PHYSICO-CHEMICAL AND HEAVY METALS ASSESSMENT OF 'NZU CLAY' AND ITS EFFECT ON HAIRS OF CONSUMERS

BY

RACHEAL UJOR AKPA
M.Sc/SCI/36802/2012-2013

DEPARTMENT OF CHEMISTRY,
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA.

JANUARY, 2016

PHYSICO-CHEMICAL AND HEAVY METALS ASSESSMENT OF 'NZU CLAY' AND ITS EFFECT ON HAIRS OF CONSUMERS

BY

Racheal Ujor, AKPA, B. Sc. (EBSU, 2009)
M.Sc./SCIE/36802/12-13

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (M.Sc) DEGREE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE,
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA.

JANUARY, 2016

DECLARATION

I declare that the work in this thesis entitled "Physico-chemical and heavy metals assessment of 'Nzu clay' and its effect on hairs of consumers" has been carried out by me in the Department of Chemistry, Ahmadu Bello University, Zaria. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma in this or any other institution.

AKPA, Racheal Ujor	----------	----------
(M. Sc/SCIE/36802/12-13)	Signature	Date

CERTIFICATION

This thesis entitled "Physico-chemical and heavy metals assessment of 'Nzu clay' and its effect on hairs of consumers" by Racheal Ujor AKPA meets the regulations governing the award of the degree of Master of Science (M.Sc) in Analytical Chemistry of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

Dr. K. I. Omoniyi Sign_____ Date_____
Chairman, Supervisory Commitee

Dr. S. E. Abechi Sign_____ Date_____
Member, Supervisory Committee

Prof. V. O. Ajibola Sign_____ Date_____
Head of Department

Prof. K. Bala Sign_____ Date_____
Dean, School of Postgraduate Studies

DEDICATION

To my Sweet Mum and Siblings, who believed and stood by me!

ACKNOWLEDGEMENTS

I am grateful to the Almighty God for His faithfulness and infinite mercy, inspiration, protection and abundant provisions that I enjoyed throughout the duration of my study.

I would like to offer my most sincere gratitude to my supervisors, Dr. K. I. Omoniyi and Dr. S. E. Abechi for their guidance, support, advice and patience, without them, this thesis would never be completed.

I acknowledge Prof. V. O. Ajibola (Head of Chemistry Department), Dr. F. O. Okibe (P. G. Coordinator), Dr. Hamisu Ibrahim (Seminar Coordinator), Prof. C. E. Gimba, Prof. A. O. Oyewale, Prof. A. Uzairu, Prof. J. O. Amiputan, Late Prof. J. F. Iyun, Prof. G. I. Ndukwe, Dr. J. D. F. Habila, Dr. S. O. Idris, Dr. E. D. Paul, Dr. O. J. Ocholi and the other staff members of Chemistry Department for their kindness and support during my study.

My sincere gratitude goes to Dr. I. A. Olatubosun from Obafemi Awolowo University for his selfless effort in helping me carry out the analysis, Mrs Owoade Latifat and Mr Madaki Bala for their assistance in laboratory analysis and interpretation of results.

I heartily appreciate my friend and confidant, Mr. Ijimdiya S. J. whose unwavering love, encouragement, prayers and support has led to the completion of this work and also my sincere gratitude goes to Mrs Olumuyiwa Bamishe for being sensitive and understanding.

To my Mother (Mrs Akpa. B.), sisters (Rhoda, Blessing, Helen, Ruth, Bernice and Grace) and only brother Ezra Akpa, to my Inlaws Mr. Chibuzor Mbah and Mr. Oliver Eze, to my Nephew Samuel Mba, Nieces Adah Mbah, and Oliver Goodness C. - You are the best part of my life. Thank you for your unwavering love, confidence, endearment, and devoted heart that has been my platform for exploits.

My profound appreciation goes to my friend and senior colleague, Mr. Francis Adikwu, for his selfless assistance and encouragement, course mates viz: Mr. Mike Abatyough, Mr. Okibe Godwin, Mrs Judith Mmereole, Miss Baraya Kyalla, Miss Made Ali, Mrs. Opeyemi Oludipe for their love and assistance during the course of the programme and to my bosom friend Mrs Omoyakhi Christy for always being there.

I recognize Mr. Omiogbemi Bello, Mr. Babatunde Victor, Mr. Michael Yakubu, Mr. Ibrahim Isah, Mrs. Esther Ben, Mrs. Ronke Oyeleke, Miss Zainab Azeez, Miss Chinomnso and all other members of Deeper Life Campus Fellowship (PG and Staff arm) for their spiritual nourishment, guidance and support, and to you who through patience and interest is reading this piece.

ABSTRACT

The assessment of the quality of the geophagious 'Nzu Clay' obtained from two hills in Ozanogogo, Ika South LGA, Delta State and Uzella river, Owan West LGA in Edo State Nigeria, with the highest cation exchange capacity, bulk density and dispersibility index, 10.800±0.424 meq/100g, 0.915±0.120 gcm^{-3}, 80.00±1.414 respectively was investigated while the pH range from 4.4 to 4.6. The concentrations of heavy metals in 'Nzu clay' obtained from the hill side were significantly higher at ($P < 0.05$) compared to the clay from Uzella river. The concentration of heavy metals in the clay from the river side was in the order: Zn □ Pb □ Cu □ Ni □ Cr □ Cd while the one from hill side showed that Cr □ Cu □ Zn □ Pb □ Ni □ Cd. The heavy metals in all the 'Nzu clay' exceeded their standard limit in soil according to WHO, 2010. The hair of addicted consumers of the clay above 5 years had mean values greater than that in addicted consumers of the clay below 5 years with concentrations of the heavy metals greater than the non addicted consumers as follows, As: 25.60 ± 1.1$mgkg^{-1}$, Cd: 4.35 ± 0.82, Cr: 112.47 ± 22.9, Cu: 4.04 ± 0.72, Ni: 7.62 ± 1.46, Pb: 2.99 ± 0.68 and Zn: 0.17 ± 0.22 mg/kg For consumers of the clay above 5 years, similarly the concentration of 22.44 ± 0.39, 2.59 ± 0.09, 66.06 ± 3.18, 0.52 ± 0.38, 3.95 ± 0.08, 1.14 ± 0.04, 0.12 ± 0.03 $mgkg^{-1}$ were recorded for As, Cd, Cr, Cu, Ni, Pb and Zn respectively for consumers below 5 years. These values exceeded the recommended dietary allowance in solid food by World Health Organization (WHO) National Agency for Food and Drug Administration and Control (NAFDAC). The levels of radioactive elements in 'Nzu Clay' obtained using Hyper Pure Germanium detector indicated that the average specific activities of ^{40}K, ^{238}U and ^{232}Th ranged from 54.45 ± 32.45 to 127.60 ± 14.7, 21.35 ± 6.28 to 38.75 ± 4.67 and 26.83 ±

13.94 to 44.51 ± 1.16 Bq/kg respectively. The radionuclides detected in ‘Nzu Clay’ are all lower than the worldwide averages by United Nations Scientific Committee on the Effects of Atomic Radiation, (UNSCEAR) 2000. The mean absorbed dose rate by the ‘Nzu Clay’ was 48.86 nGy/h, and is within the world average of 60nGy/h. The mean Annual Gonadal Equivalent Dose (AGED) in the ‘Nzu Clay’ was 207.1Sv/y, which is relatively high. The radium equivalent activity index, representative Gamma Index (Iyr), external hazard index (Hex) and internal hazard index (Hin) indicated a negligible health hazard in consuming the ‘Nzu Clay’. The XRD analysis revealed that the ‘Nzu clay’ was dominantly kaolinite and quartz. Based on the results obtained in this study, it is recommended that the ‘Nzu Clay’ be continually banned with appropriate defined measures.

TABLE OF CONTENTS

Title page		i
Cover page		iii
Declaration		iv
Certification		v
Dedication		vi
Acknowledgement		vii
Abstract		viii
CHAPTER ONE		
1.0 INTRODUCTION		1
1.1	Clay	1
1.2	'Nzu Clay'	1
1.3	Some of the Proffered Reasons for Geophagy in Humans	3
1.4	History of Clay	5
1.5	Physical and Chemical Properties of Clay	7
1.6	Uses of cay	9
1.7	Radionuclides of Specific Interest in Clays and the Environment	11
1.7.1	Pathways of radionuclides in the environment	12
1.7.2	Hazardous radionuclides and their impacts on human health	13
1.8	Gamma-ray Spectroscopy	15
1.8.1	Assessments of radioactivity levels	17
1.8.2	Biomonitor of Accumulated Heavy Metals in Human	17

1.9 Justification for the Study 18

1.10 Aim and Objectives of the study 19

CHAPTER TWO

2.0 LITERATURE REVIEW 21

2.1 Kaolin 21

2.2 Organoleptic and Granulometric Properties of Edible Clays 24

2.2.1 Cation exchange capacity 24

2.2.2 Bulk density 24

2.2.3 Water absorption index of the clay 25

2.2.4 Dispersibility of the clay 25

2.3 Heavy Metals in Clay 26

2.3.1 Arsenic 27

2.3.2 Chromium 27

2.3.3 Lead 29

2.3.4 Nickel 29

2.3.5 Zinc in clay samples 29

2.4 Health Impact of Heavy Metal 31

2.4.1 Arsenic 31

2.4.2 Cadmium 32

2.4.3 Lead 32

2.5 Radioactivity in Soil, Clay, Sand Samples 33

2.6 Selected Instrumentation Used in the Study 39

2.6.1 Theory and Instrumentation of X-Ray Diffraction Analysis 39

2.6.2 Procedure for XRD analysis 40

2.7 Theory and Instrumentation of Hyper Pure Gammanium Detector For Radioactivity Measurement 41

2.7.1 Hyper-pure germanium detector configuration 42

2.7.2 Planar configuration 42

2.7.3 Electric field and capacitance 44

2.7.4 Operational characteristics of HPGe 45

2.7.5 Energy resolution 46

2.8 Theory and Instrumentation of Atomic Absorption Spectroscopy for Metal Analysis 47

2.9 Structure of Hair 49

2.9.1 Hair as a superior bio-indicator of heavy metals compared to blood and urine 50

2.9.2 Hair analysis as a tool in assessing human exposure to heavy metals through geophagy and the limitations 52

CHAPTER THREE

3.1 MATERIALS 55

3.1.1 List of apparatus/equipments 55

3.1.2 List of reagent 55

3.1.3 Sampling of the clay types 56

3.2 Method 58

3.2.1 Quality assurance/Preparation of standard solution 58

3.2.2 Sampling of hair from addicted and non-addicted consumers of ‘Nzu clay’ 60

3.2.2a Processing of raw ‘Nzu Clay’ Sample 60

3.2.2b Sample preparation 62

3.2.3 Determination of some physico-chemical properties of the 'Nzu Clay' samples 62

3.2.4 Determination of the cation exchange capacity of the clay by the $Bacl_2$ compulsive exchange method 65

3.2.5 Digestion of 'Nzu clay' Samples for determination of total Cd, Cr, Cu, Ni, Pb and Zn contents 66

3.2.6 Measurement of the radioactivity in the clay samples 68

3.2.6 Radiation hazard indices 69

3.2.7 X-ray diffraction analysis of the 'Nzu Clay' samples using X-ray diffractometer 73

3.2.8 Statistical analysis 74

CHAPTER FOUR

4.0 RESULTS 75

CHAPTER FIVE

5.0 DISCUSSION 91

5.1 Physicochemical Parameters of the Raw and Processed/Finished 'Nzu clay' Samples 92

5.1.1 Correlation between similar physiochemical properties of the various sampling sites 96

5.2 Heavy metals concentration in 'Nzu clay' and in the hair of addicts and non addicts 97

5.2.1 Concentration of Arsenic in hair of addicts and in 'Nzu clay' samples 97

5.2.2 Concentration of Cadmium in the 'Nzu clay' samples and in hair of addicts 98

5.2.3 Concentration of Chromium in the 'Nzu clay' samples and in hair of addicts 99

5.2.4 Concentration of Copper in the 'Nzu clay' samples and in hair of addicts 100

5.2.5 Concentration of Nickel in the 'Nzu clay' samples and in hair of addicts 101

5.2.6 Concentration of Lead in the 'Nzu clay' samples and in hair of addicts 103

5.2.7 Concentration of Zinc in the 'Nzu clay' samples and in hair of addicts 104

5.3 Concentration (Bq/kg) of Radioactive Elements in 'Nzu clay' Samples 105

5.3.1 Level of the health risk hazard of radioactive elements in 'Nzu Clay' samples 107

5.4 Mineral composition of 'Nzu clay' by XRD method 110

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION 111

6.1 Summary 111

6.2 Conclusion 113

6.3 Recommendation 115

REFERENCE 116

LIST OF FIGURES

Figure:

1.0:	Silica tetrahedral and aluminum octahedron structure	8
2.0:	Classification of silicates	23
2.1:	Planar HPGe detector (p-type)	43
2.2:	Partial depletion of a planar detector	45
2.3:	Electric field variation of a planar detector	45
2.4:	Comparison of NaI(Tl) and HPGe spectra for ^{60}Co	47
2.5:	A typical Absorption spectroscopic block chart	48
2.6:	Human Hair Follicle and surrounding tissues	49
3.1:	Map of Delta State showing Ika Local Government Area in brown	57
3.2:	Raw 'Nzu Clay' hill in Ozanogogo village, Ika South LGA Delta State	57
3.3:	'Nzu clay' samples from hill and river source	61
3.4:	Mass attenuation coefficient of SiO_2 and Pb as a function of gamma-ray energy	69
4.1:	Concentration of Arsenic in hair samples of Addicts and Non-addicts	78
4.2:	Concentration of Cadmium in 'Nzu clay' samples and hair samples of Addicts and Non-addicts	79
4.3:	Concentration of Chromium in 'Nzu clay' samples and hair samples of Addicts and Non-Addicts	80
4.4:	Concentration of Copper in 'Nzu clay' samples and hair samples of	

Addicts and Non-addicts 81

4.5: Concentration of Nickel in 'Nzu clay' samples and hair samples of Addicts and Non-addicts 82

4.6: Concentration of lead in 'Nzu clay' samples and hair samples of Addicts and non addicts 83

4.7: Concentration of Zinc in 'Nzu clay' samples and hair samples of Addicts and Non addicts 84

LIST OF TABLES

Table:

2.1:	Some heavy metals and their target organs in man	31
2.2:	X-ray diffraction ‘d’ values of clay fraction	41
4.1:	Physicochemical Parameters of Raw and Finished Clay Samples	76
4.2:	Correlation between Similar Physiochemical Properties of the various Sampling Sites	77
4.3:	Target and intervention values for some metals for a standard soil (DPR-EGASPIN, 2002)	85
4.4:	Permissible limits for metals in solid food by FAO/WHO (2008)	86
4.5:	Concentration (Bq/kg) of Radioactive Elements in the ‘Nzu Clay’ Samples	88
4.6:	Presents the Health Risk Hazard of Radioactive Elements in ‘Nzu Clay’ Samples	89
4.7:	Name and Formula of the Minerals in the ‘Nzu Clay’ Samples using XRD method	90
4.8:	Crystallographic Properties of ‘Nzu Clay’ Samples by XRD method	91

LIST OF APPENDICES

Appendix

IA: Heavy Metals Concentrations of the 'Nzu Clay' from hill and water site

IB: Distribution and mean concentration of heavy metals in hair of non addicts of 'Nzu clay'

IC: Distribution and mean concentration of heavy metals in hair of > 5 yrs addiction

ID: Distribution and mean concentration of heavy metals in hair of < 5yrs addiction

IE: Heavy Metals Concentrations in Hair Samples of 'Nzu Clay' Addicts

II: Spectra of 'Nzu Clay' samples analysed using Hyper Pure Gammanium Detector.

IIIB: Concentration (Bq/kg) of Radioactive Elements in the 'Nzu Clay' Samples (one-way anova)

IIIC: Calculations on Hazard Index of Radioactive Element

IVA: X-ray diffraction of 'Nzu Clay' sample on CuKα in the 2θ region, glancing angle 15º – 75º

IVB: X-ray diffraction of 'Nzu Clay' sample on CuKα in the 2θ region, glancing angle 15º – 75º Stick Pattern

GLOSSARIES AND ABBREVIATIONS

Hanks solution: Simultaneous body fluid

Radioactive element: elements that can spontaneously emit ionizing radiation (gamma rays, alpha particles, neutrons, positrons, electrons etc) as a result of nuclear reaction or direct breakdown of an unstable nucleus.

Radioactivity: A property of unstable atoms to transmute on their own, without any external stimulus and in the process to release a characteristic radioactive emission.

Becquerel (Bq): The decay of one nucleus per second.

Gamma rays: A form of electromagnetic radiation.

Nuclide: An atomic specie characterized by the number of its protons, neutrons and its charge.

The Absorbed Dose: This expresses how much energy remains present in the material affected by radiation and is described with the unit radiation (rad) absorbed dose or Gray (1 Gray = 100 rad).

Effective equivalent dose: Characterizes the sum of all organ absorbed doses multiplied by the accompanying tissue weighting factor. 'Effective' means that the tissue weighting factors take into account the fatalities caused by radiation, as well as genetic damage only into the first subsequent generation.

ICRP: International Committee on Radiological Protection

ICDD: International Centre for Diffraction Data

JCPDS: Joint Committee on Powder Diffraction Standards

CHAPTER ONE

1. INTRODUCTION

1.1 CLAY

Animals are instinctively drawn to clay, especially when it is in the form of mud. Animals lick the clay or if injured, roll around in it to obtain relief from their injuries. It has now been observed that many varieties of species have evolved to ingest clay to counteract environmental and man-made toxins. Many herbivorous animals will eat clay after ingesting herbs loaded with tannins, a toxic substance (Domini *et al.,* 2004). The practice of eating clay for gastrointestinal ailments and applying clay topically as bandaids for skin infections is as old as mankind and one that continues today among traditional ethnic groups as well as numerous animal species (Carretero, 2002).

1.2 Nzu Clay

'Nzu clay' – also known (according to language/locality) as Argile, Calabar stone, Calabash clay, Ebumba, La Craie, Mabele, Ndom, Poto and Ulo – is a generic term used for naming these Nigerian geophagical materials. This material is available in a variety of forms including powder, moulded shapes and blocks. Though native to Africa, it is available in the UK in ethnic stores and markets. 'Nzu clay' is used for facial masks or soap. Though the consumption of this chalk cuts across sex and age, it is greater among women, especially during pregnancy (Callahan, 2003). Geophagia in Nigeria is noted to be especially associated with pregnant women who consume earth materials to alleviate the symptoms of morning sickness (Abraham, 2002).

This chalk which occurs naturally and made up of fossilized sea shells may be prepared artificially. It is prepared as a combination of clay and mud, with other ingredients like sand, wood ash and sometimes salt being mixed to them, it is then moulded and heated to produce the final product (Callahan, 2003). Calabash chalk has the structure of aluminium silicate hydroxide, which is a member of the kaolin clay group with a possible formula $Al_2Si_2O_5(OH)_4$ (Dean *et al*., 2004). Multi-elemental analysis by energy dispersive x-ray fluorescence spectroscopy (EDXRF) quantified 22 elements in 'Nzu clay' including lead and aluminium, as well as persistent organic pollutants (Dean *et al*., 2004). Another report had established the presence of arsenic (Campbell and Belfast, 2002). Lead and other toxic elements present in the clay have been reported to be associated with numerous gastrointestinal disorders including nausea, ulcer, gastritis etc. (Caraterro, 2002). This geophagic material is consumed by oral route, and several pollutants have been reported to be present in 'Nzu clay'. The most severe risk of eating clay is a total blockage of the lower intestine, which can only be remedied by surgery (Padilla and Torre, 2006).

Pica is the ingestion of any unusual substance. Many definitions have been proposed for this word, among them "the craving for oral ingestion of a given substance that is unusual in kind or quantity" and it is defined as manifestations of false or craving appetite leading to the deliberate ingestion of a bizarre selection of foods, non-nutritive substances and non-food items (Parry and Parry, 1992). Commonly cited items of pica are hair (*trichophagia*), burnt matches (*cautopyreiophagia*), feaces (*coprophagia*), lead paint chips (*plumbophagia*), leaves, grass and plant sterns (*foliophagia*), starch (*arnylophagia*), stones (*lithophagia*) and soil (*geophagia*) (Callahan, 2003).

People have often speculated that geophagy occurs as a result of a desire or need for salt. Examination of the literature, however, indicates this is unlikely in most cases for example, in some areas salt is actually added to clay before ingestion. (Vermeer, 1998) noted that among certain tribes in Nigeria salt is added to soil before it is eaten.

1.3 Some of the Proffered Reasons for Geophagy in Humans

Soil has been eaten for a variety of reasons throughout history, these can be grouped accordingly, as; medicinal use, for cosmetics, use during pregnancy, as a famine food, as a food additive or condiment, and for religious or ceremonial purposes (Dean *et al*., 2004). Worldwide, the medicinal properties ascribed to clays are numerous. Soil has been used to treat a multitude of diseases and ailments. Soil has been used both internally and externally, for example, it has been used externally to treat bubonic plague, eczema and herpes and internally for treatment of such ailments as diarrhea and nausea which formed basis for other digestive and antibiotics production usage (Williams *et al.*, 2008). This belief can be attributed to the fact that clay acts as coating material on the gastrointestinal tract and may absorb dangerous toxins. In pharmaceuticals/cosmetics, bentonite is used as a binder in tablet manufacturing. Clays are used as thickeners in a wide variety of cosmetics including facial creams, lipsticks, shampoos and calamine lotion (Doel *et al.*, 2012). Bentonite was reported to be used in 78 different cosmetics in the USA, usually at concentrations between 1% and 10%, but reaching 80% in some paste masks (CIREP, 2003).

It is generally assumed that children ingestion rates are higher than adult rates, due primarily to children's mouthing behaviour. Consumption of clay is more predominant

among women than men. It was observed that social pattern of soil eating was less frequent among young boys than in girls where no age trend was apparent (Calabrese *et al.*, 1997). Geophagy is most commonly cited as occurring during pregnancy (Saathoff *et al*., 2002). From the 16th to the 20th century, it was widely believed to be dangerous to stop pregnant women from eating whatever they wanted. Another widely held belief is that women practising geophagy will have children which are more handsome and that clay keeps the body from being marked at birth (O'Rourke *et al*., 1967). Prevalence of geophagy among pregnant women of Malawi, Zambia, Zimbabwe, Swaziland and South Africa is estimated to be 90% (Hunter, 1993).

Soil ingestion has often been related to famine (Callahan, 2003) gives numerous examples of soil being used in this manner in China, New Zealand, New Caledonia, India, Mongolia Germany, Finland, Africa, North and South America. (Vermeer, 1998) noted that among the Tiv of Nigeria it is common to qualify a bad famine by saying that "one only had dirt to feed his children".

Not only that, soil has also been used by various people as a food additive or condiment. Soil is sometimes added to breads and wild potatoes to decrease bitterness. In 1998, bentonite was approved for use as a "Generally regarded as safe" (GRAS) food additive in the USA, (US. FDA, 2004).

Bentonite is used to bind tiny particles of iron ore, which are then formed into pellets for use as feed material for blast furnaces. Finely ground clays are used in paint industry to disperse pigment evenly throughout the paint. Without clays, it would be extremely difficult to evenly mix the paint base and colour pigment (Callahan, 2003).

In addition, soils are eaten in religious ceremonies in Mexico, Barbados, China, Burma, and Malaysia. Diatomaceous earth in China was often hailed as having a supernatural origin, and the finding and ingestion of this earth was viewed as a happy omen. Geophagy also occurs in various cultures in conjunction with the swearing of oaths (Laurie, 2008).

1.4 History of Clay

Clay has been used in bricks and pottery for millennia. Sun-dried brick were used from possibly over 10,000 years ago and kiln-fired bricks were used in the construction of a temple in the Euphrates region, considered to be more than 5000 years old. Sumerian and Babylonian builders constructed ziggurats, palaces and city walls of sun-dried bricks and covered them with more durable kiln-baked bricks, often brilliantly glazed and arranged in decorative pictorial friezes. The earliest form of pottery was earthenware (porous and coarse), which has been made for at least 9000 years. The earliest pottery yet discovered in the Middle East comes from Çatal Hüyük, in Anatolia (near modern Çumra, Turkey), and dates from 8500 years ago. The oldest translucent porcelain originated from China during the T'ang dynasty (618-907 AD). The porcelain best known in the West (where it is called chinaware) was not produced until the Yuan dynasty (1278-1368 AD). This "hard-paste" porcelain was made from petuntse, or china stone (a crushed kaolinised granite consisting of a mixture of kaolinite, sericite, feldspar and quartz), ground to powder, mixed with kaolin and fired at a temperature of about 1450 ºC. Porcelain import from China was considered a great luxury in Europe and attempts to imitate it led to discovery in Florence during 1575 of "soft-paste" porcelain (or frit porcelain), a mixture

of clay and ground glass fired at about 1200 ºC. The secret of hard-paste porcelain was discovered in about 1707 at the Meissen factory in Saxony (Germany) by Johann Böttger and Ehrenfried von Tschirnaus. English bone china was first produced around 1800, when Josiah Spode added calcined bones to the hard-paste porcelain formula (Konta, 1995).

The use of clays (probably smectite) as soaps and absorbents was reported in Natural History by the Roman author Pliny the Elder (AD 77). The use of kaolin-bearing surface on paper began in China about 400 AD when powdered kaolin was added to the pigment of paper coating (Konta, 1995).

Clays are present in soils, they may be formed in soils during soil development through the weathering of various minerals or can be found essentially without change in the parent material from which the soils were formed. Parent material, climate, topography and vegetation determine the kinds of clays that are found. Hydrothermal alteration may also lead to clay formation. As erosion acts on the landscape, clay may be suspended in water and carried until they are deposited by sedimentation (Redmond, 2009).

Clays are generally mined by highly selective open pit methods using hydraulic excavators, front-end loaders, or draglines. The clay is then processed using either a dry (air flotation) or a wet process (water washing). The wet process produces a higher cost and higher quality product than the dry process. The dry process involves crushing, drying, pulverizing and air flotation, to remove the grit particles (mostly quartz and feldspar). In the wet process, the first step is to remove the non-clay minerals, usually by extracting the grit from clay slurry in drag boxes, classifiers, and/or hydro cyclones. The

clay slurry is centrifuged and then thickened to about 30% solids in settling tanks. Further processing may involve ultra flotation and screening/filtering. In some cases flotation or high-intensity magnetic separation is used to remove iron and titanium impurities (Pattanyak *et al.,* 2014).

1.5 Physical and Chemical Properties of Clay

Clays are colloidal – sub-microscopic and held in suspension in solution. When wet, they are viscous gelatinous and sticky. When dry, clay is hard, packed and cohesive. It is composed of micelles (flat, sheet-like plates laminated into stacks). They are chemically very complex, negatively charged with very high cation exchange capacity (CEC): 10-100 meq/100g and these charge allows flocculation or de-flocculation.

Clay minerals are fine-particle-size hydrous alumino-silicates which develop plasticity when mixed with water. They vary over quite wide limit in chemical, mineralogical and physical characteristics. They are all composed of electrical neutral alumino-silicate layers which move readily over each other, giving rise to such physical properties as softness, soapy feel and easy cleavage (Manukaji, 2004). All clay minerals are of secondary geologic origin that is, they are formed as alteration products of alumino-silicate rocks in an environment in which water is present (Ijagbemi, 2002). Clay minerals are produced mainly from the weathering of feldspars and micas. They form part of a group of complex alumino-silicates of potassium, magnesium and iron, known as layer-lattice minerals (Abifarin, 1999). They are very small in size and very flaky in shape, and so have considerable surface area. These surfaces carry a negative electrical charge, a phenomenon that has great significance in the understanding of the engineering

properties of clay soils (Agha, 1998). Their layer-lattice structure comprises of tetrahedral unit, which is made up of a central silicon ion with four surrounding oxygen ions and the octahedral unit comprising of a central ion of either aluminum or magnesium, surrounded by six hydroxyl ions. In both, the metal is on the inside and the non-metallic ions form the outside (Akinbode, 1996). The layer structure is formed when the oxygen ions covalently link between units. Thus, a silica layer is a form of linked tetrahedral unit, having a general formula of $nSi_4O.10(OH)$. The spacing between the outer ions in the tetrahedral and octahedral layers is sufficiently similar for them to link together via mutual oxygen or hydroxyl ions. Two stacking arrangements are possible, giving either a two-layer or a three-layer structure (Mahmoud *et al.,* 2003). In a two-layer lattice, tetrahedral and octahedral layers alternate, while a three-layer arrangement consists of an octahedral layer sandwiched between two tetrahedral layers as seen in fig 1.0. Mineral particles are built up when the layers are linked together to form stacks (Li and Zhou, 2001; Mahmoud *et al.*, 2003).

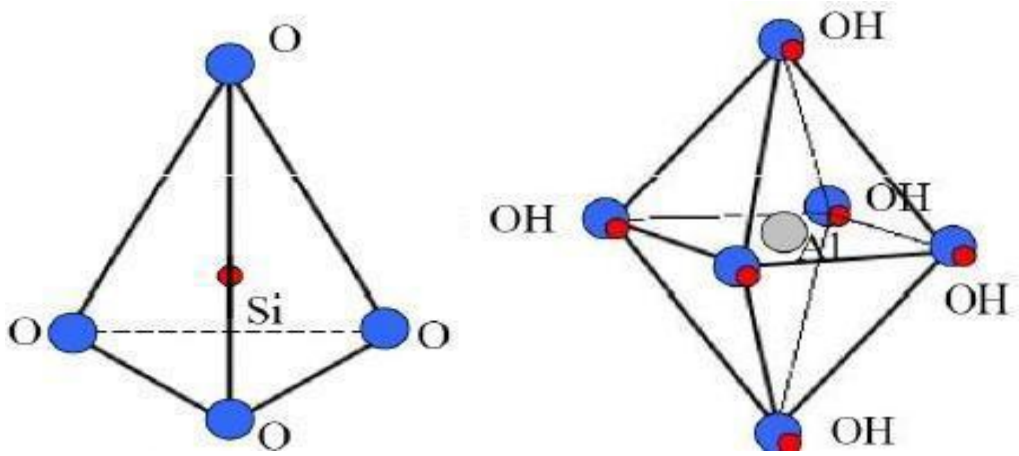


Figure 1.0: Silica tetrahedral and aluminum octahedron structure (Li and Zhou, 2001)

1.6 Uses of Clay

Clay as raw materials are used in industry and other areas of human activity. The most extensive applications are naturally in industrial branches. Many applications however, include the area called the 'formation and protection of the environment'. It is enough to be aware of the fact that industrial products utilizing clay raw materials such as porcelain, various ceramic goods, plastics, rubber goods, innumerable sorts of paper and other products influence the environment of mankind. In the formation of modern human environment, all ceramic products have a substantial significance. The building ceramic parts, manufactured bricks and roofing tiles, sanitary ceramics, easily washable tiles for exteriors and interiors in subways, airports and railway stations, shopping centres, private flats, all of them are mainly manufactured from clay raw materials (Manukaji, 2004).

Furthermore, clay minerals are of use in various paints and varnishes where they act as filler, provide protection against weathering and improves the flatting effect and adhesion of paint. Paints and varnishes filled with clay minerals also protect against corrosion and erosion (Pattanayak *et al*., 2014). A vast area of utilization of clay minerals in the protection of the environment includes their role as sorbents and retention-insulation materials. Certain clay minerals are noted for their specific adsorption properties. Kaolinite is suitable for the sorption of fluoride ions from water (Pattanayak *et al*., 2014)

Radioactive alkaline metals are most effectively sorbed by mica clay minerals, while chlorite is suitable for divalent radionuclides. Clay minerals in rivers, both in suspension and settled in muds, are important adsorbents of toxic substances in solution. The stirring properties of clay in water (including adsorption) have been known since the days of

ancient Greece and Rome. The role of clay minerals is also fundamental in agriculture, fruit growing and forestry. Clay minerals in soils are important sources of nutrients. As negatively charged colloidal bridges, they encourage a long-term proton exchange from plant roots for necessary cation released from weathering primary minerals (Speight, 2006)

In the building industries, clays and bricks are used as construction raw materials. Bricks are made up of 100% earth materials which include shales, clays, and fine-grained lateritic soils (Obaje *et al.,* 2013).

In archeology, clay minerals can serve as archaeological thermometers in the investigation of ancient ceramics. The investigation of clay minerals and argillaceous rocks in geological sciences today is an extensive region of theoretical and applied research. Clay minerals and argillaceous sediments play an important role in the oil geology and oil industry. They are of use partly as adsorbents of unwanted compounds and partly as catalysts for cracking (Speight, 2006; Ismadji, 2015).

In the southern part of Nigeria, most regions are richly blessed with natural resources like clay. These clay-based materials occur both in the plain and riverine areas (Amaefule, 1990). The use of these material resources was made possible by the application of heat in transforming the soft clay deposit into something malleable, hard, and durable. The use of these material resources was made possible by the application of heat in transforming the soft clay deposit into something malleable, hard and durable (Dinadle, 1986; Amaefule, 1990; Nweke and Ugwu, 2007).

It is believed that the history of ceramics really began with the recognition of clay as a useful raw material. The characteristic features of interest include plasticity, resistance to high temperature, malleability and complex composite formulations. The various characteristic properties of most clay products are believed to be the consequence of impurity additions and sintering firing procedure (Nweke and Ugwu, 2007). It is clear and well known that clay–based materials are especially abundant in high temperature areas like Nigeria, since it possesses the ability to resist compressional forces to a reasonable extent.

Based on the stacking arrangements and chemical composition of clay; six main groups of clay minerals may be identified: kaolinite, montmorillonite, illite, chlorite, attapulgite and vermiculite (Karpiński and Szkodo, 2015). The presence of minor amounts of mineral or soluble salt impurities in clays can restrict their uses. The more common mineral impurities are quartz, mica, carbonates, iron oxides, sulphides and feldspar (Mohammed *et al.,* 2013).

