate solution to the dealumination filtrate was precipitated by a careful evaporation of the mother liquor at 60^0C, most of the alums in the mother liquor were recovered, however this process is extremely difficult and energy consuming (Kirk Othmer, 1997; Wikipedia, 2008). During the crystallization, it was observed that the crystals of the salted alums were clearly separated from the mother liquor in which the alums were formed. This made the separation very easy when compared to that of the single alum. This clearly shows that salting the dealumination filtrate from Kankara kaolin greatly increases the yield of alum obtainable. Figure 4.4equally shows that only about 37.62% of the theoretical alum could be extracted when no salting agent was used. Though alum (single alum) is known to be insoluble in ethanol (Kirk Othmer, 1997) as was also observed by Abdul (2005), the process of sieving

the ethanol-alum precipitate also posed a little problem as was observed in the course of this work, hence some of the alum could have re-dissolved in the solution resulting in lower amount of alum extracted in the process as shown in fig 4.4.

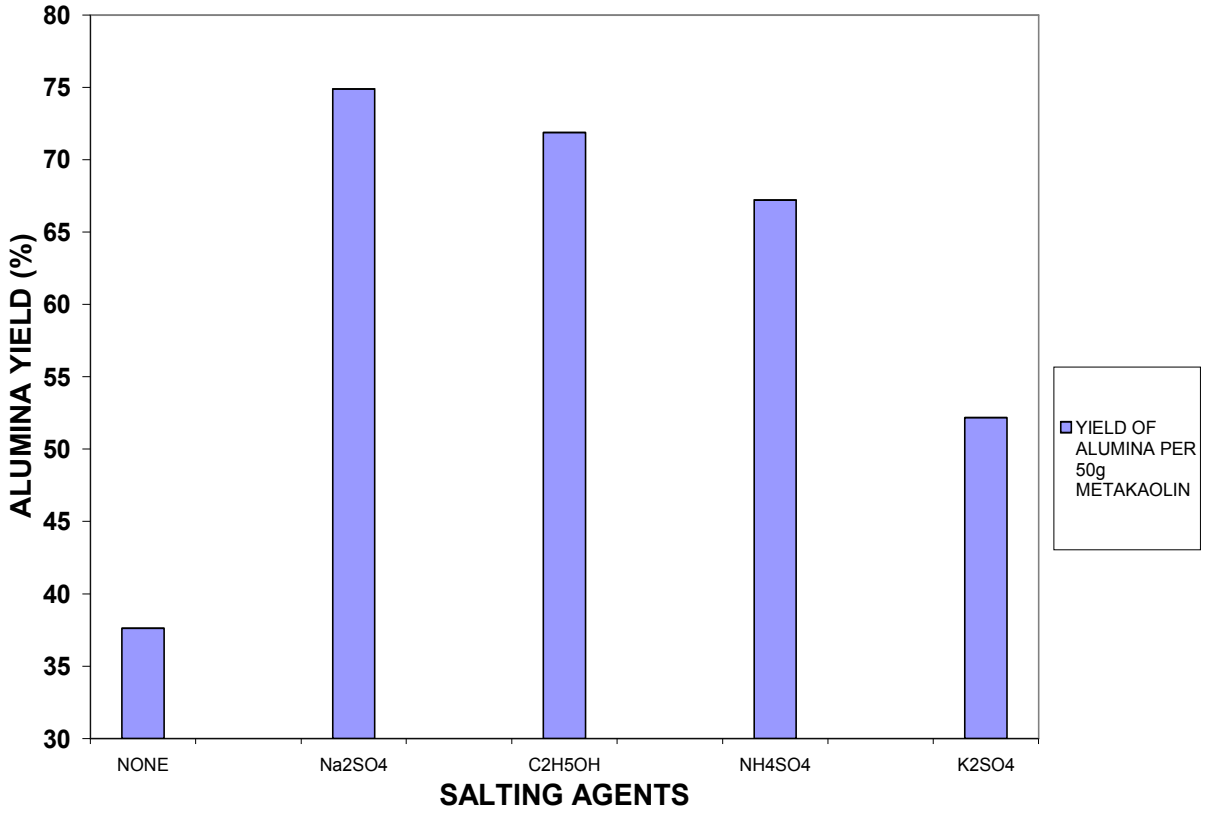


Fig 4.4: Variation of alum yield with salting agents.

