

ALUM FROM KAOLIN:  
PRODUCTION, ANALYSIS AND QUALITY STUDIES

BY

ADESINA, OLALEKAN BABATUNDE *B.Sc. (HONS)CHEMISTRY 1990*

A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, AHMADU  
BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILMENT OF THE  
REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF  
SCIENCE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY  
FACULTY OF SCIENCE  
AHMADU BELLO UNIVERSITY  
ZARIA-NIGERIA

FEBRUARY 1999

## DECLARATION


I hereby declare that this thesis contains the report of my research work and has not been presented in any previous application for a higher degree. All information from other sources are specifically acknowledged by means of references.




ADESINA, OLALEKAN BABATUNDE  
FEBRUARY, 1999.

## CERTIFICATION


This thesis entitled "ALUM FROM KAOLIN : PRODUCTION, ANALYSIS AND QUALITY STUDIES". By ADESINA, OLALEKAN BABATUNDE, meets the regulations governing the award of the degree of M.Sc. ANALYTICAL CHEMISTRY of Ahmadu Bello University and is approved for its contribution to scientific knowledge and literary presentation.

  
 DR. J. J. BONIRE  
 B.Sc., M.Sc., Ph.D  
 CHAIRMAN, SUPERVISORY COMMITTEE

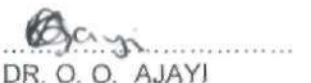
28/8/1999  
 DATE

  
 DR. (MRS) E. B. AGBAJI  
 B.Sc., M.Sc., Ph.D  
 MEMBER, SUPERVISORY COMMITTEE

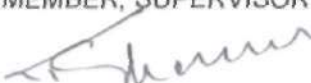
28/8/99  
 DATE

  
 DR. M. O. A. OLADIPO  
 B.Sc., M.Sc., Ph.D  
 MEMBER, SUPERVISORY COMMITTEE

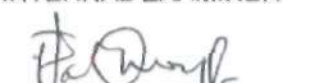
30/8/99  
 DATE

  
 DR. O. O. AJAYI  
 B.Sc., M.Sc., Ph.D  
 MEMBER, SUPERVISORY COMMITTEE

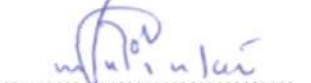
26/08/99  
 DATE

  
 DR. E. J. EKANEM  
 B.Sc., M.Sc., Ph.D  
 INTERNAL EXAMINER

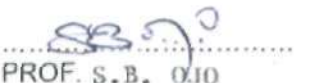
30/8/99  
 DATE

  
 PROF. J. A. A. OWOYALE  
 B.Sc., M.S.P., Ph.D  
 EXTERNAL EXAMINER

25/08/99  
 DATE

  
 DR. J. O. AMUPITAN  
 B.Sc., M.Sc., Ph.D  
 HEAD OF DEPARTMENT

4. 9. 2000  
 DATE

  
 PROF. S. B. OJO  
 B.Sc., Ph.D  
 DEAN, POST GRADUATE SCHOOL

19/02/01  
 DATE

**DEDICATION**

**TO MY WIFE:**

**OLUFUNMIKE**

**WHOSE LOVE AND SUPPORT CAN BEST BE  
DESCRIBED AS THE FAVOUR OF GOD.**

## ACKNOWLEDGEMENT

All glory of the final accomplishment of this work is given to God Almighty, who through His grace enable me to successfully complete this work at a time the natural man would have fainted. He alone should be worshipped.

I wish to thank Dr. J. J. Bonire, Dr. (Mrs.) E. B. Agbaji, Dr. M. O. A. Oladipo, and Dr. O. O. Ajayi who are my Supervisors for their numerous assistance.

I appreciate the assistance and words of encouragement received from Dr. & Mrs. Onaolapo, The Olayinkas, A. A. Abib & family, Mrs. Moji Osinuga, Prof. J. Y. Olayemi, M. O. Awofeye, Ola Audu, Mrs. R. G. Ayo and many others too numerous to mention.

Worthy of appreciation also are my parents, Mr. And Mrs. L. O. Adesina, whose support, love and care to me are far more precious than silver.

I am also grateful to Dr. John O. Adigun who was always close to me during the days the "heat" was at its peak.

For the academic and technical assistance received from the management and staff of the Centre for Energy Research and Training, ABU, Zaria, I am grateful.

To the Director/Chief Executive Officer and the management staff of the National Research Institute for Chemical Technology, I am grateful for the opportunity given to me, the financial and material provisions, and for the co-operation I enjoyed. Also I am grateful to the research and technical staff of industrial chemical department of NARICT for their immense contribution.

The expertise of Yetunde Adeniran, Mr. Samuel Ajiboye, Ademola Adigun and all who contributed "sleepless night" in view of the short notice, to type this work is highly appreciated.

Finally, I thank little Oluwatomi Adesina, who sacrificed the fatherly affection he rightly deserved at his tender age so that I can successfully complete this work.

**DEDICATION**

**TO MY WIFE:**

**OLUFUNMIKE**

**WHOSE LOVE AND SUPPORT CAN BEST BE  
DESCRIBED AS THE FAVOUR OF GOD.**

## ACKNOWLEDGEMENT

All glory of the final accomplishment of this work is given to God Almighty, who through His grace enable me to successfully complete this work at a time the natural man would have fainted. He alone should be worshipped.

I wish to thank Dr. J. J. Bonire, Dr. (Mrs.) E. B. Agbaji, Dr. M. O. A. Oladipo, and Dr. O. O. Ajayi who are my Supervisors for their numerous assistance.

I appreciate the assistance and words of encouragement received from Dr. & Mrs. Onaolapo, The Olayinkas, A. A. Abib & family, Mrs. Moji Osinuga, Prof. J. Y. Olayemi, M. O. Awolaye, Ola Audu, Mrs. R. G. Ayo and many others too numerous to mention.

Worthy of appreciation also are my parents, Mr. And Mrs. L. O. Adesina, whose support, love and care to me are far more precious than silver.

I am also grateful to Dr. John O. Adigun who was always close to me during the days the "heat" was at its peak.

For the academic and technical assistance received from the management and staff of the Centre for Energy Research and Training, ABU, Zaria, I am grateful.

To the Director/Chief Executive Officer and the management staff of the National Research Institute for Chemical Technology, I am grateful for the opportunity given to me, the financial and material provisions, and for the co-operation I enjoyed. Also I am grateful to the research and technical staff of industrial chemical department of NARICT for their immense contribution.

The expertise of Yetunde Adeniran, Mr. Samuel Ajiboye, Ademola Adigun and all who contributed "sleepless night" in view of the short notice, to type this work is highly appreciated.

Finally, I thank little Oluwatomi Adesina, who sacrificed the fatherly affection he rightly deserved at his tender age so that I can successfully complete this work.

## ABSTRACT

Alums have been produced from kaolin clay using two processes of production: the base leached process and the acid leached process. Kaolin clay which has some quantity of potassium in it as part of its constituent members gave alum samples that have above the stoichiometric value of 8.23% in it.

The base leached process gave a yield of  $29.20 \pm 1.07\%$  of alum using the raw kaolin and  $31.87 \pm 1.13\%$  of alum using calcined kaolin clay. Also, the acid-leached process gave a yield of  $47.35 \pm 1.64\%$  of alum using raw kaolin and  $59.47 \pm 1.32\%$  of alum using the kaolin clay

Kaolin was blended with aluminium rich material such as alumina ( $Al_2O_3$ ) and aluminium scraps to bring the quantity of the potassium in the alums to the stoichiometric values.

X-ray fluorescence technique was used for the elemental analysis of the alums. This technique is good for analysing solid samples without having to solubilise them.

The coagulative activities of the produced alums and the commercially available alums were assessed using both domestic water and tannery waste water samples.



## TABLE OF CONTENTS

	Page
Title Page	i
Declaration	ii
Certification	iii
Dedication	iv
Acknowledgement	v
Abstract	vi
Table of Contents	vii
Abbreviations	x
<b>CHAPTER ONE</b>	<b>1</b>
1.0 Introduction	1
1.1 Alums	1
1.2 Uses of alums	1
<b>CHAPTER TWO</b>	<b>4</b>
2.0 Literature Review	4
2.1 Alums and their raw materials	4
2.2 Analysis of alums	5
2.3 Radionuclide X-ray fluorescence analytical technique	5
2.3.1 X-ray fluorescence methods	6
2.3.2 Physical Background	6
2.3.3 Analytical Principle	7
2.4 Basic experimental technique	8
2.4.1 Excitation of fluorescence X-rays	8
2.4.2 Detection of fluorescence X-rays	8
2.4.2.1 Scintillation detectors	8
2.4.2.2 Proportional counters	9
2.4.2.3 Solid state detectors	9
2.4.3 Energy selection	9
2.4.4 Techniques for minimising interference	10
2.4.4.1 Matrix effects	10
2.4.4.2 Heterogeneity effects	11

2.4.4.2	Heterogeneity effects	11
2.4.5	Determination of individual elements	11
2.5	Alums: Their Chemistry and mode of action	13
2.5.1	Hydrolysing action of aluminium metal	14
2.6	Quality test on alums	15
	<b>CHAPTER THREE</b>	<b>16</b>
3.0	Materials and methods	16
3.1	Sample collection	16
3.2	Sample pre-treatment	16
3.3	Determination of aluminium from kaolin	17
3.4	Preparation of alum samples	17
3.4.1	From kaolin clay	18
3.4.1.1	Base-leached process	18
3.4.1.2	Acid-leached process	18
3.4.2	From calcined kaolin	19
3.4.3	From aluminium scraps	19
3.4.4	From Isan and Ara clays	20
3.4.5	From modified raw material	20
3.4.5.1	From kaolin mixed with alumina	20
3.4.5.2	From kaolin mixed with aluminium scraps	21
3.5	Elemental, sulphate ion and water content of the alum samples	21
3.5.1	Determination of aluminium in the alum samples	22
3.5.2	Determination of sulphate ion in the alum samples	23
3.5.3	Determination of potassium in the alum samples	23
3.5.4	Determination of total water content	24
3.6	X-ray fluorescence (XRF) analysis	24
3.6.1	Sample preparation for XRF	24
3.6.2	Instrumentation	24
3.6.3	Measurements	25
3.6.4	Precision and accuracy	26
3.7	Coagulative properties of alum samples	27
3.7.1	The Jar test	27

3.7.2	Turbidity	28
3.7.3	Electrical conductivity	28
3.7.4	Alkalinity	29
3.7.5	pH	29
	<b>CHAPTER FOUR</b>	<b>30</b>
4.0	<b>Results and measurement</b>	<b>30</b>
4.1	Preparation of alum samples	30
4.2	From Isan and Ara clays.	31
4.3	Analysis of the samples	31
4.3.1	Standardisation of the XRF equipment	31
4.3.2	XRF analysis of kaolin	32
4.3.3	XRF analysis of Isan and Ara clays	32
4.3.4	The aluminium content of kaolin	32
4.4	Composition of the prepared alum samples	33
4.4.1	Alums from kaolin and aluminium scraps	33
4.4.2	Results of the compositional analysis of alums prepared from mixed raw materials	34
4.5	XRF analysis of both prepared commercial alums	35
4.5.1	Alums produced from kaolin mixed with alumina	36
4.5.2	Alums produced from kaolin mixed with aluminium scraps	37
4.6	Coagulatives properties of the alum samples	37
	<b>CHAPTER FIVE</b>	<b>40</b>
	Conclusion and suggestion for further work	40
	References	42
	Appendix	46

## ABBREVIATIONS

Abbreviation	Meaning
XRF	X-ray fluorescence
PVC	Polyvinyl chloride
AOAC	Association of Official Analytical Chemists
CERT	Centre for Energy Research and Training
ppm	Parts per million
KC1	Kaolin clay sample 1
KC2	Kaolin clay sample 2
KC3	Kaolin clay sample 3
KC4	Kaolin clay sample 4
ISWT	Isan clay (white)
ISBK	Isan clay (black)
ISRD	Isan clay (red)
ARWT	Ara clay (white)
ARBK	Ara clay (black)
ARRD	Ara clay (red)
BLKA	Base-leached kaolin alum
BLKA (C)	Based-leached kaolin (calcined) alum
ALKA	Acid-leached kaolin alum
ALKA (C)	Acid-leached kaolin (calcined) alum
TT1A	Toothpaste tube alum
CSI	Federal superphosphate alum
CS2	Lagos drury alum

## CHAPTER ONE

### 1.0 INTRODUCTION.

#### 1.1 ALUM

In the context of this work alum is a dodecahydrate double sulphate of aluminum and either potassium, sodium, chromium or ammonium. A fifth common alum is ammonium ferric sulphate dodecahydrate (Anderson and Bobbin, 1971).

Potash alum  $KAl(SO_4)_2 \cdot 12H_2O$

Soda alum  $NaAl(SO_4)_2 \cdot 12H_2O$

Ammonium alum  $NH_4Al(SO_4)_2 \cdot 12H_2O$

Chrome alum  $KCr(SO_4)_2 \cdot 12H_2O$

Ferric alum  $NH_4Fe(SO_4)_2 \cdot 12H_2O$

They are formed by mixing hot concentration of their component sulphate; the resulting solutions are cooled and the solid alum, being less soluble than their component sulphate, crystallises out.

#### 1.2. USES OF ALUM

The uses of alum are many and varied. They are majorly used as coagulant for suspended dirt in water in the purification of water for town use, as astringent and bactericide (Mokuhara, 1968; Liptrot, 1985), sizing of paper and dyeing of fabrics (Whitney *et al.*, 1978), tanning of leather (Polyakar *et al.*, 1982; Klockemkamper *et al.*, 1992), hardening of plaster of Paris and in fire extinguishers and locally for cleaning slimy sludge and materials. For water treatment alone in Nigeria, the big municipalities like

Ibadan and Kano are spending 42 and 65% of their annual recurrent costs respectively, on water supply (Salako and Akinola, 1989).