1.7 Radionuclides of Specific Interest in Clays and the Environment

With regard to internal exposure from ingestion of clay being part of the immediate pathways leading to contamination of food and the environment, the most important radionuclides to be assessed in the environment are:

i. Alpha emitters: ^{238Pu}, $^{239+240}$Pu, ^{241}Am, ^{242}Cm

ii. Beta emitters: ^{89}Sr, ^{90}Sr and tritium

iii. Gamma emitters: ^{134}Cs, ^{137}Cs (^{137m}Ba), ^{I31}I

In general, the radionuclides of major importance in the contamination of clay/soil or food and environmental samples (materials which are part of the pathways leading to food) are:

Air: ^{131}I, ^{134}Cs, ^{137}Cs

Water: ^{3}H, ^{89}Sr, ^{90}Sr, ^{131}I, ^{134}Cs, and ^{137}Cs

Milk: ^{89}Sr, ^{90}Sr, ^{131}I, ^{134}Cs, ^{137}Cs

Meat: ^{134}Cs, ^{137}Cs

Other foods: ^{89}Sr, ^{90}Sr, ^{134}Cs, ^{137}Cs

Vegetation: ^{89}Sr, ^{90}Sr, ^{95}Zr, ^{95}Nb, ^{103}Ru, ^{106}Ru, ^{131}I, ^{134}Cs, ^{137}Cs, ^{144}Ce

Soil/Clay: ^{90}Sr, ^{134}Cs, ^{137}Cs, ^{238}Pu, $^{239+240}Pu$, ^{241}Am, ^{242}Cm, ^{234}Th, ^{235}U, ^{40}K

The levels of radionuclides in the environment/clay and food have been extensively compiled by UNSCEAR (2008). This group of radionuclides is most likely to be of concern in terrestrially produced foods. Biological concentration processes in fresh water and marine systems can result in very rapid transfer and enrichment of specific radionuclides (EPA, 2008).

1.7.1 Pathways of radionuclides in the environment

Some levels of radiation are naturally present in surface and ground water, but other degrees of radiation exposure come from contact with rocks, clay and soil that have been contaminated with artificially produced radionuclides such as ^{239}Pu, $^{137}Cs^{90}Sr$, ^{241}Am and

^{131}I. Release of radionuclides into environmental materials is part of the immediate pathways to the commonly encountered hazardous radionuclides through accidents, poor waste disposal or other means. Contamination of clay/soil and water sources can occur from dust transported by wind from uranium mine sites and waste deposits (Neves *et al*., 2008).

1.7.2 Hazardous radionuclides and their impacts on human health

Natural sources of radioactivity are all around and man-made radioactive materials are vital part of medicine and industry. Exposure to some radiation, natural or man-made is inevitable. We live with radiation every day, therefore we must understand its risks. Radiation is known to cause cancer in humans and other adverse health effects, including genetic defects in children of exposed parents or mental retardation in the children of mothers exposed during pregnancy (EPA US, 2007).

Eighty percent of that exposure comes from natural sources of radon gas, the human body, outer space, rocks and clay/soil. The remaining 20 percent comes from man-made radiation sources, primarily medical x-rays. Radioactive materials that decay spontaneously produce ionizing radiation, which have sufficient energy to strip away electrons from atoms (creating two charged ions) or to break some chemical bonds. Any living tissue in the human body can be damaged by ionizing radiation in a unique manner. When ionizing radiation, it strikes an organism's cells and may injure the cells. If radiation affects a significant number of cells, it can eventually lead to cancer. At extremely high doses, this type of exposure can cause death. In general, there is no safe level of radiation exposure (EPA, 2008).

In the Chernobyl nuclear plant disaster which occurred in Ukraine 1986, some 60 radionuclides were emitted from the reactor (Balonov, 2008), but only a few were considered to present serious health hazards to humans and animals. Immediately after the disaster, the main health concern involved is radioactive iodine-131, with a short half-life (eight days). It can be relatively transferred to humans rapidly from the air and through consumption of contaminated milk and leafy vegetables. Iodine becomes localized in the thyroid gland (EHP, 2010). Today, there is concern about contamination of the soil with strontium-90 (half-life approximately 30 years) which occurs in the clay/soil, food and water. It can be deposited in bones and remain in the body for long periods. In addition, ^{90}Sr could cause problems in areas close to the reactor, but at greater distances its deposition levels are low (EHP, 2010).

Uranium mining and the use of nuclear reactors are common sources of radionuclides. They are primarily contained in radioactive wastes, which present serious threats to human health. It also causes lung cancer and death in uranium miners. Long-term exposure to radon leads to an elevated risk of leukemia (Yablokov, 2009).

Cesium-137 and 134 isotopes of cesium have relatively longer half-lives (^{134}Cs has a half-life of 2 years while that of ^{137}Cs is 30 years). These radionuclides cause longer-term exposures through the ingestion pathway and through external exposure from their deposition on the ground. The radionuclide can be ingested or inhaled and resides in muscle, tissue, bones and fat. The geochemical characteristics of this radionuclide are fairly similar to those of nonradioactive ^{55}Cs (El-Reefy, 2004). Therefore, ^{137}Cs released into the atmosphere becomes strongly adsorbed by clay minerals and also by organic matter in soils. It has received particular attention in the marine environment due to its

long environmental half-life, high radio-toxicity and easy assimilation by animal and plant tissues. It is usually present as simple cation with high solubility and mobility in marine environments, depending particularly on the sorption of ^{137}Cs to sediment surfaces (El-Reefy, 2004).

1.8 Gamma-ray Spectroscopy

There are a lot of methods and techniques that are applied in the determination of naturally occurring radionuclide in geological, biological and environmental media such as rocks, soil, air and natural wastewater. However, quantitative gamma-ray spectroscopy is a powerful technique available for the non-destructive analysis of samples from such media (Yousef *et al.*, 2007). The basic principles involved in the use of gamma-ray spectroscopy include:

i. Energy Calibration: Energy calibration is simply to assign the correct energy value to the corresponding channel number. The pulse height is assumed to be proportional to the energy of the incident particle. In gamma-ray spectroscopy, the pulse height scale must be calibrated in terms of absolute gamma-ray energy if various peaks in the spectrum are to be properly identified. In many applications, the gamma-rays expected to appear in the spectrum are well known in advance and the corresponding peaks can be identified by inspection. In other applications, unknown gamma-ray spectra may occur and hence a spectra calibration gamma-ray source is used to supply peaks of known energy in the spectrum. Accurate calibration should involve a standard source with gamma-ray energies that are not widely different from those to be measured in the unknown spectrum. It is also useful to have multiple calibration peaks at various points

along the measured energy range of interest. The selection of standards to be used for gamma-ray spectrometer calibration depends on the energy range of interest (Bernard *et al*., 1998; Glenn *et al.*, 2000).

ii. Detection Efficiency: In principle, all detectors give rise to an output pulse or signal for a quantum of radiation, which interacts within its active volume. Radiation such as gamma-ray must first undergo a considerable interaction in the detector crystal before detection is possible because gamma photons can travel large distance between interactions, detectors are often less than 100% efficient. It then becomes necessary to have a precise figure for the detector efficiency in order to relate the number of pulses counted to the number of photons incident on the detector (Gilmore and Hemingway, 1995; Knoll, 2002).

iii. Intrinsic efficiency:

$$\square int = \frac{no.of\ pulses\ at\ the\ detector\ output}{no.of\ radiation\ quanta\ incident\ on\ detector} \qquad 1.1$$

The intrinsic efficiency of a detector is a detector property and is independent of the geometry. The intrinsic efficiency of a detector depends on the detector material, the radiation energy and the physical thickness of the detector in the direction of the incident radiation.

iv. Absolute Efficiency (photopeak)

$$\varepsilon_{abs} = \frac{no.of\ pulses\ recorded\ in\ photopeak}{no.of\ radiation\ quanta\ emitted\ by\ source} \qquad 1.2$$

The absolute efficiency is dependant not only on detector properties but also on the details of the counting geometry such as the distance from the source to the detector. By

using many calibration sources with known activities, the absolute efficiency of the detector for each gamma-ray line can be calculated from the formula:

$$abs = \frac{N}{A \times P\gamma} \qquad 1.3$$

(Gilmore and Hemingway, 1995; Knoll, 2002).

1.8.1 Assessments of radioactivity levels

Identification and assessment of low radioactivity levels in different samples emitting gamma rays by High purity Germanium detectors (HPGe) requires two types of calibration such as energy calibration and photopeak detection efficiency calibration. Energy calibration is necessary to identify different isotopes from the respective gamma ray energy lines, while photopeak detection efficiency determination is necessary for quantitative assessment of the radioactivity levels for each radioisotope (Gilmore and Hemingway, 1995).

1.8.2 Biomonitor of accumulated heavy metals in human

Trace element analysis on hair samples has been widely used to assess wildlife and human exposure to different contaminants present in the environment or at the workplace. Several advantages were mentioned for the use of this biological material in monitoring studies (Wenning, 2000; ATSDR, 2001), namely:

(i) The less invasive character of hair collection procedures that avoid veninpucture,

(ii) The stability of hair, as a biological material, which facilitates the storage and transport processes,

(iii) The higher concentrations of residues usually found in hair samples, when compared to those on blood and urine, and

(iv) The capacity of hair to accumulate metals during extended periods, at least 1 year of exposure.

The World Health Organization (WHO), Environmental Protection Agency (EPA), and International Atomic Energy Agency (IAEA) have recommended the use of hair as an important biological material for worldwide environmental monitoring (Samanta *et al.,* 2004).

1.9 Justification for the Study

Clay eating is a global practice that exists among humans as well as animal species. Several researches carried out on 'Nzu clay', a geophagious material has revealed abnormally high amount of heavy metals. These heavy metals have the capacity to bioaccumulate in human system.

Hair testing can complement conventional blood and urine analysis as it enlarges the window of detection and by segmentation, permits differentiation between long-term therapeutic use and single exposure. So, there is a sound motivation for investigating the elements contained in hair of group of people that ingest 'Nzu clay' habitually. The levels of the selected heavy metals in the hair of addicts (long and short term addicts) of 'Nzu clay' will signal the long and short term implication of consuming the clay.

Exposure to some radiation, natural or man-made is inevitable. We live with radiation everyday; therefore, we must understand its risks. Radiation is known to cause cancer in humans and other adverse health effects, including genetic defects in the children of exposed parents or mental retardation in the children of mothers exposed during pregnancy (EPA, US, 2007). The presence of natural radioactivity in soil results in external and internal exposure to humans. People who ingest 'Nzu clay' are exposed to radioactive element that is natural in soil. There is the need for the clay/soil to be analyzed to determine the radioactive contaminants and the level of contamination to its low levels since radioactive contamination pose a health risk. This would provide information on the safety of consuming the products which is sourced from different environment in the South Eastern part of Nigeria.

1.10 Aim and Objectives of the study

The aim of this work was to evaluate the activity concentration of radionuclides, physico-chemical properties of 'Nzu clay' at the raw and processed stages and to assess the level of heavy metal exposure in 'Nzu clay' addicts using biological samples (hair).

This aim was achieved through the following set objectives:

i. Ascertaining the physico-chemical parameters of 'Nzu clay' (swelling power, dispersibility, bulk density, water absorption index, cation exchange capacity and pH);
ii. determining the crystallographic particle size distribution of the raw and finished product of the clay using X-ray Diffraction (XRD);

iii. determining the activity concentration of radioactive elements in ‘Nzu clay’ using Hyper-pure Germanium Detector and

iv. assessing the level of As, Cd, Cr, Cu, Pb, Ni, and Zn in ‘Nzu clay’ samples and in the hair of addicted consumers (less than and above five (5) years) of the clay to compare with those of non-consumers of the clay.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Kaolin

The name "kaolin" is derived from the word Kau-Ling, or high ridge, the name given to a hill near Jau-chau Fu, China, where kaolin was first mined. Kaolin, commonly referred to as china clay, is a clay that consists mainly of kaolinite (85–95%) (Sepulveda *et al.*, 1983; Bish, 1993).

Kaolinite, the main constituent of kaolin, is formed by rock weathering. It is white, grayish-white, or slightly colored. It is made up of tiny, thin, pseudo hexagonal, flexible sheets of triclinic crystal with a diameter of 0.2–12 μm. It has a density of 2.1–2.6 g/cm^3. The cation exchange capacity of kaolinite is considerably less than that of montmorillonite, in the order of 2–10 meq/100 g, depending on the particle size, but the rate of the exchange reaction is rapid, almost instantaneous. The process of kaolin formation is called kaolinization (Grim, 1968; Farmer, 2000).

Kaolinite formation occurs in three ways:

i. Crumbling and transformation of rocks due to the effects of climatic factors (Zettlitz type);
ii. transformation of rocks due to hydrothermal effects (Cornwall type) and
iii. formation by climatic and hydrothermal effects (Mixed type).

The type of clay mineral formed during the decay of rocks containing aluminium silicates is influenced by the climate, the aluminium/silicon ratio, and pH. Conditions conducive

for kaolinite formation are strong dissolution of Ca^{2+}, Mg^{2+} and K^{+} ions and the presence of H^{+} ions (pH 4–5) (Parker, 1988; Lee *et al.,* 1999; Balan *et al.,* 2014). It has number of properties relevant to medicine. However, is an excellent adsorbent and will adsorb not only lipids and proteins, but also viruses and bacteria (Lipson and Stotzky, 1983; Farmer, 1998; Frost *et al.,* 2001; Balan *et al.,* 2010).

Kaolin is used in a large number of different cosmetic products, such as eye shadows, blushers, face powders, mascaras, foundations, makeup bases and others. In 1998, kaolin was reported to be used in 509 different cosmetics in the USA, usually at concentrations between 5% and 30%, but reaching 84% in some paste masks (CIREP, 2003). Classification of kaolinite as member in the silicates family is shown in Fig 2.0

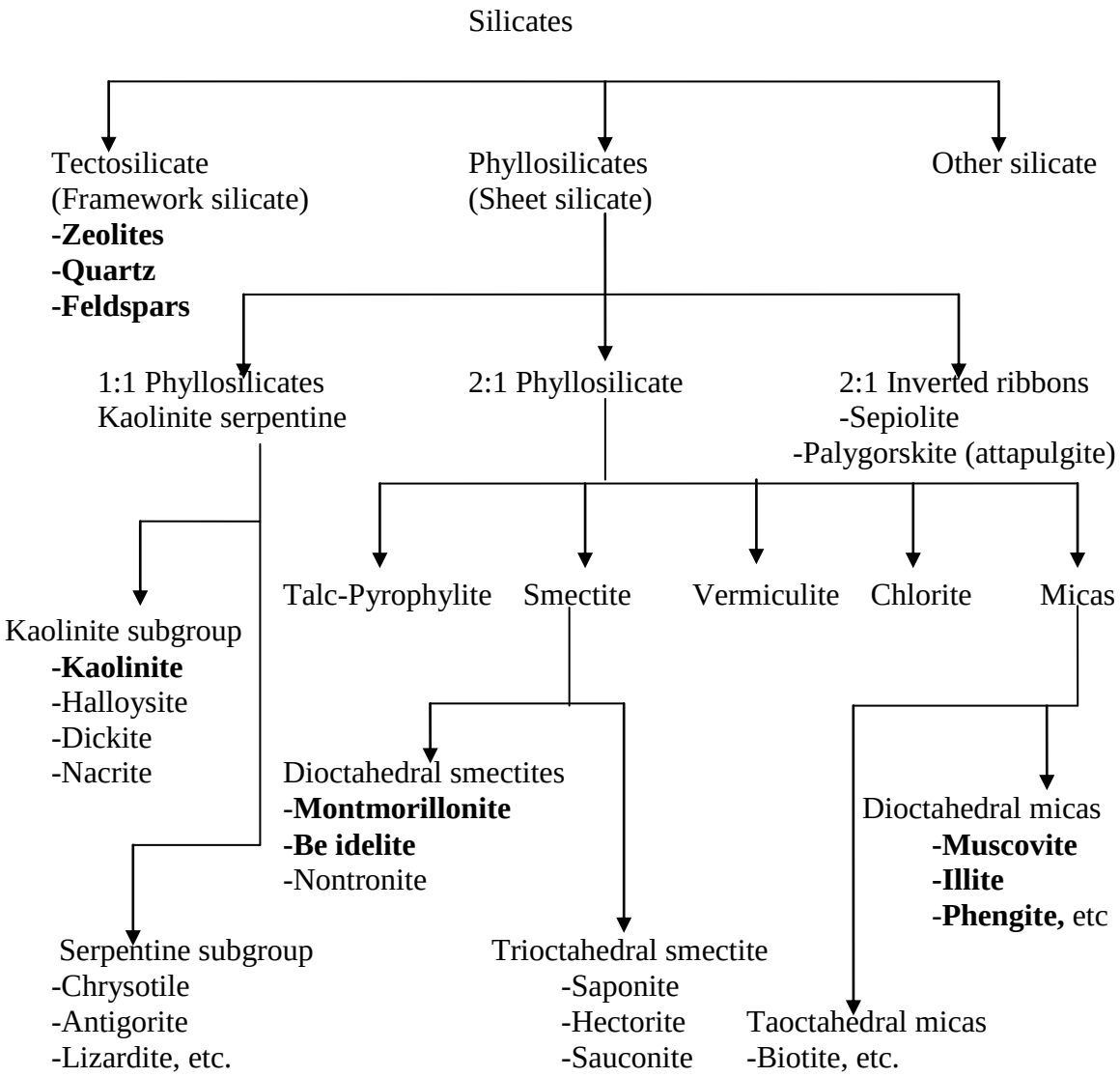


Figure 2.0 Classification of silicates (Bailey, 1980b; Rieder *et al.*, 1998).

Minerals that can be frequently found in bentonite or kaolin are in bold; the main components are in large typeface. *Illite* is a component of common soil and sediments and is classified as mica.

2.2 Organoleptic and Granulometric Properties of Edible Clays

2.2.1 Cation exchange capacity

The cation exchange capacity (CEC) is the amount of exchangeable cation per unit weight of dry soil that plays an important role in soil fertility, or the amount of negative charge in soil that is available to bind positively charged ions (cations). Hydrogen (H^+) and aluminum (Al^{3+}) ions are the predominant cation occupying the CEC in soils. It depends especially on the pH, clay mineral and on the soil organic matter content. Soil texture also influences the CEC of the clay. Higher quantities of clay and organic matter result to higher CEC. The CEC of a soil is a good indicator of the nutrient holding and buffer capacity of the soil, but in itself is not particularly useful for managing soil properties (James, 2001).

Amounts of negative and positive charges are both expressed in milliequivalents. A milliequivalent takes into account both the weight and the charge of the cation. One milliequivalent of negative charge on a clay particle is neutralized by one milliequivalent of cation.

The predominant clay mineral in most clay soils is kaolinite which has a CEC of 5 meq/100 g. Other clay minerals, such as smectite and vermiculite, have in excess of 100 meq/100 g CEC, but occur in limited amounts in some soils (Ngole *et al.,* 2010).

2.2.2 Bulk density

The bulk density of a powder is the ratio of the mass of an untapped powder sample to its volume including the contribution of the interparticulate void volume. Hence, the bulk

density depends on both the density of powder particles and the spatial arrangement of particles in the powder bed. The bulk density is expressed in grams per cubic centimeter (g/cm^3), although the international unit is kilogram per cubic meter (1 g/cm^3 = 1000 kg/m^3), because the measurements are made using cylinders. It may also be expressed in grams per cubic centimetre (g/cm^3).

The bulking properties of a powder are dependent upon the preparation, treatment and storage of the sample. The particles can be packed to have a range of bulk densities and moreover, the slightest disturbance of the powder bed may result in a changed bulk density.

The bulk density of a powder is determined by measuring the volume of a known mass of powder sample that may have been passed through a sieve into a graduated cylinder. The bulk density of soil depends greatly on the mineral make up of soil and degree of compaction, soil high in organics and some friable clay may have a bulk density well less than 1 g/cm^3 (Miller and Donahue, 1990).

2.2.3 Water absorption index of the clay

Water absorption capacity is the ability of the clay to absorb water and swell for improved consistency. It is desirable in food systems to improve yield and consistency and give body to the food (Osundahunsi *et al.,* 2003).

2.2.4 Dispersibility of the clay

The main difference between dispersive and nondispersive clays is the amount and type of cation. The lower the content of dissolved salts in the water, the greater the susceptibility of sodium saturated clays to dispersion. The presence of exchangeable sodium is an important chemical factor contributing towards dispersive behavior in soil (Bell and Walker, 2000). Another property that enhances the susceptibility of clay soils to dispersion is total dissolved salts (TDS) in the pore water. In other words, sodium saturated clays are more susceptible to dispersion as the dissolved salt concentration in the water decreases (Bell and Bruyn, 1997).

2.3 Heavy Metals in Clay

Heavy metals enter the surroundings by natural means and through human activities. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others (Morais *et al.*, 2012).

Njinga *et al*., (2014), employed the use of Instrumental Neutron Activation Analysis (INAA) and two irradiation regimes developed based on short lived and long lived radionuclides to determine the activity concentration of trace and heavy metals in clay samples from parts of Lapai, Mokwa, Lavun, Gbako and Wushishi in Niger State Nigeria. The gamma-rays from the activated samples were measured using the HPGe detector and twenty four elements namely: Na, Mg, Al, Ti , V, K, Mn, Dy, Cr, Fe, As, Br, La, Sm, Yb, Sc, Co, Rb, Cs, Ba, Eu, Lu, Hf, and Ta were obtained quantitatively. Arsenic

(As) and chromium (Cr) which are known to be heavy metals fall in the range of 0.64 50 ± 0.16 ppm – 1.63 50 ± 0.06 ppm and 29.20 50 ± 0.36 ppm – 74.80 50 ± 0.23 ppm respectively. The concentrations of La, Sm, Co, Ba, and Cr also known to be toxic were obtained within the range of 56.20 ± 21 – 102.00 ± 43 ppm, 8.14 ± 0.32 – 13.10 ± 0.2 ppm, 6.22 ± 0.22 – 21.50 ± 0.26 ppm, 218.00 ± 28 – 711.00 ± 41 ppm and 29.20 ± 23 – 80.80 ± 21 ppm respectively in all the ten composite clay samples.

Agene *et al.*, (2014) analyzed several edible clays such as Montmorillonite, Chabazite-Na, Diaspore, Faujasite-Na, Lizardite-1M, Montmorillonite 15A, lizardite and Montmorillonite collected across Nigeria from Bauchi, Benue, Gombe, Kogi, Nasarawa, Osun and Plateau States. Geochemical analysis was carried out using the XRD and ICP-OES to determine the heavy metals in the clay. Heavy metals analyzed for were Al, As, Cr, Cu, Fe, Pb, Se and Zn. The result of the analysis indicated that the heavy metals were very high in concentrations for all the clay samples collected. The levels of contamination of As, Pb, and Se in the clays from all the states under study was also exceptionally high ($P < 0.05$).

2.3.1 Arsenic

Many As compounds adsorb strongly to soils and are therefore transported only over short distances in groundwater and surface water. Arsenic is associated with skin damage, increased risk of cancer and problems with circulatory system (Scragg, 2006).

2.3.2 Chromium

Chromium is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of

the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of Cr containing wastes (Smith *et al*., 1995). Chromium (VI) is the form of Cr commonly found at contaminated sites. Chromium can also occur in the +3 oxidation state, depending on pH and redox conditions. Chromium (VI) is the dominant form of Cr in shallow aquifers where aerobic conditions exist. Chromium (VI) can be reduced to Cr^{3+} by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions, often encountered in deeper groundwater.

Chromate and dichromate adsorb on soil surfaces, especially iron and aluminum oxides. Chromium (III) is the dominant form of Cr at low pH (<4). Chromium (VI) is the more toxic form of chromium and is also more mobile. Chromium (III) mobility is decreased by adsorption to clays and oxide minerals less than pH 5 and low solubility above pH 5 due to the formation of solid $Cr(OH)_3$ (Chrostowski *et al*., 1991). Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr^{3+} increases as soil pH increase. Most of Cr released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith *et al*., 1995). It has been reported that chromium is associated with allergic dermatitis in humans (Scragg, 2006).

2.3.3 Lead

Typical mean Pb concentration in surface soils worldwide average 32 mg kg^{-1} and ranges from 10 to 67 mg kg^{-1} (Kabata-Pendias and Pendias, 2001). The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust.

2.3.4 Nickel

The major sources of nickel contamination in soil are peculiar to metal plating industries, combustion of fossil fuels, and nickel mining and electroplating. Nickel is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions, it usually takes a long time for nickel to be removed from air. The slarger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic soils however, Ni becomes more mobile and often leaches down to the adjacent groundwater (Khodadoust *et al.,* 2004).

2.3.5 Zinc in Clay Samples

Zinc is a chalcophilic element like copper and lead and a trace constituent in most rocks. Zinc rarely occurs naturally in its metallic state, but many minerals contain zinc as a major component from which the metal may be economically recovered. Sphalerite (ZnS) is the most important ore mineral and the principal source for zinc production (WHO, 2003). For non-contaminated soils and clays worldwide, (Adriano, 2001) reported average zinc concentrations of 40–90 $mgkg^{-1}$, with a minimum of 1.00 $mgkg^{-1}$ and a maximum of 2000 $mgkg^{-1}$ in Springer-Verlag soil, New York, low levels were found in

sandy soils (10–30 mg kg^{-1}), while high contents were found in clays (95 mg kg^{-1}). The fate and transport of zinc (Zn^{2+}) in the environment is dependent on cation exchange capacity, pH, organic matter content, nature of complexing ligand and the concentration of the metal in the soil. As pH increases, there is an increase in negatively charged binding sites on clay particles, which facilitates the adsorption of zinc ions and removal from solution. Zinc mobility increases with low pH under oxidizing conditions and low cation exchange capacity. The presence of competing metal ions and organic ions such as humic material may cause the adsorption of Zn^{2+} ions, particularly in soils with an elevated pH, via ligand exchange reactions. These reactions reduce the solubility of zinc in soil/clay solution and therefore, reduce its mobility and limit its bioavailability (Le-Coultre, 2001).

The recommended dietary allowance (RDA) for zinc is 11 mg day^{-1} in men and 8 mg day^{-1} in women. These correspond to approximately 0.16 mg kg^{-1} day^{-1} for men and 0.13 mg kg^{-1} day^{-1} for women. Higher RDAs are recommended for women during pregnancy and lactation. The Reference Dose (RfD) is determined using the lowest-observed-adverse-effect-level (LOAEL) (60 $mgday^{-1}$) and an uncertainty factor of 3. US EPA has established Reference Dose (RfD) for Zn to be 0.3 mg kg^{-1} day^{-1} calculating with an average bodyweight of 70 kg US, EPA (2006). Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Greany, 2005).

2.4 Health impact of Heavy Metals

Table 2.1 Some heavy metals and their target organs in man

Heavy Metals	Target Organs	Organ screened for analysis
Arsenic	Most organ of the body, especially Lungs, skin, gastrointestinal system	Urine, hair and finger nails
Cadmium	Brain, heart, blood vessel, kidney and lungs	Blood, urine (ATSDR, 1993)
Lead	Bones, brain and Gastrointestinal tract	Blood, urine and hair
Copper	Lungs, skin and gastrointestinal tract, kidney and bones	Blood, urine, hair and finger nails (Itodo *et al.*, 2009).

(Abdulrahman and Itodo, 2006).

2.4.1 Arsenic

Low levels of arsenic exposure can cause nausea and vomiting, reduced production of erythrocytes and leukocytes, abnormal heart beat, pricking sensation in hands and legs, and damage to blood vessels. Long-term exposure can lead to the formation of skin lesions, internal cancers, neurological problems, pulmonary disease, peripheral vascular disease, hypertension and cardiovascular disease and diabetes mellitus (Smith *et al.,* 2000). In chronic arsenic poisoning, diarrhea and vomiting do occur. Tremors and peripheral neuritis are present in some cases. The afferent and motor sensory nerves in the lower extremities are attacked. Ankle jerk disappears, and leg muscle atrophy begins. Arsenic stimulates the horny layer of the skin, which leads to the appearance of dark brown scales. Skin keratoses frequently result from prolonged arsenic exposure. These

may become malignant. Chronic arsenicosis results in many irreversible changes in the vital organs and the mortality rate is higher. In spite of the magnitude of this potentially lethal toxicity, there is no effective treatment for this disease (Mazumder, 2008).

2.4.2 Cadmium

Cadmium and its compounds are classified as Group 1 carcinogens for humans by the International Agency for Research on Cancer (Henson and Chedrese, 2004). Cadmium can cause both acute and chronic intoxications (Chakraborty *et al.*, 2013). Cadmium is highly toxic to the kidney and it accumulates in the proximal tubular cells in higher concentrations. The main symptoms following ingestion of cadmium at doses above about 0.07 mg kg^{-1} in humans are nausea, vomiting, and abdominal pain. Cadmium can also cause bone mineralization either through bone damage or by renal dysfunction. Studies on humans and animals have revealed that osteoporosis (skeletal damage) is a critical effect of cadmium exposure along with disturbances in calcium metabolism, formation of renal stones and hyper calciuria. If cadmium is ingested in higher amounts, it can lead to stomach irritation and result in vomiting and diarrhea. On very long exposure time at lower concentrations, it can become deposited in the kidney and finally lead to kidney disease, fragile bones and lung damage (Bernard, 2008).

2.4.3 Lead

Lead is not an essential element. It is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys (Baldwin and Marshall,

1999). Inhalation and ingestion are the two routes of exposure, and the effects from both are the same. Pb accumulates in the body organs (brain), which may lead to poisoning (plumbism) or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower intelligence quotient (IQ), shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to lead (NSC, 2009).

Lead poisoning from a variety of domestic and industrial sources is a subject of concern because it affects the nervous system of children given to eating non-food items such as dirt and clay and its effects are so severely and permanently damaging to the foetuse and newborns of mothers ingesting clay (Martin and Griswold, 2009). The signs and symptoms of acute lead poisoning are a sweet metallic taste, salivation, vomiting, intestinal colic and lowered body temperature. In addition, there may be cerebral edema, convulsions and coma. Chronic lead poisoning has central nervous system manifestations (Morais *et al.,* 2012).

2.5 Radioactivity in Soil, Clay and Sand Samples

El-Aydarous (2007) determined the activity and concentration of ^{226}Ra, ^{232}Th and ^{40}K in clay soil samples from El Taif, in Saudi Arabia. The soil activity ranges from 13 ± 1.2 to 33 ± 3.4 $Bq.kg^{-1}$ for ^{226}Ra , 11 ± 1 to 27 ± 4.2 $Bq.kg^{-1}$ for ^{232}Th and 129 ± 5.7 to 230 ± 11 $Bq.kg^{-1}$ for ^{40}K with mean values of 23.8 ± 2.4, 18.6 ± 1.7 and 162.8 ± 7.6 $Bq.kg^{-1}$, respectively. The measured activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in clay soil was

lower than the world average of 35, 30 and 40 $Bq.kg^{-1}$, respectively. All the clay soil samples from El Taif, in Saudi Arabia had radium equivalent activities lower than the limit set in the Organization for Economic Co-operation and Development (OECD) report (370 $Bq.kg^{-1}$). The overall mean outdoor terrestrial gamma dose rate was 28.98 $nGy.h^{-1}$ and the corresponding outdoor annual effective dose was 0.04 $mSvy^{-1}$ (El-Aydarous, 2007).

The radioactivity concentrations for ^{226}Ra, ^{232}Th, ^{40}K, and ^{210}Pb in 40 clayey soil samples collected from Northwest Libyan coast in the Tripoli region using high resolution γ-ray spectroscopy indicated that the samples at depths 50-70 cm were 6.7 ±1.9 Bq/kg for ^{226}Ra, 4.2 ±1.1 Bq/kg for ^{232}Th, 26.6 ±5.9 Bq/kg for ^{40}K and 9.2±3.9 Bq/kg for ^{210}Pb. The range of the absorbed dose rate obtained for the clay soil samples was from 2.7 n $Gyh^{-1}$to 6.1 nGy h^{-1} with an average of 4.4 ± 1.3 $nGyh^{-1}$, while the average effective dose rate was 0.0054 ±0.0016 m Sv $y^{-1}$with the range 0.0033 -0.0075 m Sv y^{-1} (El-Kameesy, 2008).

Sowole, (2014) assessed the radioactivity concentrations of ^{40}K, ^{238}U and ^{232}Th in surface soil samples of major markets at Sagamu, Ogun State in Nigeria with the use of gamma spectrometry using Sodium Iodide Thallium doped NaI (TI) detector coupled with a pre-amplifier base to a multiple channel analyzer (MCA). The highest radioactivity concentrations of ^{40}K and ^{238}U were obtained from Falawo market soil samples with values 1274.26 ± 4.26 Bq/kg and 40.72 ± 3.12 Bq/kg, respectively, while that of ^{232}Th was obtained from Sabo soil sample with value 115.62 ± 16.39 Bq/kg. All values were above the permissible range according to (UNSCEAR, 2000).

Faanu *et al*., (2010) assessed the public exposure to naturally occurring radioactive materials from mining and mineral processing activities of Tarkwa Goldmine in Ghana using Neutron Activation Analysis (NAA). The mean activity concentration of ^{238}U, ^{232}Th and ^{40}K in the soil, water and dust were measured and the total annual effective dose to the public estimated to be 0.69mSv which compared well with the typical world average.

Agbalagba *et al.,* (2012) carried out the analysis of naturally occurring radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in soil samples collected from the environment of the oil and gas field of Delta state. The activity concentration of the samples ranged from 19.2 ± 5.6 $Bqkg^{-1}$ to 94.2 ± 7.7 $Bqkg^{-1}$ with mean value of 41.0 ± 5.0 $Bqkg^{-1}$ for ^{226}Ra, 17.1 ± 3.0 $Bqkg^{-1}$ to 47.5 ± 5.3 $Bqkg^{-1}$ with mean value of 29.7 ± 4 $Bqkg^{-1}$ for ^{232}Th and 107.0 ± 10.2 $Bqkg^{-1}$ to 712.4 ± 38.9 $Bqkg^{-1}$ with a mean value of 412.5 ± 20.0 $Bqkg^{-1}$ for ^{40}K. The values obtained strongly agree with the world range and values reported in other countries. The study also examined some radiation hazard indices, the mean values obtained were: 98.5 ± 12.3 $Bq.kg^{-1}$ for Radium equivalent activity (Ra_{eq}), 0.8 $Bqkg^{-1}$ for Representative level index (Iγ), 54.6 $nGyh^{-1}$ for Absorbed Dose rates (D), 0.07 μSvy^{-1} for Annual Effective Dose Rates (Eff Dose), 0.3 for External Hazard Index (Hex) and 0.4 for Internal Hazard Index (Hin). These calculated hazard indices were well less than their permissible limit in soils (Agbalagba *et al.,* 2012).

The concentration of ^{238}U, ^{232}Th and ^{40}K as well as other trace elements, anions and the physical parameters of water and soil samples in a goldmine and its surrounding in Ghana using NAA was determined by (Faanu *et al*., 2010). The result shows that the concentration of ^{238}U, ^{232}Th and ^{40}K and the mean Th/U ratio in all the soil samples

compared well with the result of normal continental crust rock and the activity concentration of the soil samples were all less than WHO recommended guideline values.

Isinkaye *et al.,* (2013) carried out radiochemical and elemental analysis of clay soils collected from different locations within Ekiti State using gamma spectrometric measurements. The results show that the mean concentrations of uranium ranged from 2.2 ± 1.0 mg/kg to 3.2 ± 1.1 mg/kg, thorium ranged from 4.0 ± 0.5 mg/kg to 5.7 ± 1.7 mg/kg, while potassium presented in % by weight ranged from 0.4 ± 0.2 to 1.3 ± 0.3.