Potassium alum is known to be soluble in dilute sulfuric acid and also in water (table 2.1 referred), some of which possibly re-dissolved in the acid-water mixture resulting in less than expected alum yield when potassium sulfate solution was used. The same reason goes for the ammonium alum. However, as the concentration of the potassium sulfate in solution increases, the alum yield was also observed to increase (fig 4.5 referred). The point KC on figure 4.5 represents the yield of alum when crystals of potassium sulfate (43.5g equivalent of 500ml of 0.5M solution) were used directly on the filtrate. This is due to the fact that as the concentration increases, a super saturated environment was created because as solubility

reduces, precipitation increases at the same temperature and pressure (Kirk Othmer, 1997; Perry and Green, 1997, Wikipedia, 2008).

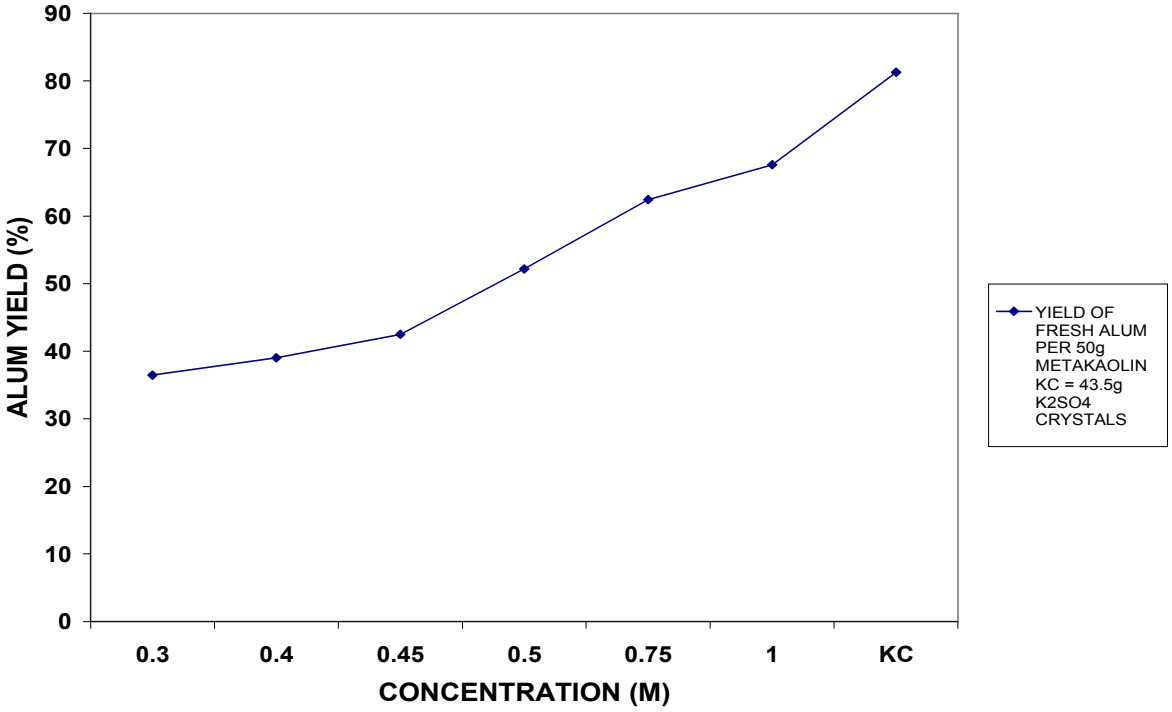


Fig 4.5: Effect of variation of concentration of potassium sulfate solution on alum yield from dealumination filtrate

4.8 **Effect of salting agents on alum quality**

Table 4.4 shows the variation of some oxides in the salted alums. Silica (SiO_2) is interestingly absent in all of these alums as can be observed, confirming the suitability of these alums in public and waste water treatment processes. It was also observed that at the drying conditions, the alums (particularly soda, potash and ammonia alums) puffed or swelled (as shown in Plate I-III) after loosing their water of crystallization (Kirk Othmer, 1997), this property accounts for soda alum's application in baking powder production. The soda, potassium and ammonium alums showed a loss in weight of 47.38%, 46.64% and

47.88% respectively when heated at 250^0C for 6 hours, which are in agreement with literature (Kirk Othmer, 1997).