Due to the large consumption of alum in Nigeria, an inward look towards its local production from available local raw materials has become necessary towards conservation of foreign exchange.

Alums have been reportedly made in commercial quantities from bauxite and alum shale (Kirk Othmer, 1992). In Nigeria, the alum produced by the National Fertilizer Company at Kaduna is from alumina (aluminum oxide) which is imported into the country (National Superphosphate and Fertilizer Company, Kaduna, 1998).

In Nigeria, Kaolin exists rather abundantly as a solid mineral (Lee, 1981; Austen, 1984). Deposits have reportedly been found in Kankara in Katsina state, Ifon in Ondo state, Aiyetoro in Ogun state, Nfamosin in Cross Rivers state and some parts of Kaduna state. It is primarily an aluminum silicate ( $\text{Al}_2\text{Si}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ ) (Lee, 1981; Austen 1984), and is a raw material for the manufacture of ceramics, pharmaceutical tiles and refractory bricks.

The pivot of this work was therefore the production of alum from kaolin and alum thus produced would have to be analysed for its constituents side by side commercially used alums.

Scraps of aluminum metal litter the streets of many towns in Nigeria. Another idea of this work was to find a more profitable use for these scraps of aluminum metal, e.g. the production of alum.

Alums are usually produced by direct reaction of the clay after purification with

sulphuric acid. The acid is a by-product in fertilizer production in Nigeria. This project was designed with that in view.

Methods of analysis of alums are many and varied, but the XRF method, from available literature, has not been used before. It is a method that analyses solids directly without having to solubilize the solids. Thus it is most likely to give the most reliable results of the elemental components of the sample. This project was therefore, designed to make use of the XRF method in studying the samples of alum synthesized. Thereafter, the coagulative properties of the alums would need to be compared with alums available in the market.

**The aim of this project therefore can be summarized thus:-**

- 1) development of methods of synthesis of alum from kaolin and possibly scrap aluminum metal.
- 2) Elemental analysis of the samples of alum so produced and
- 3) A qualitative study of the properties including coagulative ability of the alums.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 ALUMS AND THEIR RAW MATERIALS

From the available literature, the raw materials for the production of alum are not many. Bauxite has been a common raw material (Carl E. Skay, 1963). Aluminum containing clays have also been used (Walter C. Saeman, 1964). "Al -ashes" from the aluminum industry have also been used (Stefan Wiatrowski, 1955). The alum manufacturing company at Kaduna Nigeria uses alumina (Federal superphospahte and fertilizer company, Kaduna, 1998) while Kagbu (M. Sc. Thesis, 1988) has reported the synthesis of alum from kaolin using an undisclosed process.

Apart from these not many other raw materials appear to have been reported for the synthesis of alum from available literature.

By definition, alums are supposed to be double salts of an alkali metal and aluminum sulphate. In the context of this work however, ammonium aluminum sulphate dedecahydrate has also been classified as an alum (Anderson and Robbin, 1971). The Federal superphosphate and fertilizer company at Kaduna produces single salt aluminum sulphate and sells it as alum. And since that performs the functions of alums, it appears that the activity of alums largely depends on the aluminum sulphate content.

The process of producing alum from bauxite involves first roasting the bauxite and separation of the iron content before treatment with sulphuric acid (Stefan Wiatrowski, 1955). Since alums are partially or completely sulphates of aluminum, a direct reaction of the raw material with sulphuric acid at one stage or another is common to all methods of



preparing alum (Stefan Wiatrowski, 1955; Carl E. Skay, 1963; Walter C. Saeman, 1964; Kolawole *et al.*, 1986).

## 2.2 ANALYSIS OF ALUMS

The study of the elemental content of alums has been diverse. According to Kenner and O'Brien, 1971, atomic absorption spectrometry can be used to analyse the constituents that occur in traces in alums, while gravimetric method was used for the determination of aluminium, iron and silica which occur substantially in alums.

Kagbu (1988), also reported the use of atomic absorption spectrometry and gravimetric method for the determination of trace elements and major constituents of alums respectively.

However, the use of X-ray fluorescence technique for the study of the elemental components of alums does not appear to be common.

## 2.3. RADIONUCLIDE X-RAY FLUORESCENCE ANALYTICAL TECHNIQUE

Radionuclide X-ray fluorescence analysis is one of a number of X-ray spectrometric techniques available for determination of elements in different materials. All forms of X-ray spectrometry involve the bombardment of a sample with radiation of sufficient energy to eject inner shell electrons from the atoms in the sample. The ejected electrons are immediately replaced by electrons from outer shells, with simultaneous emission of X-rays with energies characteristic of the electron transitions (and hence of the elements) responsible for their emission.

### 2.3.1 X-ray fluorescence (XRF) methods

There are two main methods of exploring the quantitative capabilities of XRF technique. The first, which has been used analytically for many years, is wavelength - dispersive method, in which the X-rays from the specimen are highly collimated and dispersed according to the Bragg law by a diffracting crystal, then collected at an angle corresponding to the characteristic wavelength to be measured.

The second method is the energy - dispersive type, in which the X-rays from the specimen are incident on a detector that gives an output charge pulse precisely proportional to the energy of the X-ray absorbed (Bhukhalter, 1971; Clayton and Packer, 1979, Agarwal, 1979).

The main variation in these two methods however is in the different types of excitation radiation that can be employed.

### 2.3.2 Physical Background

The interaction of low-energy photons (100 keV) with matter is mostly photo-electric in nature. Photons of sufficient energy eject electrons, as a rule, from the K shell. The probability of interactions with a K electron is fairly high for photons with energy exceeding the binding energy of the K electron.

When a valency is produced in any of the higher binding energy levels in the electronic structure of an atom, an electron from an outer shell fills it. This results in either the emission of an X-ray of energy of the electrons in the two shells involved, or in the emission of an electron from an outer shell (called an Auger electron). The fraction of

vacancies filled in a given shell with accompanying X-ray emission is filled by Auger processes is the Auger yield. (Shenberg *et al.*, 1973).

### 2.3.3 Analytical Principle

Analysis by X-ray fluorescence consists of determining the content of specific elements in a sample by producing vacancies in the electronic structures and analysing the photons emitted as a consequence.

The element from which the photons are emitted may be identified from the energy of the characteristic X-rays emitted (Agarwal, 1979; Bhurkhalter, 1971). The characteristic X-ray spectrum of the sample consists of individual peaks corresponding to the elements present; the intensity of these peaks is a function of the concentration of the elements.

For analytical purposes the most important radiation is that associated with transitions of electrons to the K shell. For heavy elements, peaks of the L series are also convenient for analysis.

Alpha-, beta-, gamma- and X-ray - emitting radionuclides can all be used for the excitation of characteristic X-rays. However, the most extensively used are X-ray sources.

The necessary condition for occurrence of K or L X-rays is that the energy of exciting radiation is greater than the binding energy of the electron in the K or L shell of the atom excited.

## 2.4 BASIC EXPERIMENTAL TECHNIQUE

### 2.4.1 Excitation of fluorescence X-rays

Alpha, beta and gamma radiation (primary sources) and X-ray and bremsstrahlung (secondary sources) can be used for the excitation of fluorescence X-rays by radionuclides. In energy dispersive X-ray fluorescence spectroscopy, the high excitation efficiency is achieved when the energy of the exciting radiation is restricted to an energy which is just above the absorption edge of the element to be determined (Clayton and Packer, 1979).

### 2.4.2 Detection of fluorescence X-rays

There are three types of detectors most often used for the detection of fluorescence X-rays. These include: scintillation detectors, proportional counters and solid state detectors. Detectors are chosen so that the detection efficiency will be at a maximum for the energy to be determined. Two criteria are used in the choice of the detector for XRF analysis - the detector resolution and the energy interval in which they can be used.

#### 2.4.2.1 Scintillation detectors

Scintillation detectors are used for X-ray energies above 5 keV. The great advantages of scintillation detectors are their simplicity, almost unlimited service life and especially high sensitivity over a wide energy range.

Scintillation detectors are suitable for samples in which not more than four elements are to be determined, the atomic numbers of which differ from one another by at least 7 - 10.

#### 2.4.2.2 Proportional Counters

Proportional counters offer the advantage of higher resolution coupled with an ability to discriminate against back-scattered primary radiation if the correct filling gas is chosen. Argon, xenon, neon, krypton, methane or mixtures of He -CH<sub>4</sub>, Ar - CH<sub>4</sub>, Xe - CH<sub>4</sub>, He - *isobutane* are used as filling gases. These counters can be used as efficient detectors up to X-ray energies of approximately 20 keV, which includes K X-rays from light and medium atomic weight elements and L X-rays of heavy elements.

The good resolving power of proportional counters means that the elements to be detected need differ in atomic number of as little as 2-3.

#### 2.4.2.3 Solid-state detectors

Solid-state detectors of the lithium - rifled silicon type (Si/Li) and also germanium (Langherich *et al.*, 1973), are clearly superior for detection of medium and heavy element K X-rays. The main advantage of these detectors is their ability to collect a complete and well resolved spectrum simultaneously from a wide range of elements in the sample. The solid state detectors have to be cooled with liquid nitrogen while in operation, but this is not considered to be a significant practical drawback. (Papez and Cameron, 1973).

#### 2.4.3 Energy selection

In radionuclide XRF analysis, characteristic peaks of the elements to be determined in the sample and also a number of components of accompanying undesirable radiation are detected. The energy selection is done to improve the resolution of the detecting system, and in this way to increase the specificity and sensitivity of the determination.

The most important techniques for improving the energy selectivity of the detector are:

- i) selection of the radiation sources to obtain high efficiency of excitation of the element to be determined, with minimum of background,
- ii) use of absorption filters which can isolate a fairly narrow energy band,
- iii) choice of detector type,
- iv) electronic pulse - amplitude discrimination by means of single channel or multi-channel analysis.

#### 2.4.4 Techniques for minimizing interference

The precision of radionuclide XRF analysis may be affected by the presence of other elements (matrix effect) and by the particulate nature of the sample (heterogeneity effects).

##### 2.4.4.1 Matrix effect

The absolute value obtained in an XRF determination depends on the correct choice of standards for calibration. Ideally, the standards should be physically and chemically equivalent to the sample. In practice, however, variations in the physical and chemical composition of the sample relative to the standards will give rise to errors, owing to their effect on the intensity of the emitted characteristic X-radiation, unless corrections are applied. This is known as matrix effect (Shenberg *et al.*, 1973; Anderman and Kemp, 1958; Bhurkhalter, 1971).

For a homogeneous specimen there are two matrix effects namely the matrix absorption effect and the matrix enhancement effect.

The matrix absorption effect causes a decrease in the intensity of fluorescence radiation and is due to absorption of the fluorescence radiation by heavy elements in the matrix.

The matrix enhancement effect is due to the enhancement of the relevant fluorescence radiation by the presence of other elements in the matrix e.g. when chromium is determined in steel, the  $K_{\text{peak}}$  of chromium is enhanced by the  $K_{\text{peak}}$  of iron.

A rigorous theoretical treatment of the matrix effects is difficult and no satisfactory theoretical model exists. There are, however, various empirical methods, which often yield acceptable degrees of correction (Wheeler *et al.*, 1976).

#### 2.4.4.2 Heterogeneity effects

In heterogenous systems (powders, slurries, natural samples of minerals and rocks), absorption of X-rays varies from particle to particle, depending on the sizes and mass attenuation coefficient. This means that the resulting intensity of the fluorescence radiation is a function of the particle size and composition.

The heterogeneity effects can be eliminated by fusion, or reduced by fine grinding and by increasing the energy of the exciting radiation (Wheeler *et al.*, 1976).

#### 2.4.5 Determination of Individual elements

The elements determined by radionuclide XRF analysis can be divided into five groups according to their atomic number ( $Z$ ) and the energy of the emitted fluorescence radiation ( $E_f$ ). They are:-

- 1) Light elements ( $z \leq 20$ ;  $E_f < 4 \text{ keV}$ )

- 2) Elements Sc - Zn ( $z = 21 - 30$ ;  $E_f = 4 - 9$  keV)
- 3) Elements Ga - Ba ( $z = 31 - 57$ ;  $E_f = 9 - 33$  keV)
- 4) Lanthanides ( $z = 58 - 71$ ;  $E_f = 33 - 55$  keV)
- 5) Heavy elements ( $z = 71$ ;  $E_f = 55 - 99$  keV)

Characteristic K peaks for the group of light elements have very low energy. Only proportional counters are satisfactory detectors for this low-energy radiation.

Detection of the fluorescence radiation of the elements from scandium to zinc is simple (proportional, scintillation and solid-state detectors) and therefore radionuclide X-ray fluorescence determination is often used for these elements.

Radionuclide XRF analysis is most advantageous for elements of medium atomic number (Ga-Ba). Scintillation detectors are mostly used, but proportional counters and solid - state detectors can also be used.

Radionuclide XRF analysis has not been widely used for the determination of lanthanides, because of the interference of the energies of the characteristic  $K_\alpha$  and  $K_\beta$  peaks in the fluorescence spectra of the individual lanthanides and the insufficient resolving power of the detection system.

The heavy elements can be determined by means of their K or L peaks. Scintillation and solid state detectors are suitable. Some difficulties in shielding the excited radiation of energy about 100 keV are encountered when the fluorescence radiation (K series) heavy elements is excited.



## 2.5 ALUMS: THEIR CHEMISTRY AND MODE OF ACTION.

It has long been established that, when added to water, aluminum and iron salts will react with alkalinity present in water. The reaction was thought to yield the insoluble material of aluminum or ferric hydroxide represented as  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$  (Packham, 1962, Laitinen *et al.*, 1973).