The concentration of naturally occurring radioactive elements in soil from abandoned quarries in Abeokuta, Nigeria was measured using High Purity Gammanium Detector (HPGE) by (Gbadebo, 2011). The result confirmed the presence of ^{40}K, ^{232}Th and ^{236}U in appreciable amount. The maximum mean equivalent dose obtained in the studied area was lower than the maximum permissible limits of ^{40}K, ^{232}Th and ^{238}U.

Yousef *et al*., (2007) showed that, the activity concentration of radionuclides in surface clay soil samples around Kitchener Drain area in the North Nile Delta at the coast of Mediterranean sea ranged from 17.05 to 99.15 for ^{40}K,1.23 to 32.15 for ^{232}Th and 1.61 to 50.90 ($Bq.Kg^{-1}$) for ^{238}U using gamma-ray spectroscopy. The absorbed dose rate in (nGy/h) due to the natural radioactivity of the samples under study was in the range of 1.73 nGy/h to 47.03 nGy/h.

Chowdhury *et al*., (2005) determined the activity concentrations of naturally occurring radioactive materials in clay soil samples of an elevated radiation background area in southern districts of Bangladesh (n = 9); using a NaI(Tl) gamma ray spectrometric

technique, with an aim of evaluating the environmental radioactivity and the radiation hazard. The activity of ^{226}Ra in the clay soil ranged from 25 to 55 Bq kg^{-1}with a mean value of 42 ± 7 Bq kg^{-1}, that of ^{232}Th in the soil ranged from 52 to 108 Bq kg^{-1} with a mean value of 81 ± 14 Bq kg^{-1}, while the activity of ^{40}K in soil ranged from 549 to 1762 Bq kg^{-1} with a mean value of 833 ± 358 Bq kg^{-1}. The previous background radiation survey by the Bangladesh Atomic Energy Commission showed that the external background radiation level of this region is approximately 2 times (1.0 mGy y^{-1}) (higher than the world average value of 0.5 mGy y^{-1} reported by (UNSCEAR, 2000).

Ibrahim *et al*., (2013) determined ^{226}Ra, ^{232}Th, and ^{40}K natural activity concentrations in soils and sediments of some mining areas in Central Nasarawa State Nigeria, using Sodium Iodide-Thallium Gamma Spectroscopy. The mean natural activity concentrations were lower compared to the World average value, except ^{232}Th which was higher than the world average value with a difference of 20.23 Bq/kg. The evaluated annual mean effective dose was 0.04 ± 2.7 mSv/yr which was less than the annual dose limit for the public. The mean Radium equivalent activity was 141.56 ± 7.2 Bqkg-1. The average background radiation absorbed dose was 5.81 ± 0.08 mSv/y which was higher compared to worldwide average of 1mSvy^{-1} given by (UNSCEAR, 2000; IAEA, 2003).

Akram *et al*., (2006) determined the concentration of natural radionuclides in the bottom sediments and clay of Karachi Harbour/Manora channel area of Pakistan using gamma spectrometry technique. The activity in the sea sediment samples from these area was found to vary from 18.5 ± 4.3 to 29.1 ± 3.8 Bqkg^{-1} for ^{226}Ra 11.7 ± 1.2 to 27.7 ± 4.2 Bqkg^{-1} for ^{228}Ra and 332.2 ± 19.3 to 729.2 ± 36.7 Bqkg^{-1} for ^{40}K. The mean values of radium equivalent activity, absorbed dose rate and annual effective dose were 89 Bqkg^{-1},

44nGy.h^{-1} and 0.055 mSv.y^{-1}, respectively. The value of effective dose was much less than level of 1.0 mSv.y^{-1} as recommended by the International Commission on Radiological Protection (ICRP).

Lawluvi *et al*., (2011) investigated the levels and hazards associated with ^{238}U, ^{232}Th and ^{40}K in beach sands from some renowned tourist resorts in the Greater Accra region of Ghana using HPGe. The total absorbed dose rate and the annual effective doses were calculated. The specific activities ranged from 11.0 -31.8 Bq kg^{-1} for ^{238}U, 0.5-1.5 Bq kg^{-1} for ^{235}U, 10.9-103.7 Bq kg^{-1} for ^{226}Ra, 16.8-231.2 Bq kg^{-1} for ^{232}Th and 68.3 -183.9 Bq kg^{-1} for ^{40}K.

El-Daly and Hussein, (2008) measured the radioactivity levels of ^{226}Ra (^{238}U) in clay soil samples collected from North Western desert of Egypt using gamma-ray spectroscopy. The results obtained indicate that the radioactivity levels of ^{226}Ra (^{238}U) for clay soil samples ranged from 14.82 to 26.56 Bq kg^{-1} with mean average value of 22.12 Bqkg^{-1}, while for ^{232}Th the highest value was 20.99 Bq kg^{-1} and the lowest value was 3.91 Bq kg^{-1} with the average value being 10.27 Bq kg^{-1}, for^{40}K the activity ranged from 382.98 to 58.02 Bq kg^{-1} with the average value being 180.04 Bq kg^{-1}.

The work by (Ashnani *et al*., 2010) indicated that the average activity concentration of ^{226}Ra, ^{40}K and ^{232}Th in soil and sediment samples from Aras river, Ardabil Province, North-West of Iran and south west of Caspian Sea using high performance germanium detector (HPGD), had the average activity concentrations of ^{40}K and ^{226}Ra being 263.75 ± 6.18 Bqkg^{-1} and 4.42 ± 0.46 Bqkg^{-1} respectively in the soil and sediment samples. The average concentrations of activity of ^{232}Th was 20.24±1.18Bqkg^{-1}. One-third of the

samples had activity of ^{40}K being more than the allowable limits while the other natural activities were in the background range.

2.6 Selected Instrumentation Used in this Study

2.6.1 Theory and Instrumentation of X-Ray Diffraction Analysis

X-ray powder diffraction (XRD) is the most widely used for the identification of unknown crystalline materials (minerals, inorganic and organic compounds). Other applications include: characterization of crystalline materials, identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions, measurement of sample purity. With specialized technique, XRD can be used to determine crystal structure using Rietveld refinement and the determination of modal amount of minerals (quantitative analysis) (Bish and Post, 1989; Chiari *et al.*, 2003).

Empyrean diffractometer is commonly used with a copper anode material manufactured by Pan analytical. It works with a combination of other components like the water chiller which cools the x-ray tube and maintains a uniform temperature. There is also compressed air that helps in opening and closing the cabinet door. The goniometer forms the central part of the Empyran diffraction system. It contains the basic axes in X-ray diffractometry which includes the omega and 2 theta axes. The X-ray tube, incident beam optics, the sample stage and the diffracted beam optic including the detector are mounted on a specific position on the goniometer. The goniometer is set up in vertical mode and can be configured for theta-theta and alpha-1 diffraction geometries. The goniometer

radius is 240 mm. The diffractometer consist of three basic elements such as an X-ray tube, a sample holders and an X-ray detector (Chettle, 2005).

2.6.2 Procedure for XRD analysis

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towards a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectral consist of several components, the most common being K_α and K_β. K_α consists in part $K_{\alpha 1}$ and $K_{\alpha 2}$. Also $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering by foils or crystal monochrometers is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded when the gonometry of the incident X-rays impinging the sample satisfies Bragg equation;

$$n\lambda = 2d \sin \theta \qquad 2.5.1$$

where n is the interger, λ is wavelength and d is distance of lattice planes.

Constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor (Bish and Post, 1989; Chettle, 2005).

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed goniometer. For typical powder patterns, data is collected at 2θ from ~5° to 75° angles that are preset in the X-ray scan.

Table 2.2 Possible minerals in clay and the corresponding 'd' values using XRD

d(Å)	Possible mineral	JCPDS-ICDD file no.
4·2754, 1·5441, 1·3864	Quartz	01-075-8320
3·4354, 2·5505, 1·3781	Alumina	1-088-2112.
2·6990, 1·6957, 2·2001	Hematite	00-33-0664
3·8057, 3·4354, 2·2903	Tridymite	-
3·3462, 3·0965, 2·2844	Illite	00-26-0911
4·1876, 2·5509, 3·4023	Kaolinite	00-006-0221

(ICDD, 2001; Hubbard *et al.,* 2003).

2.7 Theory and Instrumentation of Hyper Pure Gammanium Detector for Radioactivity Measurement

High Purity Germanium (HPGe) gamma-ray detectors are of greater advantages over other Gamma detectors in terms of energy resolution, efficiency, sensitivity, ease of spectrum analysis and in a wide range of applications both fixed-installed and *in situ.*

2.7.1 Hyper-pure germanium detector configuration

Though the sample for HPGe is already very high in purity, the material is further purified with the zone refining technique. The germanium is melted in a crucible using radio-frequency (RF) heating coils. The underlying principle is that impurities concentrate in the liquid phase leaves the solid purer than the original melts as a liquid freezes and solid appears.

Each zone refiner coil melts a small section of the germanium in the crucible. As the RF coils are slowly moved along the length of the crucible, the molten zone moves with them. Thus, the germanium melts as the coil approaches and freezes as the coil moves away. The impurities tend to remain in the molten section, which leads to a higher concentration of impurities in the liquid than the solid. In this way, the impurities are swept to one end. This sweeping operation is repeated many times, until the impurities are concentrated at one end of the ingot. This end is then removed, leaving the remaining portion much purer than the original starting material. The improvement or reduction in the impurity concentration actually realized is about a factor of 100 or more at the completion of this process.

Large single crystals of germanium are grown using the Czochralski technique. A precisely cut seed crystal is dipped into the molten germanium and then withdrawn slowly, while maintaining the temperature of the melt just above the freezing point. The rate of crystal withdrawal and temperature of the melt are adjusted to control the growth of the crystal (Gilmore and Hemingway, 1995).

2.7.2 Planar configuration

In a planar HPGe detector configuration using a p-type crystal, the electric contacts are provided on the two flat surfaces of a germanium crystal.

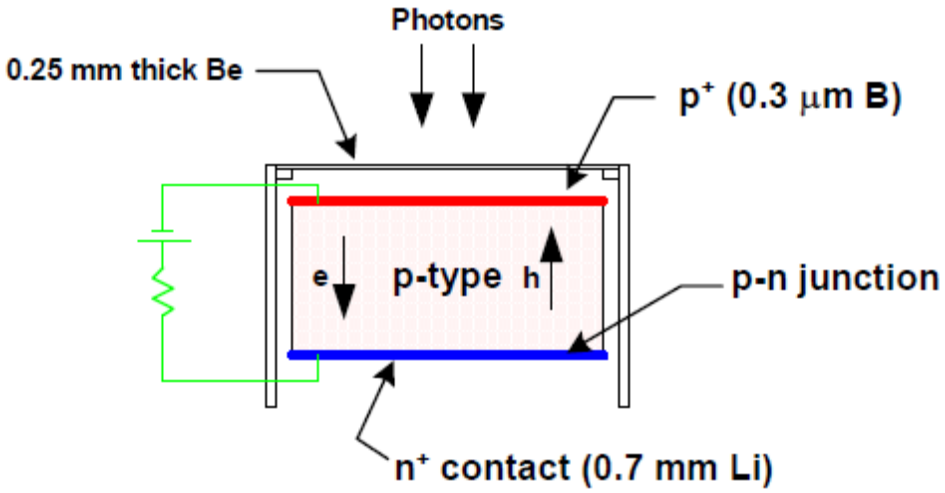


Figure 2.1 Planar HPGe detector (p-type) (Knoll, 1999).

A lithium evaporation and diffusion to form the n^+ contact is performed over one of the surface. This lithium-diffused layer is about several hundred μm thick. The depletion region is formed by reverse biasing n^+-p junction. The surface of the opposite side is modified to the p^+ layer by ion implantation of boron acceptor atoms to increase the conductivity near the surface. Since both materials are p-type, no semiconductor junction exists at this side instead, the p+ layer provides the electric contact to collect the charge carriers created by the radiation. The thickness of the implanted boron layer is so thin (a few tenths of μm). It is a suitable entrance window for low energy photons (Knoll, 1999)

To make a reverse bias, a positive high voltage is applied to the n^+ contact with respect to the p+ surface. The depletion region is formed at the region close to the n^+ contact and

then expanded deeply into the p-side as the bias voltage is raised. Once the detector is fully depleted, further increase of the bias (overvoltage) does not make any effect on the sensitive volume however, it makes the electric field stronger, which subsequently shortens carrier collection times and reduces the risk of carrier losses (recombination and trapping).

Planar HPGe detectors can also be fabricated starting with high-purity n-type crystals. Similarly, n^+ and p^+ contacts are provided on both sides. Reverse biasing also requires the application of a positive voltage to the n^+ side. In this case, the depletion region is expanded from the p^+ contact.

When fully depleted and operated with a sufficient overvoltage, the electric field inside the crystal is almost uniform and charge carriers drift under a constant electric field.

2.7.3 Electric field and capacitance

The electric field in HPGe detectors governs the charge carrier collection process. The signal pulse shape and the timing behaviour are consequently dependent on the variation of the electric field strength. The governing equation is Poisson's equation:

$$\nabla 2V = -\rho / \varepsilon \qquad 2.6.1$$

The charge density ρ is given as $\rho = -eN_A$ for p-type crystals and as $\rho = eN_D$ for n-type crystals. For convenience, p-type crystals are assumed in the following derivation.

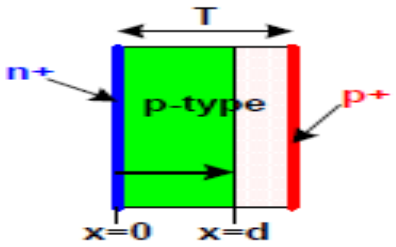


Figure 2.2: Partial depletion of a planar detector (Knoll, 1999)

Where x = 0 represents the n+ contact position. The electric field is obtained by integrating the Poisson's equation.

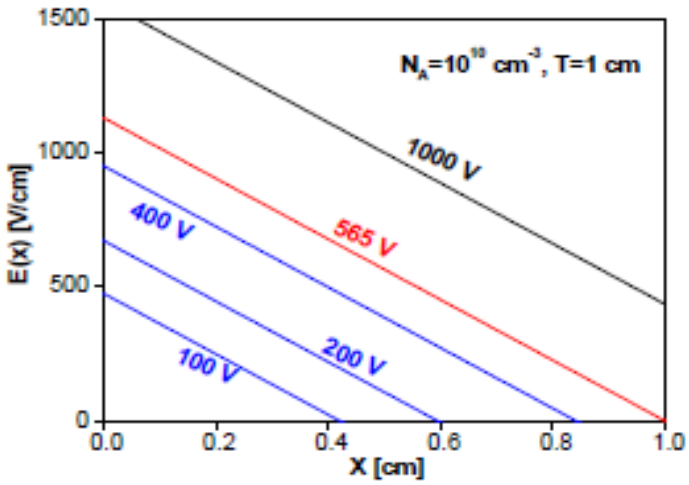


Figure 2.3: Electric field variation of a planar detector (Knoll, 1999)

2.7.4 Operational characteristics of HPGe

Although silicon detectors can be operated at room temperature in principle, operating germanium detectors at room temperature is impossible due to the small band gap energy, which generates an intolerable leakage current. Therefore, germanium crystals must be cooled to reduce the leakage current. HPGe detectors are allowed to warm to room

temperature when they are not in operation, however, they are always maintained at LN2 temperature practically.

The Ge crystal is encased in a vacuum tight container (cryostat) to reduce thermal conduction between the crystal and the air. The basic function of a cryostat is to cool the germanium detector to LN2 temperature. The germanium detector preamp is normally included as part of the cryostat package. Since the preamp should be located as close as possible so that the overall capacitance can be minimized, the preamp is installed together. The input stages of the preamp are also cooled. The entire cold assembly is maintained by the cryostat under high vacuum for both thermal insulation and protection of the internal components from contamination.

All of the cryostat materials around the detector should be as low as possible to reduce photon scatter. Hence, aluminum, magnesium, beryllium, Teflon and Mylar are used whenever possible.

2.7.5 Energy resolution

The most important characteristic of HPGe detectors is their excellent energy resolution. In Fig. 2.6, two spectra from an HPGe and a NaI(Tl) are compared for a ^{60}Co source. The great superiority of the HPGe detector allows the separation of many closely spaced gamma lines, which is very beneficial for measuring multi-gamma emitting radioactive sources.

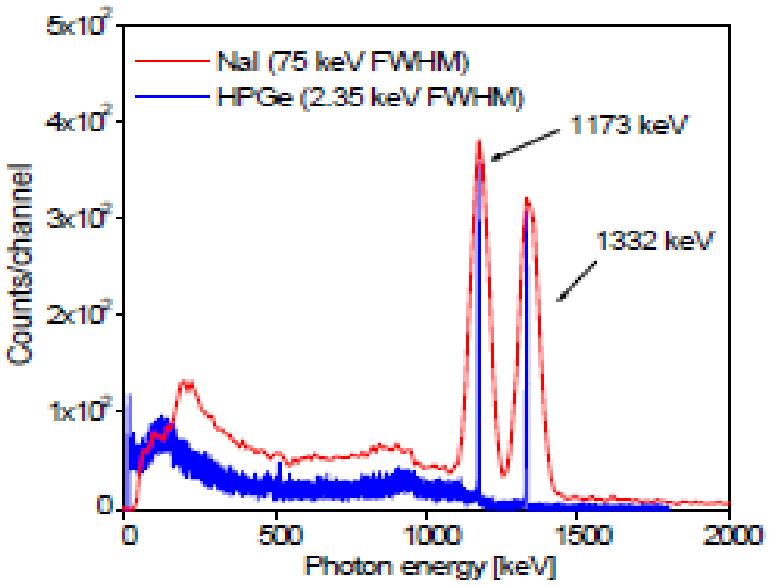


Figure 2.4 Comparison of NaI(Tl) and HPGe spectra for ^{60}Co (Knoll, 1999)

The energy resolution of the HPGe photon spectroscopy system is governed by the variation in the number of charge carriers, variation in the charge carrier collection, and the contribution of electronic noise. Hence, the FWHM of a peak in the spectrum can be represented as

$$W^2_T = W^2_D + W^2_X + W^2_E \qquad 2.6.2$$

Where W values on the right-hand side are peak widths expected due to carrier statistics, carrier collection and electronic noise.

2.8 Theory and instrumentation of Atomic Absorption Spectroscopy for Metal Analysis

Atomic absorption spectroscopy (AAS) is a spectro-analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation

(light) by free atoms in the gaseous state. It is the study of absorption spectra by means of electromagnetic radiation through an atomic medium that is selectively absorbing. This produces pure electronic transitions free from vibration and rotational transitions.

Atomic absorption methods measure the amount of energy (in the form of photons of light, and thus a change in the wavelength) absorbed by the sample. Specifically, a detector measures the wavelength of light transmitted by the sample and compares them to the wavelengths, which originally passed through the sample. A signal processor then integrates the change in wavelength, which appear in the readout as peaks of energy absorption at discrete wavelengths in (fig. 2.7)

The technique makes use of absorption spectrometry to assess the concentration of an analytic in a sample. It requires standards with known analytic content to establish the relation between the measured absorbance and the analytic concentration and relies therefore on the Beer-Lambert law (Thomas, 2000)

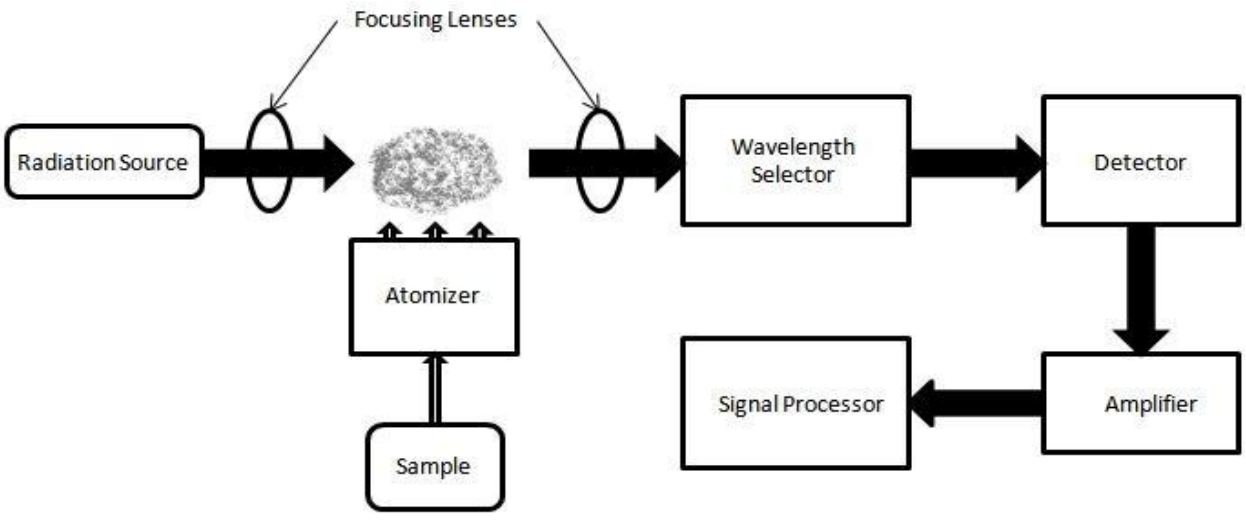


Figure 2.5: A typical absorption spectroscopy block chart (Thomas, 2000).

2.9 Structure of Hair

Human hair starts to grow during the third month of faetal life. Hair fibres are then created through a cyclic pattern of cell proliferation and differentiation that continues through life (Sen, 1996). Hair consists of a strong exterior layer or cuticle, a cortex and an inner layer called the medulla. Most trace elements detected in hair reside in the cuticle, which is made up of polymerized protein in a homogeneous high-sulphur protein matrix. This protein matrix consists primarily of the amino acid the amino acid cysteine. While hair is growing, the matrix cells at the papilla of the follicle have a high rate of metabolic activity, which causes them to absorb elements introduced in the diet (Katz and Katz, 1992).

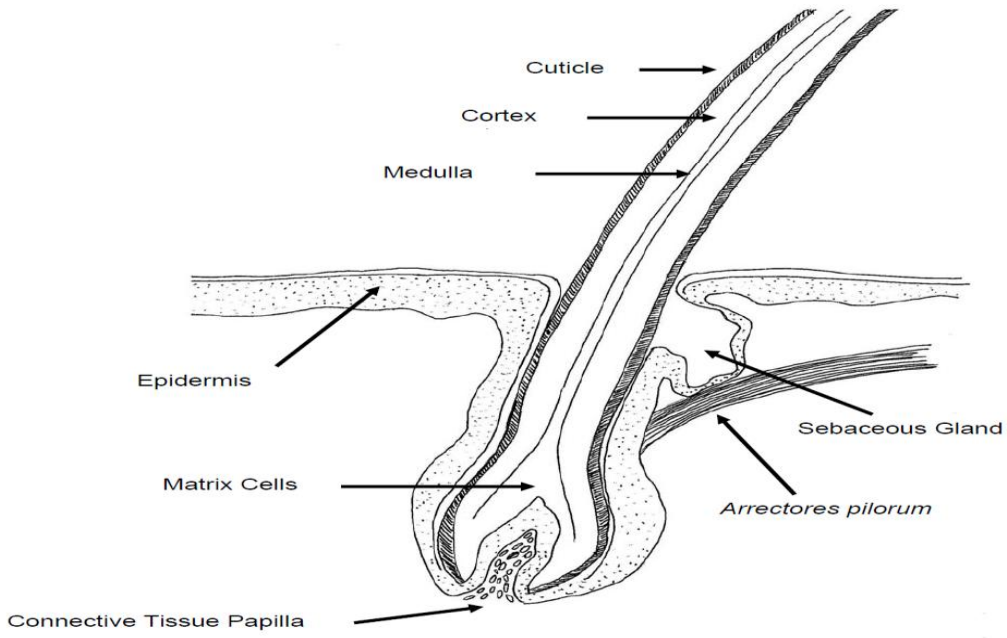


Figure 2.6 Human Hair Follicle and surrounding tissues (Katz and Katz, 1992).

The growing hair is exposed to metabolic activities for a short time as it approaches the skin's surface and hardens through keratinization. The trace elements accumulated during growth are then sealed into the hair (Katz and Katz, 1992). Once it grows past the skin's surface, hair is isolated from the body's ongoing metabolic activity (Graf, 1978; Koons and Peters, 1994). There are five primary sources of elements to growing hair which include matrix cells, the connective tissue papilla, eccrine secretions, apocrine secretions, and the epidermis. The elements obtained through ingestion or environmental exposures are applied to hair through endogenous deposition from the connective tissue papilla and matrix cells. Eccrine sweat exogenously deposits salts high in sodium and potassium on the hair. Other trace elements deposited through sweat include nitrogen, calcium, phosphorus, magnesium, copper, manganese and iron (Sanford, 1994). According to (Katz and Katz, 1992), the link between hair growth and heavy metal concentrations in the body suggests hair functions as an excretory organ for arsenic and other potentially toxic metals. This suggestion has been confirmed by (Foo *et al*., 1993).

The endogenous deposition sources previously mentioned are not the only sources of elements on hair. Exogenous depositions of trace elements also occur and are influenced by exposure to soil, water, air and bacteria.

2.9.1 Hair as a superior bio-indicator of heavy metals compared to blood and urine

Since the middle of the 20th Century, the determination of trace and heavy element levels in human scalp hair has become increasingly popular for monitoring environmental exposures, evaluating heavy metal poisonings, assessing nutritional status and diagnosing diseases. Blood and urine analysis are the more traditional approach to evaluating trace

and heavy element levels in the human body, but the biokinetics as well as changing environmental factors often result in fluctuating trace element concentrations in blood and urine. Hair, on the other hand, is considered by some to be a metabolic end product providing a more permanent record of the trace elements associated with health and disease and of trace elements assimilated from the environment (Goulle and Kintz, 1996; Goyer and Clarkson, 2001) described the body tissues as being in a state of dynamic equilibrium or homeostasis which tend to maintain stability with coordinated responses to compensate for changes in the physiological system with hair as a exception.

Unlike the other body compartments, hair is a metabolic end product that is thought to incorporate trace elements into its structure during its growing process. During the growth phase of a hair cycle, the matrix cells at the papilla of the hair follicle show intense metabolic activity and produce hair at a rate of approximately 0.3 mm/day (Rodushkin, 2003).

The developing hair is exposed to this metabolic milieu for only a short period of time during which trace elements from the blood are partitioned into the nascent hair. As the growing hair approaches the skin surface, it undergoes a hardening process or keratinization and the trace elements accumulated during its formation are sealed into the protein structure of the hair. It is in this way that the trace element concentrations of the hair are possibly related to the trace elements in the body. The efficacy of hair analysis for evaluating systemic arsenic intoxication was asserted by (Wolfsperger *et al*., 1994; Paulsen *et al*., 1996; Wang, *et al.*, 2009), the authors noted that the exposed subjects with the highest hair arsenic concentrations displayed the cutaneous signs of arsenic poisoning including stomach pain, headaches, diarrhea and vomiting.

Wilhelm *et al.*, (1994) reported correlations between the concentrations of lead in the hair of children and the clinical signs of lead poisoning. Strain and his co-workers reported that zinc-deficient Egyptians were found to have mean hair zinc level approximately half that of the normal Egyptian population.

The data collected in a lead poisoning surveillance project established a correlation between concentrations of lead in the blood (BPb) and the concentrations of lead in the hair (HPb) of children with confirmed plumbism; BPb = 0.02757 HPb + 39.79, where BPb is the whole blood lead concentration expressed as μg/100 mL and HPb is the concentration of lead in the hair expressed as mg/kg. For the 11 data points reported, the correlation coefficient r, was 0.854 with p less than 0.001.

2.9.2 Hair analysis as a tool in assessing human exposure to heavy metals through geophagy and the limitations

One of the most difficult issues regarding fatal clay addiction lays in the diagnosis of less apparent forms of the syndrome where no history of individual or maternal consumption is available and where no physical features have manifested (Wang *et al*., 2009).

In opposition, some limitations were described for hair analysis, mainly the occurrence of exogenous contamination that contributes to a differential increase in the total contents of different contaminants (ATSDR, 2001).

Constraints pointed out for the use of hair analysis according to (ATSDR, 200), are:

(i) The lack of correlation between concentrations of trace elements in hair and in other target organs (e.g. liver, kidney), or body fluids (e.g. blood, urine);

(ii) The lack of scientific knowledge about kinetics of incorporation of trace elements in hair and;

(iii) The insufficiency of epidemiological data to support predictions of health effects, related with a specific concentration of each element, in hair.

In spite of these constraints, scalp hair has been considered a good screening tool to assess the likely occurrence of environmental exposures and to justify more extensive and expensive studies including all the population concern.

Takako *et al.,* (2011) carried out elemental mapping of hair sections in Ehime, Japan, using synchrotron radiation micro beam X-ray fluorescence (μ-SXRF). Relative affinities of 11 metals and metalloids determined by adsorption experiment were: Hg^{2+}> Pb^{2+}> Cu^{2+}> Cr^{3+}> Cd^{2+}> $As^{(III)}$> $Se^{(IV)}$> Zn^{2+}> Co^{2+}> $Sb^{(III)}$> Ni^{2+}.

Nida *et al.,* (2014). analyzed the concentration of Hg in hair samples of 200 residents of Karachi, Pakistan using cold vapor atomic absorption spectroscopy (CVAA) technique for mercury concentration. The effects of age, gender, working status, location, food and smoking habit were investigated. Control region showed a positive correlation between Hg and age of donor while no such correlation was observed for polluted regions. Mercury exposure through cosmetic usage in female was only pronounced in control region. These results indicate that environmental pollution dominates other potential factors. Elevated mean level of mercury was noticed for regular fish consumers than rarely fish consumers. 95.33% of the samples contained Hg greater than the permissible level of 2 $\mu g \cdot g^{-1}$ set by WHO.

Akan *et al.,* (2012) determined the concentration of Cu, Zn, Co, Mn, Fe, Cr, Cd, As, Ni and Pb in samples of hair and nail collected from different subjects with respect to sex, age and occupational exposure to heavy metals in Maiduguri metropolis, Borno State, Nigeria using Flame Atomic Absorption Spectrophotometer (AAS, Unicam 969). Also hair and nail samples were collected from smoker and non-smoker subjects for heavy metals determination. High concentrations of all the metals under study were observed to accumulate in the subjects. It was also observed that of all the metals studied, Zn showed the highest concentrations while Cu showed the least levels. Significantly high levels of heavy metals were observed in smokers, compared to a non-smoker. ($P < 0.05$). The levels of all the metals studied were significantly higher in the toenails compared to fingernail samples ($P < 0.05$). The levels of all the metals studied were statistically higher in male subjects compared to female subjects ($P < 0.05$). The concentrations of heavy metals in nail samples were significantly higher than hair samples.

CHAPTER THREE

3.1 MATERIALS

3.1.1 List of Apparatus/equipments

Top load (Denver instrument XP-600)

Baird and Tatlock Auto bench centrifuge (weigh in excess of 18.14kg)

Analytical weighing balance (Sartorium ED224S, max 220g; d=0.1mg)

Jenway pH meter (3505)

Sension 5 Conductivity meter (Hach product) England

Hotplate; Jenwang 1000, England

Reciprocating shaker; Line instruments,Inc 3527

AAS – VARIA AA2404FS, England

Hiper Pure Gammanium detector, by Canberra; model GC8023, S/N9744

X-Ray Diffractory machine; Bruker-AXS-type D8 ADVANCE diffractometer, with Cu Ka1 radiation (wavelength 1.5406λ),

Colony Counting Machine; STUART-Scientific Sc5, UK

Autoclave; Astell ASB300 England

Incubator; Gallankamp IH-150 England

Hot air oven; D-91126 Schwabach FRG, Germany

3.1.2 List of reagent

Calcium chloride dihydrate

Sodium hydrogen tetraoxophosphate (V1)

Anhydrous Magnesium tetraoxosulphate (V1)

Potassium chloride

Anhydrous Potassium hydrogen tetraoxophosphate (V1)

Sodium chloride

D-Glucose

Phenol red sodium salt

Saline Solution

3.1.3 Sampling of the clay types

Raw ‘Nzu clay’ was collected from each of two ‘Nzu clay’ hills in Ozanogogo village of Ika South Local Government area, Delta State, in the Eastern part of Nigeria. Two samples were obtained from each of the raw ‘Nzu clay’ hills using randomized sampling technique. The raw clays were processed to finished ‘Nzu clay’ making a sum of four samples. A sample of already prepared ‘Nzu clay’ sourced from Uzella river, in Owan west LGA Edo State made up the fifth ‘Nzu clay’ sample.

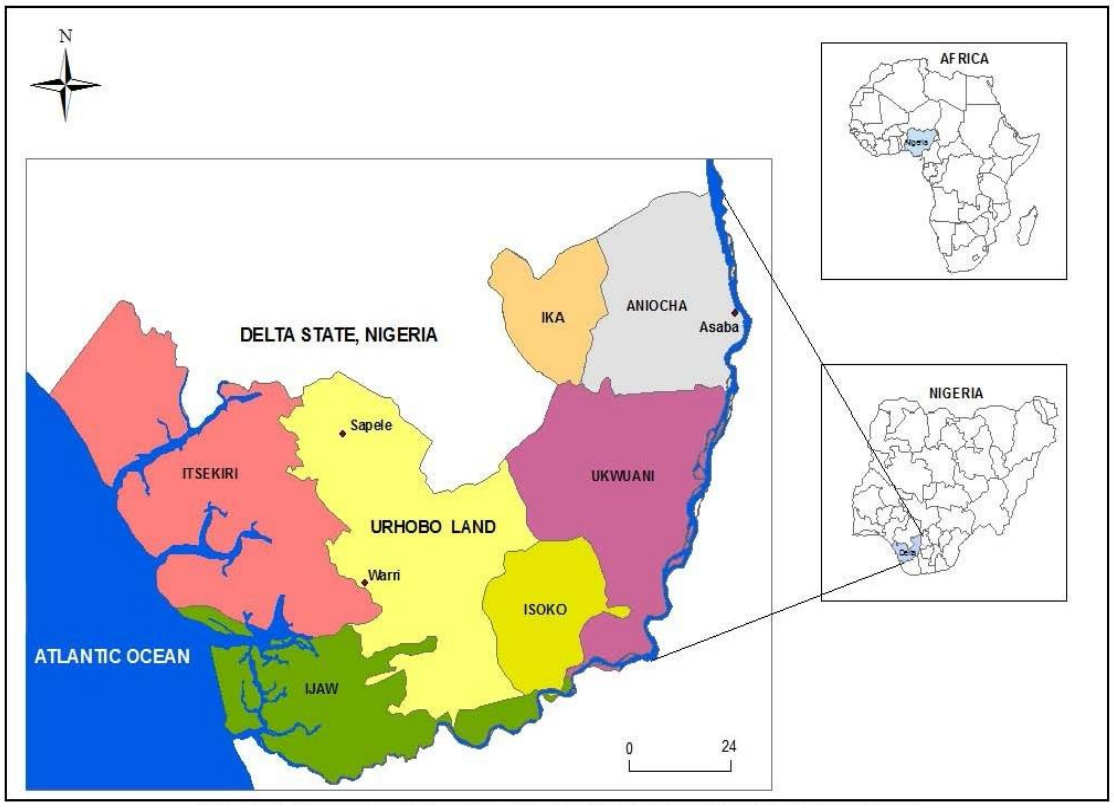


Figure 3.1 Map of Delta State showing Ika Local Government Area in brown (Francis, 2008).