Table 4.4 Variation of oxides with salting agents

	OXIDES (WT %)					
SALTING AGENTS	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**MgO**	**Na_2O**
NONE	ND	ND*	0.195	0.125	0.275	0.130
Na_2SO_4	ND	0.0345	0.335	0.195	0.185	12.022
C_2H_5OH	ND	0.140	0.210	0.185	0.400	0.135
$(NH_4)_2S0_4$	ND	0.185	0.215	0.260	1.690	0.115
K_2SO_4	ND	23.300	ND	0.210	0.445	0.090

*ND=Not detectable

The ferric content of the produced alums is significantly low making it desirable and suitable for metallurgical applications and for water treatment (0.5% Fe max. Acquah et al, 1978; Harrison, 2004).



Plate I: Puffed Ammonia Alum



Plate II: Puffed Potassium Alum



Plate III: Puffed Soda Alum

4.8.1 **Potassium alum**

Table 4.4 reveals that the potassium alum obtained from Kankara kaolin is suitable for making pure alumina for refractory and catalytic applications and for the metallurgical industry in the production of aluminum metal, as the potassium will serve as a fluxing agent by reducing the melting point of the alumina ore, enhancing the separation of the aluminum metal by any of the processes chosen (Peters et al, 1974, Answers.com, 2008). Table 4.5 also shows that variation in the concentration of the potassium sulfate solution has little or no impact on the quality of the alum obtained. The presence of some of the metal oxides in this alum may not be unconnected with the ability of potassium to form complexes with the respective metal. For example, potassium can combine with iron to form iron alum; $KFe(SO_4)_2.12H_2O$ (Kirk Othmer, 1997). Plate IV shows photographs of potassium alum of well defined crystal structure obtained from Kankara kaolin. Thus, the suitability of Kankara kaolin for the production of commercial and analytical grade alums cannot be overemphasized as have already been alluded to by previous investigators.

Table 4.5: Effect of concentration of K_2SO_4 solution on alum quality.

	OXIDES IN WT %								
CONCENTRATION (M)	**Al_2O_3**	**SiO_2**	**SO_3**	**K_2O**	**CaO**	**Fe_2O_3**	**MgO**	**CuO**	**Na_2O**
0.30	14.01	ND	58.86	23.00	ND	0.13	0.24	0.06	0.14
0.40	14.00	ND	60.98	22.80	ND	0.20	0.28	0.06	0.15
0.45	12.01	ND	60.90	23.40	ND	0.19	0.18	0.06	0.12
0.50	12.09	ND	60.01	23.20	ND	0.23	0.23	0.06	0.10
0.75	14.00	ND	59.10	23.50	ND	0.18	0.25	0.06	0.11
1.00	14.00	ND	59.08	23.50	ND	0.17	0.25	0.06	0.11



Plate IV: Photograph of Potassium Alum Crystals from Kankara Kaolin.

4.9 **Effect of ammonium salts on alum yield and quality**

Fig 4.6 shows the variation in alum yield when different salts of ammonia were used in obtaining ammonium alum. 2 volume of 20wt % ammonia solution (hydroxide) per volume of dealumination filtrate, 500 ml solution of 0.5M ammonium sulfate (this solution contains 33g ammonium sulfate) and 33g of ammonium sulfate crystals were used as salting agents. It was observed that rapid nucleation occurred when the ammonia solution was added to the filtrate and cooling was not needed at all. This must have resulted from the formation of

ammonium sulfate and ammonium alum. The alumina yield is observed to be lower because of the difficulty in handling ammonia solution, mixing was really difficult as ammonia gas (with its pungent and choking smell) was continuously been given off from the solution, hence the process was carried out in a fume chamber. The highest yield was obtained when the ammonium sulfate crystals were used directly. The difference in alum yield between the use of ammonium sulfate solution and the crystals was due to the level of saturation arising from the concentration of the various resulting solutions. Though both contain the same mass of ammonium sulfate, the solution from the crystals (i.e. filtrate + crystals) is more concentrated and hence more saturated. This condition increases the amount of alum crystals precipitated under the same condition (Cheresources.com, 2008). It can also be observed that the alum from the direct crystal salting is of a higher quality than the others, particularly with regards to the MgO content (table 4.6 referred).