In these reactions an acid was produced which reduced the pH of the solution and consumed alkalinity in approximately the ratio of 1 mg/L of commercial filter alum.

Alum acts as a coagulant in two ways: For most water purification, enough alum is added to precipitate  $\text{Al}(\text{OH})_3(\text{s})$ . This covers the colloids with a gelatinous and sticky sheath. It also provides additional targets for the original solids to hit in the flocculation tank, thereby accelerating the flocculation of the particles into larger aggregates. These targets are necessary in coagulating waters having low turbidity, since excessive process times are needed to aggregate the primary solids alone. This mode of coagulation, in which considerable quantities of aluminum hydroxide are formed, has been termed 'sweep coagulation' (Sanks, 1980).

A second mechanism of coagulation by alum is absorbing positively charged aluminum monomers and polymers on negative colloids, thereby neutralizing the charges on the particles and rendering them sticky or unstable so that aggregates are formed when contacts occur. This type of coagulation can only be used for high turbidity waters. In many cases, less coagulation may be needed than for low turbidity waters, since a precipitate is not needed.

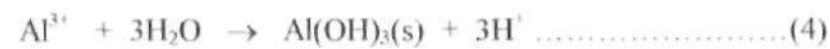
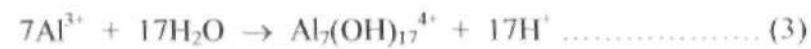
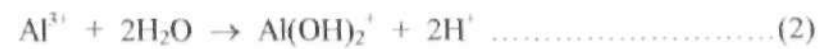
In order to estimate the chemical feed requirements, a minimum dosage of 35 mg/L of alum is necessary for turbidity coagulation but additional alum or acid may be

required to lower the pH (Sanks, 1980).

### 2.5.1 Hydrolyzing action of aluminum metal

Hydrolyzing metal ions such as  $\text{Al}^{3+}$  from aluminum sulphate added to water assist in destabilizing the suspended particles.

When alum is added to water, they dissolve readily. The sulphate ions disperse through out the liquid as  $\text{SO}_4^{2-}$ . The aluminium ion is hydrolysed and is completely surrounded by six water molecules with a net charge of +3. However, under the pH condition used the trivalent metal hydrolyses to form different species.



The ions  $\text{AlOH}^{2+}$  and  $\text{Al(OH)}_2^+$  shown in reactions (1) and (2) are monomers, since each contain only one aluminum atom. Although their charges are less than +3, they are an effective coagulant for negative colloids because they are readily adsorbed on the surface of many solids. Ions such as  $\text{Al}_7(\text{OH})_{17}^{4+}$  may resemble polymers, since they contain several aluminum atoms. Such ions are strongly adsorbed on most negative colloids and are good coagulants.

$\text{Al(OH)}_3(\text{s})$  denotes the solid, amorphous, gelatinous precipitate of aluminum hydroxide that is formed in most coagulation plants. Alum acts as an acid; since protons are liberated into solution in reaction 1 to 4 above.

The aluminum species that are formed when alum is added to water depend primarily on the pH of the water and on the amount of alum added (Sanks, 1980).

## 2.6 QUALITY TEST ON ALUMS

In assessing the quality of alums usually, the turbidity, conductivity, alkalinity and pH of the water treated with the alum are studied (Muyibi *et al.*, 1995).

In this work therefore, the quality of the alums synthesized were assessed along this line side by side samples of alum obtained commercially.

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 SAMPLE COLLECTION

Kaolin clay samples were collected from the kaolin deposit in Kankara, Katsina State.

Clay samples were collected from two villages, Ara and Isan, in Ekiti State.

Toothpaste aluminum collapsible tubes were collected from the refuse dumps around Basawa, Zaria.

Alumina ( $\text{Al}_2\text{O}_3$ ), was purchased from a scientific and Chemicals store in Zaria, Kaduna State.

Alum samples were collected from the Federal Superphosphate and Fertilizer Company, Kaduna, Kaduna State and Drury Chemicals in Lagos, Lagos State for comparison purpose.

#### 3.2 SAMPLE PRE-TREATMENT

All the clay samples were each mixed with large amount of water; the coarse and heavy stones were allowed to settle first, leaving a supernatant of the slurry of the fine particles of the clay. The slurry was carefully decanted and allowed to settle over a period of 24 hours.

The settled clay samples were then transferred into petri dishes, dried in an oven at  $105\text{ }^\circ\text{C}$  and ground to fine powder using an Agate mortar. This procedure ensured adequate homogenisation of the samples.

The toothpaste tubes were cut open and washed thoroughly with water to remove all the dirt and the remaining paste on the wall of the scraps. The coatings on the aluminum scraps were removed using acetone to obtain a paint-free aluminum scrap.

### 3.3 DETERMINATION OF ALUMINUM FROM KAOLIN

A 2.00 g quantity of kaolin was dissolved in 200 cm<sup>3</sup> of water in a 600 cm<sup>3</sup> beaker. About 5.00 g of pure ammonium chloride was added to it and heated just to boiling. Ammonia solution was added to adjust the pH to between 7 and 8. The solution was boiled again for about 2 minutes and filtered at once through a quantitative ashless filter paper and the precipitate was washed thoroughly with a 2 percent solution of ammonium chloride.

The filter paper with the precipitate was placed in a previously weighed and dried platinum crucible, charred and ignited at 1000 °C for 15 minutes (Vogel, 1978). The quantity of alumina obtained was calculated thus:

$$\frac{\text{Weight of residue}}{\text{Weight of sample taken}} \times \frac{100}{1} = \%Al_2O_3.$$

The quantity of aluminum, therefore, was determined by multiplying %Al<sub>2</sub>O<sub>3</sub> by a factor of 0.5292.

### 3.4 PREPARATION OF ALUM SAMPLES

Alum was produced using two processes. They are base leached process and acid leached process. Each of the production process was carried out in triplicates and the percentage yield calculated.

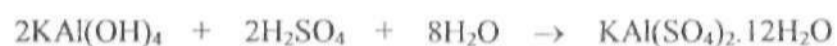
### 3.4.1 FROM KAOLIN CLAY

#### 3.4.1.1 Base-leached process

30.00 g of kaolin was digested in 250 cm<sup>3</sup> portion of 2 mol dm<sup>-3</sup> KOH solution with stirring and heating. This digestion process was for a period of 2 hours in a fume cupboard.



The resulting mixture was filtered to remove the undissolved solid material. Then a 100 cm<sup>3</sup> portion of 9 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution was added to the filtrate. This was later evaporated to  $\frac{3}{4}$  volume and allowed to cool to obtain alum crystals.



The alum crystals were recrystallised in distilled water and the crystals obtained were allowed to dry at 105 °C in an oven.

#### 3.4.1.2 Acid leached process

A 30.00 g of kaolin was digested in 100 cm<sup>3</sup> portion of 9 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution with stirring and heating for a period of 2 hours in a fume cupboard. The mixture was later filtered to remove the undissolved material. Then 250 cm<sup>3</sup> portion of 2 mol dm<sup>-3</sup> KOH solution was added to the filtrate.

This was concentrated to about  $\frac{3}{4}$  volume and allowed to cool to obtain the alum crystal. These crystals were recrystallised in distilled water and the crystals obtained were allowed to dry at 105 °C in an oven.

### 3.4.2 FROM CALCINED KAOLIN

Kaolin was calcined in the furnace at about 860 °C. This was to increase the surface area of the kaolin that is available for reaction. Then 30.00 g quantity of the calcined kaolin was used for the production of alum using both base-leached and acid-leached processes described in sections 3.4.1.1 and 3.4.1.2 respectively.

The percentage yield of alum was calculated using the expression below:

$$\% \text{ Yield} = \frac{\text{Weight of product obtained}}{\text{Expected weight of product}} \times \frac{100}{1}$$

The expected weight of product can then be calculated using the expression.

$$\text{Expected weight} = \frac{\text{Weight of kaolin} \times \% \text{ Al in kaolin} \times \text{Molecular weight of alum}}{\text{Atomic mass of aluminum}}$$

The molecular weight of kaolin [Al<sub>2</sub>(OH)<sub>4</sub>Si<sub>2</sub>O<sub>3</sub>] is 258.16.

$$\therefore \% \text{ Al in kaolin} = \frac{54}{258.16} \times \frac{100}{1} = 20.92\%$$

The molecular weight of alum [KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O] is 474.

$$\text{Therefore, expected yield} = \frac{30 \times 0.2092 \times 474}{27} = 110.18 \text{ g.}$$

### 3.4.3 From Aluminum Scraps

A 10.00 g of aluminum scraps was shredded into 250 cm<sup>3</sup> portion of 2 mol dm<sup>-3</sup> KOH solution and warmed in a fume cupboard to facilitate the dissolution of the scraps. There was effervescence of hydrogen gas during this process.



The resulting mixture was filtered to remove any undissolved component of the scrap. Then a 100 cm<sup>3</sup> portion of 9 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution was added to the filtrate. The mixture was evaporated to ¾ volume and allowed to cool to obtain the alum crystals (Kolawole, *et al.*, 1986; Lambert and Muir, 1976).



These alum crystals were crystallised in distilled water and the crystals obtained allowed to dry in the oven at 105 °C.

The preparation was carried out in triplicate and the percentage yield calculated as follows:

$$\% \text{ Yield} = \frac{\text{Weight of alum obtained}}{\text{Expected weight of alum}} \times \frac{100}{1}$$

The expected weight of alum from 10.00 g of aluminum scrap is:

$$\frac{10 \times 474}{27} = 175.56 \text{ g.}$$

#### 3.4.4 From Isan and Ara Clays

Isan and Ara clays were used for the production of alum using the base leached and acid leached processes described in sections 3.4.1.1 and 3.4.1.2 respectively.

#### 3.4.5 FROM MODIFIED RAW MATERIAL

##### 3.4.5.1 From kaolin mixed with alumina

Different mixture ratios of both kaolin and alumina were used in the production of alum. The weight ratios of kaolin:alumina that were used are:



(i) 20.00 g:10.00 g; (ii) 15.00 g:15.00 g; (iii) 10.00 g:20.00 g and (iv) 5.00 g:25.00 g.

The above mixture ratios of both kaolin and alumina were used to produce alum samples using both the base leached process and acid leached process described in sections 3.4.1.1 and 3.4.1.2 respectively.

#### 3.4.5.2 From kaolin mixed with aluminum scraps

The different weight ratios of kaolin:aluminum scraps that were used to produce alum include:

(i) 30.00 g:1.00 g; (ii) 30.00 g:2.00 g; (iii) 30.00 g:3.00 g and (iv) 30.00 g:4.00 g

The above mixture ratios of both kaolin and aluminum scraps were used to produce alum samples through base leached and acid leached processes described in sections 3.4.1.1 and 3.4.1.2 respectively. But the 30.00 g:4.00g mixture of kaolin:aluminum scraps ratio required 120 cm<sup>3</sup> portion of 9 mol/dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution for the base leached process to produce alum.

However, care was taken not to evaporate the alum liquor to dryness since that would have produced burnt alum and the product may eventually dissociate (Kirk othmer, 1992).

### 3.5 ELEMENTAL, SULPHATE ION AND WATER CONTENT OF THE ALUM SAMPLES.

Alum [KAl(SO<sub>4</sub>)<sub>2</sub> .12H<sub>2</sub>O], which is a double salt (Wade and Banister, 1973) contains its compositional elements and the water of crystallization in stoichiometric quantity. The stoichiometric values of these elements are thus calculated as follows :

Molecular Mass of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} =$

$$39 + 27 + (96 \times 2) + (18 \times 12) = 474$$

$$\therefore \text{The concentration of K} = \frac{39}{474} \times \frac{100}{1} = 8.23\%$$

$$\text{Al} = \frac{27}{474} \times \frac{100}{1} = 5.70\%$$

$$\text{SO}_4^{2-} = \frac{192}{474} \times \frac{100}{1} = 40.51\%$$

$$\text{H}_2\text{O} = \frac{216}{474} \times \frac{100}{1} = 45.57\%$$

### 3.5.1 Determination of Aluminum in the Alum Samples

#### *Reagents Preparation*

##### **Preparation of 0.01 mol dm<sup>-3</sup> aluminum ion solution**

About 1.185 g of the Alum sample was accurately weighed and dissolved in distilled water in 250 cm<sup>3</sup> volumetric flask and was made up to mark with distilled water.

##### **Preparation of 0.01 mol dm<sup>-3</sup> EDTA solution**

1.40 g of the disodium salt of ethylenediaminetetraacetic acid was dissolved in distilled water in a 500 cm<sup>3</sup> volumetric flask and shaken very well. Then distilled water was added to make up to 500 cm<sup>3</sup> mark.

##### **Preparation of 0.01 mol dm<sup>-3</sup> zinc sulphate solution**

A 1.61 g quantity of zinc sulphate was dissolved in distilled water in a 1 dm<sup>3</sup> volumetric flask and shaken to dissolve. Distilled water was added to make up to 1 dm<sup>3</sup> mark.

**Procedure:**

A 25.00 cm<sup>3</sup> portion of 0.01 mol dm<sup>-3</sup> aluminum ion solution each of the alum samples was taken in a clean conical flask and a slight excess of 0.01 mol dm<sup>-3</sup> EDTA solution added. The pH was adjusted to between 7 and 8 with ammonia solution. The solution was then heated to ensure complete complexation of the aluminum, and was later allowed to cool. The pH of the solution was, once again, adjusted to between 7 and 8 and later titrated against 0.01 mol dm<sup>-3</sup> ZnSO<sub>4</sub> solution using Eriochrome Black as indicator.

The colour changed from blue to wine red at the end point. Every cubic centimetre difference between the volume of 0.01 mol dm<sup>-3</sup> ZnSO<sub>4</sub> solution used in the back titration corresponds to 0.2698 mg of aluminum (Vogel, 1971).