Figure 3.2 Raw 'Nzu Clay' hill in Ozanogogo village, Ika South LGA, Delta State

3.2 Method

3.2.1 Quality assurance/Preparation of standard solution

All the reagents used were of analytical grade. The preparation of the standard solutions for calibration were carried out as follows:

(a) $BaCl_2.2H_2O$ (0.1M) extracting solution

Hydrated barium chloride (24.428 g) was accurately weighed and introduced into a 1000.00 cm^3 volumetric flask containing about 800 cm^3 of distilled water and then made up to mark with distilled water.

(b) $BaCl_2.2H_2O$ (2mM) equilibrating solution

Barium chloride (20 cm^3) of 0.1M concentration was accurately measured and poured into a 1000.00 cm^3 volumetric flask and then made up to mark with distilled water.

(c) $MgSO_4.7H_2O$ (0.1M) solution

Magnesium sulphate (24.648 g) was accurately weighed and poured into 1000.00 cm^3 volumetric flask containing about 800 cm^3 of distilled water, it was then made up to mark with distilled water.

(d) $MgSO_4.7H_2O$ solution (1.5mM and 5mM)

Magnesium sulphate solution (0.1 M) was measured (15.00 cm^3) using a measuring cylinder, this was carefully transferred into a 1000.00 cm^3 volumetric flask and diluted

with distilled water and then made up to mark. The same procedure was repeated using 50 cm^3 of 0.1 M magnesium sulphate solution.

(e) H_2SO_4 (0.05 M)

Concentrated sulphuric acid (2.80 cm^3) was accurately measured and poured into a 1000.00 cm^3 volumetric flask containing about 800.00 cm^3 distilled water and then made up to mark with distilled water (Hanks, 2007).

(f) Hanks solution

Hank solution is a simulanous body fluid. It was prepared thus: 0.4 g potassium chloride, 0.06 g potassium phosphate monobasic (anhydrous), 0.8 g sodium chloride, 0.04788 g sodium phosphate dibasic(anhydrous), 1.0 g D-Glucose and 0.011g Phenol Red•Na of the total salt compound was all suspended in 900 cm^3 tissue culture grade water with constant, gentle stirring until the powder is completely dissolved. A 0.350 g of sodium bicarbonate powder was added for 1000.00 cm^3 of solution and stirred until dissolved.

pH was adjusted to 0.2 - 0.3 pH units less than the desired pH using 1M HCl or 1M NaOH since the pH tends to rise during filtration. The final volume was made up to mark to 1000.00 cm^3 with tissue culture grade water. The solution was immediately sterilized by filtering through a sterile membrane filter with a porosity of 0.22 micron, positive pressure was used rather than vacuum to minimize the loss of carbon dioxide. The desired amount of sterile solution was aseptically dispensed into sterile containers, the liquid solution was then stored at 15-30°C and in dark till use (Hanks, 2007).

3.2.2 Sampling of hair from addicted and non-addicted consumers of 'Nzu clay'

Sixty market vendors in Benin Edo State and Zaria Kaduna State, Nigeria were questioned orally about the origins and use of 'Nzu clay' and twenty (20) 'Nzu clay' addicts were identified and issued questionnaires that sought to reveal the age, sex, geographic location, occupation, duration of addiction to clay eating, type of hair treatments used, quantity, and quality (type) of clay ingested. The questionnaire revealed that ten of the respondents are addicts of the clay for more than five years and five are addicts (consuming the clay) for less than five years (3 - 5 years).

Hair samples were obtained from individual addicted consumers of 'Nzu clay' from Zaria city, Kaduna State. The consumers of the 'Nzu clay' were categorized according to age and duration of 'Nzu clay' consumption. So after thoroughly educating the respondents about the essence of the research, approximately 0.5 g of hair was collected from each person addicted to the clay for less than five years, consumers above five years and non consumers of the clay (n = 15) using a sterilized stainless steel scissors. The scissors was cleaned with acetone after each hair collection as a precaution. The hairs were then put into separate Ziploc bags for storage, the hair samples were then washed with non-ionic detergent and rinsed with distilled water, it was then oven dried for 3 days at 60-70 ^{o}C and stored in an airtight plastic bag prior to its digestion, so as to assess the level of exposure of the persons to heavy metals in correlation to the duration of exposure.

3.2.2a Processing of raw 'Nzu Clay' sample

Raw 'Nzu clay' from Uzella river, Owan West LGA lies beneath the water. After this is brought out, the water is allowed to drain out a little then the clay is mixed with hands to

form a smooth paste. The paste is then moulded and cut into shapes/blocks before it is laid on an elevated metal hook net. Fire is set up under the elevated metal net a little distance away from it and the 'Nzu clay' is heated to dryness. The finished 'Nzu clay' becomes ash in colour when completely processed.

Sample of raw 'Nzu clay' obtained from hill of Ozanogogo, Ika South LGA Delta State is also locally processed by first drying it under the sun in open air and then crushing the clay to powder using a porcelain mortar and pestle, appropriate amount of salt is being dissolved in water and then mixed with the clay until it is sticky and malleable enough to be moulded with ease, the clay is then shaped into blocks and laid on metal hook net and heated, following the procedure mentioned above.

Figure 3.3: 'Nzu clay' samples from hill and river source

Site 1R raw clay from Hill of site 1 from Ozanogogo (ash-white). Site 2R raw clay from hill of site 2 from Ozanogogo (red-ash), site 1F processed clay from site 1 Ozanogogo,

Ika South LGA Delta State and site 3F processed/finished 'Nzu clay' from Uzella river, Owan West LGA Edo State.

3.2.2b Sample preparation

All glassware and plastic used for collection and preparations were cleaned by soaking in 10% nitric acid (HNO_3) for at least 12 hr and then rinsed several times with the double distilled water. 'Nzu clay' samples were oven-dried at 40^{o}C for 48 hr prior to disaggregation using a porcelain mortar and pestle and sieving through 2000 µm aperture nylon mesh.

3.2.3 Determination of some physico-chemical properties of the 'Nzu Clay' samples

(a) Determination of swelling power of the clay

Swelling power was determined by the method described by (Takashi and Sieb, 1988; Hirsch and KoKini, 2002). It involves weighing 1.00g of each clay samples from each of the hills and the processed clay from the river side into different 10.00 cm^3 centrifuge tube. Then 5.00 cm^3 of Hanks solution was added to each set-up and mixed gently with a glass stirrer, the slurry was then heated in a water bath at a temperature of 100 ℃ for 15 min. During heating, the slurry was continuously stirred gently using a glass stirrer in order to prevent clumping of the clay. At the end of 15 min, the tube containing the paste was centrifuged at 3000 rpm for 10 min, after which the supernatant was decanted immediately after centrifuging. The weight (gcm^{-3}) of the clay was then taken and recorded.

$$Swelling\ power\ =\ \frac{weight\ of\ wet\ mass\ of\ the\ clay}{Weight\ of\ the\ dry\ clay} \quad 3.1$$

(b) Determination of dispersibility of the clay

Dispersibility was determined by using the method described by (Kulkarni *et al*., 1991). Five grammes of each of the clay sample (site1R, site 1F, site 2R, site 2F, and Site 3FC) was weighed into separate 100.00 cm^3measuring cylinder, Hanks solution was then added to each 100.00 cm^3 cylinder to mark. The set up was stirred vigorously using a glass stirrer and allowed to stand for 3 h. The volume of the settled particles in each set up was recorded and then subtracted from 100. The differences are reported as percentage dispersibility.

$$\%\ Dispersibility\ =\ 100\ -\ volume\ of\ settled\ particle \quad 3.2$$

(c) Determination of bulk density of the clay

The bulk density was determined by the method of (AOAC, 1990). A 5.00 g amount of each of the clay samples (site1R, site 1F, site 2R, site 2F, and Site 3FC) was weighed into separate 50.00 cm^3 graduated measuring cylinder. The samples were packed by gently tapping the cylinder on the bench top 10 times from a height of 5.00 cm. The volume of each of the samples was then recorded.

$$Bulk\ density\ (g/ml)\ =\frac{weight\ of\ the\ sample}{volume\ of\ the\ sample\ after\ tapping} \quad 3.3$$

(d) Determination of water absorption index of the clay

Water absorption index was determined using a method described by (Solusulski, 1962; Hirsch and KoKini, 2002). The crucibles and centrifuge tubes were dried in an oven at

105℃ for 20 min and then allowed to cool in a desiccator. After cooling the crucible, the centrifuge tubes were weighed and 1.00 g each of the clay samples (site1R, site 1F, site 2R, site 2F, and Site 3FC) were weighed into each of the tube. Exactly 10.00 cm^3 of Hank's solution was added and then stirred gently with a stirring rod for 30 min. Each of the tube containing a clay type was centrifuged at 4000 rpm for 15 min, the supernatants was then decanted and discarded. The residue remaining in each of the tubes was weighed and recorded.

Water absorption index was calculated as:

$$\frac{weight\ of\ tube + residue\ after\ centrifuge - weight\ of\ empty\ tube}{Weight\ of\ sample} \times 100 \qquad 3.4$$

(e) pH of the clay

An aliquot dispersion of 1g each of the clay sample (site 1R, site 1F, site 2R, site 2F, and Site 3FC) was poured into a 10 cm^3 beaker and shaken in water for 5 minutes and the clay pH was determined using a glass electrode coupled pH meter (Jenway; model 3505).

All the above parameters were determined in triplicates and the mean and standard deviations recorded.

3.2.4 Determination of the cation exchange capacity of the clay by the $BaCl_2$ compulsive exchange method

The compulsive exchange method is the method recommended by the Soil Science Society of America (Sumner and Miller, 1996) because it is a highly repeatable, precise and direct measure of a soil's CECb. This method was used to determine the CECb at the pH and ionic strength of the clay samples for an estimate of the CECe.

(a) Procedure for the determination of cation exchange capacity

The clay sample from each of the clay type considered (site 1R, site 1F, site 2R, site 2F, and Site 3FC) was weighed (2.00 g) into separate funnel containing medium grade filter paper. The clay sample in each set-up was slowly leached with 20 cm^3 of 0.1M $BaCl_2.2H_2O$ allowing each addition to soak into the clay sample before adding more. The clay sample was again leached with 60 cm^3 of 2mM $BaCl_2.2H_2O$ in six 10 cm^3 portions, allowing each addition to soak into the clay. The last 10 cm^3 of leachate was saved separately for pH determination. After leaching, the filter paper and the clay of each set-up was carefully transferred to a pre-weighed 125 cm^3 flask and 10.0 cm^3 of 5mM $MgSO_4$ was added. Occasional shaking of the volumetric flask was done for about 1 hr.

Conductivity of the 1.5 mM $MgSO_4$ solution was measured using Conductivity meter (Sension 5, Hach product) giving a value of ~300 μS or μmhos. Then an additional 0.100 cm^3 of 0.1 M $MgSO_4$ was poured whenever the conductivity of the sample solution was not 1.5x this value (~300 μS); this ceases when it is this value. The amount of 0.1M $MgSO_4$ added was then noted. The pH of the solution was determined.

A 0.05M H_2SO_4 solution was added drop-wisely to the solution if it is not within 0.1 units of the previously measured value of the last 10 cm^3 of sample leachate until pH is in appropriate range. Distilled water was added with mixing until the solution conductivity is that of the 1.5mM $MgSO_4$. The solution pH and conductivity was adjusted alternately until the end points were reached then the outside of the flask was wiped, dried using a clean towel and then weighed for a final solution weight (W_f).

(b) Calculations of CECe

a. Total solution (cm^3) [assumes 1cm^3 weighs 1 g]

final tube weight (g) - tube tare weight (g) - 2 g [weight of clay used]

b. Mg in solution, not on CEC (meq)

Total solution (cm^3) x 0.003 (meq/ cm^3) [1.5 mM $MgSO_4$ has 0.003 meq/cm^3]

c. Total Mg added (meq)

0.1 meq [meq in 10 cm^3 of 5 mM $MgSO_4$] + meq added in 0.1M $MgSO_4$

[cm^3 of 0.1 M $MgSO_4$ x 0.2 meq/ cm^3 (0.1 M MgSO4 has 0.2 meq/ cm^3)]

d. CEC (meq/100g) = (c - b) x 50

[Total Mg added - Mg in final solution × 50 so as to convert from 2 g of clay to 100 g].

3.2.5 Digestion of 'Nzu clay' samples for determination of total Cd, Cr, Cu, Ni, Pb and Zn contents

The samples of clay collected from the two sites were tagged site1R, site 1F, site 2R, site 2F, and site 3FC. The processed/finished samples collected from the river side were tagged site 3FC. For each digested mixture using aqua regia (1:3 of ultra-pure 70% HNO_3 and pure 37% hydrochloric acid (HCl)). A selected weight (1.00 g) of a clay sample was mixed with 30 cm^3 of aqua regia overnight and then digested for three hour at maximum temperature of 170 °C on a hot plate. Warm distilled water was occasionally added in drops to avoid drying up of the mixture. The filterate was then made up to the 100 cm^3 mark in volumetric flasks by using double distilled water. Each digested sample was then filtered using a no 42 Whatman filter paper. The digestion for each clay type was carried out in triplicate (n = 3) inside a fume cupboard. For each solution of the clay being

digested, the levels of As, Cd, Cr, Cu, Ni, Pb and Zn were then determined using atomic absorption spectrophotometer (VARIAN AA2404FS, England) at Multi-user Laboratory, Ahmadu Bello University Zaria, Kaduna State in January 2015.

(a) Digestion of hair samples of 'Nzu clay' Addicts for Determination of As, Cd, Cr, Ni, Pb and Zn contents

Exactly 0.25 g of dried hair sample from a respondent (addict of 'Nzu clay') was weighed into a beaker and digested in 12 cm^3 of *aqua regia* ($^1/_3$ HNO_3 and ¾ HCl acid) this was heated on a hot plate digestion block inside a fume cupboard. The maximum digestion temperature was 120 ^oC, so as to avoid loss of material, each beaker had a glass lid.

Digestion continued until a clear and colourless solution was obtained in each digest. Each sample took 2-3 hr to be completely digested. Warm distilled water was occasionally added to prevent drying up of the digest. The clear solution obtained was allowed to cool, filtered with Whatman no. 42 paper and diluted to a final volume of 100.00 cm^3 with double distilled water following the method of (Ming and Lena, 2001). This solution obtained was stored in a plastic container until analysis was done using Atomic Absorption Spectrophotometer (model VARIA AA2404FS, England) at the multi-user Laboratory, Ahmadu Bello University Zaria, Kaduna State, Nigeria.

(b) Determination of Total Cd, Cr, Cu, Ni, Pb and Zn contents in the clay and hair samples

The sample solution is aspirated into a flame and the sample element is converted to atomic vapour. Most of the atoms in the flame remain in the ground state and it is this ground state atoms that are measured in atomic absorption. These ground state atoms can

absorb radiation of a particular wavelength that is produced by a special source made from that element (the element being analyzed). The wavelength of radiation given off by the source is the same that this sample element would give off if it were to emit radiation, since it is the same element with the source. The absorption follows Beer's law, that is, the absorbance is directly proportional to the path length in the flame and to the concentration of atomic vapour in the flame (Mendham *et al*., 2008). The machine runs in triplicate and the average absorbance of the sample was calculated by referring to the appropriate calibration curve drawn by the in-built computer interface. The concentrations were equally read out from the computer print-out.

3.2.6 Measurement of the radioactivity in the clay samples

The radioactivity concentrations were measured at Centre for Energy Research and Development (CERD), Obafemi Awolowo University (OAU), Ile-Ife using Hiper Pure Gammanium detector model GC8023, Canberra.

'Nzu clay' samples were crushed to a powder form which was then collected through a 0.85 mm mesh sieve. After that, the sample was then placed in an oven at about 90°C until constant weight was achieved. Due to the high density of 'Nzu clay' (~ 4 g/cm^3). Pure silica powder (SiO_2, 2.46g/cm^3) was used to get samples with densities nearly equal the density of reference material. Silica has an appropriate mass attenuation coefficient for gamma rays as shown in Fig.3.4 (Hubbell and Seltzer, 1996).

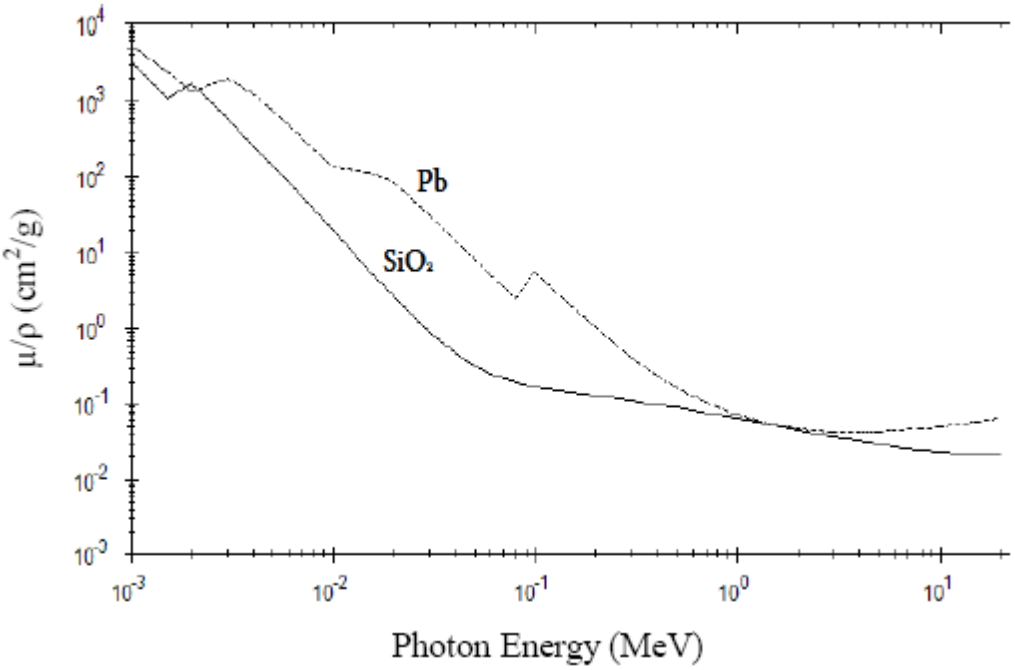


Figure 3.4: Mass attenuation coefficient of SiO_2 and Pb as a function of gamma-ray energy (Hubbell and Seltzer, 1996).

In order to confirm that the use of silica does not affect the rate of self-absorption of the emitted gamma-rays, two masses of 'Nzu clay' samples (20 and 40 g) were used and then the appropriate amount of silica needed for each mass to fill the 240 ml plastic beakers added. Silica and 'Nzu clay' were mixed well to get a homogenous sample which was then sealed for more than 28 days to reach the secular equilibrium between ^{226}Ra and its short lived products. The same geometry and size were used for both measured and reference material samples. The measurements are then collected for 20 to 24 hour (Hubbell and Seltzer, 1996).

3.2.6 Radiation hazard indices

Various radiation health hazard indices analysis are being used in radiation studies to arrive at a reliable conclusion on the health status of a radiated or irradiated person and

the environment (Avwiri *et al.*, 2013; Agbalagba and Onoja, 2011; Zarie and Al-Mugren, 2010) in order to assess the radiation hazards associated with any study samples, the following quantities need to be understood.

(a) Absorbed dose rate

This expresses how much energy remains present in the material affected by radiation and is described with the unit radiation absorbed dose (rad) or Gray (1 Gray = 100 rad). One Gray means that in 1 kilogram of a given substance, 1 watt-second or 1 Joule of energy remains present. Conversion factors to transform specific activities C_{Ra}, C_{Th} and C_K of uranium, thorium and potassium respectively into absorbed dose rate is calculated as given by (UNSCEAR, 2000).

$$D\ (nGy/h) = C_K 0.0414 + C_{Ra} 0.461 + C_{Th} 0.623 \qquad 3.5$$

About 98% of the external γ dose rate from ^{238}U series is delivered by the ^{226}Ra sub series. So disequilibrium, between ^{226}Ra and ^{238}U will not affect the results of dose calculations from the measurement of ^{226}Ra. The world average is 60nGy/h, according to (UNSCEAR, 2000).

(b) Radium equivalent activity (Ra_{eq})

The radium equivalent activity is a weighted sum of activities of the ^{226}Ra, ^{232}Th and ^{40}K radionuclides based on the estimation that 1Bq/kg of ^{226}Ra, 0.7Bq/kg of ^{232}Th, and 13Bq/kg of ^{40}K produce the same radiation dose rates. Radium equivalent (Ra_{eq}) is a common index used to compare the specific activities of materials containing ^{238}U, ^{232}Th and ^{40}K by a single quantity, which takes into account the radiation hazards associated

with them (Kohshi *et al.*, 2001; Avwiri *et al.*, 2013). The activity index provides a useful guideline in regulating the safety standard dwellings. The radium equivalent activity index is given as (Beratka and Mathew, 1985):

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_{K} \quad 3.6$$

Where C_{Ra}, C_{Th} and C_K are the radioactivity concentration in Bq/kg of ^{238}U, ^{232}Th, and ^{40}K respectively. The use of a material whose concentration exceeds 370 Bq/kg is discouraged to avoid radiation hazards (UNSCEAR, 2000).

(c) Annual gonadal equivalent dose (AGED)

The activity bone marrow and the bone surface cells are considered as organs of interest by UNSCEAR, (2000). The AGED for the resident of a building using a material with given activity concentration of ^{238}U, ^{232}Th and ^{40}K is calculated using the equation slated by (IAEA, 2003a).

$$AGED\ (Sv/yr) = CRa3.09 + CTh4.18 + Ck0.314 \quad 3.7$$

where $\mathbf{C_{Ra}}$, $\mathbf{C_{Th}}$ and $\mathbf{C_k}$ are the radioactivity concentration of ^{238}U, ^{232}Th and ^{40}K. The maximum AGDE permissible limit is 1mSv/y.

(d) External hazard index (Hex)

Many radionuclides occur naturally in terrestrial soils and rocks and upon decay, these radionuclides produce an external radiation field to which all human beings are exposed. In terms of dose, the principal primordial radionuclides are ^{232}Th, ^{238}U and ^{40}K. Thorium and uranium are head series of radionuclides that produce significant human exposure.

The external hazard index (Hex) is defined by (Beretka and Mathew, 1985)

$$Hex = \frac{CRa}{370} + \frac{CTh}{259} + \frac{\mathrm{Ck}}{4810} \quad 3.8$$

Where C_{Ra}, C_{Th} and C_K are the radioactivity concentrations in Bq/Kg of ^{238}U, ^{232}Th and ^{40}K respectively. The value of this index must be less than unity for the radiation hazard to be negligible Hex value equal to unity corresponds to the upper limit of Raeq (370Bq/Kg) (Berekta and Mathew, 1985; Dragovic *et al*., 2006).

(e) Internal hazard index (Hin)

The internal hazard index (Hin) is given as (Beretka and Mathew, 1985; Kohshi *et al.*, 2001).

$$Hin = \frac{CRa}{185} + \frac{CTh}{259} + \frac{\mathrm{Ck}}{4810} \quad 3.9$$

H_{in} should be less than unity for the radiation hazard to be negligible. Internal exposure to radon are very hazardous, this can lead to respiratory diseases like asthma and cancer.

(f) Representative gamma index (Iyr)

This is used to estimate the - radiation hazard associated with the natural radionuclide in specific investigated samples. The representative gamma index as (Avwiri *et al.*, 2013)

$$Iyr = \frac{CRa}{150} + \frac{CTh}{100} + \frac{Ck}{1500} \quad 3.10$$

This gamma index is also used to correlate the annual dose rate due to the excess external gamma radiation caused by superficial materials. It is a screening tool for identifying materials that might become health concern when used by humans.

Values of Iyr ≤ 1 corresponds to an annual effective dose of less than or equal to 1mSv, while Iyr ≤ 0.5 corresponds to annual effective dose less or equal to 0.3mSv (Beretka and Mathew, 1985; IAEA, 2003; Avwiri *et al.*, 2013).

(g) Annual effective dose equivalent (AEDE)

The annual effective dose equivalent in other words is the largest amount of ionizing radiation a person may receive according to radiation prote ction guidelines. It combines both internal andexternal dose and has replaced the concept of maximum permissible dose for occupational exposures per year. This is calculated from the absorbed dose rate by applying dose conversion factor of 0.7Sv/Gy and the occupancy factor for outdoor and indoor was 0.2 (5/24) and 0.8 (19/24) respectively Beretka and Mathew (1985). AEDE is determined using the following:

AEDE (Outdoor) (μSv/y) = Absorbed dose (nGy/h) × 8760h × 0.7Sv/Gy × 0.2×10^{-3}

AEDE (Indoor) (μSv/y) = Absorbed dose (nGy/h) × 8760h × 0.7Sv/Gy × 0.8×10^{-3}

The world average value for absorbed dose and annual effective dose equivalent rate are 60ηGyh-1 and 1.0mSvy-1 (ICRP, 1991; UNSCEAR, 2000).

3.2.7 X-ray Diffraction analysis of the 'Nzu Clay' samples using X-ray diffractometer

X-ray Diffraction Analysis was carried out in the Geoscience Laboratory, Kaduna. The 'Nzu clay' sample of each group was finely grounded to pass through 63 microns. The powdered sample was then prepared using the sample preparation block and compressed in the flat sample holder to create a flat, smooth surface that was later mounted on the sample stage in the XRD cabinet.

The sample was analyzed using the reflection–transmission spinner stage using the theta-theta settings. Two-theta starting position was 0.00483 and ends at 75.000 with a two-theta step of 0.026 at 3.57 seconds per step. Tube current was 40 mA and the tension was 45 VA. Fixed divergent slit size of 1^{o} was used and the goniometer radius was 240 mm.

The intensity of diffracted X-rays was continuously recorded as detector rotate through their respective angles. Peak intensity occurs when the mineral contains lattice planes with d-spacing appropriate to diffract X-ray at that value of 0 (Theo, 2002; Maslen *et al*., 2004).

3.2.8 Statistical analysis

One-way ANOVA was employed in comparing the level of heavy metals in the 'Nzu clay' by site $P < 0.05$ using Duncan Multiple range test. The level of heavy metals in the clay and in the hair samples above 5 yr and less than 5 yr was compared and also the derived values from radioactivity in the clay samples by site (location) at $P < 0.05$. Results are presented as mean ± standard deviation; the number of replicate measurements ($n = 3$), using Statistical Package for Social Sciences (SPSS), software for windows version 20.0 (IBM SPSS Statistics 20.0). $P \leq 0.05$ was considered to indicate significant difference. Least Significant Difference (LSD) was used to determine which means differ.

CHAPTER FOUR

4.0 RESULTS

Table 4.1 shows some physicochemical parameters of 'Nzu clay' samples, these include: the cation exchange capacity (CEC), bulk density, dispersibility, water absorption index, swelling power and pH of raw and finished clay samples obtained from sites 1 and 2 of hill side in Ozanogogo, Ika south LGA of Delta State and site 3 from Uzella river, Owan west LGA, Edo state.

Table 4.2 shows correlation between similar physiochemical properties of the various sampling sites; site 1R, site 2R are sample codes for raw 'Nzu clay' obtained from two (2) hill site in Ozanogogo, Ika south LGA of Delta State. Site 1F, site 2F are processed/finished clay from same sites, while site 3F is sample code for 'Nzu clay' obtained from Uzella river, Owan west LGA, Edo state.

The concentration of individual heavy metals such as As, Cd, Cr, Cu, Ni, Pb and Zn in processed 'Nzu clay' obtained from Uzella river, Owan west LGA Edo state (WS) and Ozanogogo, Ika South LGA, Delta state (HS) in comparison with the concentration of heavy metals in hairs of addicted consumers of the clay above five years (FA), below five years (FB) and in non consumers of the clay (NA) are presented in figure 4.1 to 4.6.

Table 4.1; Physicochemical Parameters of Raw and Finished Clay Samples from Site 1, Site 2 from Hill Side in Ozanogogo, Ika south LGA Of Delta State and site 3 from Uzella river, Owan West LGA, Edo State.

Properties	**Raw Samples**		**Finished Samples**		
	Site 1	Site 2	Site 1	Site 2	Site 3
CEC (meq/100g)	10.800±0.424	10.200±0.989	10.250±1.202	9.870±0.671	9.725±0.035
Bulk density(g/cm^3)	0.725±0.212	0.710±0.000	0.915±0.120	0.880±0.169	0.570±0.014
Dispersibility	80.000±1.414	80.000±0.000	77.250±0.353	74.750±3.880	76.500±0.707
Water absorption index	1.930±0.056	1.745±0.777	1.775±0.106	1.780±0.282	2.230±0.000
Swelling Power	1.680±0.028	1.685±0.049	1.555±0.636	1.590±0.424	2.070±0.000
pH	5.150±0.494	5.250±0.494	4.500±0.141	4.500±1.141	4.500±0.000

Table 4.2: Correlation between Similar Physiochemical Properties of the various Sampling Sites

Properties	site1 R	site2 R	site 1F	site 2F	site 3F
CEC	**site1 R** 1.000[a]	1.000[a]	1.000[a]	0.988[a]	1.000[a]
Bulk density	**site 2R**	1.000[b]	1.000[b]	0.999[b]	1.000[b]
Dispersibility	**site 1F**		1.000[c]	0.999[c]	1.000[c]
Water absor-tion index	**site 2 F**			1.000[d]	0.999[e]
pH	**site 3 F**				1.000[f]

Correlation of physiochemical parameters of Nzu clay samples from site 1, 2 and 3 for both raw(R) and finished/processed (F) 'Nzu clay' samples.
Where, a: cation exchange capacity, b: bulk density, c: dispersibility, d: water absorption capacity, e: swelling power, f: pH.

site1R: raw 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)
site2R: raw 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)
site1F: processed/finished 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)
site2F: processed/finished 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)
site3F: processed/finished 'Nzu clay' from site 3 (Uzella river, Owan West LGA Edo State)

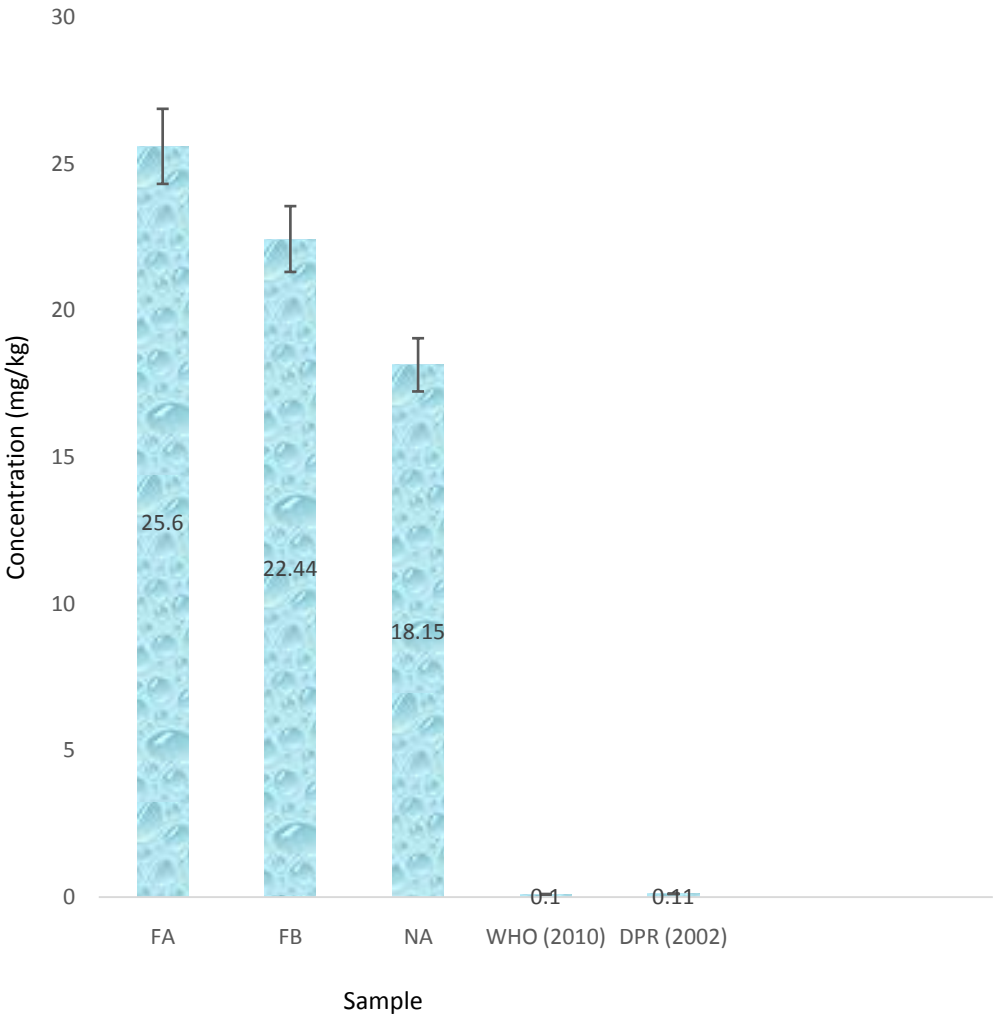


Figure 4.1: Concentration of Arsenic in hair samples of Addicts and Non-addicts

Where
FA: consumer of 'Nzu clay' above Five years
FB: consumer of 'Nzu clay' below Five years
NA: Non Addicts of 'Nzu clay'
WHO: World Health Organization
DPR: Department of Petroleum Resources