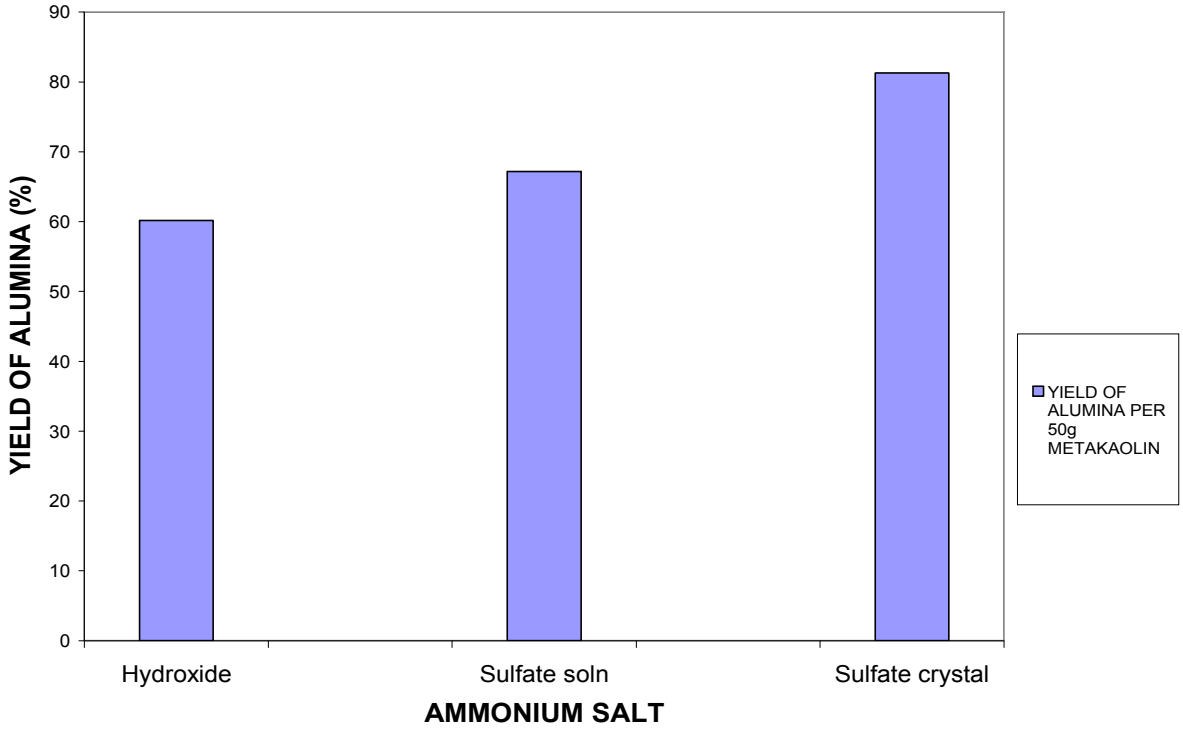


Fig 4.6 Variation of alum yield with ammonium salts

Table 4.6 Variation of the quality of ammonium alums

AMMOINIUM SALTS	Al_2O_3	SiO_2	SO_3	K_2O	CaO	Fe_2O_3	MgO	CuO	Na_2O	NiO
Hydroxide	7.33	0.34	87.63	0.09	0.23	0.265	0.755	0.07	0.125	0.0075
Sulfate solution	17.20	ND	73.21	0.185	0.215	0.260	1.69	0.055	0.115	ND
Sulfate crystals	17.80	ND	74.60	O.13	0.20	0.23	0.44	0.08	0.18	ND

The ease of preparation of ammonium alum by doping the dealumination filtrate with ammonium sulfate crystals coupled with the enhanced quality as observed makes this method preferred to the other ammonium salting methods for alum production from Kankara kaolin. This alum also meets commercial requirements for water treatment purposes (Acquah et al, 1978), for alumina production for catalytic and refractory applications (Richardson, 1992; Steven et al, 2008; Haznan et al, 2008).