**3.5.2 Determination of sulphate ion in the alum samples**

1.00 g of each of the alum samples was dissolved in 100 cm<sup>3</sup> volumetric flask (with 30 cm<sup>3</sup> of 1:4 HCl) and later made up to mark with distilled water.

10.00 cm<sup>3</sup> portion of the solution was taken in a conical flask and subsequently, 6 cm<sup>3</sup> of 10% BaCl<sub>2</sub> solution was added. The solution was boiled for 15 minutes on a hot plate. It was later filtered using an ashless filter paper and the precipitate was later ashed and ignited in the furnace at 860 °C for one hour (Vogel, 1971).

**3.5.3 Determination of Potassium in the Alum Samples**

Preparation of the standard solution for the calibration curve for potassium using a flame photometer required the dissolution of approximately 1.90 g of KCl salt in 1 dm<sup>3</sup> of distilled water. This solution contains the equivalent of 1.00 mg of solution per cubic centimeter.

The stock solution was diluted to give five solutions containing 25, 20, 15, 10 and 5 ppm of potassium ions. The potassium content of the various Alum samples was determined using a flame photometer (Vogel, 1971)

A calibration curve was prepared for the potassium ion.

#### 3.5.4 Determination of total water content.

An accurately weighed quantity of Alum sample was placed in a previously ignited crucible and heated in a furnace at 130 °C to a constant weight. (AOAC, 1970).

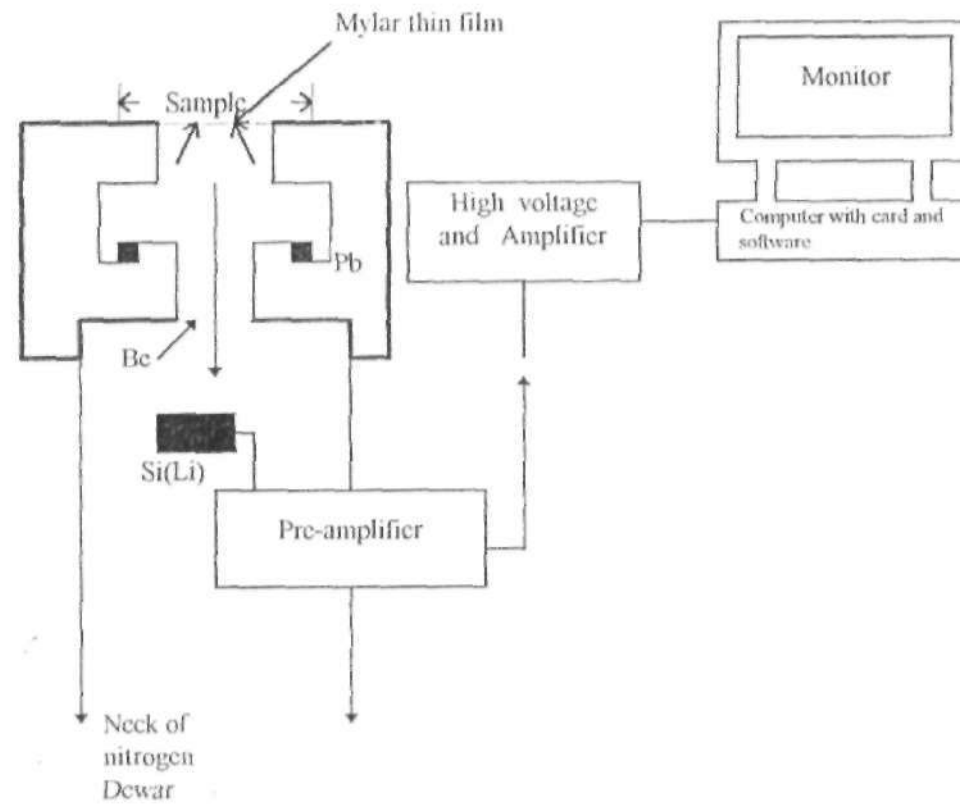
### 3.6 X - RAY FLUORESCENCE (XRF) ANALYSIS

#### 3.6.1 Sample Preparation for XRF

2.00 g each of all clay, alum and reference samples was ground to fine powder to allow homogenization of the samples. About 3 - 4 drops of a binder (PVC in toluene) was added to the pre-weighed sample and mixed together very well and later pressed into a pellet.

#### 3.6.2 Instrumentation

The XRF set-up used for this work consists of a silica Si (Li) detector, and its pre-amplifier (model SL G-13-3-170), Computer controlled high voltage bias amplifier (model 9300/7), a computer based Emcaplus card acquisition system and interchangeable radioisotope sources ( $^{55}\text{Fe}$  and  $^{109}\text{Cd}$ ). The experimental set up is as shown in the block diagram in figure 1.



**Figure 1: The X - ray Fluorescence (XRF) set up at the Centre for Energy Research and Training (CERT) A.B.U., Zaria.**

The energy dispersive X-ray fluorescence spectrometer in CERT, is combined with a dedicated computer for easy data reduction. Also the computer carries out peak location, energy assignment, element identification, smoothening, background subtraction, normalization, matrix correction, curve fitting inter-element correlation and data print out.

### 3.6.3- Measurements

The direct comparison method, with the necessary corrections for absorption using as guide Compton scattered peaks and peak ratio was used.

(Shenberg *et. al.*, 1973)

Information obtained directly from the XRF measurement consists of photopeaks of the elements analyzable by radionuclide source employed as the primary X-rays. A complete display of the elements present in the sample is called a spectrum.

Each spectrum is treated with data reduction software, AXILS, which carries out the integration of areas enclosed by each peak less the background. The results so obtained were further corrected for counting-time.

A set of standard reference materials which is comparable with the unknown samples matrix as well as in composition was also analyzed.

The final concentration of the given element in the unknown sample was obtained by comparing count rates of the element in the sample with the standard which also has the concentration of some element already established.

$$\frac{\text{Count rate of element A sample}}{\text{Concentration of element A sample}} = \frac{\text{Count of element A standard}}{\text{Concentration of element A standard}}$$

#### 3.6.4 Precision and Accuracy

Precision and accuracy depend on the element to be measured, the form of the sample, the concentration of the element, the concentration and variations in concentration of the other elements present, exciting source and the counting-time (Papez and Cameron, 1973).

Other systemic factors as sample composition and sample preparation also contribute to precision and accuracy.

The accuracy test was carried out using four certified reference materials having similar matrices and properties as the unknown samples. The certified reference samples

include:-

- i) Obsidian Rock 278
- ii) Basalt Rock 688
- iii) USGS AG V-1 and
- iv) USGS G.2

### 3.7 COAGULATIVE PROPERTIES OF ALUM SAMPLES

Some physical and chemical characteristics of water samples were determined in order to assess the coagulative properties of the Alum samples. The determined parameters include Turbidity, Electrical conductivity, Alkalinity and pH.

Two water samples were used in the assessment of the coagulative properties of the Alum samples

The water samples are :-

- i) Tannery waste water - which is an example of industrial waste water and
- ii) Ahmadu Bello University dam water - which is an example of domestic water source.

#### 3.7.1 The Jar Test

Five grams of alum was dissolved in distilled water in a 250 cm<sup>3</sup> volumetric flask and later made up to mark to give a 2.00% stock solution of alum.

Appropriate volumes of the prepared alum solution was put in 1 dm<sup>3</sup> quantity each of the test water samples put in a 1 dm<sup>3</sup> beaker placed under a jar test apparatus. A custom-made glass baffle was then inserted in the beaker to enhance coagulation. The

paddle was inserted into the beaker and the apparatus switched on at a set speed of 100 rpm. (i.e. revolution per minute) for rapid mix. After 30 seconds, the speed was reduced to 30 rpm for slow mixing and flocculation for about 30 minutes.

A settling time was allowed and the characteristics of the water were determined again (Muyibi and Okuofu, 1995).

### 3.7.2 Turbidity

Turbidity is caused by the scattering of light in all directions by undissolved substances. The turbidity of water is of interest for two main reasons. Firstly, turbidity is an important parameter for characterizing water quality.

Secondly, knowledge of turbidity allows an estimate to be made of the concentration of undissolved substances

The turbidity measurements were carried out by placing the test water in the sample bottle in the instrument and recording the reading using a turbidimeter.

### 3.7.3 Electrical Conductivity

The electrical conductivity of water is related to its concentration of dissolved mineral salts. The determination of electrical conductivity provides a rapid and convenient means of estimating the concentration of electrolytes which, for waters to be used for public supply, is not far from the concentration of dissolved solid matter.

The electrical conductivity was determined by placing the test water samples in the water cell of the instrument for measurement. The electrolytic conductivity measuring set model MC - 1, Mark V was used for all the measurements.



#### 3.7.4 Alkalinity

Alkalinity of water is the capacity of that water to accept hydrogen ions ( $H^+$ ). Alkalinity is usually imparted by the bicarbonate ( $HCO_3^-$ ), carbonate ( $CO_3^{2-}$ ) and hydroxide ( $OH^-$ ) components of the natural or treated water.

It was determined by titrating the sample of water with 0.02 N  $H_2SO_4$  solution using phenolphthalein and methyl orange. Phenolphthalein was used to determine the portion of alkalinity contributed by all the hydroxide and half of the carbonate, corresponding to a pH of 8.2 at end of titration. Methyl orange was used to determine the alkalinity contributed by all the form of alkalinity corresponding to a pH of 4.3 at the end of titration.

#### 3.7.5 The pH

The pH is used as a function of the acidity or alkalinity of a substance. The electrode system was standardized before measurements using buffer solutions with pH values near upper and lower limits of the range to be determined.

The pH of the water samples were determined using the Crison micro pH 2000

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSIONS

#### 4.1 PREPARATION OF ALUM SAMPLES

The relative yield of alum obtained from kaolin and aluminum scraps is as shown in table 1 (see appendix).

The alum samples studied in this work were synthesized by two major methods: the acid leached and base leached processes. The base leached method has been reportedly used in the synthesis of alum from aluminum metal (Kolawole *et. al.*, 1986). Within the limits of available literature, the use of the base-leached process for the production of alum from kaolin in this work is a novel development. The production of alum through the acid leached method appears to be a completely new development of this work. Kagbu (M. Sc., 1988) did report the production of alum from kaolin but no mention of how the alum was produced from kaolin. Therefore, within the limit of available literature this work can claim the development of the acid-leached method for the production of alum from kaolin and also the application of the base-leached to clay materials like kaolin in the production of alum. It was observed from table 2 that the highest yield of alum was 66.52% obtained from aluminum scraps. This may be attributed to the fact that the scraps were almost pure aluminum metal. The calcined kaolin samples gave higher yields of alums than the kaolin samples in the natural state. This can be attributed to the calcination process which had increased the surface area of the kaolin clay thereby allowing more of the aluminum content of kaolin for reaction. Also the volatile components of the kaolin could have been evaporated off during the calcination, making the calcined kaolin relatively richer in aluminum.

However, the acid-leached process gave the higher percentage yield of alum in both calcined and natural kaolin clay samples. The highest percentage yield of 59.47% alum was obtained from the calcined kaolin clay using the acid-leached process while the base leached process using the uncalcined kaolin clay gave the lowest percentage yield of 29.20% alum.

#### **4.2 FROM ISAN AND ARA CLAYS**

There was no alum produced from both Isan and Ara clays using both base leached and acid leached processes.

#### **4.3 ANALYSIS OF THE SAMPLES**

##### **4.3.1 Standardization of the XRF equipment**

The accuracy check of the results was carried out using four certified reference materials having similar matrices and properties as the unknown samples. The results obtained from the exercise are displayed in tables 3, 4, 5 and 6 in the appendix.

From these results, it is clear that the results obtained in this work showed good agreement with the certified value since the ratio of the analysis and literature value is approximately one.

The X-ray spectra obtained were analysed to find the area of different X-ray peaks using the computer program for analysis of highly complex multichannel X-ray spectra produced by Si (Li) detector (Van Espen *et al.*, 1979).

#### 4.3.2 XRF analysis of Kaolin

The result of the XRF analysis of kaolin clay is presented in table 7 in the appendix.

Potassium was found to be already present in the Kaolin sample. Potassium is one of the constituent elements of interest in the alum to be produced. With the exception of potassium, calcium, iron and silicon all the other elements detected were in trace amounts. The concentration of titanium and zinc present in the kaolin were so small that they were below the detection limit of the technique.

#### 4.3.3 XRF analysis of Isan and Ara clays

The result of the XRF analysis of Isan and Ara clays are as presented in table 8 in the appendix. From the result it can be seen that potassium was below the detection limit of the equipment or it was completely absent in the clay samples. All other elements determined appear to be present in little quantities. But what is note worthy is that Isan and Ara clay did not yield any alum. Further work on the clay samples, like the determination of the aluminum content were therefore stopped

#### 4.3.4 The aluminum content of kaolin.

This determination had to be carried out using another method - gravimetric determination of aluminum as aluminum oxide - because the XRF analytical method could not be used to quantify aluminum metal.

Kaolin was found in the average to contain  $14.29 \pm 0.63\%$  of aluminum.

#### 4.4 COMPOSITION OF THE PREPARED ALUM SAMPLES

##### 4.4.1 Alums from kaolin and aluminum scraps

This study was carried out using flame photometry for the determination of potassium; complexometric titration with EDTA for the determination of aluminum, gravimetric determination of sulphate and the AOAC method for determining water.

The result is presented in table 9 in the appendix.

The result shows that the alum samples produced from kaolin have very high potassium content (about 23% K) using the two processes of production.

This finding is opposed to the about 8% potassium that is expected to be present in alums, from a theoretical calculation of the amount of potassium present in  $KAl(SO_4)_2 \cdot 12H_2O$ . This development led in the course of this work to the modification of the kaolin raw material.