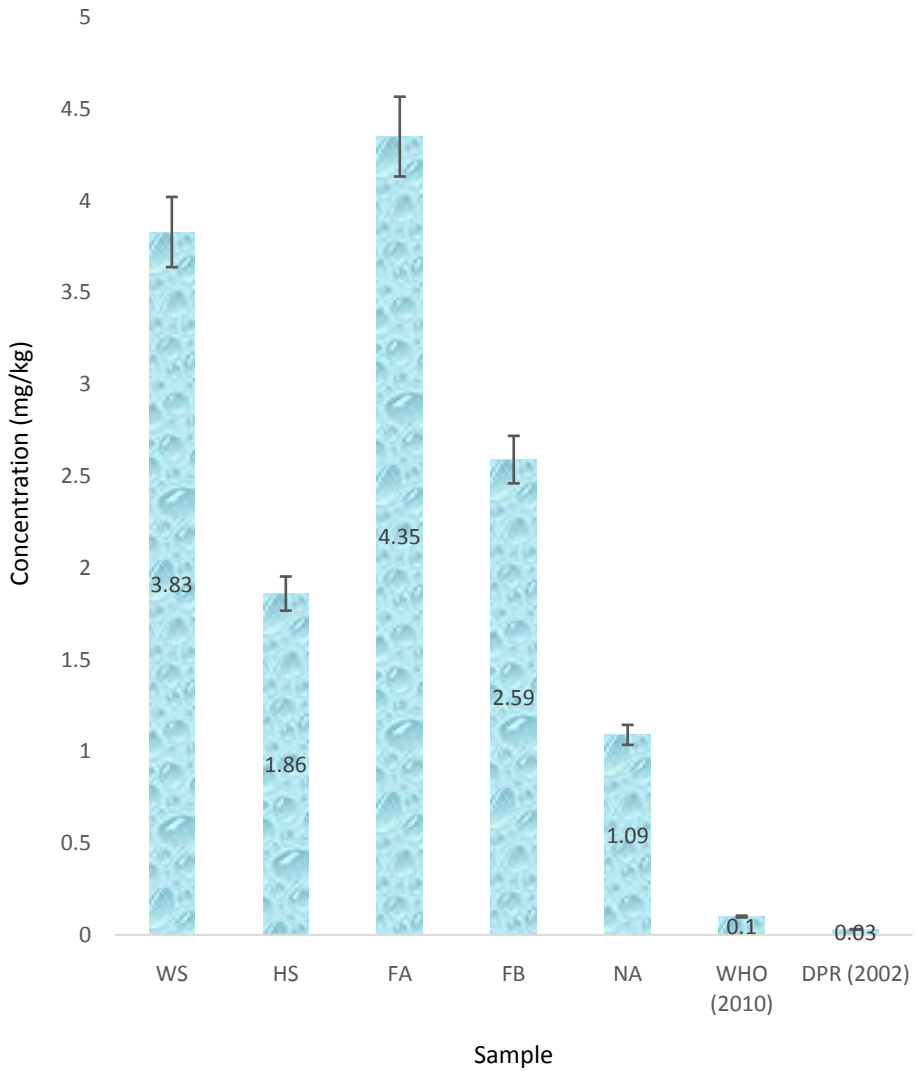


Figure 4.2: Concentration of Cadmium in 'Nzu clay' samples and hair samples of Addicts and Non-addicts

Where
WS: 'Nzu clay' from Water side
HS: 'Nzu clay' from Hill side
FA: consumer of 'Nzu clay' above Five years
FB: consumer of 'Nzu clay' below Five years
NA: Non Addicts of 'Nzu clay'
WHO: World Health Organization
DPR: Department of Petroleum Resources

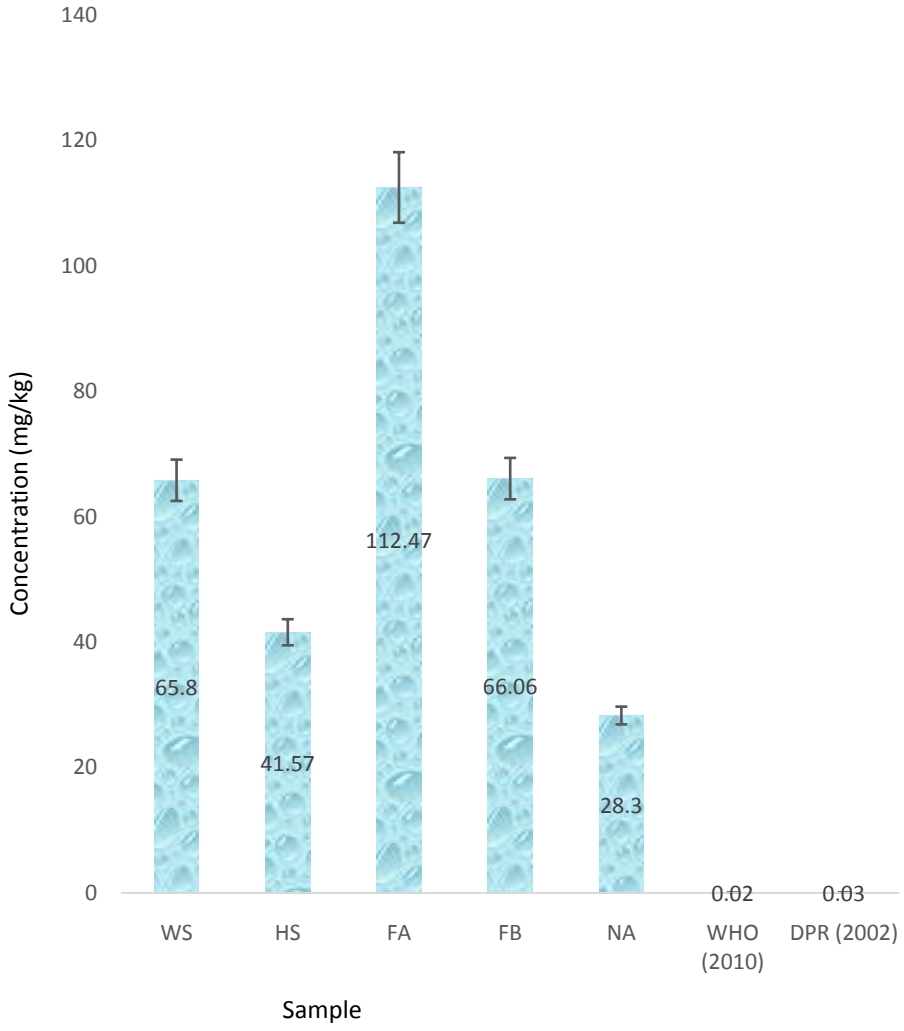


Figure 4.3: Concentration of Chromium in 'Nzu clay' samples and hair samples of Addicts and Non-addicts

Where
WS: 'Nzu clay' from Water side
HS: 'Nzu clay' from Hill side
FA: consumer of 'Nzu clay' above Five years
FB: consumer of 'Nzu clay' below Five years
NA: Non Addicts of 'Nzu clay'
WHO: World Health Organization
DPR: Department of Petroleum Resources

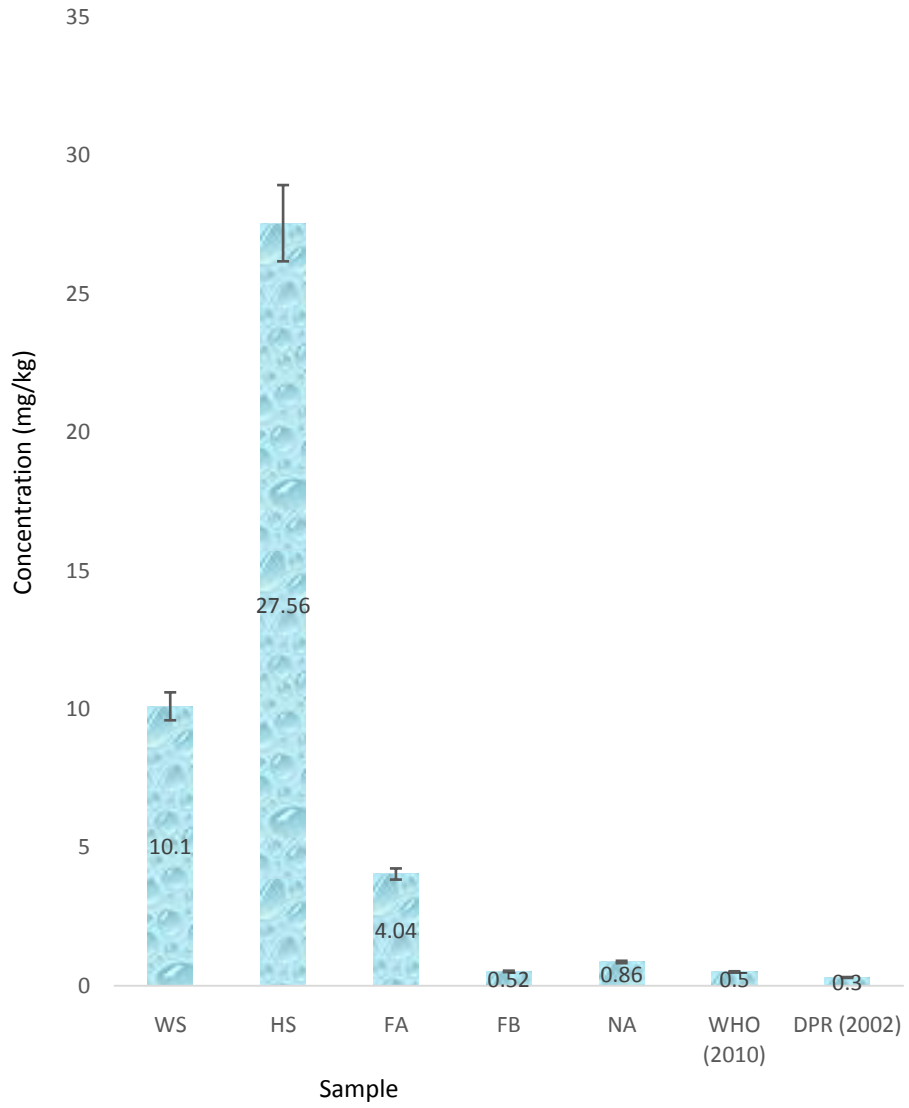


Figure 4.4: Concentration of Copper in 'Nzu clay' samples and hair samples of Addicts and Non-addicts

Where
WS: 'Nzu clay' from Water side
HS: 'Nzu clay' from Hill side
FA: consumer of 'Nzu clay' above Five years
FB: consumer of 'Nzu clay' below Five years
NA: Non Addicts of 'Nzu clay'
WHO: World Health Organization
DPR: Department of Petroleum Resources

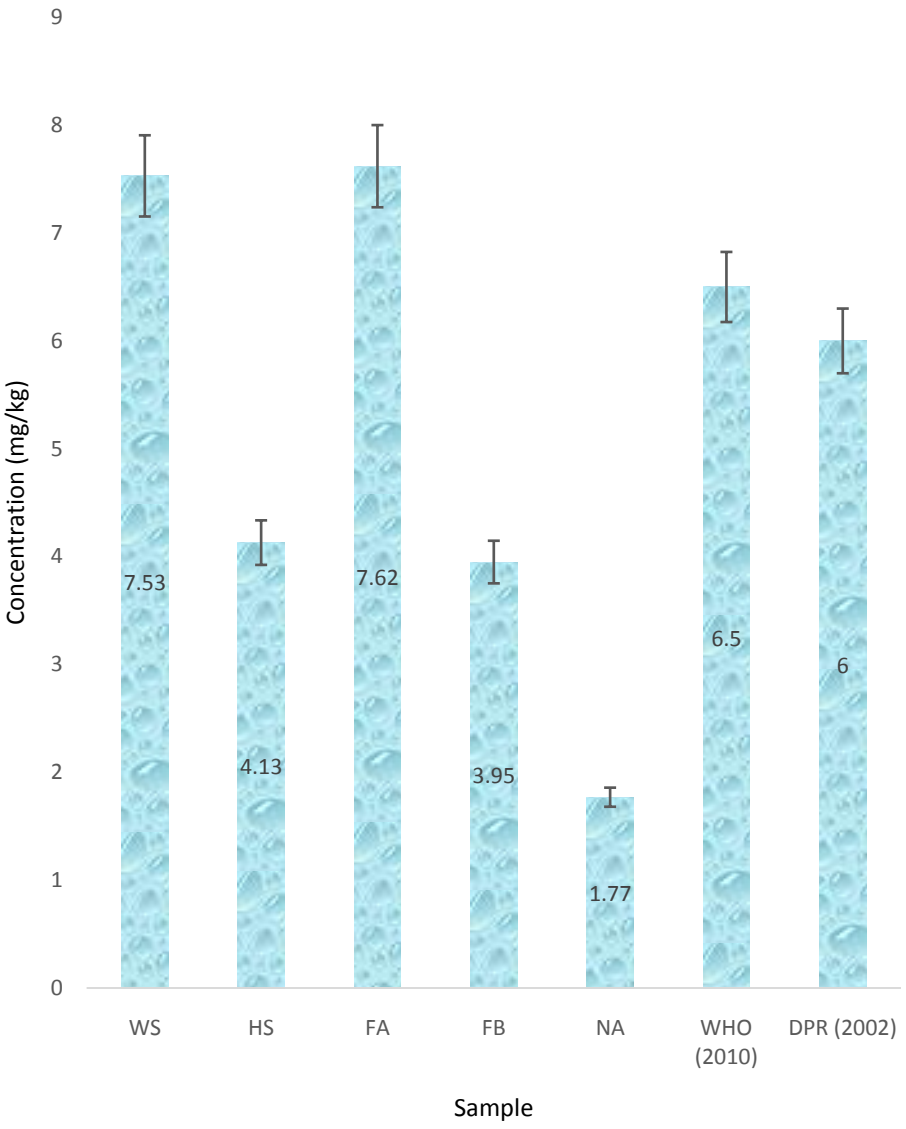


Figure 4.5: Concentration of Nickel in 'Nzu clay' samples and hair samples of Addicts and Non-addicts

Where
WS: 'Nzu clay' from Water side
HS: 'Nzu clay' from Hill side
FA: consumer of 'Nzu clay' above Five years
FB: consumer of 'Nzu clay' below Five years
NA: Non Addicts of 'Nzu clay'
WHO: World Health Organization
DPR: Department of Petroleum Resources

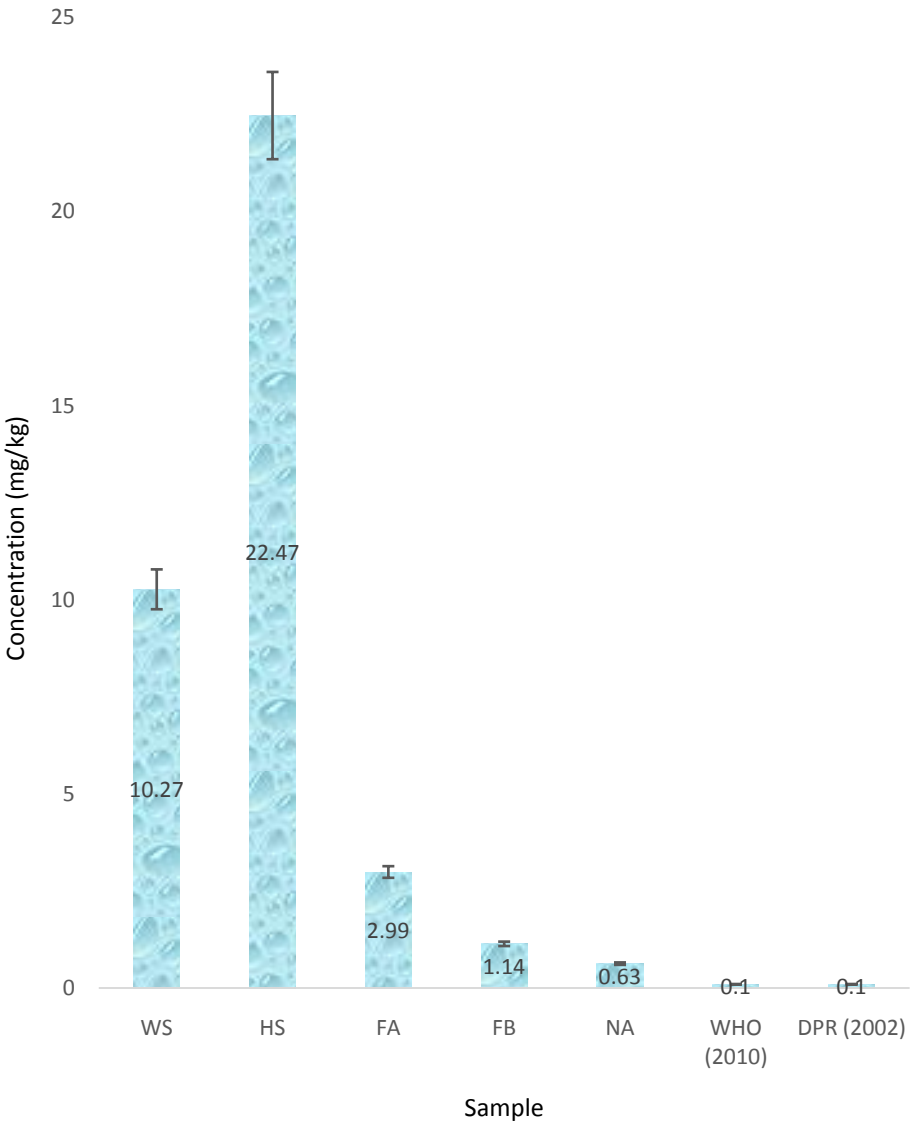


Figure 4.6: Concentration of lead in 'Nzu clay' samples and hair samples of Addicts and Non-addicts

Where
WS: 'Nzu clay' from Water side
HS: 'Nzu clay' from Hill side
FA: consumer of 'Nzu clay' above Five years
FB: consumer of 'Nzu clay' below Five years
NA: Non Addicts of 'Nzu clay'
WHO: World Health Organization
DPR: Department of Petroleum Resources

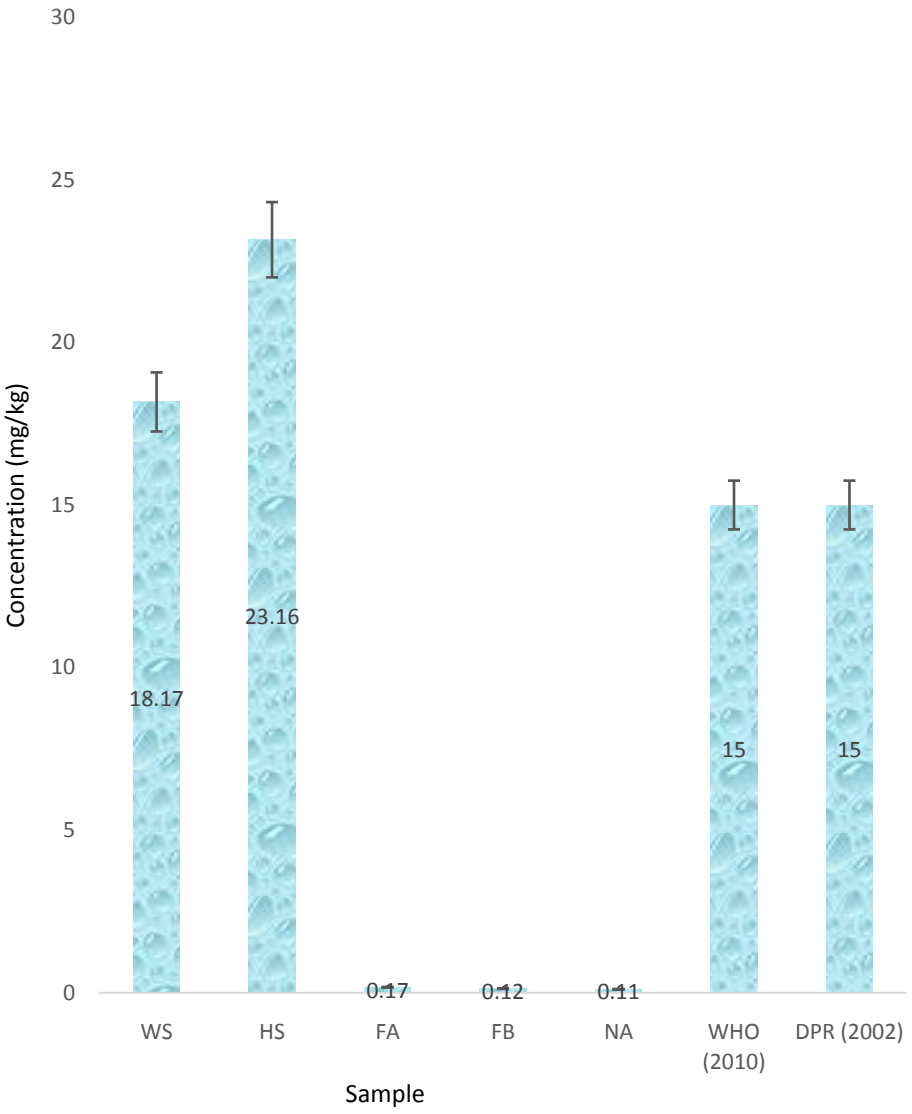


Figure 4.7: Concentration of Zinc in 'Nzu clay' samples and hair samples of Addicts and Non-addicts

Where
WS: 'Nzu clay' from Water side
HS: 'Nzu clay' from Hill side
FA: consumer of 'Nzu clay' above Five years
FB: consumer of 'Nzu clay' below Five years
NA: Non Addicts of 'Nzu clay'
WHO: World Health Organization
DPR: Department of Petroleum Resources

Table 4.3 Target and Intervention Values for Some Metals for a Standard Soil (DPR-EGASPIN, 2002)

Metal	Target value ($mgkg^{-1}$)	Intervention value ($mgkg^{-1}$)
Ni	140.000	720.000
Cu	0.300	10.000
Zn	—	—
Cd	100.000	380.000
Pb	35.000	210.000
As	200.000	625.000
Cr	20.000	240.000

Table 4.4 Permissible limits for metals in solid food by FAO/WHO (2008)

Solid food	FAO/WHO (mg kg^{-1})	NAFDAC
Zn	0.010	-
Cu	0.500	0.300
Cd	0.010	0.200
Pb	0.200	0.300
Ni	0.450	-
Cr	0.020	-
As	0.100	-

Table 4.3 shows the target and intervention values for some metals for a standard soil according to Environmental guidelines and standards for the petroleum industry, Department of Petroleum resources DPR-EGASPIN (2002) Lagos, Nigeria.

Table 4.4 shows concentration (Bq/kg) of radioactive elements (^{40}K, ^{238}U and ^{232}Th) in the raw and processed/finished 'Nzu Clay' Samples from hill of two sites in Ozanogogo of Ika south LGA, Delta State and processed/finished 'Nzu Clay' Samples from water side in Uzella river, Owan West LGA, Edo State. The highlight on bold signifies the highest activity concentration of radioactive element respectively.

Table 4.6 presents the health risk hazard of radioactive elements in 'Nzu Clay' samples while Table 4.5 presents the name and formula of the minerals in the 'Nzu clay' samples using the XRD method.

Table 4.7 presents X-ray diffraction method of 'Nzu Clay' sample on CuKα in the 2θ region, glancing angle 15º – 75º in the raw and finished 'Nzu Clay' Samples from hill of two sites in Ozanogogo of Ika south LGA, Delta State and finished 'Nzu Clay' Samples from water side in Uzella river, Owan West LGA Edo state.

Table 4.9 presents the microscopic and colonial morphology of bacteria isolates of the finished 'Nzu clay' samples from the three sites.

Table 4.10 shows bacteria count (colony counts of bacteria) isolated from the finished 'Nzu clay' samples from three sites.

Table 4.5 Concentration (Bq/kg) of Radioactive Elements in the 'Nzu Clay' Samples

SAMPLES	K-40	U-238	Th-232
SITE 1 R	92.28 ± 30.91^{b}	21.35 ± 6.28^{a}	26.83 ± 13.94^{a}
SITE 2 R	54.45 ± 32.45^{b}	29.08 ± 18.22^{a}	30.84 ± 22.2^{a}
SITE I F	127.60 ± 14.7^{b}	34.45 ± 4.45^{a}	44.51 ± 1.16^{a}
SITE 2 F	125.90 ± 2.77^{b}	26.72 ± 13.31^{a}	28.38 ± 14.53^{a}
SITE 3 FC (WS)	108.14 ± 7.97^{b}	38.75 ± 4.67^{a}	36.24 ± 2.13^{a}
World Mean Range (UNSCEAR, 2000)	400(140 – 850)	35(17 – 60)	30(11 – 64)

Subscript a,b: significant difference at ($P < 0.05$) ANOVA
site1R: raw 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)
site2R: raw 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)
site1F: processed/finished 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)
site2F: processed/finished 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)
site3F: processed/finished 'Nzu clay' from site 3 (Uzella river, Owan West LGA Edo State)

Table 4.6 : Health Risk Hazard of Radioactive Elements in 'Nzu Clay' Samples

Site	ADR (nGy/h)	Raeq (Bq/kg)	AGED (Sv/y)	EHI (eq)	IHI (eq)	RGI (1yr)
Site1R:	30.36	66.83	207.10	0.18	0.24	0.47
Site2R:	34.84	77.37	234.64	0.21	0.29	0.54
Site1F:	48.86	107.90	330.79	0.29	0.39	0.76
Site2F:	35.17	76.99	239.58	0.21	0.28	0.54
Site3FC:	44.88	98.89	303.68	0.22	0.33	0.59
World Mean Range:	60	370	1.00	1.00	1.00	1.00

(UNSCEAR, 2000), Raeq = radon equivalent activity, AGED = annual Gonadal equivalent dose, EHI = external hazard index, IHI = internal hazard index, RGI = representative gamma index.

site1R: raw 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)

site2R: raw 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)

site1F: processed/finished 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)

site2F: processed/finished 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)

site3F: processed/finished 'Nzu clay' from site 3 (Uzella river, Owan West LGA Edo State)

Table 4.7 Name and Formula of the Minerals in the 'Nzu Clay' Samples using XRD method

Sample	Mineral name	Compound name	Chemical formula	Crystal system
Site 1R	Kaolinite	Aluminium silicate hydroxide	$Al_2Si_2O_5(OH)_4$	Monoclinic
Site 1 F	Quartz /Kaolinite	Silicon Oxide / Aluminium silicate hydroxide	SiO_2 / $Al_2Si_2O_5(OH)_4$	Hexagonal/Monoclinic
Site 2 R	Kaolinite	Aluminium silicate hydroxide	$Al_2Si_2O_5(OH)_4$	Monoclinic
Site 2 F	Quartz/Kaolinite	Silicon Oxide / Aluminium silicate hydroxide	SiO_2 / $Al_2Si_2O_5(OH)_4$	Hexagonal/Monoclinic
Site 3 FC	Quartz /Kaolinite	Silicon Oxide / Aluminium silicate hydroxide	SiO_2 / $Al_2Si_2O_5(OH)_4$	Hexagonal/Anorthic

JCPDS and ICDD Reference file number;
Silicon oxide: 01-075-8320
Aluminum silicate hydroxide: 00-006-0221

Table 4.8 Crystallographic Properties of 'Nzu Clay' Samples by XRD method

Sample	a(Å)	b(Å)	c(Å)	Alpha	Beta	Gamma	VOC	Z	RIR
Site1 R	5.16	8.93	7.39	90	104.5	90	329.68	2	-
Site1 F	4.92/5.16	4.92/8.93	5.41/7.39	90/90	90/104.5	120/90	113.53/329.68	3/2	3.03/-
Site2 R	5.16	8.93	7.39	90	104.5	90	329.68	2	-
Site2 F	4.92/5.16	4.92/8.93	5.41/7.39	90/90	90/104.5	120/90	113.53/329.68	3/2	2.91
Site3Fc	4.91/5.14	4.91/8.93	5.41/7.37	90/91.8	90/104.5	120/90	113.1/327.34	3/-	3.06/-

site1R: raw 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)
site2R: raw 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)
site1F: processed/finished 'Nzu clay' from site 1 (Ozanogogo village Ika South LGA Delta State)
site2F: processed/finished 'Nzu clay' from site 2 (Ozanogogo village Ika South LGA Delta State)
site3F: processed/finished 'Nzu clay' from site 3 (Uzella river, Owan West LGA Edo State)
VOC: volume of cell
RIR: Reference Intensity Ratio

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physicochemical Parameters of the Raw and Processed/Finished 'Nzu clay' Samples

The physicochemical parameters of the raw and process 'Nzu clay' samples are presented in Table 4.1. The cation exchange capacity of the raw and finished/processed sample of the 'Nzu clay' from site1 has a mean value of 10.800 ± 0.424 and 10.250 ± 1.202meq/100 g, respectively. This indicates that the processing of the clay which includes salting and heating does not have any significant effect on the 'Nzu clay' samples from site1. Samples from site 2 have a mean value of 10.200 ± 0.989meq/100 g and 9.870 ± 0.671meq/100 g for the raw and finished/processed 'Nzu clay' respectively. This indicates that processing have a significant effect on the cation exchange capacity of the clay samples from site 2 as ions are affected by the processing temperature causing a reduction in the CEC of the processed 'Nzu clay'.

The cation exchange capacity of 'Nzu clay' from site 3 has a mean value of 9.725 ± 0.035meq/100 g. This compare significantly to the CEC in finished 'Nzu clay' from site 2. Raw 'Nzu clay' from site 1 has the highest cation exchange capacity while the processed/finished clay from site 3 have the lowest cation exchange capacity (Table 4.1). The predominant clay mineral in most soil is kaolinite which has a standard CEC value of 5 meq/100 g (James, 2001). The mean CEC value of 'Nzu Clay' in this study exceeds 5 meq/100 g. Hence, the tendency to exchange its cation with the minerals in the body is

high; this is also an index of its high adsorptive capacity for cations and ability to enrich the host with cations.

James, (2001) noted that the CEC of a soil is a good indicator of the nutrient holding and buffer capacity of the soil. 'Nzu clay' have high tendency to exchange essential metals like Ca for toxic ones when ingested, this makes the clay suitable for mineralization in the consumers although soils with high CECs may cause iron deficiency anaemia due to decreasing the absorption and bioavailability of iron and hypokalemic myopathy by gastrointestional potassium depletion (Chaushev *et al.,* 2003). Hypokalemic myopathy due to habitual ingestion of soil has been reported in South Africa (Chaushev *et al.,* 2003).

The bulk density of the 'Nzu clay' as presented in Table 4.1 shows the bulk density of the raw and processed/finished 'Nzu clay' from site 1 have a mean value of 0.725 ± 0.212 and 0.915 ± 0.120 g/cm^3, respectively. This indicates that salting and processing temperature have a significant effect on the bulk density of the clay as there is increase in the packing of the 'Nzu clay' powder. The raw and finished 'Nzu clay' from site 2 have a mean bulk density of 0.710 ± 0.000 g/cm^3 and 0.880 ± 0.169 g/cm^3 respectively. This is also an increase in the bulk density of the processed 'Nzu clay'. The bulk density of clay samples from site 3 has recorded mean value of 0.570±0.014 g/cm^3. This is significantly low compared to the processed 'Nzu clay' from site 1 and site 2 and could be as a result of the particle size of the clay. On the other hand, the processed/finished 'Nzu clay' from site 1 had the highest bulk density while processed/finished clay from site 3 had the lowest bulk density. The finer the texture, the lower the bulk density of the clay powder.

The values of bulk density of the 'Nzu clay' from the three sites, fell well less than the internationally accepted range of 1.0 to 1.7 g/cm^3 for clay soils (USDA, 2014).

The dispersibility (%) of the raw and processed/finished 'Nzu clay' obtained from site 1 have a mean value 80.00 ± 1.414 and 77.250 ± 0.353, respectively (Table 4.1). Dispersibility value for the clay that was raw and processed/finished being obtained from site 2 had a mean value of 80.00 ± 0.000 and 74.750 ± 3.880 respectively, while the mean value obtained for the dispersibility of 'Nzu clay' obtained from site 3 was 76.500 ± 0.707 which compared well with the processed sample from site 1. The raw 'Nzu clay' from site 1 and site 2 had the highest dispersibility while the processed/finished clay from site 2 had the lowest value of 74.750 ± 3.880. Result from site 1 and site 2 showed that the raw clay samples were better dispersed in water than the processed/finished 'Nzu clay' as they possessed higher dispersibility than the finished clay. The raw and processed/finished 'Nzu clay' obtained from the three sites studied have good dispersibility since they show values above 70%.

Water absorption index of the raw and processed/finished clay from site1 recorded the value 1.930 ± 0.056 and 1.775 ± 0.106 g/cm^2, respectively showing a slight reduction in value as a result of processing of the clay. The mean values for raw and processed/finished clay from site 2 was 1.745 ± 0.777 and 1.780 ± 0.282 g/cm^2, respectively implying that there was no effect of processing temperature on the finished clay. 'Nzu clay' from site 3 recorded the highest absorption index value of 2.230±0.000 g/cm^2 which may be traced to the location of site 3 being more of sedimentary nature from the river side while the raw 'Nzu clay' from site 2 had the lowest water absorption index of 1.745 ± 0.777.

The swelling power of the clay had values that relates to that of the respective water absorption index which may be as a result of the organic matter, texture and bulk density of the 'Nzu clay'. The swelling power for samples from Site 1 was 1.680 ± 0.028 and 1.555 ± 0.636 for the raw and processed/finished clay respectively. The swelling power for 'Nzu clay' from Site 2 have values of 1.685 ± 0.049and 1.590 ± 0.424 respectively while the processed/finished clay from site 3 had the highest value of being 2.070 ± 0.000. This may be due to the particle size of the clay as it has a finer texture than the 'Nzu clay' obtained from the hill sides, while processed/finished clay from site 1 have the lowest swelling power with a value of 1.555 ± 0.636. The results showed that processing had a slight effect on the degree of exposure of the internal structure of the clay mineral to the action of water as the processed/finished clay from site 1 and site 2 as values indicates a reduction in swelling ability of the 'Nzu clay'.

The pH of the 'Nzu clay' from site 1 had value of 5.150 ± 0.494 and 4.500 ± 0.141 for the raw and processed/finished clay respectively, however, the raw and processed/finished clay from site 2 had values of 5.250 ± 0.494 and 4.500 ± 1.141 respectively while the processed/finished 'Nzu clay' from site 3 has the pH value 4.500 ± 0.000. The pH of the processed/finished clay from site 1, site 2 and site 3 indicated higher acidity. Processing temperature and salting of the clay could account for this increased acidity. Ingestion of 'Nzu clay' may prevent the stomach pH from dropping to levels that are favorable for Fe dissolution, thereby reducing their bioavailability to the geophagic individual even where the Fe concentration in the ingested soil is high**.** Low pH of the processed/finished clay could account for the slightly sour taste, and the addition of salt to the 'Nzu clay' could be one of the major reasons why people, especially the pregnant

women crave for this clay. This could be some of the reasons why consumption of clay is reported to control excessive secretion of saliva and reduce nausea (Ibeanu *et al.,* 1997).

The colours of the raw 'Nzu clay' from site 1 and site 2 is ash-white while the processed/finished 'Nzu clay' has light grey-ash colour. On the other hand, the processed/finished 'Nzu clay' from site 3 is dark grayish-ash in colour.

5.1.1 Correlation between similar physiochemical properties of the various sampling sites

Table 4.2 shows the correlation between physiochemical properties of 'Nzu clay' from site 1, site 2 and site 3. Raw 'Nzu clay' from site 1 correlates well in cation exchange capacity with that of raw clay from site 2, processed clay from site 1 and site 3 at r = 1.00 and also correlates well at r = 0.988 processed/finished clay from site 2.