4.10 **Effect of scale-up on alum yield**

Fig 4.7 shows the yields of alum obtained when different amounts of metakaolin were separately dealuminated at the same condition in a scale-up attempt. It was observed that as the mass of metakaolin increased per batch, the yield of alum also increased. This can be explained as a consequence of the higher amount of energy available for the reaction, since it is known to be endothermic (Aderemi and Oludipe, 2001; Aderemi et al, 2001). This energy is supplied by the exothermic heat of hydration of sulfuric acid as it mixes with the water-metakaolin suspension. This observation is somewhat at variance with the usual experience in the chemical process industries, which shows that as a process is scaled up, the relative yield/conversion reduces due to problems of local overheating, improper mixing e.t.c. These problems where absent in this scale up owing to the fact that the mixing of the acid with water generated much heat sufficient to effect both stirring of the mixture and

provide for the heat of reaction and consequently results in enhanced yield/conversion. This is also corroborated in fig 4.8.

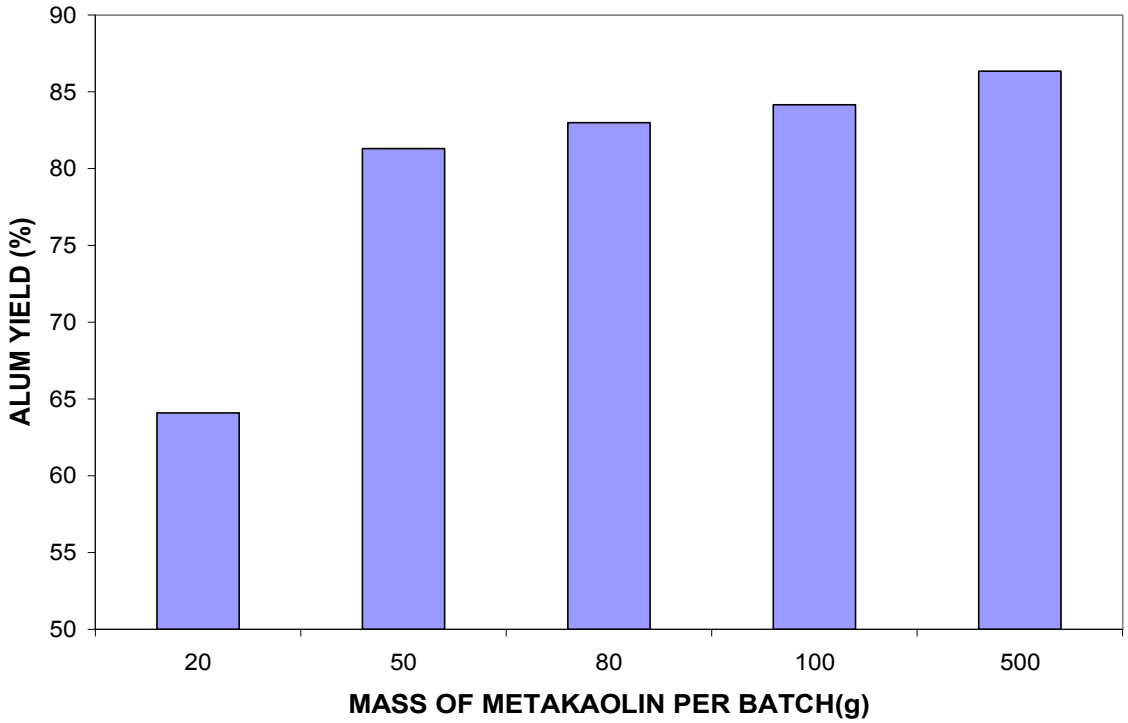


Fig 4.7 Variation of alum yield with mass of metakaolin per batch

Fig 4.8 shows the variation of alum yield with quantity of acid used per batch for the dealumination of 100g metakaolin. It was observed that as the quantity of acid (see appendix A) increased per batch for a fixed amount of metakaolin, the alum yield increased. But when the cost of acid is of importance and considering the cheap cost of kaolin in Nigeria, the 2 folds acid quantity will be preferred particularly in a scaled up process.