Alum produced from scrap aluminum through the base leached method has a potassium content of 8.10% which is close to the theoretical 8.23% potassium content in alum. However, the commercial samples of alum obtained from Federal Superphosphate and Fertilizer Company in Kaduna and Drury Chemicals in Lagos did not contain potassium.

The percentage concentration of aluminum in the kaolin based alum samples were lower than the theoretically expected value. This may be due to the fact that the 14.29% concentration of aluminum in the kaolin clay is low compared to the aluminum scraps which is almost pure aluminum metal.

The sulphate content of the produced alum samples from kaolin was found to be within the range of 34.50% to 36.90% for the base-leached process and within the range of 33.99% to 38.96% for the acid leached process.

#### 4.4.2 Results of the compositional analysis of alums prepared from mixed raw materials

With the high potassium content of the alum samples prepared from kaolin, it became necessary to find a way of reducing the potassium concentration to about the stoichiometric value in  $KAl(SO_4)_2 \cdot 12H_2O$ . Therefore mixtures which will increase the aluminum content of the alums were tried in the preparation of alum.

Kaolin/alumina mixtures (in varying ratios) were experimented upon as raw materials for the alum production. Both methods i.e. the base leached method and the acid leached method were used.

Table 10 shows the compositional assay of the alums prepared from the mixtures.

The result shows that only small amount of kaolin mixed with rather large amount of alumina (ratio 1:2 up to 1:5) gave alum products ion and water contents are near to those expected theoretically. This was found to be rather unsatisfactory economically in view of the high cost of alumina which is being imported.

Kaolin was therefore mixed with aluminum metal (scraps) directly, and the mixture used as raw material in another series of alum production.

Table 11 shows the analysis result of the alum samples obtained from the kaolin/aluminium scrap mixtures. The results show that these apparently is a better method

of obtaining alum from kaolin mixed with relatively small amount of aluminum scraps gave alums with composition very close to the theoretical values.

This therefore, potentially, is an economically and chemically viable method of preparing alum from kaolin. Scrap aluminum can be easily obtained even from waste materials like aluminum cans, tubes, foils and so on. It could even be an effective way of ridding the environment of aluminum waste materials.

#### 4.5 XRF ANALYSIS OF BOTH PREPARED AND COMMERCIAL ALUMS

Alum samples were also analysed using XRF technique to determine the trace element concentration. It was observed from table 12 that titanium, zinc, yttrium and vanadium were no longer present in the prepared alum samples though were found in kaolin raw material in trace amount. Also iron, strontium and zirconium were not detected in the prepared alums but present in trace amount in the Lagos Drury alum; although these elements were detected in the raw material used for the preparation of alum i.e kaolin. This suggests that the processes developed for the production of alum were effective in removing the impurities.

The alums samples from the two companies did not contain potassium, while its concentration in the aluminum scraps based alum was within the stoichiometric range at 8.27%. However the concentration of potassium in the kaolin based alum samples were exceptionally high. The high values of potassium can be attributed to the fact that the kaolin clay contained certain amount of potassium before being used for the production of alum as earlier reported.

But calcining the kaolin clay before its use in producing alum, it was discovered that not only did it give increased percentage yield of alum with the same quantities of reagents used; the amount of potassium in the alum produced was reduced from 45.30% to 28.95% for the base-leached process and it was reduced from 46.20% to 27.84% for the acid-leached process.

The distribution of other elements in the alum samples is uniform and generally in trace amounts.

#### 4.5.1 Alums produced from kaolin mixed with alumina

*Alums produced from different mixture ratio of kaolin and alumina were analysed for the trace element concentration.*

The result which is presented in table 13 shows that the concentration of potassium in the alums produced from the mixed raw material of kaolin and alumina was still very high at 27.68% for the 20g:10g mixture ratio of kaolin alumina and 12.22% for the 5g:25g mixture ratio of kaolin. Alumina respectively, though there was reduction in the initial concentration of within 45.30% - 46.20% using the uncalcined kaolin clay.

The distribution of the trace element concentration of alum produced from the above mixture ratios of kaolin and alumina were so low that they were below the detection limit of the technique or were not present again; with the exceptions of rubidium having very low concentration.



#### 4.5.2 Alums produced from kaolin mixed with aluminum scraps

The result of the XRF analysis of alums produced from the mixture of kaolin and aluminum scraps is presented in table 14.

The result show a reduction in the initial high concentration of potassium to 27.82% for the 30g:1g mixture ratio and 12.27% for the 30g:4g mixture ratio of kaolin:aluminum scraps respectively..

However, the concentration of the trace elements of the alums were so low or no longer present that the technique could not detect it except for calcium and rubidium whose concentrations were very low.

#### 4.6 COAGULATIVE PROPERTIES OF THE ALUM SAMPLES

The World Health Organisation (WHO) have set standards for drinking water parameters even though no such standard was set for tannery waste water (WHO, 1985).

The standard values are shown below:

pH range - Not less than 6.5 and not greater than 9.2.

Turbidity - Maximum acceptable concentration is 5 units.

Maximum allowable concentration is 25 units.

The characteristics of the tannery water were determined again after treatment with the different dosages of all the alum samples so as to assess their coagulative activities. The results of these tests are presented in tables 15-18.

Comparing the coagulative activities of the prepared alum samples with the companies own on industrial waste water such as tannery effluent, it was established that the prepared alum samples, especially from the kaolin based raw material, performed

better in terms of turbidity removal from the waste water and also that the prepared alums removed the dissolved salts in the waste water better than one of the industrial/commercial alums [this was reflected in the reduction of the electrical conductivity of the treated water (Table 16)]

The alum sample that has greater turbidity removal effect is the one produced from kaolin through acid leached process and alum from a mixture of kaolin and alumina in the ratio 20g:10g respectively using the base leached process. Also the alum produced from calcined kaolin through the acid leached process was found to be best suited for the removal of the dissolved salts of the tannery waste water.

However, alum samples from the companies were found to have increased the turbidity and dissolved salts content of the tannery effluent.

The alkalinity of the treated water was determined and it was found that it was generally comparable for all the prepared and commercial alum samples. Also the determined pH values were comparable for all the samples though found to be acidic.

The second water sample employed in this work is the university dam water at Ahmadu Bello University, Zaria. The water was collected and analysed for the physico-chemical characteristics before treatment with alum and the results presented in tables 19-22

It can be seen from tables 19-22 that the extent to which each alum sample reduced the turbidity of the water is low, but they are below the maximum allowable turbidity units of 25 given by the World Health Organisation (WHO, 1985).

Though the amount of dissolved salts in the raw water was small as it only gave conductivity value of 18  $\mu\text{mohs/cm}$ , there was appreciable reduction of the dissolved salts

in the water when treated with aluminium scraps based alum, alums from kaolin mixed with alumina and Lagos Drury alum.

The pH of the drinking water is also important and WHO gave the tolerable pH limit for domestic water not to be less than 6.5 and not greater than 9.2. However, it is the alum samples from calcined kaolin, kaolin mixed with alumina, kaolin mixed with aluminium scraps and Drury company alum in Lagos that gave treated water samples with pH values within this range.

The result of the alkalinity determinations are generally comparable with all the alum samples and were appreciably reduced.

The optimum dosage of alum required for the treatment of water samples from rivers was found through the determination of the various parameters above (i.e. turbidity, conductivity, alkalinity and pH) to be 30 mg/L.

## CHAPTER FIVE

### CONCLUSION AND SUGGESTION FOR FURTHER WORK.

Kaolin, a locally available raw material, has been successfully utilized in the production of alum. Two methods of preparation of alum were described through leaching with acid and base. The percentage yield of the alum from the acid leached process was higher than that obtained through the base-leached process.

However, alum samples produced from kaolin contained more than the stoichiometric quantity of potassium. The process of calcining the kaolin clay before its use for alum production caused a reduction in the potassium content of the alum from  $42.50 \pm 0.79\%$  to  $23.75 \pm 0.48\%$  for the acid leached process.

A modification of the raw material, kaolin by blending with either alumina or aluminum scraps helped in reducing the hitherto high concentration of potassium to approximately stoichiometric quantity.

The X-ray fluorescence technique used in the analysis of alum samples was demonstrated to be an accurate and precise method of analysis of samples with the precision that is better than 10%. It is also a sensitive, multielement technique of analysis due to its ability to determine concentration values in the  $\mu\text{g/g}$  range i.e. ppm level.

The results of the XRF analysis of the alum samples show that these alums samples are relatively pure since the concentrations of both the trace elements and heavy metals are only in ppm range or below the detection limit of the analytical technique.

Prepared alum samples had better coagulative performance in the tannery waste water treatment compared to the performance of commercially available ones.

It was the alum sample from the acid leached that gave the best coagulative performance with the optimum alum dosage of 30 mg/l.

The treatment of domestic water with the alum samples had comparable coagulative activities. It was found that the process of calcination of the kaolin before the production of alum did not only increase its yield of alum but also improved its performance in the coagulation process.

Though the prepared alum samples performed creditably well in coagulation activities, further work could be done to ascertain its suitability in the tanning of leather and fixing of dye on fabrics in the textile industry.

## REFERENCES

- Agarwal, B. K. (1979). X-ray spectroscopy. Springer series in Optical science, Springer - Verlag Berlin, **15**, pp. 53 - 119.
- Aghadinuno, M. C. K. (1986). Alums: versatility in composition synthesis, structure and uses. *Journal of Science Teachers Association of Nigeria (JSTAN)*, **24**, pp.233-238.
- Anderman, G. and Kemp, J.W. (1958). Scattered X-ray as internal standard in X-ray Emission Spectroscopy. *Analytical Chemistry*, **30**: 8, pp. 1306 - 1309.
- Anderson, J. D. and Bobbin S. A. (1971). The production of potable water, Encyclopedia of science and technology, McGraw - Hill, New York, vol. 7, pp. 326.
- Austen, G.T. (1984) Shreves chemical Process Industry McGraw - Hill Books Limited, London 5<sup>th</sup> edition pp. 50-55.
- Bhurkhalter, P. G. (1971) Radioisotopic X-ray analysis of silver ores using Compton scattered for Matrix compensation. *Analytical Chemistry*, **43**: 1, pp. 11-17.
- Birks, L. S. and Brooks, E. J. (1950). Applications of X-ray fluorescence spectroscopy in mineral analysis. *Analytical chemistry*, **43**: 1, pp. 10 7.
- B'lees (1989). The chemistry of atmospheric Pollution. *Chemistry in Britain*, **25**: 1, pp. 38.
- Calhoun, W. A. and Powell H.E. (Jr) (1957). Laboratory investigation of bauxite ore from Quapaw deposit U.S. Bur. Of mines, Rept. Invest. No. 5366, pp11 (C.A.52: 3281).
- Carl E. S. (1963). Aluminum sulphate production (to American Cyanamid Co). U.S. 3,079,228, pp4. (C.A. 58: 12207).
- Environmental Health engineering Laboratory Manual, Department of water resources and environmental engineering. Ahmadu Bello University, Zaria.
- Everyman's Encyclopedia, vol. I, pp. 233.
- Ewing, G.W. (1975). Instrumental methods of Chemical Analysis, McGraw - Hill Kogashuka Limited, Tokyo.
- Fox, D. L. and Jefferies, H. E. (1981). Applications of X-ray fluorescence techniques. *Analytical chemistry*, **53**, pp. 1R - 15R.

- Gauntlett, R.B. and Packham, R.F. (1973). The removal of organic compounds in the production of potable water. *Chemistry and Industry*, pp. 812 - 817.
- Goffer, Z. (1976). Archaeological Chemistry. A source book on Applications of Chemistry to Archaeology, chemical analysis series, vol 5.
- Grant, J. and Robinson, D. (1978) Alum; Encyclopedia of Chemical Technology, John Wiley, New York, Vol. 2, pp. 249.
- Grimshaw, R. W. (1971). The chemistry and Physics of clays, Ernest Benn Limited, London, 4<sup>th</sup> Edition, pp., 66.
- Hanson, V.F. (1973): Spectroscopic analysis of mineral ones. *Applied spectroscopy*, **27**, pp. 309.
- Kagbu, J. A. (1988): Comparative analytical studies of some samples of local produced and imported alums used for water treatment (MSc. Thesis).
- Kirk-Othmer (1992); Encyclopedia of chemical technology, 2<sup>nd</sup> edition, vol 2, pp. 58-65.
- Kirk-Othmer (1971) Encyclopedia of chemical Technology 4<sup>th</sup> edition, vol 2, pp 330 - 342.
- Klockenkamper, R., Knoth, J. Prange, A. and Schmenke, H. (1992). *Analytical chemistry* **64**, pp. 1115A - 1124A.
- Kolawole, G.A., Patel, K.S. and Aghadinuno, M.C. (1988). The feasibility of commercial production of alum from aluminum scraps. *Journal of Science Teachers Association of Nigeria*, **28**: pp. 231 - 233.
- Laitinen H.A (1973) Chemical Analysis McGraw - Hill Book Co. New York. Pp. 105 - 113.
- Lambert, J. and Muir, T.A. (1976). Practical chemistry 3<sup>rd</sup> edition Heinemann Educational Books, London, pp 110 - 111.
- Langheirich, A.P. Forster, J.W. and Linn, (Jr.) T.A. (1973), Current status and potential of solid state Detectors in Industrial and Field Applications In: Nuclear Techniques in the Basic metal Industries. Proceedings of a symposium, Helsinki, IAEA, Vienna.
- Larrabee, B.G. and Shaffner, T.J. (1981). Analytical chemistry, Vol. 53, pp. 163r - 174R.
- Lee J.D. (1981). A New Concise Inorganic Chemistry, Nostrand Reinhold Co. Limited, London, 3<sup>rd</sup> edition pp. 78 - 80.