Raw 'Nzu clay' from site 2 correlates well in bulk density with that of processed samples from site 1, site 2 and site 3 at r = 1.00. Processed/finished 'Nzu clay' from site 1 correlates well in dispersibility with that of the processed/finished 'Nzu clay' from site 1, site 2 and site 3 at r = 1.00. The processed/finished 'Nzu clay' from site 2 correlate well in swelling power with processed/finished 'Nzu clay' from site 3 at r = 0.99. The significant positive correlations observed among the physic-chemical parameters possibly suggest a strong association between these parameters.

5.2 Heavy Metals Concentration in 'Nzu clay' and in the Hair of Addicts and Non-addicts

Appendix IA, shows the concentration of the heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in the processed/finished 'Nzu clay' obtained from the hill in Ozanogogo, Ika South LGA Delta State and from Uzella river, Owan West LGA Edo State by Atomic Absorption Spectrometry. Appendix IB, IC and ID - indicate the distribution of heavy metal (As, Cd, Cr, Cu, Ni, Pb and Zn) in the hair of addict of the clay above five years, less than fives of addiction and non addicts of the clay while Appendix IE shows the heavy metal concentrations (Mean ± Sem in mg/kg) in Hair Samples of 'Nzu Clay' Addicts above five years, less than five years and non consumers of the clay. One-way ANOVA was employed in comparing the level of heavy metals in the 'Nzu clay' by sites, and also the variation of the metals in hair of addicted consumers of the clay above 5 yrs, less than 5 yr and that of the non-addicts $P < 0.05$ using Duncan Multiple range test.

5.2.1 Concentration of Arsenic in hair of Addicts and in 'Nzu clay' samples

Figure 4.1 shows the concentration of As in the hair of consumers of the 'Nzu clay' above five years has the range of 23.51 to 29.81 $mgkg^{-1}$ with a mean ± SEM value of 25.60 ± 1.1$mgkg^{-1}$, As in consumers of the clay less than five years range from 21.10 to 23.30 $mgkg^{-1}$ having a mean± SEM value of 22.44 ± 0.39 $mgkg^{-1}$ while the concentration of As in non-addicts have the range 18.15 to 25.60$mgkg^{-1}$ with a mean ± SEM value of 18.15±0.27$mgkg^{-1}$ in (fig 4.1). This indicates significant difference between the levels of the metals in the hair of addicts by variation of years of addiction compared to the non addicts ($P < 0.05$).

The concentration of As in the hair of the addicts studied is significantly very high at ($P < 0.05$) compared to the recommended dietary allowance RDA by the (WHO, 2010) and (DPR, 2002) which is 0.11mgkg^{-1}. Exposure to arsenic has therapeutic effect on cancer of the cervic (Hung-Chin *et al.,* 2010). Arsenic can also cause high blood pressure and other cardiovascular diseases in pregnant women (Richard, 2007). Long-term exposure of As can lead to the formation of skin lesions, internal cancers, neurological problems, pulmonary disease, peripheral vascular disease, hypertension and cardiovascular disease and diabetes mellitus (Smith *et al.,* 2000).

5.2.2 Concentration of Cadmium in the 'Nzu clay' samples and in hair of addicts

Figure 4.2 shows the concentration of Cd in the 'Nzu clay' from the hill side Ozanogogo village, Ika South LGA Delta State and Uzella river, Owan West LGA Edo State had a mean ± SEM value of 1.86 ± 0.03 (mgkg^{-1}) and 3.83 ± 0.14 mgkg^{-1} respectively in (fig 4.2). There is a significant difference between the location sites at ($p \leq 0.05$) (Appendix IA). The mean concentration of Cd from water side is higher being of more sedimentary form than 'Nzu clay' from hill side. It is clearly evident that consumption of 'Nzu clay' have the tendency to bioaccumulate in the body of addicts according to the duration of addiction as indicated in the analysis carried out in the hair of the groups concerned. However, the concentration of Cd in the 'Nzu clay' sample was less than the target value for Cd in standard soil which is 100 mgkg^{-1} according to (DPR-EGASPIN, 2002).

Concentration of Cd in the hair of addicts of 'Nzu clay' above five years, the range is from 3.22 to 7.60 mgkg^{-1}, having a mean value of 4.35 ± 0.82, the concentration of Cd in the hair of addicts of 'Nzu clay' being less than five years range from 2.28 to 2.71mgkg^{-1}

with a mean value of 2.59 ± 0.09 while the concentration of Cd in non-addicts range from 0.94 to 1.44mgkg^{-1}, having a mean value of 1.09 ± 0.09. There is a significant difference at ($p \leq 0.05$) (Appendix IE) between the years of addiction above five years and less than five years in comparison to the concentration of Cd in non-addicts. Concentration of Cd in all the addicts and the non-addicts exceed the recommended dietary allowance limit (RDA) according to (WHO, 2010) and Department of Petroleum Resources (DPR, 2002) which are values 0.1 and 0.03 respectively. Cadmium is highly toxic to the kidney and it accumulates in the proximal tubular cells in higher concentrations. The main symptoms following ingestion of cadmium at doses above about 0.07 mg kg^{-1} in humans are *nausea*, vomiting, and abdominal pain. Cadmium can also cause bone mineralization either through bone damage or by renal dysfunction (Chakraborty *et al.*, 2013).

5.2.3 Concentration of chromium in the 'Nzu clay' samples and in hair of addicts

The mean ± SEM (mgkg^{-1}) concentration of Cr in the 'Nzu clay' from water side (WS) is 65.8 ± 2.50 which is significantly high at ($P \leq 0.05$) (Appendix IA) compared to its counterpart from hill side (HS) with mean Cr concentration of 41.57 ± 2.07 in (fig 4.4). The values in the clay are above the target value in a standard soil which is 20 (mg kg^{-1}) according to (DPR-EGASPIN, 2002). The RDA for Cr according to (WHO, 2010) is 0.02 and department of petroleum resources (DPR) is 0.03 which is also infinitesimal compared to the concentration of Cr in the hair of both the addicts and non addicts of the clay as clearly seen in (fig 4.4) and Appendix IA.

Fig 4.4 and appendix IE indicates the chromium concentrations (Mean ± Sem in mg/kg) in hair samples of 'Nzu clay' addicts above five years, less than five years and non-addict

of the clay. The concentration of Cr in the hair of addicts of 'Nzu clay' above five years range from 83.11 to 204.11 $mgkg^{-1}$, having a mean value of 112.47 ± 22.9, however, the concentration of Cr in addicts less than five years range from 59.30 to 75.04 $mgkg^{-1}$ the mean value was 66.06 ± 3.18 while the concentration of Cr in the hair of non-addicts range from 16.34 to 54.67 $mgkg^{-1}$, the mean level was 28.3 ± 6.75. This result showed significant difference at (P □ 0.05) (Appendix IE) in the level of Cr in the hair of addicts less than and greater than five years compared to the level in the hair of non-consumers of 'Nzu clay'. Results obtained from different *in vitro* and *in vivo* experiments have shown that chromate compounds can induce DNA damage in many different ways and can lead to the formation of DNA adducts, chromosomal aberrations, sister chromatid exchanges, alterations in replication and transcription of DNA (O'Brien *et al.,* 2001; Matsumoto *et al.,* 2006) as the long term bioaccumulation of Cr in the hair of the addicts calls for caution. Chromium is also associated with allergic dermatitis in humans, headache and inhibition of adenosine triphosphate (ADTP) during respiration (Scragg, 2006).

5.2.4 Concentration of copper in the 'Nzu clay' samples and in hair of addicts

The mean ± SEM concentration of Cu in the 'Nzu clay' samples being collected from the hill side in Ozanogogo site 1 and 2 was 27.56 ± 0.78 $mgkg^{-1}$, while that of its counterpart from the water in Uzella river, Owan West LGA Edo State was 10.10 ± 0.61 $mgkg^{-1}$ in (fig 4.4). The concentration of Cu from hill side is significantly high at (p □ 0.05) compared to the target and intervention value (mg kg^{-1}) according to DPR-EGASPIN (2002) which is 0.30 and 10.00 respectively in (Fig 4.4, Appendix IA).

Figure 4.4 shows the concentration of Cu in the hair of addicts of 'Nzu clay' for above five years. This ranged from 3.14 to 6.91 $mgkg^{-1}$, the mean value was 4.04 ± 0.72 $mgkg^{-1}$. However, Cu in the hair of the addict of the clay for less than five years range from 0.08 to 2.02$mgkg^{-1}$having a mean ± SEM value of 0.52 ± 0.38. From the result (Appendix IC and ID), the concentration of Cu in the hair of non-addicts of the 'Nzu clay' ranged from 0.86 to 1.28 the mean ± SEM value was 0.86 ± 0.16 $mgkg^{-1}$. This shows that ingestion of the clay does not have a significant effect on the bioaccumulated heavy metals by the consumers of the clay for less than five years. This may be due to the fact that Cu is one of the essential metals needed in the human body and also the cation exchange capacity of the clay to replace readily available cation in the body. The concentration of Cu in the hair of addicts above five years was at a higher concentration value due to the bioaccumulation of the metals over the years. It is of note that the concentration of Cu in the hair of non-addict is significantly higher at (P □ 0.05) (Appendix **E**) than that in addicts less than five years, and also higher than the RDA according to (WHO, 2010) which is 0.5 $mgkg^{-1}$. This may be due to environmental and physiological factors, status of living and metabolism of the individuals.

In humans, Cu helps in the production of blood haemoglobin, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation (Martínez and Motto, 2000).

5.2.5 Concentration of nickel in the 'Nzu clay' samples and in hair of addicts

The mean ± SEM ($mgkg^{-1}$) concentration of Ni in the 'Nzu clay' samples obtained from the hill side at Ozanogogo, Ika South LGA Delta State and water side at Uzella, Owan

West LGA Edo State are 7.53 ± 0.30 and 4.13 ± 1.00 respectively, the 'Nzu clay' from the water side (WS) had higher Ni concentration than its hill side counterpart. The clay from both sites had higher Ni concentration than the permissible limit in standard soil, the value being 6.5 and 6 $mgkg^{-1}$ according to (WHO, 2010) and (DPR, 2002) respectively but Ni concentration in the clay was lower than the target limit of Ni in clay which is 140 $mgkg^{-1}$ as set by (DPR-EGASPIN, 2002) as seen in (Table 4.3).

Figure 4.5 shows that the concentration of Ni in the hair of the addicts of 'Nzu clay' above five years range from 4.73 to 11.49 $mgkg^{-1}$ having a mean value of 7.62 ± 1.46, on the other hand, concentration of Ni in the hair of addicts of the clay less than five year range from 3.80 to 4.27$mgkg^{-1}$, the mean value was 3.95 ± 0.08 while the concentration of Ni in the hair of non addicts range from 1.26 to 2.77 $mgkg^{-1}$ having a mean value of 1.77 ± 0.28. This value of Ni recorded in the hair of non-consumers of the clay is significantly lower than the levels in the hair of the addicts less than five years; also the levels in the hair of addicted consumers for less than five years is less than the concentration of Ni in addict of the 'Nzu clay' above five years at (P □ 0.05). Addict less than and above five years of addiction to 'Nzu clay' had a mean value of Ni in the hair (3.95 and 7.62 respectively) being higher than the permissible limit set by (FAO/WHO, 2008) which is 0.45 $mgkg^{-1}$ as seen in Table 4.4 and Appendix IE. Concentration of Ni in hair of addicts of the clay above five years is significantly higher than the permissible limit at (P □ 0.05). Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. High level of Ni poisoning causes new born weight reduction, and reduced pregnancy length (Khodadoust *et al.,* 2004).

5.2.6 Concentration of Lead in the 'Nzu clay' samples and in hair of addicts

The mean ± SEM ($mgkg^{-1}$) concentration of Pb in 'Nzu clay' obtained from the water side in Uzella river, Owan West LGA Edo State and hill side in Ozanogogo, Ika South LGA Delta State were 10.27 ± 1.79 and 22.47 ± 1.52 respectively (fig 4.6), with concentration of Pb in the 'Nzu clay' samples from the hill side being significantly higher than the clay obtain from the hill side in Ozanogogo at (P 0.05) although both are lower than the target value for standard soil of 35.00$mgkg^{-1}$ as set by (DPR-EGASPIN, 2002).

Figure 4.6 shows that the concentration of Pb in the hair of 'Nzu clay' addicts above five years, this ranged from 2.02 to 5. 69 $mgkg^{-1}$, having a mean value of 2.99 ± 0.68. The concentration of Pb in the hair of addicts less than five years ranged from 1.00 to 1.21$mgkg^{-1}$, having a mean value of 1.14 ± 0.04, while the concentration of Pb in the hair of non-addicts to 'Nzu clay' ranged from 0.27 to 0.95 $mgkg^{-1}$, the mean level of Pb was 0.63 ± 0.11. All the mean values compared to the concentration of Pb in the hair of all addicts and non addicts exceeds the permissible limit of 0.1 set by (WHO, 2010) and (DPR, 2002). It is anticipated that the level of Pb above this permissible limit may accumulate in the body organ such as the brain, which may lead to poisoning (plumbism) or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk of impaired development, lower intelligence quotient (IQ), shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to lead (NSC, 2009).

5.2.7 Concentration of zinc in the 'Nzu clay' samples and in hair of addicts

Figure 4.6 shows The concentration of Zn in 'Nzu clay' obtained from water side at Uzella river and hill side at Ozanogogo was 18.17 ± 0.33 and 23.16 ± 1.00 respectively with the 'Nzu clay' from hill side being significantly higher than the clay from the water side (P □ 0.05) using Duncan Multiple range test ANOVA. The mean value of Zn in the clay is higher than the target value of 15 $mgkg^{-1}$as set by (WHO, 2010) and (DPR, 2002) in standard soil.

The concentration of Zn in the hair of addicts of 'Nzu clay' above five years, ranged from 0.12 to 0.24 $mgkg^{-1}$, with a mean value of 0.17 ± 0.22, on the other hand, concentration of Zn in the hair of addicts less than five years ranged from 0.05 to 0.19 $mgkg^{-1}$, with a mean value of 0.12 ± 0.03 while that of the non addicts ranged from 0.06 to 0.19$mgkg^{-1}$, having a mean value of 0.11 ± 0.02. The variation of concentration of Zn in the hair of addicts less than five years and in the addicts to 'Nzu clay', above five years and non addicts were of no significant difference at (P □ 0.05) and also correspond to the RDA for zinc which is 11 mg day^{-1} in men and 8 mg day^{-1} in women, these correspond to approximately 0.16 mg kg^{-1} day^{-1} for men and 0.13 mg kg^{-1} day^{-1} for women (EPA, 2006). Zinc is a trace element that is essential for human health. Zinc shortages can cause birth defects. The distribution of Zn in the hair of all the groups: addicts less than five years, above five years and non-addicts to 'Nzu clay' were closely the same which indicate that Zn does not bioaccumulate in the body due to cation exchange capacity of the 'Nzu clay'. The non-parametric Analysis of Variance (ANOVA) revealed that the differences observed in the levels of the Zn among the hair samples were not statistically significant (P □ 0.05) (Appendix IE).

The concentration of heavy metals in the hair of the addicted consumers of 'Nzu clay' for a period above five years is alarmingly higher than that recorded in the addicts of the clay for less than five years, this is undoubtedly attributed to long years of addiction to the clay.

The concentration of heavy metal in the 'Nzu clay' obtained from the water side is in the order: Zn □ Pb □ Cu □ Ni □ Cr □ Cd while the level of heavy metals in the 'Nzu clay' from the hill side is in the order: Cr □ Cu □ Zn □ Pb □ Ni □ Cd. Therefore, the consumption of 'Nzu clay' should continually be discouraged as it poses grievous health risk to the consumers due to the bioaccumulation of heavy metals at levels higher than the recommended dietary allowance (RDA) in solid food substances by WHO/FAO/NAFDAC.

The order of the heavy metal contamination of the hair of addicted consumers of 'Nzu clay' for above five years is: Cr □ As □ Ni □ Cd □ Pb □ Zn. The concentration of the heavy metals in the hair of the addict of the clay less than five years is in the order: Cr □ As □ Ni □ Cd □ Pb □ Cu □ Zn, while the order of concentration of heavy metals in the non-addicts used as control is in the order: Cr □ As □ Cd □ Ni □ Cu □ Pb □ Zn, with Cr having the highest concentration of 66.06 ± 3.18 in the hair of addicts above five years and Zn having the least concentration of 0.11±0.02 in hair of the non-addicts of the clay.

5.3 Concentration (Bq/kg) of Radioactive Elements in 'Nzu clay' Samples

Table 4.5 and Appendix IIIA represents the level of radioactive elements (one-way ANOVA) in the raw and processed/finished 'Nzu clay' obtained from Ozanogogo, Ika

South LGA of Delta State and the processed/finished 'Nzu clay' obtained from Uzella river, Owan West LGA Edo State. Appendix II shows spectral of radioactivity in the clay. The activity concentration of ^{40}K range from 54.45 ± 32.45 to 127.60 ± 14.7 Bq/kg in the raw clay from site 2 at Ozanogogo, had the lowest activity concentration of 54.45 ± 32.45, the processed/finished 'Nzu clay' from site 1 had the highest activity concentration of ^{40}K being 127.60 ± 14.7 Bq/kg. All these values fall below the permissible limit of 400(140 – 850) Bq/kg recommended by United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 2000). However, it is of note that processing of the 'Nzu clay' causes significant increase in the activity concentration of ^{40}K at ($P < 0.05$) also as indicated in table 4.5.

Activity concentration of ^{238}U in the 'Nzu clay' had value range 21.35±6.28 to 38.75±4.67 Bq/kg, with the raw clay obtained from site 1 at Ozanogogo having the lowest activity concentration being 21.35 ± 6.28 while the processed/finished clay from site 3 have the highest activity concentration of ^{238}U being 38.75±4.67 Bq/kg,. All the values of ^{238}U falls within the allowance limit for ^{238}U in the world mean and range for a standard soil according to (UNSCEAR, 2000) which is 35 (mean)17 – 60 range. Table 4.4 shows the increase in concentration of ^{238}U in the processed/finished clay from the three sites except the processed/finished clay obtained from site 2 at Ozanogogo which is 26.72 ± 13.31.

Activity concentration of ^{232}Th in the 'Nzu clay' range from 26.83 ± 13.94 to 44.51 ± 1.16 Bq/kg, with the raw 'Nzu clay' from site 1at Ozanogogo having the lowest concentration of ^{232}Th being 26.83 ± 13.94, while the processed/finished clay from same site have the highest concentration of ^{232}Th. This indicates that processing temperature

increases the activity concentration of ^{232}Th. It is of note that the processed/finished clay from all the three sites had higher activity concentration of ^{232}Th than the raw clay counterpart except for the processed/finished clay from site 2 at Ozanogogo having a value of 28.38±14.53, while the value of ^{232}Th in the raw clay was 30.84±22.2. However the activity concentration of ^{232}Th in the 'Nzu clay' from all sites fall within the allowance limit of the world mean range which is 30 (mean) 11 – 64 (range) according to UNSCEAR (2000). This study compare well with the work carried out by (Agbalagba *et al.*, 2012) on the analysis of naturally occurring radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in soil samples collected from oil and gas field environment of Delta state. The activity concentration of the samples ranged from 19.2 ± 5.6 Bqkg^{-1} to 94.2 ± 7.7 Bqkg^{-1} with mean value of 41.0 ± 5.0 Bqkg^{-1} for ^{226}Ra, 17.1 ± 3.0 Bqkg^{-1} to 47.5 ± 5.3 Bqkg^{-1} with mean value of 29.7 ± 4 Bqkg^{-1} for ^{232}Th and 107.0 ± 10.2 Bqkg^{-1} to 712.4 ± 38.9 Bqkg^{-1} with a mean value of 412.5 ± 20.0 Bqkg^{-1} for ^{40}K. The values obtained are in good agreement with the world range and values reported in other countries.

5.3.1 Level of the health risk hazard of radioactive elements in 'Nzu clay' samples

Table 4.6 presents the absorbed dose rate (nGy/h) of radioactive element in the raw 'Nzu clay' samples from site 1 at Ozanogogo had the lowest absorbed dose rate of 30.36 while the processed/finished clay from site 1 had the highest absorbed dose rate value 48.86. These values fall below the world allowance limit of value 60nGy/h as stated by (UNSCEAR, 2000).

The result of radium equivalent activity (Ra_{eq}) in the 'Nzu clay' samples obtained from the three sites (two hill sites in Ozanogogo and one site at Uzella river) shows that raw

‘Nzu clay’ from site 1 had the lowest value of 66.83 Bq/kg, while the processed/finished clay from site 1 have the highest radium equivalent activity 107.90 Bq/kg as calculated (Appendix IIIC). The range of the radium equivalent activity in ‘Nzu clay’ is above the mean value 79.47Bq/kg as given by (Beratka and Matthew, 1985) and less than the permissible limit set by (UNSCEAR, 2000) with value 370 Bq/kg.

The raw ‘Nzu clay’ from site 1at Ozanogogo, had the lowest annual gonadal equivalent dose (AGED) 207.1Sv/y, while processed/finished clay from site 3 at Ozanogogo had the highest annual gonadal equivalent dose value of 303.68Sv/y. All calculated values (table 4.6 and Appendix IIIC) were less than the permissible limit of 1000Sv/y set by (UNSCEAR, 2000).

Following from table 4 and Appendix IIIC, the External hazard index (Hex) of the raw ‘Nzu clay’ from site 1 at Ozaogogo had the lowest calculated value of 0.18eq while the highest value of 0.29eq was calculated for the in processed/finished ‘Nzu clay’ from the same site. This shows that processing of the clay have effect on the activity concentration of the radioactive elements in the clay. Therefore, increasing the health risk hazard of the clay. The external hazard index of the clay samples calculated indicated that it poses no risk to human health, since their values are less than unity as stipulated by (UNSCEAR, 2000).

The internal hazard index (Hin) of the raw clay from site 1 at Ozanogogo had the lowest value 0.24eq, while processed/finished clay from the same site, site 1 had a calculated value of 0.39, the entire values are less than unity which is the permissible limit by (UNSCEAR, 2000).

Representative Gamma index (1yr) of the raw 'Nzu clay' from site 1 at Ozanogogo had the lowest value of 0.47, while that of processed/finished clay from site 1 have the highest calculated value 0.76. Representative Gamma index indicated that there was no health risk hazard recorded since the entire 'Nzu clay' have value less than unity as indicated by (UNSCEAR, 2000). The hazard indexes in this study agrees with (Agbalagba *et al.,* 2012) who also examined some radiation hazard indices oil fields environment of Delta State Nigeria, the mean values obtained were: 98.5 ± 12.3 $Bq.kg^{-1}$ for radium equivalent activity (Ra_{eq}), 0.8 $Bqkg^{-1}$ for Representative level index (Iγ), 54.6 $nGyh^{-1}$ for the Absorbed Dose rates (D), 0.07 μSvy^{-1} for Annual Effective Dose Rates (Eff Dose), 0.3 for External Hazard Index (Hex) and 0.4 for Internal Hazard Index (Hin). These calculated hazard indices were well less than their permissible limit (Table 4.6) and also the results obtained from (Sowole, 2014), the hazard index for surface soil samples of major markets at Sagamu, Ogun State in Nigeria with the use of gamma spectrometry using Sodium Iodide Thallium doped NaI (TI) detector, ascertained the mean external hazard index (Hex) and mean internal hazard index (Hin) for all the soil samples from Falawo market calculated to be 0.616 Bq/kg and 0.691Bq/kg respectively, and that of Awolowo market were 0.566 Bq/kg and 0.634 Bq/kg respectively. For Sabo market the mean values were calculated to be 0.594 Bq/kg and 0.658 Bq/kg respectively. All the values obtained were less than 1.0 Bq/kg as recommended for safety by (UNSCEAR, 2000).

Appendix IIIC presents the calculation of the hazard index of all 'Nzu clay' from the three sites. The ingestion of 'Nzu clay' pose no health risk to human, and are safe for pharmaceutical, cosmetics and industrial application.

5.4 Mineral Composition of 'Nzu clay' by XRD Technique

Table 4.7 and Appendix IVA presents the minerals found in 'Nzu clay' and the chemical formulae of the 'Nzu clay' obtained from two sites (hills) of Ozanogogo, Ika South LGA Delta State and one site Uzella river, Owan West LGA, Edo State. The characterization of XRD patterns as provided by XRD equipment indicates the presence of pure kaolinite (Aluminium silicate hydroxide) with chemical formula of $Al_2Si_2O_5(OH)_4$ in the raw 'Nzu clay' from Site 1 and site 2 at Ozanogogo, having monoclinic crystal system.

XRD analysis for mineralogical investigation revealed that the 'Nzu clay' are dominantly composed of the mineral quartz (Silicon oxide) with the chemical formula SiO_2 and hexagonal crystal system in the processed/finished clay obtained from site 1 and site 2 at Ozanogogo than Kaolinite (Aluminium silicate hydroxide) with chemical formula of $Al_2Si_2O_5(OH)_4$ having monoclinic crystal system (Appendix IVB).

Quartz (Silicon oxide) with chemical formula SiO_2 having hexagonal crystal system is dominant in the processed/finished 'Nzu clay' obtained from site 3 at Uzella river, than Kaolinite (Aluminium silicate hydroxide) with chemical formula of $Al_2Si_2O_5(OH)_4$ having anorthic crystal system. The mineral (kaolinite) in the clay of site 3 at Uzella river has crystal system (anorthic) that is different from crystal system in the kaolinite contained in 'Nzu clay' from the two hills of Ozanogogo, Ika South LGA, Delta State as seen in table 4.7. Availability of the nutrient in the clay and eventually in the stomach is influenced by the texture and mineralogy of the clay.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

This study indicates that there was significant difference in the concentration of the analyzed metals at ($P < 0.05$) between the raw 'Nzu clay' and the processed/finished 'Nzu clay' as there was disparity in the physico-chemical parameters determined in the clay. The bulk density (g/cm^3) of raw and processed/finished 'Nzu clay' had a mean value of 0.72 ± 0.212 and 0.915 ± 0.120 respectively, showing increase in bulk density of the processed clay. Dispersibility (%) in the raw and processed/finished clay was 80.00 ± 1.414 and 74.750 ± 3.880, respectively. This showed decrease in the dispersibility of the processed/finished clay. Water absorption and swelling power of processed/finished 'Nzu clay' obtained from Uzella river have the highest values 2.230 ± 0.000 and 2.070 ± 0.000 respectively. The pH of the raw and processed/finished 'Nzu clay' was 5.150 ± 0.494 and 4.500 ± 0.141 respectively, showing increased acidity in the clay.

The mean value of CEC of the raw and processed/finished clay range from 9.725 ± 0.035 meq/100 g to 10.80 ± 0.424 meq/100g. This indicates that processing condition have no significant effect at ($P < 0.05$) on the cation exchange capacity of the clay as ions are unaffected by the processing temperature of the processed 'Nzu clay'. There is correlation between the physicochemical parameters at range 98.8% to 100% as shown in (table 4.1)

The concentration of heavy metals in the processed/ finished 'Nzu clay' obtained from the hill side in Ozanogogo, Ika South LGA and Uzella river, Owan West LGA, Edo State had mean ± SEM ($mgkg^{-1}$) value of Cd as 1.86 ± 0.03 and 3.83 ± 0.14 respectively, Cr 41.57 ± 2.07 and 65.8 ± 2.50 respectively, Cu 27.56 ± 0.78 $mgkg^{-1}$, and 10.10 ± 0.61$mgkg^{-1}$respectively, Ni 7.53 ± 0.30 and 4.13 ± 1.00 respectively, Zn 22.47 ± 1.52 and 10.27 ± 1.79 respectively. Heavy metals in the clay samples obtained from the hill and water side exceed the allowance limit for standard soil by (DPR-EGASPIN, 2002) (Table 4.3).

The hair of the addicts of 'Nzu clay' analyzed using Atomic Absorption Spectroscopy, revealed that the addicts of the clay for above 5 yr have the mean value of As being 25.60 ± 1.1$mgkg^{-1}$, Cd 4.35 ± 0.82, Cr 112.47 ± 22.9, Cu 4.04 ± 0.72, Ni 7.62 ± 1.46, Pb 2.99 ± 0.68 and Zn 0.17 ± 0.22; while the addicts of the clay for less than 5yr had the mean value for As being 22.44 ± 0.39 $mgkg^{-1}$, Cd 2.59 ± 0.09, Cr 66.06 ± 3.18, Cu 0.52 ± 0.38, Ni 3.95 ± 0.08, Pb 1.14 ± 0.04, and Zn 0.12 ± 0.03. This shows increased variation in the concentration of the heavy metals studied at ($P < 0.05$) as the years of consumption of the clay increased. All the addicts and non addicts of the clay have concentration of the heavy metals in the levels that exceed the recommended dietary allowance in solid food by FAO/WHO and NAFDAC as shown in Table 4.4.

The levels of radioactive elements in the raw 'Nzu clay' indicated that the lowest activity concentration (Bq/kg) of ^{40}K, from site 2 was 54.45 ± 32.45,^{238}U from the clay of site 1 recorded 21.35 ± 6.28 and ^{232}Th from the clay of site 1 at Ozanogogo was 26.83 ± 13.94. Furthermore, the processed/finished clay have higher activity concentration (Bq/kg) of ^{40}K being 127.60 ± 14.7 from site 1, site 3F (Uzella river) ^{238}U 38.75 ± 4.67 and site 1

^{232}Th 44.51 ± 1.16. These values indicate that ^{40}K had the highest activity concentration (Bq/kg) of 127.60 ± 14.7 in the edible clay samples, while ^{238}U and ^{232}Th had values that are close in range 38.75 ± 4.67 and 44.51 ± 1.16 respectively. The radionuclides detected in 'Nzu Clay' were all lower in levels than the worldwide average values 400, 35 and 30 for ^{40}K, ^{238}U and ^{232}Th respectively as stated by (UNSCEAR, 2000).

The mean absorbed dose rate by the 'Nzu Clay' was calculated to be 48.86 nGy/h, this is within the world average which is 60nGy/h according to (UNSCEAR, 2000). The mean value of the Annual Gonadal Equivalent Dose (AGED) in the 'Nzu Clay' was 207.1Sv/y, which is relatively high and could pose risk to the activity of the bone marrow and the bone surface cells. The values of the radium equivalent activity index, representative Gamma Index (Iyr), external hazard index (Hex) and internal hazard index (Hin) were less than unity, this indicated that there is a negligible health hazard in consuming the 'Nzu Clay' from Ozanogogo.

X-ray diffraction of 'Nzu Clay' sample on CuK_{α} in the 2θ region, glancing angle 15º – 75º in the raw and finished 'Nzu Clay' investigated for the mineralogy reveals that the 'Nzu clay' is dominantly composed of the mineral kaolinite, compound name; aluminium silicate hydroxide ($Al_2Si_2O_5(OH)_4$) and quartz, silicon (IV) oxide (SiO_2).

6.2 Conclusion

'Nzu clay' obtained from the hill of two sites in Ozanogogo, Ika South LGA, Delta State and one site in Uzella river, Owan West LGA Edo State revealed that the health risk could result from the high levels of some studied heavy metals that were above the threshold limits. Heavy metal contaminant in 'Nzu clay' obtained from the water side

were in the order of Zn □ Pb □ Cu □ Ni □ Cr □ Cd; while in the 'Nzu clay' from the hill side had the metals in the order: Cr □ Cu □ Zn □ Pb □ Ni □ Cd. Heavy metals obtained from the hill and water side had exceeded the tolerable limit in soil (WHO, 2010) and (DPR, 2002).

Results derived from analysis on the hair of the addicts greater than 5yr and less than 5yr in comparison with those in the non-addicts show discrepancies at ($P < 0.05$), the heavy metal concentrations in addicts greater than 5yr were higher than the concentration of heavy metals in addicts less than 5yr, while addicts of the clay less than 5yr have higher concentration of heavy metals than the non addicts. As, Cd Cr Cu Ni Pb were all higher in concentrations than the permissible limit set by WHO/NAFDAC, except for Zn which was lower than the permissible limit of 15 $mgkg^{-1}$ by WHO/NAFDAC and does not reflect bioaccumulation which may be as a result of the essentiality of Zn in the human body and the CEC of the clay.

Radioactive elements ^{40}K, ^{238}U and ^{232}Th in the 'Nzu clay' are within the tolerable limit of 400, 35 and 30 Bq/Kg respectively by (UNSCEAR, 2000).The calculated mean value of health hazard indexes; absorbed dose rate, annual gonadal equivalent dose (AGED), radium equivalent activity index, representative Gamma Index (Iyr), external hazard index (Hex) and internal hazard index (Hin) were all within the world mean range. However, continuous consumption of the clay over the years can be biomagnified which may result to risk of fatal cancerous growth in organs of addicts of the clay.

Most of the clay samples obtained from the three sites were predominantly a mixture of the mineral kaolinite $Al_2Si_2O_5(OH)_4$ and quartz, SiO_2. The presence of the minerals;

Kaolinite and Quartz may account for the reason why 'Nzu clay' have a unique flavor and taste which appeals to the appetite than the other clays with other minerals such as halloysite, illite, mica, bentonite and feldspar that are not ingested by man. All the clay samples varied in texture, aroma, taste and colour.

This study shows that most of these elements in the clays are far above the WHO standard which could lead to toxicity of the body and result to result to gastrointestinal disorder, kidney failure, reduced pregnancy length, intelligence decline in children, brain disorder and even death.

6.3 Recommendation

The recommendations made from the findings of the study are:

i. Further research should be carried out on the concentration of heavy metals in addicts of 'Nzu clay' using blood and nails as bioindicator to compare with findings made from using hair as bioindicator in this study.
ii. Mines should not be located where these edible clays are naturally sited or processed to avoid exposure to harmful radionuclides.
iii. The study also recommends that the consumption of 'Nzu clay' be continually banned and the ban enforced by the law enforcement agencies such as NAFDAC, ministry of environment and ministry of health, since the presumed benefits is out-weighed by the high levels of toxic heavy metals in the clay and in the hair of the addicted consumers likewise the microbial load.

REFERENCES

Abdulrahman, F. W. and Itodo, A. U. (2006). Canned fish poisoning: High level of some toxic metals. *Medical and Pharmacitical Sciences* 2(1): 10-14.

Abifarin, M. S. (1999). Investigation on local refractory materials for high temperature applications. Mechanical Engineering Depertment, Federal University of Technology, Minna, p. 17

Adriano, D. C. (2001). Trace Elements in terrestrial environments-biogeochemistry, bioavailability and risks of metals, *Springer, New York*, pp. 31-35.

Agbalagba, E. O., Avwiri, G. O. and Chad-Umoreh, Y. E. (2012). γ-Spectroscopy measurement of natural radioactivity and assessment of radiation hazard indices in soil samples from oil fields environment of Delta State, Nigeria. *Journal of Environmental Radioactivity*, 109(1): 64-70.