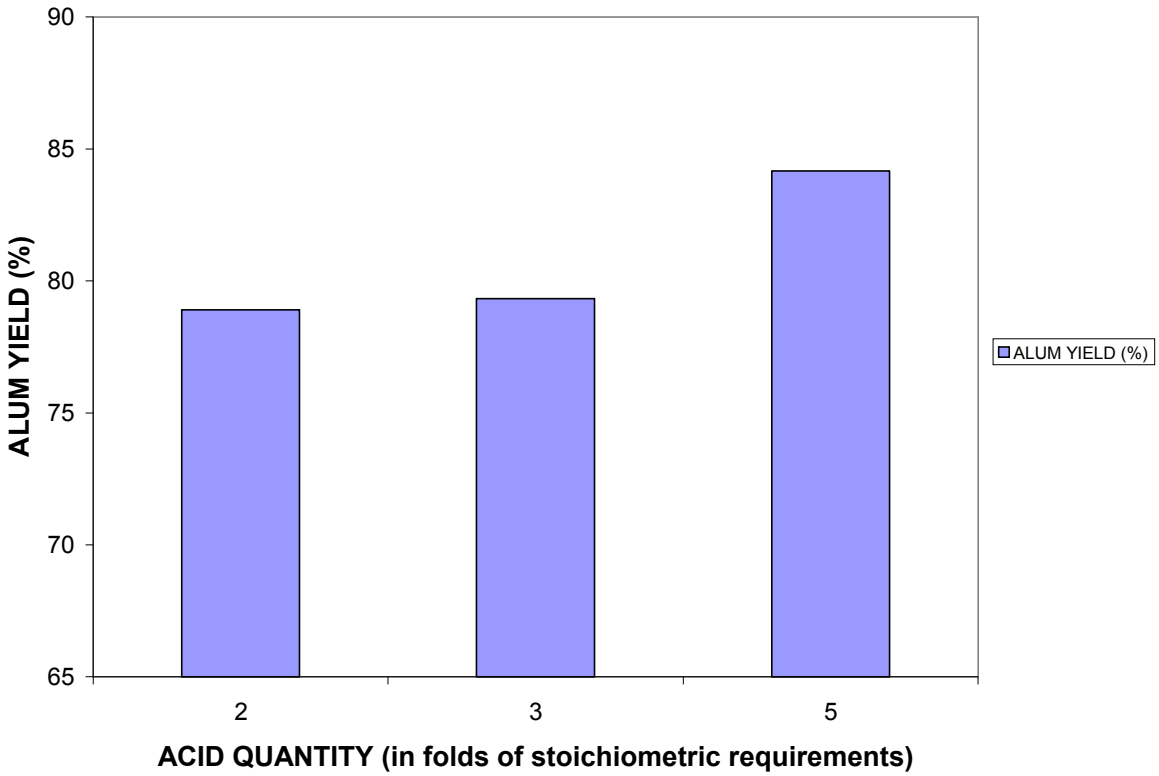


Fig 4.8 Variation of alum yield with the quantity of acid

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be drawn from the results of this work:

1. 0.91kg of fully beneficiated Kankara kaolin was obtained per kg of raw Kankara kaolin, while 0.8585kg of metakaolin was obtained per kg of beneficiated kaolin that was calcined at 750^0C for 2 hours.
2. Metakaolin with silica to alumina ratio of 2 to 1, which is in agreement with literature expectation, was produced by the beneficiation of Kankara kaolin.
3. Silica-free alums were produced from Kankara kaolin.
4. The yield of alum obtained from fully beneficiated Kankara kaolin was found to be 8.38% higher than that from the raw kaolin.
5. The quality of the alum from the fully beneficiated kaolin was found to be 85.97% higher than that from the raw kaolin in terms of their magnesium oxide content.
6. The use of salting agents was found to increase the yield of alum from the dealumination filtrate of Kankara kaolin by about 53.72%, and that the highest yield of 81.30% was obtained when ammonium and potassium sulfate crystals were separately added directly to the dealumination filtrate.
7. It was found that using only the heat of dissolution of acid in water for the dealumination of Kankara kaolin, an alum recovery yield of about 81.30% was obtained in comparison with 87.36% when extra heat from oil bath at 100^0C for

three hours was used, while 85% alum recovery was reported by Aderemi (2002) using heat from oil bath at 100^0C.