- Liptrot, G.F. (1985). Modern Inorganic chemistry, Oxford University Press, 4<sup>th</sup> Edition pp 208 - 209, 377 - 381.
- Mokuhara M. (1955) The agglutination of bacteria by alum. *Japan Journal Bacterial*, **6**, pp. 89 - 93 (C.A. 48: 83171).
- Moore, C. B. (1981) Analytical Chemistry, vol. 53, pp. 38R-44R.
- Muyibi, S.A. and Okuofu, C.A. (1995). Coagulation of low turbidity surface waters with MORINGA OLEIFERA seeds *International Journal of Environmental studies*, **48**: pp. 263-273.
- Nielson, K. K. (1978). Progress in X-ray fluorescence correction methods using scattered radiation. *Advances in X-ray analysis*, **22**: pp. 303 - 315.
- Official Method of analysis of the association of Official Analytical chemistry (1970). 11<sup>th</sup> edition pp. 11.
- Orlova, S.I. Peptin N.N. and Shneerson, A.L. (1931). Formation of alum by action of nitrogen oxides on the salts of chronic acid. *Zhur. Obshchei Khim*, **1**, pp. 31-38 (C.A. 26: 563).
- Packham, R. F. (1962) The coagulation process II effect of pH on the precipitation of Aluminum Hydroxide. *Journal of Applied Chemistry*, **15** pp. 18-23.
- Papez, K. and Cameron, J.F. (1973) Application of energy - Dispersive x-ray fluorescence analysis in the basic metal Industries. Proceeding of a symposium, Helsinki, IAEA, Vienna.
- Polyakor, A. A. Shakhalin, A.A. and Tazyhetsetskaya, T.A. (1982). Methods for preserving and disinfecting hides (C.A 96: 11432+).
- Reney, H. (1956) Treatise on Inorganic chemistry, Elsevier, London, vol. 1, pp. 343 - 344.
- Salako, M. A. and Akinola, J. K. (1989). "Municipal water supply costs" *15<sup>th</sup> WEDC Conference Proceedings* PP 15 - 18.
- Sanks, R. L. (1980) Water treatment plant design Ann Arbor Science 3<sup>rd</sup> edition pp. 65-70, 283 - 289.
- Shenberg, C., Haim, B.A. and Amiel, S. (1973) Accurate. determination of copper in mixtures and ores by radioisotope excited X-ray fluorescence spectrometric analysis using Peak ratios. *Analytical chemistry*, **45**: pp. 1804 - 1008.



- Stefan W. (1955): Utilization of Industrial wastes in chemical processes. *Chemik*, **8.**, pp. 9 - 12 (C. A. 52: 4887).
- Sweeney, R.A., Gehrie, C.W. and Rexroad, P.R. (1981); *Analytical Chemistry*, **53**, pp. 28R - 38R.
- Tuyosi A. (1939). Preparation of pure ammonium alum from the solutions obtained by the sulphuric acid extraction process. *J. Soc. Chem. Ind. Japan* **42**: suppl. Binding pp. 33 - 34 (C.A. 33: 4385).
- Van Espen P., Nulleus, H. and Maenhaut, W. (1979). *Microbeam Analysis* (edited by D. E. Newbury) San Francisco press.
- Vogel A. I. (1971) *Quantitative Inorganic Analysis* pp. 436, 462, 837.
- Wade, K. and Banister, A.J. (1973). Alums: *Comprehensive Inorganic Chemistry*, edited by Bailar, (Jr) J.C. , Pergamon press, oxford, vol., 1, pp. 1056.
- Walter C. S. (1964). Aluminum sulphate (to Olin Mathieson Chemical corp). U. S. 3, 143, 392. Pp. (C. A. 61: P. 9196).
- Wheeler, B.D., Martell, D.M. and Cooper, J. A. (1976). Chemical analysis of Nickel Ores by Energy Dispersive X - ray Fluorescence. *Advances in X-ray Analysis*, **20**: 423 - 429.
- Whitney, R. P., Horn, W.M.V. ; and Carey, C. (1978); Paper: *Encyclopedia of Chemical Technology* vol. 14, pp. 129.
- Wilson, D.C. (1982); The Definition of Special Waste. *Chemistry and Industry*, **8**, pp. 253-259.

## APPENDIX

**Table 1: Yield of alum (g) per 100g of raw material.**

Raw material	Process	Amount of alum obtained (g)
Kaolin	Base leach	107.75 ± 4.00
Kaolin	acid leach	173.99 ± 5.88
Calcined kaolin	base leach	117.04 ± 4.15
Calcined kaolin	Acid leach	218.42 ± 4.86
Aluminum scraps	Base leach	1167.16 ± 19.42

**Table 2: Percentage yield of produced alums**

Raw material	Process	% Yield
Kaolin	Base leach	29.20 ± 1.07
Kaolin	Acid leach	47.35 ± 1.64
Calcined kaolin	Base leach	31.87 ± 1.13
Calcined kaolin	Acid leach	59.47 ± 1.32
Aluminum scraps	Base leach	66.52 ± 1.11

*Table 3. Comparison of the results of XRF analysis of Obsidian Rock 278 with their certified values.*

Elements	Literature values	This work	This work/Lit. val.
Si (%)	34.0	33.60	0.99
K(%)	3.44	3.98	1.16
Ca(%)	0.70	0.72	1.03
Ti(%)	0.15	<0.17	<1.13
V	15.0	14.9	0.99
Fe (%)	1.05	1.25	1.19
Co	1.50	1.68	1.12
Zn	55.0	<73.4	<1.33
Rb	127	123	0.97
Sr	63.5	622	0.98
Y	41.0	41.8	1.02
Zr	295	296	1.00
Nb	n.d	16.8	-

Note: n.d = not determined.

Table 4: Comparison of the results of XRF analysis of Basalt Rock 688 with their certified values

Elements	Literature values	This work	this work /Lit. value.
Si(%)	22.5	22.2	0.99
K(%)	0.16	0.18	1.13
Ca(%)	8.68	8.75	1.01
Ti(%)	0.70	0.65	0.93
V	250	226	0.90
Fe (%)	5.93	5.98	1.01
Co	49.7	49.9	1.00
Zn	58.0	<79.6	<1.37
Rb	1.91	n.d	-
Sr	169	156	0.92
Y	17.0	17.4	1.02
Zr	60.6	60.0	0.99
Nb	n.d.	<13.0	-

Note: n.d = not determined.

**Table 5: Comparison of the results of XRF analysis of AG V-1 with their certified values**

Elements	Literature values	This work	This work /Lit. val.
Si(%)	27.4	22.1	0.81
K(%)	2.41	2.05	0.85
Ca(%)	3.53	2.40	0.68
Ti(%)	0.63	0.60	0.95
V	121	133	1.10
Fe(%)	1.60	1.92	1.20
Co	15.3	<28.0	<1.83
Zn	88.0	86.7	0.99
Rb	67.3	68.2	1.01
Sr	662	650	0.98
Y	20.0	20.9	1.05
Zr	227	223	0.98
Nb	15.0	<25.5	<1.70

Table 6: Comparison of the results of XRF analysis of G.2 with their certified values.

Elements	Literature values	This work	This work /Lit. val.
Si(%)	32.2	34.3	1.07
K(%)	3.71	3.05	0.82
Ca(%)	1.40	1.25	0.89
Ti(%)	0.28	0.40	1.43
V	36.0	38.5	1.07
Fe(%)	1.60	1.84	1.15
Co	4.60	<10.7	<2.33
Zn	86.0	84.5	0.98
Rb	170	194	1.14
Sr	478	452	0.95
Y	11.0	11.8	1.07
Zr	309	295	0.95
Nb	12.0	12.6	1.05

Table 7 Elemental composition of kaolin clay in ppm.

Elements	Kaolin sample 1	Kaolin sample 2	Kaolin sample 3	Kaolin sample 4
K(%)	7.49	6.62	7.45	8.00
Ti(%)	<0.33	<0.35	<0.31	<0.38
V	58.70	64.00	45.50	61.00
Ca(%)	0.33	0.33	0.39	0.42
Fe(%)	0.10	0.19	0.14	0.14
Zn	96.50	90.10	89.30	90.00
Pb	84.50	70.00	139.00	174.00
Rb	31.20	32.10	53.50	38.60
Y	31.20	40.60	<15.70	22.20
Zr	108.00	137.00	131.00	133.00
Sr	<15.70	93.50	40.00	37.30
Si(%)	14.70	17.30	15.30	14.90

**Table 9: Elemental, sulphate ion and water composition of alum.**

Samples	K(%)	Al(%)	SO <sub>4</sub> <sup>2-</sup> (%)	H <sub>2</sub> O(%)
Kaolin alum (base leached)	40.50 ± 0.79	1.70 ± 0.63	34.50 ± 0.69	22.50 ± 0.38
Kaolin alum (acid leached)	41.60 ± 0.65	1.48 ± 0.79	33.99 ± 0.65	22.70 ± 0.35
Calcined kaolin alum (base leached)	23.75 ± 0.48	2.90 ± 0.82	36.90 ± 0.90	35.60 ± 0.49
Calcined kaolin alum (acid leached)	23.13 ± 0.82	3.65 ± 0.73	38.96 ± 0.61	33.90 ± 0.40
Aluminum scrap alum	8.10 ± 0.63	6.80 ± 0.65	40.78 ± 0.57	44.14 ± 0.72
Commercial sample 1	Nil	5.68 ± 0.33	40.51 ± 0.33	38.80 ± 0.36
Commercial sample 2	Nil	5.73 ± 0.17	44.73 ± 0.48	35.20 ± 0.61
Stoichiometric value	8.23	5.70	40.51	45.57

**Table 8: Elemental composition of Isan and Ara clays in ppm (except otherwise stated)**

Elements	ISWT	ISBK	ISRD	ARWT	ARBK	ARRD
K	Nil	Nil	Nil	Nil	Nil	Nil
Ti(%)	1.17	626.00	514.00	591.00	554.00	571.00
V	564.00	626.00	514.00	591.00	554.00	571.00
Ca(%)	0.38	054	0.21	073	0.64	0.86
Fe(%)	12.20	9.42	14.00	6.75	7.73	6.42
Zn	<92.60	<92.70	<95.00	<93.90	<90.50	<92.80
Pb	<75.40	<58.00	<56.60	83.10	<65.40	<81.10
Rb	218.00	175.00	66.10	256.00	245.00	260.00
Y	45.00	53.50	24.90	39.50	42.50	35.70
Zr	95.80	255.00	197.00	364.00	335.00	464.00
Sr	57.20	186.00	136.00	112.00	125.00	129.00
Si(%)	14.50	14.60	14.50	15.00	14.90	15.40



**Table 10: Elemental, sulphate ion and water composition of alums produced from kaolin mixed with alumina**

Samples	K(%)	Al(%)	SO <sub>4</sub> <sup>2-</sup> (%)	H <sub>2</sub> O(%)
K(b)	23.86 ± 0.65	4.39 ± 0.22	40.81 ± 0.45	30.86 ± 0.33
K(a)	22.23±0.63	4.63±0.64	42.10±0.82	30.44±0.51
L(b)	16.25±0.63	4,55±0.38	40.66±0.40	38.09±0.48
L(a)	15.20±0.36	4.67±0.63	40.25±0.31	39.42±0.33
M(b)	9.69±0.31	5.88±0.30	40.23±0.38	43.67±0.36
M(a)	11.15±0.79	6.39±0.36	40.85±0.50	41.16±0.46
N(b)	7.92±0.95	6.02±0.48	40.92±0.29	44.19±0.42
N(a)	8.23±0.48	5.88±0.63	40.96±0.87	44.53±0.21
Stoichiometric value	8.23	5.70	40.51	45.57

**Table 11: Elemental, sulphate ion and water composition of alums produced from kaolin mixed with aluminum scraps**

Samples	K(%)	Al(%)	SO <sub>4</sub> <sup>2-</sup> (%)	H <sub>2</sub> O(%)
W(b)	22.82±0.82	4.38±0.17	36.33±0.69	35.69±0.38
W(a)	22.29±0.65	4.53±0.18	36.52±0.90	35.73±0.35
X(b)	9.58±0.79	5.33±0.12	42.58±0.65	42.15±0.21
X(a)	10.42±0.65	5.41±0.63	41.77±0.73	41.76±0.40
Y(b)	8.33±0.65	6.45±0.40	42.46±0.61	42.48±0.49
Y(a)	9.58±0.79	6.21±0.16	41.21±0.57	42.25±0.36
Z(b)	9.48±0.48	5.98±0.65	41.16±0.33	42.55±0.35
Z(a)	9.27±0.48	6.01±0.73	42.04±0.65	42.21±0.34
Stoichiometric value	8.23	5.70	40.51	45.57

**Table 12: Elemental composition of alum samples**

Elements	BLKA	BLKA(C)	ALKA	ALKA(C)	TTA	CSI	CS2
K(%)	45.30	28.95	46.20	27.84	8.28	Nil	Nil
Ti	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fe	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Ca(%)	0.49	0.61	0.48	0.24	0.44	Nil	Nil
Zn	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Rb	nil	Nil	Nil	Nil	Nil	nil	Nil
Si(%)	<2.02	<9.85	<1.97	<8.65	<1.60	Nil	Nil
Y	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Sr	Nil	Nil	Nil	Nil	Nil	Nil	78.60
V	Nil	Nil	Nil	nil	Nil	Nil	Nil
Zr	Nil	Nil	Nil	Nil	Nil	Nil	72.30

Where BLKA is Base leached kaolin alum

BLKA (C) is Base leached kaolin (calciined) alum

ALKA is Acid leached kaolin alum

ALKA (C) is Acid leached kaolin (calciined) alum

TTA is Aluminum scrap alum

CS1 is Kaduna superphosphate alum

CS2 is Lagos Drury alum.