Agbalagba. E. O. and Onoja, R. A. (2011). Evaluation of natural radioactivity in Soil sediment and water samples of Niger Delta (Biseni) flood plain lakes, Nigeria. *Journal of Environmental Radioactivity*, 102(1): 667-671.

Agene, I. J., Lar, U. A., Mohammed, S. O., Gajere, E. N., Dang, B., Jeb, D. N. and Ogunmola, J. K. (2014). The Effects of Geophagy on Pregnant Women in Nigeria. *American Journal of Human Ecology*, 3(1): 1-9.

Agha, O. A. (1998). Testing of local refractory clay for producing furnace lining bricks. Mechanical Engineering Depertment, Federal University of Technology, Minna, pp. 52-65.

Akan, J., Chellube, Z., Abdulrahman, F. and Waziri, M. (2012). Hair and nail heavy metal levels in residents from Maiduguri, Borno State, Nigeria: *Academic Publishers, Burnaby, British Columbia* 6(3): 2143-2151.

Akinbode, F. O. (1996). An investigation on the properties of termite hill as refractory material for furnace lining. *Indian Foundry Journal*, pp. 11-13

Akram, M., Qureshi, R. M., Ahmad, N., Solaija, T. J., Mashiatullaa, A., Afzal, M., Faruq, M. U. and Zeb, L. (2006). Concentration of natural and artificial radionuclides in bottom sediments of Karachi Harbour/manora channel, Pakistan coast (Arabian sea). *Journal of Chemical Society of Pakistan*, 28(3): 11-14.

Amaefule, J. (1990). Explanation and production research and laboratory support needs of Nigeria petroleum industry. *Houston*, TX.

Andrew, M. J. D. and Dan, B. A. (2010). Top six toxic threats. Blacksmith Institute in New York City. Available at WWW.Wastepolluted, [Accessed July 2015]

AOAC (1990). Association of official analytical chemists. Official method of analysis. 15th Edition. *Journal of agricultural chemistry and environment.* Washington DC.

Ashnani, M. H. M., yavari, A. R. and Hassani, E. (2010). A survey of pollutions of the Aras river and the South-West of Caspian Sea case study: radioactivity pollutions. *World Applied Sciences Journal,* 9(1): 76-80.

ATSDR. (1993). Agency for toxic substances and disease registry; Toxicological profile for heavy metals. US Department of Health and Human Service.

ATSDR. (2001). Draft toxicological profile for cadmium; Agency for toxic substances and disease registry. Department of Health and Human Services. Atlanta, USA.

Avwiri, G. O., Ononugbo, C. P. and Egieya, J. M. (2013). Evaluation of natural radionuclide content in surface and ground water and excess life time cancer risk due to gamma radioactivity. *Academic Research International Journal,* 4(6): 636-647.

Avwiri, G. O., Osimobi, J. C. and Agbalagba, E.O. (2013). Evaluation of natural occurring radionuclide variation with lithology depth profile of Udi and Ezeagu Local Government Areas of Enugu State, Nigeria. *International Journal of Engineering and Applied Sciences*, 4(3): 25.

Bailey, S. W. (1980) Summary of recommendations of Association Internationale Pour l'Étude des Argiles AIPEA, nomenclature committee on clay. *American Journal for Minerals,* 65: 1–7. http://www.minsocam.org [Accessed July 2015.]

Balan, E., Calas, G. and Bish, D. L. (2014): Kaolin-group minerals: From hydrogen-bonded layers to environmental recorders. *Elements*, 10: 183-188.

Balan, E., Delattre, S., Guillaumet, M. and Salje, E. K. H. (2010). Low temperature infrared spectroscopic study of OH-stretching modes in kaolinite and dickite. *American Mineralogist,* 95: 1257-1266.

Baldwin, D. R. and Marshall, W. J. (1999). Heavy metal poisoning and its laboratory investigation. *Annalysis of Clinical Biochemistry*, 36(3): 267–300.

Balonov, M. I. (2008). The Chernobyl Forum: major findings and recommendations. *Journal of Environmental Radioactivity,* 96: 6-12.

Bell, F. G. and Walker, D. J. H. (2000). A further examination of the nature of dispersive soils in Natal, South Africa Quarterly. *Journal of Engineering Geology and Hydrogeology*, 33: 187–199

Bell, F.G. and Bruyn, A. (1997). Sensitive, expansive, dispersive and collapsive soils. *Bulletin of the International Association of Engineering Geology*, 56: 19–38.

Beretka, J. and Matthew, P. (1985). Natural radioactivity of Australian building materials, industrial wastes and byproducts. *Health physics*, 48(1): 87.

Bernard A. (2008). Cadmium and its adverse effect on human health. *Indian Journal of Medical Research*, 128(4): 557–64.

Bernard, S., Lester, A. S. and Brian, K. B. (1998). Handbook of health physics and radiological health. Williams and Wilkins, Baltimore MD, 3rd edition, for high purity gamanium detectors, p. 18

Bish, D. L. (1993). Rietveld refinement of the kaolinite structure at 1.5 K. *Clays and Clay Minerals*, 41: 738-744.

Bish, D. L. and Post, J. E. (1989). Modern powder diffraction. Reviews in mineralogy, *Mineralogical Society of America*. 20: 108.

Calabrese, E. J., Stanek, E. J., Pekow, P. and Barnes, R.M. (1997). Soil ingestion estimates for children residing on a superfund site. *Ecotoxical Environment*, 36(3): 258–268.

Callahan, G. N. (2003). Eating dirt. Emerg infectous disease, 19(8): pp. 1016–1021. http://www.cdc.gov/ncidod/EID/vol9no8/pdfs/03-0033.pdf. [Accessed August 2015]

Campbell, H. and Belfast, I. E. (2002). Department of health, social service and public safety. calabash chalk http: //www.docstoc.com|docs|54253409| [Accessed August 2015].

Caraterro, M. I. (2002). Clay minerals and their beneficial effects upon human health. A review. *Applied Clay Science*, 21(3-4):155-163.

Chakraborty, S., Dutta, A. R., Sural S., Gupta, D. and Sen, S. (2013). Ailing bones and failing kidneys: a case of chronic cadmium toxicity. *Annual Clinical Biochemistry* 50(5): 492–495.

Chaushev, P. G., Dreyer, M. J. and Gledhill, R. F. (2003). Hypokalemic myopathy due to ingestion of earth, *Journal of Neurology*, 250(2): 114-115.

Chettle, D. R. (2005). *X-Ray Spectrum*, 34: 446.

Chiari, G., Giustetto, R., and Ricchiardi, G. (2003). *European Journal of Mineralogy*, 15(1): 21–33.

Chowdhury, M. I., Kamal, M., Alam, M. N., Yeasmin, S. and Mostafa, M. N. (2005). Distribution of naturally occurring radionuclides in soils of the southern districts of Bangladesh. *Radiation Protection Dosimetry*, 1 of 5.

Chrostowski, P., Durda, J. L. and Edelmann, K. G. (1991). The use of natural processes for the control of chromium migration. *Journal for Remediation*, 2(3): 341–351.

CIREP, (2003). Final report by the cosmetic ingredient review panel on the safety of magnesium aluminium silicate, magnesium silicate, bentonite, Fuller's earth, kaolin, montmorillonite, and zeolite. *International Journal of Toxicology,* 22(1): 37–122.

Dean, B., Gano D., Knight K., Ofman J. and Fass R. (2004). Effectiveness of proton pump inhibitors in nonerosive reflux diseases. *Journal of Clinical Gastroenterology and Hapatology,* 2: 656-664.

Dinadle, A. (1986). Pottery science, materials, processes and products. Ellis Horwood Ltd. London, UK. 20-28.

Doe1, E. D., Awua, A., Achoribo, S. E., Adu-Bobi, N. A., Donko, S., BaidooI., Opata, N. S. and Ampong, A. G. (2012). Essential and toxic element present in clay obtained from Ghanaian Market. *Elixir Applied Biology*, 47: 8633-8636.

DPR-EGASPIN, (2002). Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), Department of Petroleum Resources, Lagos, Nigeria, p. 64.

Dragovic, S., Lj, J., Onjia, A. and Bacic, G. (2006). Distribution of primordial radionuclides in surface soils from Serbia and Montenegro.

El-Aydarous, A. (2007). Gamma radioactivity levels and their corresponding external exposure of some soil samples from Taif Governorate, Saudi Arabia. *Global Journal of Environmental Research,* 1(2): 49-53.

El-Daly, T. A. and Hussein, A. S. (2008). Natural radioactivity levels in environmental samples in North Western desert of Egypt. Proceedings of the 3rd Environmental physics conference, 19-23 Feb. Aswan, Egypt.

El-Kameesy, S. U. (2008). Natural radioactivity of beach sand samples in the tripoli Region, North West Libya. *Turkish Journal of Engineering and Environmental Sciences*, 32: 245–251.

El-Reefy, H. (2004). Study of gamma ray spectra for some environmental pollutants in El-Brollos Lake. B.Sc.Thesis, Tanta University. *Environmental Chemistry—Environmental Pollution and Ecotoxicology*, 73–77.

Environmental Health Perspective (EHP). (2010). Thyroid cancer after Chernobyl: increased risk persist two dacades after radioiodine exposure. Proceedings of third European congress Helsinki, Finland, June 2010, p. 14-16.

Environmental Protection Agency, EPA. (2008). Radiation protection, health effects http://www.epa.gov/ttn/atw/ [Accessed February 2015].

Environmental Protection Agency, U. S. (2007). Radionuclides (including Radon, Radium and Uranium, http://www.epa.gov/ttn/atw/ hlthef/radionuc.html [July 2015].

Faanu, A., Darko, E. O. and Ephraim, J. H. (2010). Assessment of public Exposure to naturally occurring radioactive materials from mining and processing activities of Tarkwa Gold mine in Ghana. *Journal of Environmental Monitoring Assessment*, 180: 15-29

Farmer, V. C. (1998). Differing effects of particle size and shape in the infrared and Raman spectra of kaolinite. *Clay Minerals*, 33: 601-604.

Farmer, V. C. (2000). Transverse and longitudinal crystal modes associated with OH stretching vibrations in single crystals of kaolinite and dickite. *Spectrochimica Acta*, A56: 927-930.

Foo, S. C., Khoo, N. Y., Heng, A., Chua, L. H., Chia, S. E., Ong, C. N., Ngim, C. H. and Jeyaratnam, J. (1993). Metals in hair as biological indicies for exposure. *International Archives of Occupational and Environmental Health.* 65:1432-1246.

Francis, O. (2008). Map of Delta State, Nigeria. Urhobo historical society.

Gbadebo, A. M. (2011). Natural Radionudide distribution in Granitic rocks and soil of abandoned Quarry sites, Abeokuta South Western Nigeria, *Asian Journal. of Applied Science 4* (2): 176-185

Gilmore, G. and Hemingway, J. D. (1995). Practical gamma-ray spectroscopy. John Wiley and Sons, pp. 156-161.

Glenn, F. K. (2000). Radiation detection and measurement. John Wiley and Sons, Inc, USA, 3rd Edition, pp. 44-49.

Goulle, J.P. and Kintz, P. (1996). A new tool for biological study: hair analysis. Value in medical practice. Review of the Medical Intern, 17: 826-835.

Goyer, R. A. and Clarkson, T. W. (2001). casarett and douls toxicology. The basic science of poisons. Sixth edition. McGraw-Hill Publishing Companies Inc. New York, USA, pp. 152-155.

Graf, V. B. (1978). Trace Element Levels in Human Hair at Childbirth. A M.Sc Thesis presented to the Faculty of the Graduate School University of Missouri - Columbia.

Greany, K. M. (2005). An assessment of heavy metal contamination in the marine sediments of Las Perlas Archipelago, Gulf of Panama, M.Sc. thesis, School of Life Sciences Heriot-Watt University, Edinburgh, Scotland, pp 144-148.

Grim, R. E. (1968) Clay mineralogy, second edition. New York, McGraw-Hill, p. 596.

Hanks, J. (2007). Hanks' Balanced Salt Solution and pH Control. *Tissue Culture Association Manuals,* 3: 3.

Henson, M. C. and Chedrese, P. J. (2004). Endocrine disruption by cadmium, a common environmental toxicant with paradoxical effects on reproduction. Experiment on Biological Medicine, 229(5): 383-392.

Hirsch, J. B. and Kokini, J. L. (2002). Understanding the mechanism of cross-linking agents through swelling behavior and pasting properties of cross-linked waxy maize starches. *Cereal Chemistry,* 79: 102-107.

Hubbard, B., Kuang, W., Moser, A., Facey, G. A. and Detellier, C. (2003). *Clays and Clay Minerals,* 2: 76-80

Hubbel, J. and Seltzer, S. (1996). Tables of x-ray mass attenuation coefficients and mass energy absorption coefficients. http://physics.nist.gov/PhysRefData/XrayMass Coef/cover.html.

Hung-Chih, T., Cheng-Chieh, Y., Wen-Kang, C., Wen-Huei, C., Ming-Chih C. and Fung-Jou L. (2010). Humic acid enhances the cytotoxic effects of arsenic trioxide on human cervical cancer cells. *Journal of Environmental Toxicology and Pharmacology* , 29(2): 117-125.

Hunter, J. M. (1993). Macroterme geophagy and pregnancy clays in Southern Africa. *Journal of cultural geography,* 14: 69-92.

IAEA, (2003) International Atomic Energy Agency. Guidelines for radioelement mapping using gamma ray spectrometry data, Vienna, Austria. IAEA-TECDOC-1363.

Ibeanu, G. E. L., Dim, L. A., Mallam, S. P., Akpa, T. C. and Munyithya, J. (1997) Nondestructive XRF analysis of Nigerian and Kenyan clays. *Journal of Radioanalytical Nucleic Chemistry,* 22(1): 207-209.

Ibrahim, U., Akpa, T. C. and Daniel, I. H. (2013). Assessment of Radioactivity Concentration in Soil of some Mining Areas In Central Nasarawa State, Nigeria. *Science World Journal,* 8: 2.

ICRP, (1991). Recommendations of the international commission on radiological protection. http://www.icrp.org/publication.asp. ICRP Publication 60, [Accessed October, 1993].

Ijagbemi, C.O. (2002). Development and performance evaluation of a biomass clay lined cookstove. Meng thesis, Department of mechanical Federal University of Technology Akure, Nigeria, pp 107-111.

International Centre for Diffraction Data (2001). *Mineral Powder Diffraction File Databook,* p. 942.

Isinkaye, M. O., Shitta, M. O. and Oderinde, M. O. (2013). Determination of radionuclides and elemental composition of clay soils by gamma and X-ray spectrometry. US National Library of MedicineNational Institutes of Health, 1: 74.

Ismadji S. (2015). Clay Materials for Environmental Remediation, Springer Briefs in Green Chemistry for Sustainability, DOI 10.1007/978-3-319-16712-1_2

Ismail, A. F., Yasir, M. S., Ab. Majid, A., Bahari, I., Yahaya, R. and Abd Rahman, I. (2009). Radiological studies of naturally occurring radioactive materials in some Malaysia's sand used in building construction. *The Malaysian Journal of Analytical Sciences*, 13(1): 29 – 35.

Itodo, A. U, Abdulrahman, F. W, Happiness, U. O. and Abubakar, M. N. (2009). corrosion impact on the leacheability of heavy metal ions in canned juices and beverages marketed in Nigeria . Research in science education information and communication technology. 1(1): 164.

James, J. (2001). Cation exchange capacity in soil and crop. South Carolina Turfgrasss Foundation News, pp.1-4.

Kabata-Pendias, A. and Pendias, H. (2001). Trace metals in soils and plants, CRC Press, Boca Raton, Fla, USA, 2nd edition, pp. 237-241.

Karpiński, B. and Szkodo, M. (2015). Clay minerals; mineralogy and phenomenon of clay swelling in oil & gas industry, Gdansk, University of Technology, Department of materials science and welding engineering, Gdańsk, Poland, Narutowicza, pp. 80-233

Katz, S. A. and Katz, R. B. (1992). Use of hair analysis for evaluating mercury intoxication of the human body. *Journal of Applied Toxicology,* 12:79-84.

Khodadoust, A. P., Reddy, K. R. and Maturi, K. (2004). Removal of nickel and phenanthrene from kaolin soil using different extractants, *Environmental Engineering Science*, 21(6): 691–704.

Knoll, G. F. (1999). Radiation detection and measurement. 3rd edition John Wiley and Sons, pp. 305-342.

Knolls, G. F. (2002). Atomic power laboratory, nuclides and isotopes. Chart of the nuclides, lockheed martin, USA, 16th edition.

Kohshi, C., Takao, I. and Hideo, S. (2001). Terrestrial gamma radiation in koshi prefecture, Japan, *Journal of Health Science*, 47(4): 362-372.

Konta, J. (1995). Clay and man; clay raw materials in the service of man. *Applied Clay Science,* 10: 275-33.

Koons, R. D. and Peters, C. A. (1994) Axial distribution of arsenic in individual human hairs by solid sampling graphite furnace AAS. J. Anal. Toxicol. 18: 36-40.

Kulkarni K.O., Kulkarni, D. N. and Ingle, U. M. (1991). Sorghum malt based weaning food formulation preparation, functional properties and nutritive value. *Food and Nutrition Bulletin,* 13(14): 322-327

Laurie, A. K. (2008). Micribiological investigation of geophagy in chimpazees. Department of Bothany, University of Toronto, pp. 59-63.

Lawluvi, H., Darko, E. O., Schandorf, C., Fannu, A., Awudu, A. R. and Kpeglo, D. O. (2011). Natural radioactivity concentrations in beach sands from some tourists Resorts. *Research Journal of Environmental and Earth Sciences*, 3(6): 729-736.

LeCoultre, T. D. (2001). A meta-analysis and risk assessment of heavy metal uptake in common garden vegetables, MSc Thesis, East Tennessee State University, Johnson City, TN.

Lee, S., Kim, Y.J. and Moon, H.S. (1999). Phase transformation sequence from kaolinite to mullite investigated by an energy-filtering transmission electron microscope. *Journal of the American Ceramic Society 82(1): 2841-2848.*

Li, Z. and Zhou N. (2001). Technological advancement in the preparation and application of monolithic refractories. *China's refractories*, 10(1).

Lipson, S. M., and Stotzky, G. (1983). Adsorption of reovirus to clay minerals: Effects of cation exchange capacity, cation saturation, and surface area. Applied environmental microbiology, 46: 673–682.

Mahmoud S., Ayman, H. and Mousa, A. (2003). Pretreatment effect on the catalytic activity of Jordanian bentonite. *Journal of the Clay Mineral Society,* 51(1).

Manukaji, J.U. (2004). An investigation into the use of local clays as a high temperature insulator for electric cookers. PhD Thesis Mechanical Engineering Department, Federal University of Technology, Minna, pp. 256-258.

Martin, S. and Griswold, W. (2009). Human health effects of heavy metals. *Environmental Science and Technology Briefs for Citizens,* 15: 1–6.

Martínez, C. E. and Motto, H. L.(2000). Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution,* 107(1), p. 153–158.

Maslen, E. N., Fox, A. G. and O'Keefe, M. A. (2004). X-ray Scattering, *International Tables for Crystallography,* C: 554.

Matsumoto, S. T., Mantovani, M. S., Malaguttii, M. I. A., Dias, A. L., Fonseca, I. C. and Marin-Morales, M. A. (2006). Genotoxicity and mutagenicity of water contaminated with tannery effluents, as evaluated by the micronucleus test. *Genetic Molicular Biology* 29(1): 148–58.

Mazumder G. (2008). Chronic arsenic toxicity and human health. *Indian Journal on Medical Research*, 128(4): 436–447.

Mendham, J., Denney, R.C., Barnes, J. D. and Thomas, M. J. K. (2008). Vogel's textbook of quantitative chemical analysis, *Pearson Education. 6th Edition*, p. 49.

Miller, R. W. and Donahue, R. L. (1990). Introduction to soils and plant growth. 6th edition. Prentice-Hall Inc. Englewood cliffs, New Jersey, p. 60.

Ming, C. and Lena, Q. M.(2001). Comparison of three aqua regia digestion methods, soil science society. *American Journal*, 65:491–499.

Mohammed, Y., Falah, R., Kwather. Y. and Al-Soudany, H. (2013). Improvement of Clay soil characteristics using Rice Husk Ash, *Journal of Engineering and Urbanism*, 3(1): 12-18.

Morais S., Costa, F. G. and Pereira, M. L. (2012). Heavy metals and human health, *emerging issues and practice*, pp. 227-246.

Neves, O., breu, M. M. and Vicente, E. M. (2008). Uptake of uranium by lettuce in natural uranium contaminated soils in order to assess chemical risk for consumers. *Water, Air, and Soil Pollution*, 195(1-4): 73–84.

Ngole, V. M., Ekosse, G. E. and DeJager, L. (2010). Physicochemical characterestics of geophagic soils from South Africa and Swaziland, *African Journal of Biotechnology*, 9(36): 5929–5937.

Nida, A., Shaikh, M., Talat, M., Majid, M. (2014). Monitoring of environmental mercury exposure using hair as bioindicator and the study of potential factors affecting on it in Karachi. *American Journal of Analytical Chemistry*, 5: 83-90.

Njinga, R. L., Elele, U. U. and Ewa, I. O. (2014). Elemental concentration of commonly used clay potteries from selected locations in Niger State of Nigeria. *Journal of Environmental Science, Toxicology and Food Technology*, 8: 11-21.

NSC, (2009). Lead Poisoning, *National Safety Council.* http://www.nsc.org/news resources/Resources/Documents/Lead Poisoning.pdf. [Acessed July 2011].

Nweke, E. S. and Ugwu, E. I. (2007). Analysis and characterization of clay soil in Abakaliki, Nigeria, *Journal of Total Science*, 8(2): 190-193

O'Brien, T., Xu, J. and Patierno, S. R. (2001). Effects of glutathione on chromium-induced DNA crosslinking and DNA polymerase arrest. *Molecular Mechanisms of Metal Toxicity and Carcinogenesis, Springer US,* pp. 173–182.

Obaje, S .O., Omada, J .I. and Dambatta, U. A. (2013). Clays and their Industrial Applications; Synoptic review. *Internationals Journal of Science and Technology*, ISSN 2224-3577; 3(1).

O'Rourke, D. E., Quinn, J. G., Nicholson, J. O. and Gibson, M. H. (1967). Geophagia during pregnancy. *Obstetrics and Gynecology*, 29: 581-584.

Osundahunsi, O., Fagbemi, T., Kesselman, E. and Shimoni E. (2003). Comparison of the physicochemical properties and pasting characteristics of flour and starch from red and white sweet potato cultivars. *Journal of Agricultural Food Chemistry,* 51: 2232-2236.

Padilla, F. V. and de la Torre, A. M. (2006). La pica: retrado de una entidad clinica poco conocida. *Nutricion Hospitalaria.* 21: 557–566.

Parker, S. P. (1988). McGraw-Hill encyclopedia of the geological sciences, 2nd edition. *New York,* pp. 32–33, 69–72, 400–401.

Parry-Jones, B. and Parry-Jones, W. L. L. (1992). Pica: symptom or eating disorder; A historical assessment. *British Journal of Psychiatry,* 160: 341-354.

Pattanayak, B., Muduli, S.D. and Dhal, D. K. (2014). Removal efficiences of fire clay soils through the distribution of different particle size. *International Journal of Development Research,* 4(8): 1616-1622.

Paulsen, F., Mai, S., Zellmer, U. and Alsen-Hinrichs, C. (1996). Blood and hair arsenic, lead and cadmium analysis of adults and correlation analysis with special reference to eating habits and other behavioral influences. *Gesund heitswesen,* 58: 459-464.

Redmond, W. A. (2009). Clay, microsoft encarta. *Microsoft Corporation.* [DVD].

Richard, K. (2007). A review and rationale for studying the cardiovascular effects of drinking water arsenic in women of reproductive age. *Journal of Toxicology and Applied Pharmacology,* 222(3): 344–350,

Rieder, M., Cavazzini, G., D'yakonov, Y. S., Frank-Kamenetskii, V. A., Gottardi, G., Guggenheim, S., Koval, P. V., Müller, G., Neiva, A. R., Radoslovich, E. W., Robert, J. L., Sassi, F. P., Takeda, H., Weiss, Z. and Wones, D. R. (1998). Nomenclature of micas Clays, *Clay Minerals,* 46(1): 586–595

Rodushkin, I. and Axelsson, M. D. (2003). Application of double focusing sector field ICP-MS for multi elemental characterization of human hair and nails. *Science Total Environment,* 305(1): 23–39.

Samanta, G., Sharma, R., Roychowdhury, T. and Cha- kraborti, D. (2004). Arsenic and other elements in hair, nails, and skin-scales of arsenic victims in West Bengal, India. *Science of the Total Environment,* 326(1-3): 33-47.

Sanford, M. K. and Kissling, G. E. (1994). Multivariate analyses of elemental hair concentrations from a medieval nubian population. *American Journal of Phylosophy and Anthropology,* 95: pp. 41-52.

Scragg, A. (2006). Environmental biotechnology, Oxford University Press, Oxford, UK, 2nd edition.

Sen, J. (1996*).* Determination of essential and toxic trace element concentrations in scalp hair of the bengalee population , West Bengal. Thesis submitted for the Degree of Doctor of Philosophy in Anthropology under the Auspices of the University of Calcutta, p. 306.

Sepulveda, M. J., Vallyathan, V., Attfield, M. D., Piacitelli, L. and Tucker, J. H. (1983). Pneumoconiosis and lung function in a group of kaolin workers. *American Journal on Respiratory Disease,* 127: 231–235.

Smith, A. H., Lingas, E. O. and Rahman, S. M. (2000). Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bull World Health Organization,* 78(9): 1093–1103.

Smith, L. A., Means, J. L. and Chen, A. (1995). Remedial options for metal-contaminated sites. *Journal of Analytical Toxicology,* 18: 36-40.

Solusulski, F. W. (1962). The centrifuge method for determining flour absorptivity in hard red spring wheat's. *Cereal Chemistry,* 39: 344

Sowole, O. (2014). Assessment of radiological hazard indices from surface soil to individuals from major markets at Sagamu Ogun State, Nigeria. *Science World Journal,* 9(3).

Speight, J. G. (2006). The chemistry and technology of petroleum. 4th edition, CRC press, Wyoming US. ISBN- 10: 0-8493-9067-2.

Sumner, M. E. and Miller, W. P. (1996). Cation exchange capacity and exchange coefficients, methods of soil analysis, chemical methods. SSSA Book, Series. 5.

Takako, N., Takaaki, I., Masafumi, K., Shin, T. and Shinsuke, T. (2011). Applicability of human hair as a bioindicator for trace elements exposure. *Interdisciplinary Studies on*

Takashi, S. and Sieb, P.A. (1988). Paste and gel properties of prime corn and wheat starches with and without native lipids. *Cereals chemistry,* 65; 47.

Theo, H. (2002). Space-group Symmetry. *International Tables for Crystallography, A(1).*

Thomas, G. (2000). Chasteen, Department of Chemistry, Sam Houston State University, Huntsville, Texas 77341.

United Nations Scientific Committee on the Effects of Atomic Radiation, (2000). Report to the general assembly, with scientific annexes. United Nations sales publication E.94.IX.2. United Nations, New York,

UNSCEAR, (2008). Report to the General Assembly with Scientific Annexes, Volume II. Scientific Annexes C, D and E .United Nations, New York.

US FDA, (2004). Code of Federal regulations. Direct food substances affirmed as generally recognized as safe (GRAS). Washington, DC, US Department of Health and Human Services, Food and Drug Administration, Title 1: Part 84.

USDA/NRCS. (2014). United States Department of Agriculture. Soil health guide for educators, pp 1-2.

Vermeer, D. E. (1998). Nigerian geophagical clay. A review; *Traditional Antidiarrheal Pharmaceutical science*, 227: 634-636.

Wang, T., Fu, J., Wang, Y., Liao, C., Tao, Y., Jiang, G., (2009). Use of hair as indicator of human exposure to heavy metals in an electronic waste recycling area. *Environmental pollution*, 157: 2445-2451.

Wenning, R. (2002). Potential problems with interpretation of hair analysis results. *Ensic. Science International*, 107: 5 - 12.

WHO, (2003). Poverty and health: strategy for the african region retrieved from http://www.who.int/hdp/strategy_en.pdf [Acessed July 2015].

Wilhelm, M., Lomberk, I. and Ohnesorge, F. K. (1994). Cadmium, Copper, Lead and Zinc concentration in hair and toenails of young children and family members: a follow up study, *Science Total Environment*, 141: 275-280.

Williams L. B., Haydel, S. E., Giese, R. F. and Eberi, D. D. (2008). Chemical and mineralogical characterics of french green clays used for healing. *Clay and Clay Minerals*, 56:(4): 437-452.

Wilson, M. J. (2004). Clay mineralogical and related characteristics of geophagic materials. *Journal of Chemical Ecology*, .29(7): 1525-1547.

Wolfsperger, M., Hauser, G., Gossler, W. and Schlsgenhaufen, C. (1994). Heavy metals in human hair samples from Austria and Italy. *Journal of Science Total Environment*, 156: 235 - 242.

Yablokov, A. V., Nesterenko, V. B. and Nesterenko, A. (2009). Chernobyl consequences of the disaster for the population and the environment. *Science Total Environment*, p. 1189.

Yousef, M. I., Abu El-Ela, A. and Yousef, H. A. (2007). Natural radioactivity levels in surface soil of kitchener drain in the Nile delta of Egypt. *Journal of nuclear and radiation physics,* 26(1): 246-248.

Zarie, K. A. and Al-Morgren, K. S. (2010). Measurement of natural radioactivity and assessement of radiation hazards in soil samples from Tayma area. *Isotope Radioactivity Resource,* 42(1): 1-9.

APPENDIX

Appendix IA:

Heavy Metals Concentrations (Mean ± SEM in mg/kg) of the 'Nzu Clay' Sample from the hill side in Ozanogogo of Ika south LGA in Delta State and the finished product of 'Nzu clay' samples from water side in Uzella river, Owan West LGA. Edo State.

Sample	Cd	Cr	Cu	Ni	Pb	Zn
WS	3.83±0.14^{b}	65.8±2.50^{b}	10.10±0.61^{a}	7.53±0.30^{b}	10.27±1.79^{a}	18.17±0.33^{a}
HS	1.86±0.03^{a}	41.57±2.07^{a}	27.56±0.78^{b}	4.13±1.00^{a}	22.47±1.52^{b}	23.16±0.68^{b}

Where the supscript a stands for lower and b for higher significant difference at ($P < 0.05$)

SEM: **S**tandard Error of **M**ean

WS: **W**ater **S**ide

HS: **H**ill **S**ide

Appendix IB: Distribution and mean concentration (mg/kg) of heavy metals in hair of non addicts of 'Nzu clay'

Range non addicts	**Heavy Metals**						
	Cr	**Cd**	**Pd**	**As**	**Zn**	**Cu**	**Ni**
NA_1	54.67	1.44	0.69	18.01	0.06	1.28	2.77
NA_2	24.02	0.94	0.96	17.29	0.07	0.93	1.26
NA_3	16.34	1.09	0.27	18.00	0.19	0.29	1.59
NA4	24.71	1.05	0.62	18.52	0.11	0.95	1.99
NA_5	21.86	0.95	0.59	18.91	0.13	0.86	1.26

Appendix ID:

Distribution and mean concentration (mg/kg) of heavy metals in hair of < 5yrs addiction

Range	**Heavy Metals**						
5 years below	**Cr**	**Cd**	**Pd**	**As**	**Zn**	**Cu**	**Ni**
FB_1	64.45	2.28	1.00	22.40	0.05	2.02	3.90
FB_2	71.82	2.71	1.15	23.10	0.19	0.19	3.92
FB_3	59.30	2.55	1.19	21.10	0.08	0.08	3.88
FB_4	59.70	2.59	1.17	22.30	0.11	0.11	3.80
FB_5	75.04	2.84	1.21	23.30	0.19	0.19	4.27

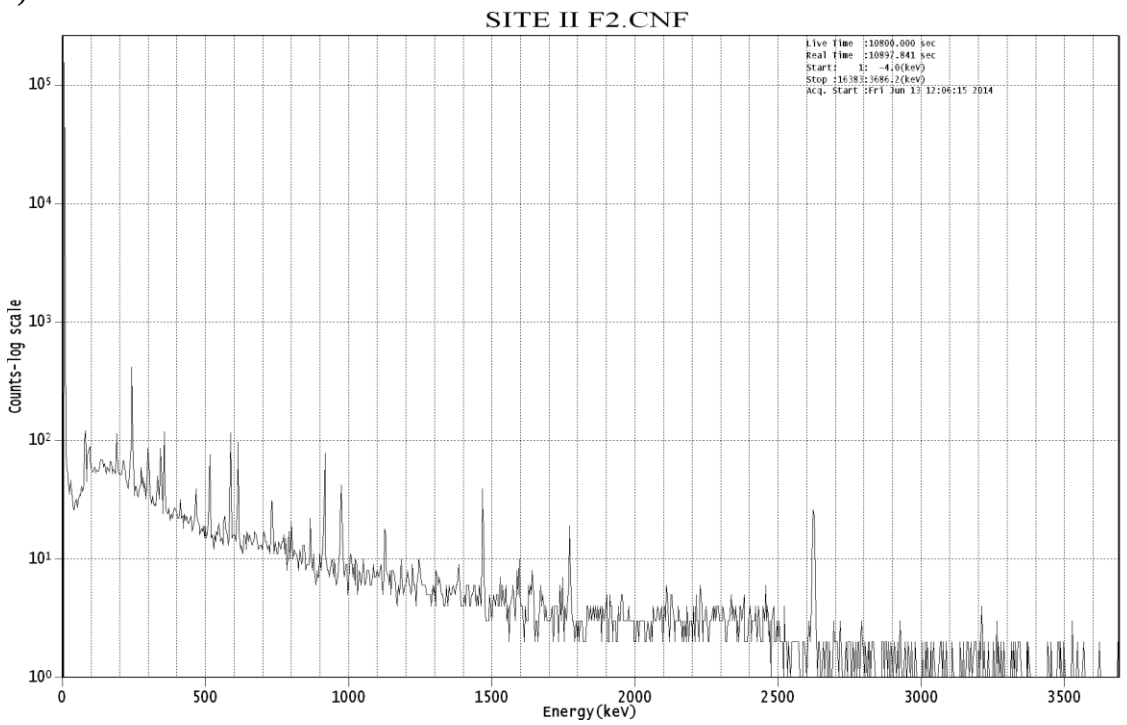
Appendix IE. Heavy Metals Concentrations (Mean ± Sem in mg/kg) in Hair Samples of 'Nzu Clay' Addicts

Samples	As	Cd	Cr	Cu	Ni	Pb	Zn
FA	25.60 ± 1.1^{c}	4.35 ± 0.82^{c}	112.47 ± 22.9^{b}	4.04 ± 0.72^{b}	7.62 ± 1.46^{b}	2.99 ± 0.68^{b}	0.17 ± 0.22^{a}
FB	22.44 ± 0.39^{b}	2.59 ± 0.09^{b}	66.06 ± 3.18^{a}	0.52 ± 0.38^{a}	3.95 ± 0.08^{a}	1.14 ± 0.04^{a}	0.12 ± 0.03^{a}
NA	18.15 ± 0.27^{a}	1.09 ± 0.09^{a}	28.3 ± 6.75^{a}	0.86 ± 0.16^{a}	1.77 ± 0.28^{a}	0.63 ± 0.11^{a}	0.11 ± 0.02^{a}

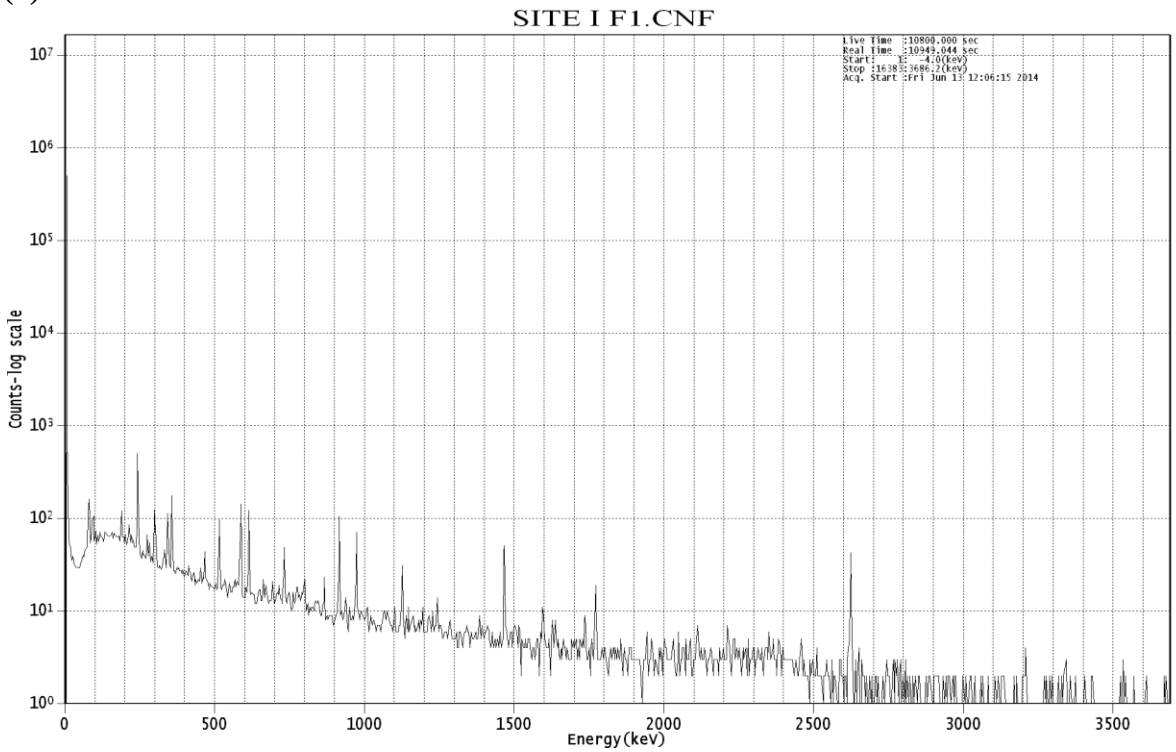
FA: Consumers of edible clay for **F**ive years and **A**bove
FB: Consumers of edible clay for **F**ive years and **B**elow
NA: **N**on-**A**ddicts
Values in the same column having the same superscripts are not significantly different while values in the same column having different superscripts are significantly different ($P < 0.05$)

Appendix II: Spectra of 'Nzu Clay' samples Analysed using Hyper Pure Gammanium Detector.