8. Ammonium alum, soda alum, potassium alum were produced from Kankara kaolin.
9. As the concentration of the potassium sulfate solution increased, the yield of alum was found to also increase, and well defined potassium alum crystals were also produced.
10. The assay of alums obtained from the open market compared more directly with the samples from unbeneficiated/raw kaolin in this investigation.
11. Need for beneficiation cannot be based on yes or no basis because the specific requirement dictates the level/extent of beneficiation to employ.
12. In a scale up attempt to test the efficacy of the results, 50g, 80g, 100g and 500g of metakaolin were each dealuminated per batch and an alum yield of 81.30%, 83.00%, 84.16% and 86.35% respectively were observed.
13. In a mini-optimization attempt, 2 folds, 3folds, and 5folds acid quantity were each used for dealumination and alum yields of 78.90%, 79.33% and 84.16% respectively, were observed.
14. 8.0kg of ammonium and potassium alum was produced from the scale up attempt.

5.2 Recommendations

It is recommended that to fully develop this process, the following should be carried out:

1. Other kaolin sources in Nigeria apart from Kankara should be investigated for their suitability for producing alum for different applications
2. A pilot plant for the production of alum from Kankara kaolin should be designed and constructed, to enable proper optimization of these processes.
3. The research for the full development of these processes should be adequately funded to enable a speedy delivery.
4. Facilities for online and real-time analysis should be procured to enhance speedy analysis and development.
5. The synergetic effect in catalysis of the oxide impurities in the alums and hence in alumina from Kankara kaolin should be investigated.

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APPENDIX A

Calculations for stoichiometric quantity of acid and amount of water of dilution of filtrate prior to crystallization are presented in this appendix

The basic dealumination equation is:

$Al_20_3(s) + 3H_2SO_4\ (aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$

102g 3 x 98g

Basis: 50g metakaolin

From XRF analysis metakaolin contains 41.1wt% Al_2O_3

50g metakaolin contains 41.1% x 50g Al_2O_3 = 20.55g

From stoichiometry

102g Al_2O_3 requires 294g.100% H_2SO_4

20.55g requires $\frac{20.55 \text{ x } 294g}{102} = 59.232g\ H_2SO_4$

Amount of 96% H_2SO_4 Required = $100 \text{ x } \frac{59.232g}{96} = 61.7g$

ρ_{96} @ 30°C = 1.826gcm^{-3}

$\therefore V_{98} = \frac{M_{98}}{\rho_{98}} = \frac{61.70}{1.826} = 33.7897cm^3$

5 fold stoichiometric quantity = 5 x 33.8825cm^3 = 168.9485cm^3

To dilute this to 60 wt% H_2SO_4

$60\rho_{60} V_{60} = 98\rho_{96}V_{96}$

= $326.887cm^3$

Amount of water to be added to dilute to 60%

$V_w = \frac{\rho_{60}V_{60} - \rho_{96}V_{96}}{\rho_w} = \rho_{60}V_{60} - \rho_{98}V_{98}$

Since ρ_w is taken as 1 gcm^{-3}

V_w = 1.510 x 326.887 - 1.826 x 168.9485 = 185.1scm^3

Pre-Crystallization Dilution

Prior to Crystallization, the filtrate from dealumination was diluted with water to simulate ≅ 38 wt% original sulfuric acid (i.e as if diluting 96 wt% to 38 wt%. This was done to depress the freezing point of the excess sulfuric acid.

$$V_{38} = \frac{60\rho_{60}V_{60}}{38\rho_{38}} = \frac{60 \times 1.51 \times 326.882}{38 \times 1.2780} = 609.824cm^3$$

Water added

$V_w = \rho_{38}V_{38} - \rho_{60}V_{60} = 1.278 \times 609.824 - 1.51 \times 326.882$

$= 285.764cm^3$

Appendix B

Calculations for reaction yields and Crystallization yields are presented in this appendix.