**Table 13: Elemental composition of alums produced from kaolin mixed with alumina (results in ppm., except otherwise stated)**

Elements	K(b)	K(a)	L(b)	L(a)	M(b)	M(a)	N(b)	N(a)
K(%)	27.68	27.20	23.52	21.12	14.96	14.69	12.89	12.22
Ti	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fe	Nil	Nil	Nil	Nil	Nil	Nil	nil	Nil
Ca	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Zn	Nil	Nil	Nil	Nil	Nil	Nil	nil	Nil
Rb	100.50	96.50	92.60	78.20	72.30	86.10	79.10	88.30
Si(%)	<20.00	<19.80	<19.60	<19.00	<18.20	<16.90	<16.00	<15.60
Y	Nil	Nil	Nil	Nil	nil	Nil	Nil	Nil
Sr	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
V	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Zr	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

Where sample K is 20g: 10g kaolin: alumina ratio.

L is 15g :15g kaolin: alumina ratio

M is 10g:20g kaolin: alumina ratio

N is 5g:25g kaolin: alumina ratio.

Table 14: Elemental composition of alums produced from kaolin mixed with aluminum scraps

Elements	W(b)	W(a)	X(b)	X(a)	Y(b)	Y(a)	Z(b)	Z(a)
K(%)	27.80	27.30	14.90	16.20	13.30	14.50	12.50	12.30
Ti	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fe	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Ca	405.00	407.00	424.00	436.00	448.00	468.00	466.00	489.00
Zn	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Rb	101.80	99.50	96.40	84.80	99.60	72.60	66.40	60.20
Si(%)	<20.20	<20.00	<19.60	<19.00	18.30	<17.70	<16.80	<15.80
Y	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Sr	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
V	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Zr	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

Where sample W is 30g: 1g kaolin: aluminum scrap ratio

X is 30g: 2g kaolin: aluminum scrap ratio

Y is 30g: 3g kaolin: aluminum scrap ratio

Z is 30g: 4g kaolin: aluminum scrap ratio.

a = acid-leached process

b = base-leached process.

**Table 15: The effect of doses of various alum samples on the turbidity (units) of tannery waste water doses of alum**

Alum samples	30mg/L	40mg/L	50mg/L
Kaolin alum (b)	461.50±0.34	462.50±0.24	464.50±0.29
Kaolin alum (b)	460.91±0.34	463.13±0.31	465.01±0.38
Calcined kaolin alum	461.01±0.33	462.79±0.39	465.04±0.26
Calcined kaolin alum	463.03±0.31	465.74±0.26	465.03±0.28
Kaolin: alumina alum (20g:10g)(b)	460.11±0.29	462.02±0.31	462.26±0.33
Kaolin: alumina alum (20g:10g)(a)	460.83±0.35	461.71±0.37	462.01±0.31
Kaolin alumina alum (15g:15g)(b)	461.05±0.26	462.77±0.32	463.11±0.39
Kaolin alumina alum (15g:15g)(a)	463.04±0.39	466.11±0.30	466.20±0.36
Kaolin alumina alum (10g:20g)(b)	460.12±0.33	462.17±0.39	462.96±0.25
Kaolin alumina alum (10g:20g)(a)	461.07±0.26	463.11±0.39	462.81±0.33
Kaolin alumina alum (5g:25g)(b)	460.34±0.33	463.17±0.38	465.08±0.44
Kaolin alumina alum (5g:25g)(a)	462.65±1.37	465.12±0.26	464.88±0.31
Kaolin : scrap metal alum (30g:1g)(b)	464.00±0.35	466.11±0.31	466.07±0.33
Kaolin,scrap metal alum (30g:1g)(a)	464.22±0.31	464.19±0.41	465.29±0.39
Kaolin scrap metal alum (30g:2g) (b)	465.06±0.37	466.44±0.4	466.38±0.35
Kaolin scrap metal alum (30g:2g)(a)	464.69±0.36	464.77±0.26	466.03±0.39
Kaolin scrap metal alum (30g:3g)(b)	463.25±0.27	465.11±0.38	465.32±0.40
Kaolin scrap metal alum (30g:3g)(a)	461.06±0.32	463.14±0.39	463.21±0.30
Kaolin scrap metal alum (30g:4g)(b)	461.31±0.33	463.26±0.40	465.26±0.33
Kaolin scrap metal alum (30g:4g)(a)	463.29±0.35	465.27±0.39	465.16±0.31
Scrap metal alum	467.50±0.29	463.16±0.36	463.06±0.33
Commercial sample 1	551.07±0.41	520.21±0.31	478.51±0.39
Commercial sample 2	550.20±0.31	511.50±0.39	493.52±0.33

Turbidity for the raw water sample is 468 units where commercial sample 1 is alum from federal superphosphate and fertilizer company, Kaduna commercial sample 2 is alum from Drury chemicals, Lagos.

a is the acid leached process.

b is the base leached process.

**Table 16: the effect of doses of various alum samples on the conductivity ( $\mu\text{mho/cm}$ ) of tannery waste water doses of alum**

Alum samples	30mg\L	40mg\L	50mg\L
Kaolin alum b	2.33±0.37	2.28±0.61	2.10±0.69
Kaolin alum a	2.30±0.28	2.30±0.22	2.10±0.30
Calcined kaolin alum b	2.30±0.21	2.30±0.26	2.10±0.19
Calcined kaolin alum a	2.30±0.21	2.00±0.16	2.08±0.21
Kaolin: alumina alum (20g:10g) b	2.33±0.23	2.20±0.18	2.25±0.22
Kaolin: alumina alum (20g:10g) a	2.37±0.23	2.28±0.21	2.20±0.16
Kaolin: alumina alum (15g:15g) b	2.44±0.22	2.31±0.19	2.30±0.16
kaolin alumina alum (15g:15g) a	2.45±0.17	2.40±0.21	2.25±0.25
Kaolin alumina alum (10g:20g) b	2.45±0.16	2.38±0.25	2.32±0.23
Kaolin alumina alum (10g:20g) a	2.41±0.25	2.40±0.21	2.28±0.17
kaolin alumina alum (5g:25g)b	2.33±0.18	2.20±0.21	2.20±0.23
Kaolin alumina alum (5g:25g) a	2.31±0.23	2.22±0.16	2.15±0.22
Kaolin scrap metal alum (30g:1g) b	2.34±0.19	2.20±0.22	2.16±0.21
Kaolin scrap metal alum (30g:1g) a	2.40±0.19	2.23±0.21	2.20±0.13
Kaolin scrap metal alum (30g:2g) b	2.33±0.16	2.33±0.22	2.21±0.19
Kaolin scrap metal alum (30g:2g)a	2.43±0.21	2.41±0.25	2.32±0.17
Kaolin scrap metal alum (30g:3g) b	2.35±0.18	2.31±0.23	2.28±0.26
Kaolin: scrap metal alum (30g:3g)a	2.44±0.15	2.33±0.23	2.28±0.27
Kaolin scrap metal alum (30g:4g) b	2.33±0.18	2.30±0.22	2.22±0.19
Kaolin scrap metal alum (30g:4g)a	2.30±0.12	2.33±0.21	2.15±0.16
Scrap metal alum	2.20±0.25	2.24±0.31	2.11±0.15
Commercial sample 1	2.61 ± 0.31	2.14±0.23	2.15±0.16
Commercial sample 2	2.70±0.29	2.20±0.21	2.11±0.23

Conductivity for the raw water sample is  $4.5 \times 10^3 \mu\text{mho/cm}$ .

**Table 17 : The effect of doses of various alum samples on the alkalinity (mg/L CaCO<sub>3</sub>) of tannery waste water.**

Alum Samples	Doses of Alum		
	30 mg/L	40 mg/L	50 mg/L
Kaolin alum b	186.51 ± 6.71	201.30 ± 4.11	193.33 ± 7.20
Kaolin alum a	216.44 ± 4.50	188.66 ± 5.15	126.37 ± 8.11
Calcined Kaolin alum b	206.16 ± 3.91	186.66 ± 4.14	122.66 ± 6.31
Calcined Kaolin alum a	230.33 ± 4.37	203.13 ± 5.05	100.03 ± 4.11
Kaolin : alumina alum (20 g : 10 g)b	211.66 ± 4.66	179.67 ± 6.11	144.44 ± 4.50
Kaolin : alumina alum (20 g : 10 g)a	246.73 ± 6.14	184.66 ± 6.46	129.67 ± 3.81
Kaolin : alumina alum (15 g : 15 g)b	213.33 ± 5.81	155.66 ± 5.45	122.63 ± 4.12
Kaolin : alumina alum (15 g : 15 g)a	251.33 ± 3.71	155.37 ± 4.88	123.67 ± 3.17
Kaolin : alumina alum (10 g : 20 g) b	212.22 ± 4.66	160.63 ± 3.67	113.67 ± 5.15
Kaolin : alumina alum (10 g : 20g)a	203.67 ± 3.67	156.67 ± 4.16	112.22 ± 6.46
Kaolin : alumina alum (5 g : 25 g)b	200.37 ± 4.41	153.17 ± 7.34	109.11 ± 3.74
Kaolin : alumina alum (5 g : 25 g)a	211.13 ± 5.42	156.67 ± 4.16	101.67 ± 5.40
Kaolin : scrap metal alum (30 g : 1 g)b	215.45 ± 5.50	153.17 ± 7.34	142.25 ± 6.31
Kaolin : scrap metal alum (30 : 1 g)a	231.47 ± 6.46	148.73 ± 6.54	111.67 ± 3.81
Kaolin : scrap metal alum (30 g : 2 g)b	213.79 ± 4.57	147.98 ± 5.11	123.51 ± 4.51
Kaolin : scrap metal alum (30 g : 2 g)a	248.49 ± 3.82	181.33 ± 4.64	126.45 ± 6.66
Kaolin : scrap metal alum (30 g : 3 g)b	206.63 ± 5.06	156.67 ± 4.71	104.39 ± 7.11
Kaolin : scrap metal alum (30 g : 3 g)a	193.33 ± 6.53	153.17 ± 7.34	120.74 ± 6.13
Kaolin scrap metal alum (30 g : 4 g)b	188.67 ± 7.41	148.67 ± 5.18	107.70 ± 5.11
Kaolin scrap metal alum (30 g : 4 g)a	203.45 ± 5.46	106.30 ± 5.47	108.30 ± 4.51
Scrap metal alum	221.77 ± 6.44	206.67 ± 7.13	157.11 ± 3.67
Commercial sample 1	212.37 ± 4.37	216.91 ± 3.77	110.31 ± 5.12
Commercial sample 2	209.73 ± 4.17	211.66 ± 5.41	156.67 ± 6.11

Alkalinity for the raw water sample is 300 mg/L CaCO<sub>3</sub>

**Table 18 : The effect of doses of various alum samples on the pH of tannery waste water.**

Alum Samples	Doses of Alum		
	30 mg/L	40 mg/L	50 mg/L
Kaolin alum b	3.35 ± 0.23	3.28 ± 0.61	3.25 ± 0.73
Kaolin alum a	3.63 ± 0.67	3.60 ± 0.29	3.58 ± 0.38
Calcined Kaolin alum b	3.63 ± 0.33	3.60 ± 0.73	3.58 ± 0.66
Calcined Kaolin alum a	3.50 ± 0.33	3.30 ± 0.41	3.25 ± 0.23
Kaolin : alumina alum (20 g : 10 g)b	3.58 ± 0.22	3.40 ± 0.38	3.40 ± 0.29
Kaolin : alumina alum (20 g : 10 g)a	3.41 ± 0.66	3.38 ± 0.33	3.35 ± 0.41
Kaolin : alumina alum (15 g : 15 g)b	3.50 ± 0.73	3.52 ± 0.63	3.41 ± 0.39
Kaolin : alumina alum (15 g : 15 g)a	3.45 ± 0.29	3.38 ± 0.21	3.41 ± 0.45
Kaolin : alumina alum (10 g : 20 g) b	3.55 ± 0.38	3.50 ± 0.31	3.45 ± 0.28
Kaolin : alumina alum (10 g : 20g)a	3.54 ± 0.70	3.55 ± 0.45	3.50 ± 0.39
Kaolin : alumina alum (5 g : 25 g)b	3.56 ± 0.39	3.50 ± 0.37	3.42 ± 0.31
Kaolin : alumina alum (5 g : 25 g)a	3.53 ± 0.26	3.48 ± 0.41	3.45 ± 0.45
Kaolin : scrap metal alum (30 g : 1 g)b	3.60 ± 0.33	3.60 ± 0.38	3.52 ± 0.22
Kaolin : scrap metal alum (30 : 1 g)a	3.52 ± 0.29	3.55 ± 0.39	3.45 ± 0.37
Kaolin : scrap metal alum (30 g : 2 g)b	3.61 ± 0.33	3.65 ± 0.27	3.65 ± 0.21
Kaolin : scrap metal alum (30 g : 2 g)a	3.66 ± 0.25	3.64 ± 0.31	3.70 ± 0.36
Kaolin : scrap metal alum (30 g : 3 g)b	3.65 ± 0.45	3.67 ± 0.33	3.67 ± 0.22
Kaolin : scrap metal alum (30 g : 3 g)a	3.62 ± 0.26	3.63 ± 0.41	3.71 ± 0.44
Kaolin scrap metal alum (30 g : 4 g)b	3.55 ± 0.31	3.60 ± 0.39	3.65 ± 0.27
Kaolin scrap metal alum (30 g : 4 g)a	3.50 ± 0.18	3.55 ± 0.32	3.60 ± 0.23
Scrap metal alum	3.65 ± 0.37	3.63 ± 0.25	3.60 ± 0.33
Commercial sample 1	3.58 ± 0.28	3.55 ± 0.31	3.53 ± 0.33
Commercial sample 2	3.55 ± 0.25	3.51 ± 0.23	3.52 ± 0.29

pH of the raw water sample is 3.15



Table 19 : The effect of doses of various alum samples on the turbidity (Units) of ABU dam water.

Alum Samples	Doses of Alum		
	30 mg/L	40 mg/L	50 mg/L
Kaolin alum b	14.21 ± 0.23	14.21 ± 0.17	14.19 ± 0.29
Kaolin alum a	14.22 ± 0.29	14.21 ± 0.26	14.20 ± 0.23
Calcined Kaolin alum b	14.23 ± 0.39	14.22 ± 0.41	14.20 ± 0.33
Calcined Kaolin alum a	14.22 ± 0.35	14.21 ± 0.41	14.23 ± 0.33
Kaolin : alumina alum (20 g : 10 g)b	14.20 ± 0.29	14.23 ± 0.36	14.21 ± 0.33
Kaolin : alumina alum (20 g : 10 g)a	14.23 ± 0.38	14.23 ± 0.31	14.11 ± 0.35
Kaolin : alumina alum (15 g : 15 g)b	14.24 ± 0.29	14.25 ± 0.31	14.11 ± 0.33
Kaolin : alumina alum (15 g : 15 g)a	14.22 ± 0.31	14.21 ± 0.31	14.33 ± 0.35
Kaolin : alumina alum (10 g : 20 g) b	14.23 ± 0.31	14.22 ± 0.30	14.22 ± 0.31
Kaolin : alumina alum (10 g : 20g)a	14.22 ± 0.28	14.11 ± 0.35	14.14 ± 0.39
Kaolin : alumina alum (5 g : 25 g)b	14.11 ± 0.35	14.13 ± 0.37	14.21 ± 0.31
Kaolin : alumina alum (5 g : 25 g)a	14.23 ± 0.30	14.14 ± 0.35	14.11 ± 0.47
Kaolin : scrap metal alum (30 g : 1 g)b	14.23 ± 0.37	14.22 ± 0.31	14.20 ± 0.33
Kaolin : scrap metal alum (30 : 1 g)a	14.22 ± 0.31	14.20 ± 0.22	14.23 ± 0.33
Kaolin : scrap metal alum (30 g : 2 g)b	14.21 ± 0.39	14.24 ± 0.37	14.23 ± 0.37
Kaolin : scrap metal alum (30 g : 2 g)a	14.22 ± 0.33	14.21 ± 0.35	14.22 ± 0.33
Kaolin : scrap metal alum (30 g : 3 g)b	14.13 ± 0.31	14.04 ± 0.37	14.02 ± 0.33
Kaolin : scrap metal alum (30 g : 3 g)a	14.21 ± 0.31	14.21 ± 0.31	14.23 ± 0.35
Kaolin scrap metal alum (30 g : 4 g)b	14.04 ± 0.39	14.10 ± 0.33	14.03 ± 0.29
Kaolin scrap metal alum (30 g : 4 g)a	14.23 ± 0.37	14.22 ± 0.39	14.12 ± 0.31
Scrap metal alum	14.21 ± 0.38	14.25 ± 0.41	14.20 ± 0.31
Commercial sample 1	14.01 ± 0.35	14.03 ± 0.33	14.21 ± 0.37
Commercial sample 2	14.20 ± 0.37	14.21 ± 0.39	14.43 ± 0.33

Turbidity of the raw water sample is 14.35 units

**Table 20 : The effect of doses of various alum samples on the conductivity of the raw water sample is 18  $\mu$ mho/cm**

Alum Samples	Doses of Alum		
	30 mg/L	40 mg/L	50 mg/L
Kaolin alum b	15.81 $\pm$ 0.17	15.83 $\pm$ 0.21	18.30 $\pm$ 0.23
Kaolin alum a	16.11 $\pm$ 0.25	18.13 $\pm$ 0.17	20.01 $\pm$ 0.21
Calcined Kaolin alum b	15.83 $\pm$ 0.19	15.82 $\pm$ 0.17	18.10 $\pm$ 0.21
Calcined Kaolin alum a	16.03 $\pm$ 0.26	18.11 $\pm$ 0.17	18.13 $\pm$ 0.21
Kaolin : alumina alum (20 g : 10 g)b	16.03 $\pm$ 0.17	15.91 $\pm$ 0.26	16.22 $\pm$ 0.23
Kaolin : alumina alum (20 g : 10 g)a	16.52 $\pm$ 0.25	16.31 $\pm$ 0.19	16.33 $\pm$ 0.26
Kaolin : alumina alum (15 g : 15 g)b	16.11 $\pm$ 0.19	16.32 $\pm$ 0.16	16.03 $\pm$ 0.21
Kaolin : alumina alum (15 g : 15 g)a	16.21 $\pm$ 0.22	16.03 $\pm$ 0.18	16.07 $\pm$ 0.23
Kaolin : alumina alum (10 g : 20 g) b	15.41 $\pm$ 0.15	15.63 $\pm$ 0.19	15.61 $\pm$ 0.22
Kaolin : alumina alum (10 g : 20g)a	15.63 $\pm$ 0.23	14.81 $\pm$ 0.17	15.84 $\pm$ 0.21
Kaolin : alumina alum (5 g : 25 g)b	14.51 $\pm$ 0.21	14.53 $\pm$ 0.17	14.12 $\pm$ 0.19
Kaolin : alumina alum (5 g : 25 g)a	14.80 $\pm$ 0.25	14.61 $\pm$ 0.21	14.63 $\pm$ 0.23
Kaolin : scrap metal alum (30 g : 1 g)b	15.52 $\pm$ 0.19	15.81 $\pm$ 0.23	15.63 $\pm$ 0.21
Kaolin : scrap metal alum (30 : 1 g)a	15.63 $\pm$ 0.17	15.83 $\pm$ 0.25	15.81 $\pm$ 0.23
Kaolin : scrap metal alum (30 g : 2 g)b	15.59 $\pm$ 0.29	15.80 $\pm$ 0.33	15.81 $\pm$ 0.21
Kaolin : scrap metal alum (30 g : 2 g)a	15.61 $\pm$ 0.41	15.60 $\pm$ 0.27	15.73 $\pm$ 0.21
Kaolin : scrap metal alum (30 g : 3 g)b	15.21 $\pm$ 0.27	15.03 $\pm$ 0.19	15.04 $\pm$ 0.19
Kaolin : scrap metal alum (30 g : 3 g)a	15.31 $\pm$ 0.25	15.13 $\pm$ 0.23	15.11 $\pm$ 0.19
Kaolin scrap metal alum (30 g : 4 g)b	14.51 $\pm$ 0.21	14.63 $\pm$ 0.23	14.61 $\pm$ 0.39
Kaolin scrap metal alum (30 g : 4 g)a	14.82 $\pm$ 0.35	14.91 $\pm$ 0.41	14.90 $\pm$ 0.27
Scrap metal alum	14.12 $\pm$ 0.29	14.50 $\pm$ 0.25	15.11 $\pm$ 0.33
Commercial sample 1	16.03 $\pm$ 0.20	15.91 $\pm$ 0.25	16.11 $\pm$ 0.23
Commercial sample 2	13.21 $\pm$ 0.23	13.50 $\pm$ 0.19	13.91 $\pm$ 0.25

Conductivity of the raw water sample is 18  $\mu$ mho/cm

Table 21: The Effect of Doses of Various Alum samples on the Alkalinity (mg/L  $\text{CaCO}_3$ ) of ABU dam Water

Alum Samples	Doses of Alum		
	30 mg/L	40 mg/L	50 mg/L
Kaolin alum b	8.51 ± 0.73	7.53 ± 0.81	5.50 ± 0.66
Kaolin alum a	7.61 ± 0.76	7.50 ± 0.69	5.51 ± 0.71
Calcined Kaolin alum b	8.01 ± 0.65	7.52 ± 0.69	5.51 ± 0.73
Calcined Kaolin alum a	7.51 ± 0.79	9.03 ± 0.73	8.52 ± 0.77
Kaolin : alumina alum (20 g : 10 g)b	9.51 ± 0.77	9.03 ± 0.66	9.02 ± 0.71
Kaolin : alumina alum (20 g : 10 g)a	9.53 ± 0.78	9.51 ± 0.77	9.03 ± 0.81
Kaolin : alumina alum (15 g : 15 g)b	9.51 ± 0.73	9.05 ± 0.66	8.11 ± 0.65
Kaolin : alumina alum (15 g : 15 g)a	9.52 ± 0.77	9.12 ± 0.63	9.03 ± 0.73
Kaolin : alumina alum (10 g : 20 g) b	9.03 ± 0.66	9.14 ± 0.73	8.53 ± 0.71
Kaolin : alumina alum (10 g : 20g)a	9.14 ± 0.76	9.03 ± 0.69	8.51 ± 0.81
Kaolin : alumina alum (5 g : 25 g)b	8.05 ± 0.71	8.12 ± 0.77	8.51 ± 0.63
Kaolin : alumina alum (5 g : 25 g)a	8.07 ± 0.71	8.03 ± 0.73	7.51 ± 0.81
Kaolin : scrap metal alum (30 g : 1 g)b	8.04 ± 0.79	7.51 ± 0.73	7.54 ± 0.75
Kaolin : scrap metal alum (30 : 1 g)a	8.51 ± 0.71	8.03 ± 0.66	8.01 ± 0.75
Kaolin : scrap metal alum (30 g : 2 g)b	8.52 ± 0.73	8.51 ± 0.71	7.11 ± 0.77
Kaolin : scrap metal alum (30 g : 2 g)a	8.54 ± 0.73	8.03 ± 0.66	8.01 ± 0.69
Kaolin : scrap metal alum (30 g : 3 g)b	8.51 ± 0.77	8.11 ± 0.73	7.52 ± 0.75
Kaolin : scrap metal alum (30 g : 3 g)a	8.50 ± 0.75	7.52 ± 0.69	7.53 ± 0.71
Kaolin scrap metal alum (30 g : 4 g)b	8.50 ± 0.73	7.50 ± 0.69	7.03 ± 0.77
Kaolin scrap metal alum (30 g : 4 g)a	8.03 ± 0.75	7.51 ± 0.66	7.04 ± 0.73
Scrap metal alum	9.52 ± 0.69	8.01 ± 0.76	7.03 ± 0.66
Commercial sample 1	9.10 ± 0.71	7.05 ± 0.73	7.01 ± 0.66
Commercial sample 2	8.53 ± 0.73	7.51 ± 0.73	7.03 ± 0.71

Alkalinity of the row water sample is 13 mg/L  $\text{CaCO}_3$

Table 22: The effect of doses of various alum samples on the pH of ABU dam water

Alum Samples	Doses of Alum		
	30 mg/L	40 mg/L	50 mg/L
Kaolin alum b	6.09 ± 0.23	6.09 ± 0.41	6.05 ± 0.21
Kaolin alum a	6.11 ± 0.33	6.09 ± 0.39	6.06 ± 0.27
Calcined Kaolin alum b	6.71 ± 0.18	6.62 ± 0.22	6.55 ± 0.33
Calcined Kaolin alum a	6.70 ± 0.25	6.61 ± 0.31	6.57 ± 0.39
Kaolin : alumina alum (20 g : 10 g)b	6.63 ± 0.41	6.60 ± 0.27	6.60 ± 0.31
Kaolin : alumina alum (20 g : 10 g)a	6.65 ± 0.23	6.63 ± 0.33	6.65 ± 0.29
Kaolin : alumina alum (15 g : 15 g)b	6.72 ± 0.27	6.65 ± 0.35	6.60 ± 0.22
Kaolin : alumina alum (15 g : 15 g)a	6.71 ± 0.39	6.61 ± 0.22	6.63 ± 0.33
Kaolin : alumina alum (10 g : 20 g) b	6.70 ± 0.45	6.72 ± 0.33	6.72 ± 0.29
Kaolin : alumina alum (10 g : 20g)a	6.73 ± 0.39	6.71 ± 0.52	6.60 ± 0.45
Kaolin : alumina alum (5 g : 25 g)b	6.65 ± 0.52	6.61 ± 0.38	6.63 ± 0.39
Kaolin : alumina alum (5 g : 25 g)a	6.60 ± 0.31	6.63 ± 0.41	6.51 ± 0.44
Kaolin : scrap metal alum (30 g : 1 g)b	6.81 ± 0.55	6.82 ± 0.28	6.51 ± 0.31
Kaolin : scrap metal alum (30 : 1 g)a	6.81 ± 0.49	6.63 ± 0.39	6.60 ± 0.37
Kaolin : scrap metal alum (30 g : 2 g)b	6.85 ± 0.38	6.80 ± 0.41	6.41 ± 0.22
Kaolin : scrap metal alum (30 g : 2 g)a	6.80 ± 0.29	6.70 ± 0.33	6.73 ± 0.39
Kaolin : scrap metal alum (30 g : 3 g)b	6.71 ± 0.33	6.65 ± 0.29	6.53 ± 0.33
Kaolin : scrap metal alum (30 g : 3 g)a	6.75 ± 0.39	6.61 ± 0.27	6.50 ± 0.41
Kaolin scrap metal alum (30 g : 4 g)b	6.65 ± 0.43	6.63 ± 0.35	6.61 ± 0.29
Kaolin scrap metal alum (30 g : 4 g)a	6.63 ± 0.25	6.60 ± 0.41	6.53 ± 0.35
Scrap metal alum	6.85 ± 0.31	6.80 ± 0.22	6.80 ± 0.39
Commercial sample 1	6.11 ± 0.44	5.97 ± 0.43	5.91 ± 0.31
Commercial sample 2	6.63 ± 0.35	6.59 ± 0.37	6.46 ± 0.39

pH of the raw water sample is 6.24

Calibration curve for determination of potassium