During the conversion of beneficiated kaolin to metakaolin at 750^0C for two hours, 56.6957g of beneficiated kaolin gave 48.675g metakaolin.

$$\% \text{ loss in weight} = \frac{56.6957 - 48.675}{56.6957} \times 100 = 14.147\%$$

The silica/ alumina mole ratio metakaolin is calculated as; (SiO_2 = 48.00wt%,

Al_2O_3 = 41.1wt %)

$$\frac{48.0}{60} \Big/ \frac{41.1}{102} = 1.9854$$

From the elemental analysis, the metakaolin contains 41.1wt % Al_2O_3, using 50g metakaolin as basis; amount of alumina present is given by 41.1 × 50 = 20.55g

185.4856g of fresh ammonium alum obtained after crystallization, when dried at 250^0C for 6 hours gave 93.8491g. This represents $\frac{185.4856 - 93.8491}{185.4856} \times 100 = 49.40$ % loss.

From the elemental analysis of the dried alum, it contains 17.80wt % alumina

Hence the amount of alumina in the alum is given as 0.1780 × 93.8491 = 16.7051g

The percentage yield of alumina by the ammonium alum is given as

$$\frac{16.7051}{20.55} \times 100 = 81.29\%$$

Table B1: Alum yield from heat of dealumination

Heating time in oil bath (hrs)	Mass of fresh ammonium alum (g)	Alum yield (%)
0	185.4856	81.29
1	185.654	81.36
2	188.7694	82.76
3	199.3434	87.36

Table B2: Alum yield from extent of beneficiation

Extent of beneficiation	Weight of fresh alum (g)	Yield of alum (%)
Raw kaolin	166.3608	72.91
Day 1 of soaking	166.124	72.81
Day 2 of soaking	167.1202	73.24
Day 3 of soaking	174.547	76.50
Sieved kaolin (S)	180.9031	79.28
Fully beneficiated kaolin (B)	185.4856	81.29

Table B3: Alum yield from salting agents

Salting agents	Wt of dried alum (g)	Wt % Al_2O_3	Wt of Al_2O_3 (g)	Alum yield (%)
NONE	40.8189	18.94	7.7309	37.62
Na_2SO_4	55.9707	14.01	15.3869	74.88
C_2H_5OH	71.8188	20.56	14.7693	71.87
$(NH_4)_2SO_4$	80.30	17.2	13.8113	67.21
K_2SO_4	82.10	13.09	10.7223	52.18

Table B4: Alum yield from ammonium salts

Ammonium salts	Wt of dried alum (g)	Wt % Al_2O_3	Wt of Al_2O_3 (g)	Al_2O_3 yield (%)
Hydroxide	93.124	8.36	12.3607	60.15
Sulfate solution	80.30	17.20	13.8113	67.21
Sulfate crystals	93.8491	17.80	16.7051	81.29

APPENDIX C

The calculation for the preparation of the solutions of the salting agents is presented here.

The reaction between ammonium sulfate and aluminum sulfate in the presence of water to give ammonium alum is given as;

$$(NH_4)_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow \underset{\text{Ammonium alum}}{(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O}$$

Molar masses: 132g 342g

But 342g of $Al_2(SO_4)_3$ contains 102g of Al_2O_3, which requires 132g of $(NH_4)_2SO_4$.

For 50g metakaolin, 20.55g Al_2O_3 will require $\frac{20.55 \times 132}{102} = 26.594g$ ammonium sulfate crystals.

1M solution of $(NH_4)_2SO_4$ contains 132g in 1000ml of water

0.5M solution contains 33g in 500ml of water

This 0.5M solution of ammonium sulfate was used for the salting which contains 19.41% excess of the stoichiometric ammonium sulfate required. This excess helps to make up for possible side reactions.