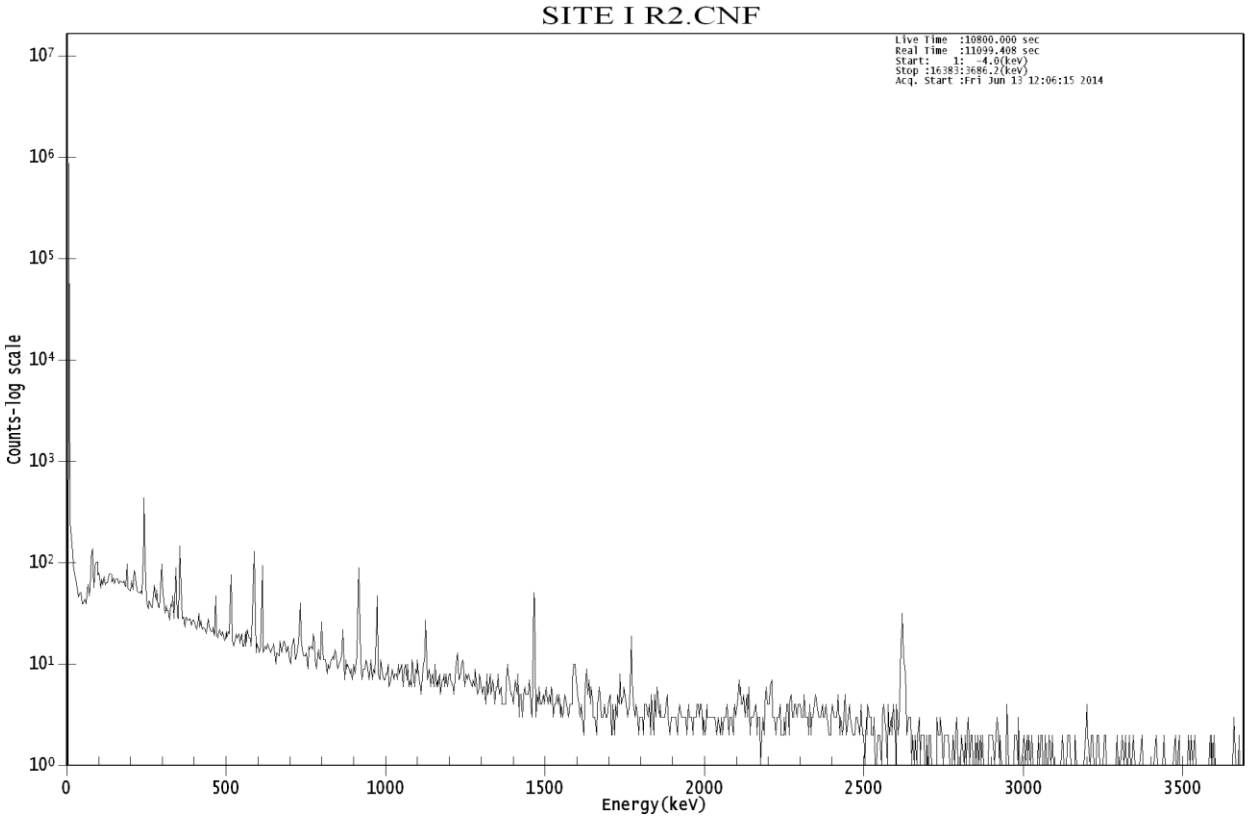
a)



(b)



(c)


SITE I R2.CNF
Live Time :10800.000 sec
Real Time :11099.408 sec
Start: 1: -4.0(keV)
Stop :16383:3686.2(keV)
Acq. Start :Fri Jun 13 12:06:15 2014
Counts-log scale
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
0
500
1000
1500
2000
2500
3000
3500
Energy(keV)

Appendix IIIA

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
R1	1.00	2	92.2800	43.71334	30.91000	-300.4688	485.0288	61.37	123.19
	2.00	2	21.3500	8.88126	6.28000	-58.4450	101.1450	15.07	27.63
	3.00	2	26.8300	19.71414	13.94000	-150.2945	203.9545	12.89	40.77
	Total	6	46.8200	41.49276	16.93935	3.2760	90.3640	12.89	123.19
F1	1.00	2	127.6050	20.79601	14.70500	-59.2397	314.4497	112.90	142.31
	2.00	2	34.4450	6.28618	4.44500	-22.0341	90.9241	30.00	38.89
	3.00	2	44.5100	1.64049	1.16000	29.7708	59.2492	43.35	45.67
	Total	6	68.8533	46.75737	19.08862	19.7845	117.9222	30.00	142.31
R2	1.00	2	53.4500	45.89123	32.45000	-358.8663	465.7663	21.00	85.90
	2.00	2	29.0850	25.75990	18.21500	-202.3585	260.5285	10.87	47.30
	3.00	2	30.8350	31.40261	22.20500	-251.3063	312.9763	8.63	53.04
	Total	6	37.7900	29.98156	12.23992	6.3263	69.2537	8.63	85.90
F2	1.00	2	125.8950	3.91030	2.76500	90.7623	161.0277	123.13	128.66
	2.00	2	26.7200	18.82318	13.31000	-142.3996	195.8396	13.41	40.03
	3.00	2	28.3800	20.54852	14.53000	-156.2412	213.0012	13.85	42.91
	Total	6	60.3317	52.32638	21.36216	5.4185	115.2448	13.41	128.66

Appendix IIIB: Concentration (Bq/kg) of Radioactive Elements in the 'Nzu Clay' Samples (one-way anova)

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
R1	Between Groups	6229.865	2	3114.933	3.929	.145
	Within Groups	2378.380	3	792.793		
	Total	8608.245	5			
F1	Between Groups	10456.579	2	5228.290	33.043	.009
	Within Groups	474.681	3	158.227		
	Total	10931.261	5			
R2	Between Groups	738.769	2	369.385	.295	.764
	Within Groups	3755.702	3	1251.901		
	Total	4494.471	5			
F2	Between Groups	12898.408	2	6449.204	24.434	.014
	Within Groups	791.844	3	263.948		
	Total	13690.252	5			

Appendix IIIC: Calculations on Hazard Index of Radioactive Element

Absorbed dose rate

$$D({}_nG_{y/h}) = 0.0414Ck + 0.461C_{Ra} + 0.623C_{Th}$$

Site IR $D({}_nG_{y/h}) = (0.0414 \times 92.28) + (0.46 \times 21.35) + (0.623 \times 26.83)$
$3.82 + 9.82 + 16.72 = 30.36\ {}_nG_{y/h}$

Site 2R $(0.0414 \times 54.45) + (0.46 \times 29.08) + (0.623 \times 30.84)$
$2.25 + 13.38 + 19.21 = 34.84$

Site IF $(0.0414 \times 127.6) + (0.46 \times 34.45) + (0.623 \times 44.51)$
$5.28 + 15.85 + 27.73 = 48.86\ {}_nG_{y/h}$

Site 2F $(0.0414 \times 125.9) + (0.46 \times 26.72) + (0.623 \times 28.28)$
$5.2 + 12.29 + 17.68 = 35.17$

Site 3FC $(0.0414 \times 108) + (0.46 \times 38.75) + (0.623 \times 36.24)$

4.47 + 17.83 + 22.58 = 44.88

Radium Equivalent activity (Ra_{ef})

$Ra_{eq} = C_{Ra} + 1.43\ C_{Th} + 0.077Ck$

Site 1R 21.35 + (1.43 × 26.83) + 0.077 × 92.28
21.35 + 38.37 +7.11 = 66.83 Ra_{eq}

Site 2R 29.08 + (1.43 × 30.84) + 0.077 × 54.45
29.08 + 44.1 + 4.19 =7.34

Site 1F 34.45 + (1.43 × 44.51) + 0.077 × 127.60
34.45 + 63.65 + 9.83 =107.9

Site 2F 26.72 + (1.43 ×28.38) +0.077 × 125.9
26.72 + 40.58 +9.69 =76.99

Site 3FC 38.75 + (1.43 ×36.24) +0.077 × 108
38.75 + 51.82 + 8.32 = 98.89

Annual Gonadal Equivalent dose

AGED (Sr/yr) = $3.09\ C_{Ra} + 4.18\ C_{Th} + 0.314\ C_k$

Site 1R (3.09 × 21.35) + (4.18 ×26 .83) + (0.314 × 92.28)
65.97 + 112.15 + 28.98 = 207.10

Site 2R (3.09 × 29.08) + (4.14 × 30.84) + (0.314 ×54.45)
89.86 + 127.68 + 17.1 = 234.64

Site 1F (3.09 × 34.45) + (4.14 × 44 .51) + (0.314 × 127.6)
106.45 + 184.27 + 40.067 = 330.79

Site 2F (3.09 × 26.72) + (4.14 × 28.38) + (0.314 × 125.9)
82.56 + 117.49 + 39.53 = 289.58

Site 3FC (3.09 × 38.75) + (4.14 × 36.24) + (0.314 × 108)
119.74 + 150.03 + 33.9 =303.68

External hazard Index

Hex = $C_{Ra}/370 + C_{Th}/259 + C_k\ /4810$

Site 1R 21.35/370 + 26.83/259 + 92.28/4810
0.06 + 0.1 + 0.02 =0.81

Site 2R 29.08/370 + 30.84/259 + 54.45/4810

0.08 + 0.12 +0.01 = 0.21

Site 1F 34.45/370 + 44.51/259 + 127.60/4810
0.09 + 0.17 + 0.03 = 0.29

Site 2F 26.72/370 + 28.38/259 + 125.9/4810
0.07 + 0.11 + 0.03 = 0.21

Site 3FC 38.75/370 + 26.24/259 + 108/4810
0.10 + 0.10 + 0.02 = 0.22

Internal hazard index (Hin)

$Hin = C_{Ra}/185 + C_{Th}/259 + C_K/4810$

Site 1R 21.35/185 + 26.83/259 + 92.28/4810
0.12 + 0.1 + 0.02 = 0.24

Site 2R 29.08/185 + 30.84/259 + 54.45/4810
0.16 + 0.12 + 0.01 = 0.29

Site 2F 26.72/185 + 28.38/259 + 125.9/4810
0.14 + 0.11 + 0.03 = 0.28

Site 3FC 38.75/185 + 26.24/259 + 108/4810
0.21 + 0.10 + 0.02 = 0.33

Representative Gamma Index I_{yr}

$I_{yr} = C_{Ra}/150 + C_{Th}/100 + C_k/1500$

Site 1R 21.35/150 + 26.83/100 + 92.28/1500
0.14 + 0.27 +0.06 = 0.47

Site 2R 29.08/150 30.84/100 + 54.45/1500
0.19 + 0.31 + 0.04 = 0.54

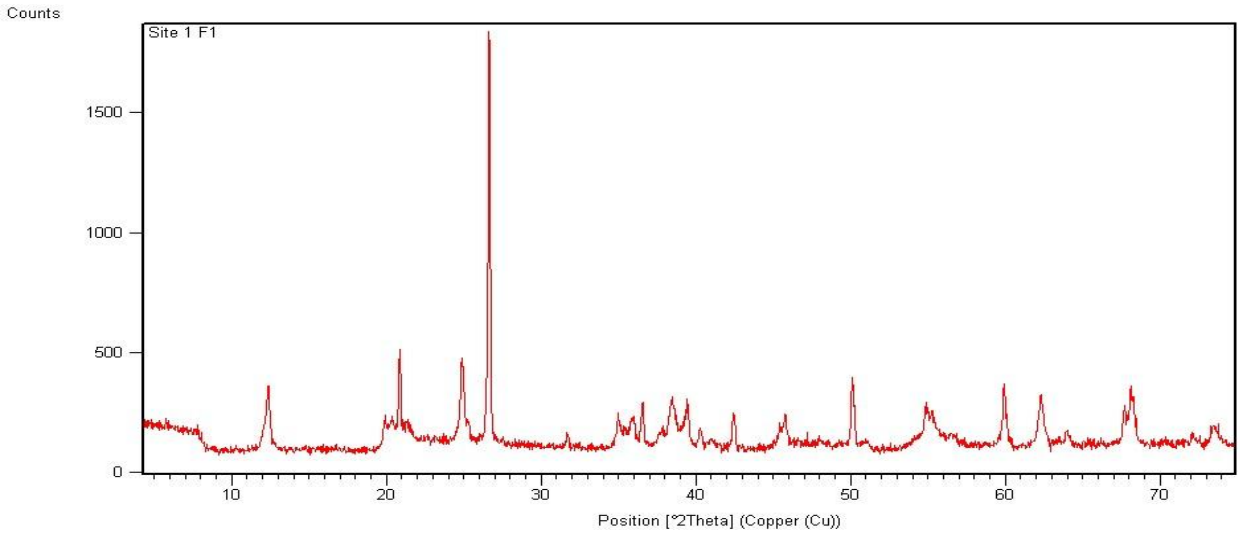
Site 1F 34.45/150 + 44.51/100 + 127.6/1500
0.23 + 0.45 + 0.09 = 0.76

Site 2F 26.72/150 + 28.38/100 + 125.9/1500
0.18 + 0.28 + 0.08 =0.54

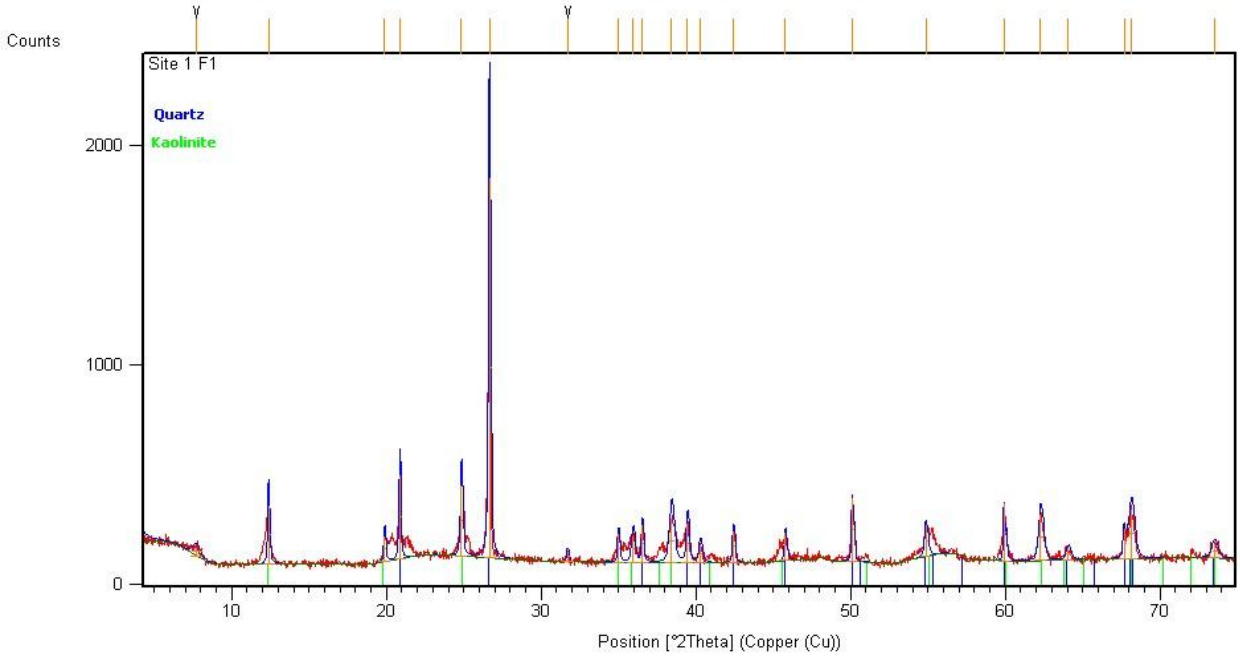
Site 3FC 38.75/150 + 26.24/100 + 108/1500
0.26 + 0.26 +0.07 = 0.59

Appendix IVA: X-ray diffraction of 'Nzu Clay' sample on CuKα in the 2θ region, glancing angle 15º – 75º

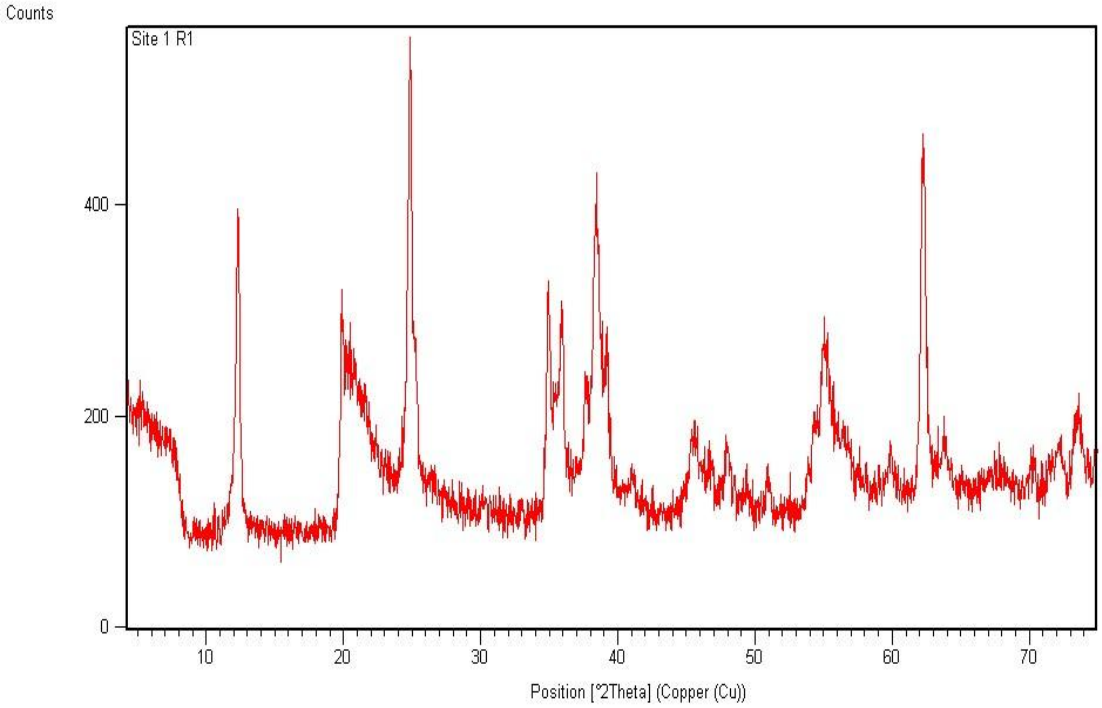
(a)



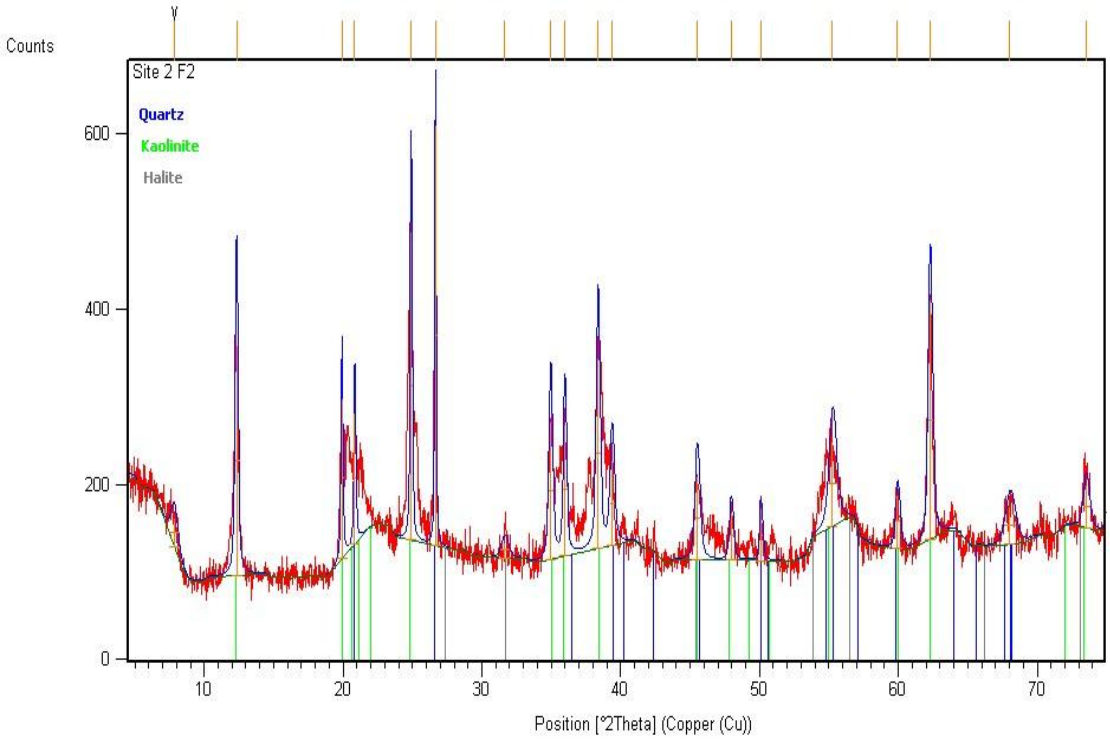
(b)



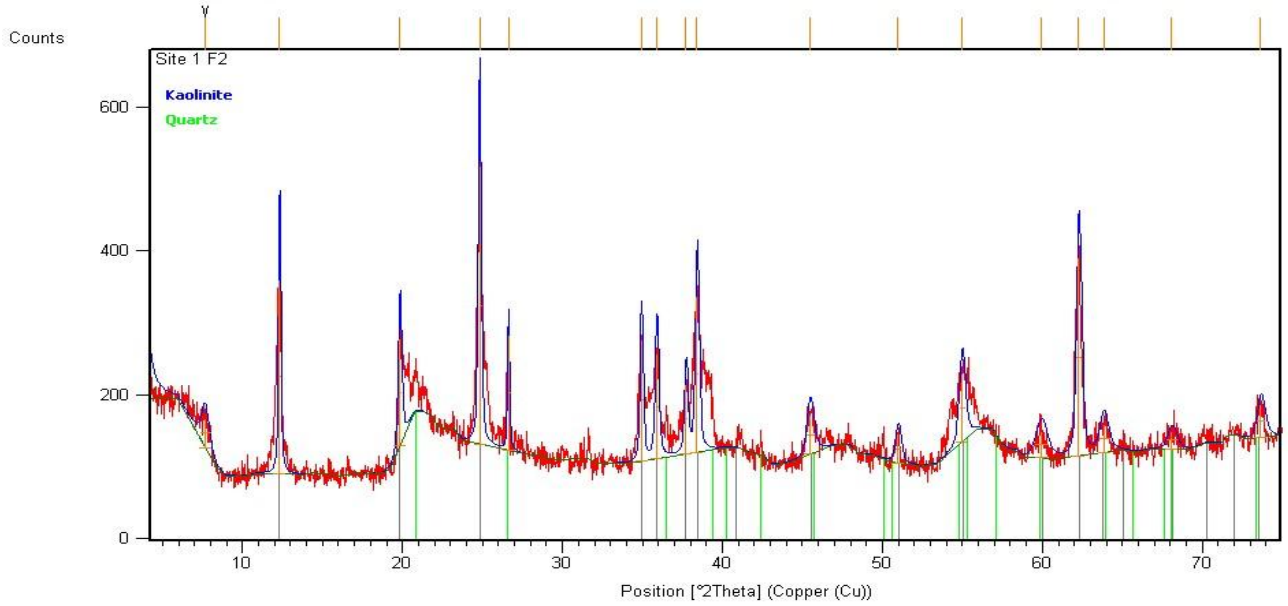
(c)


Counts
Site 1 R1
400
200
0
10
20
30
40
50
60
70
Position [°2Theta] (Copper (Cu))

(d)


Counts
Site 2 F2
Quartz
Kaolinite
Halite
600
400
200
0
10
20
30
40
50
60
70
Position [°2Theta] (Copper (Cu))

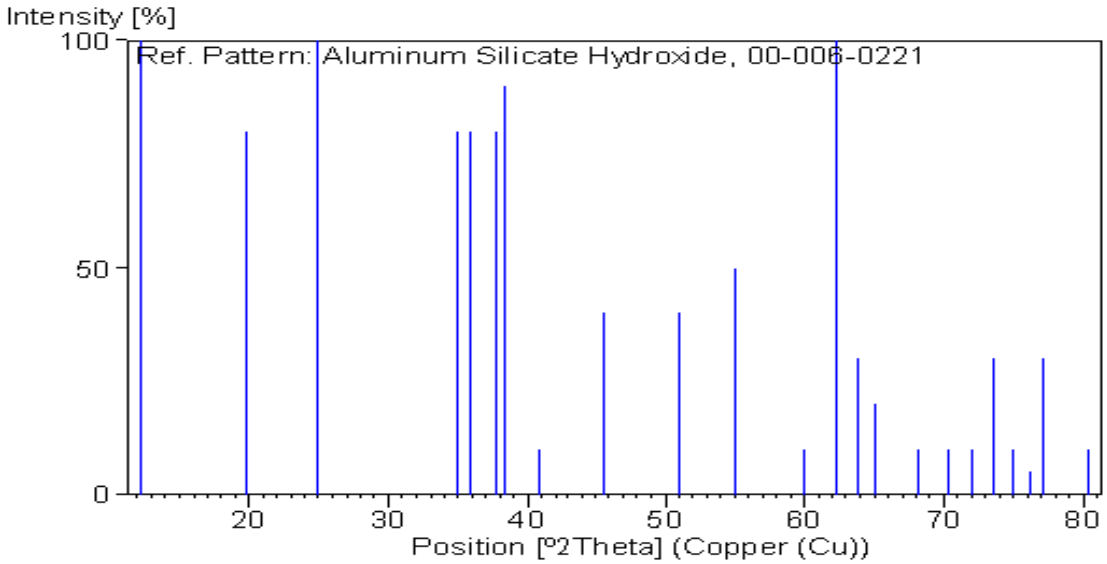
(g)



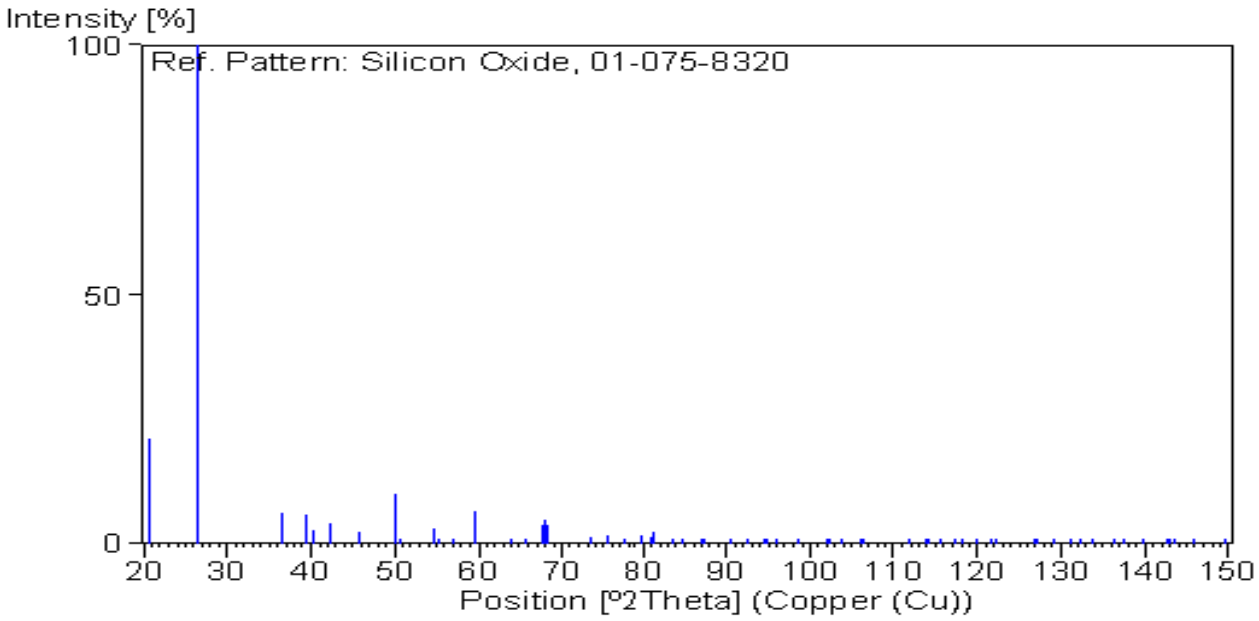
Appendix IVB

X-ray diffraction of 'Nzu Clay' sample on CuKα in the 2θ region, glancing angle 15º – 75º Stick Pattern

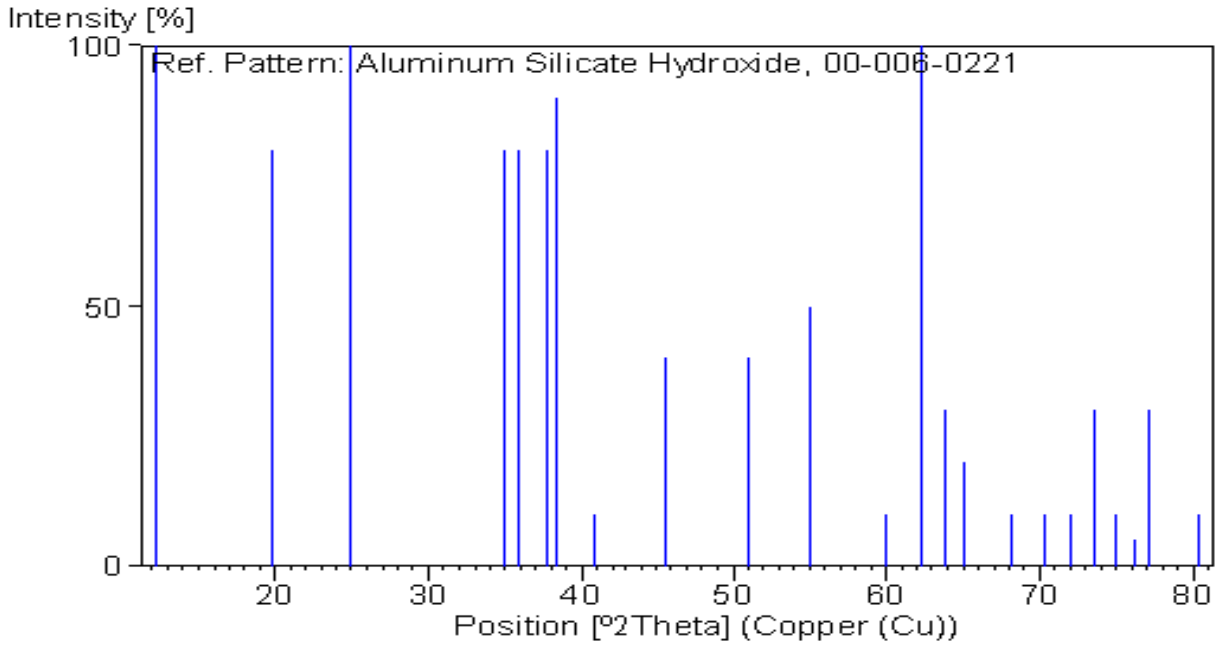
(a) Site1 R



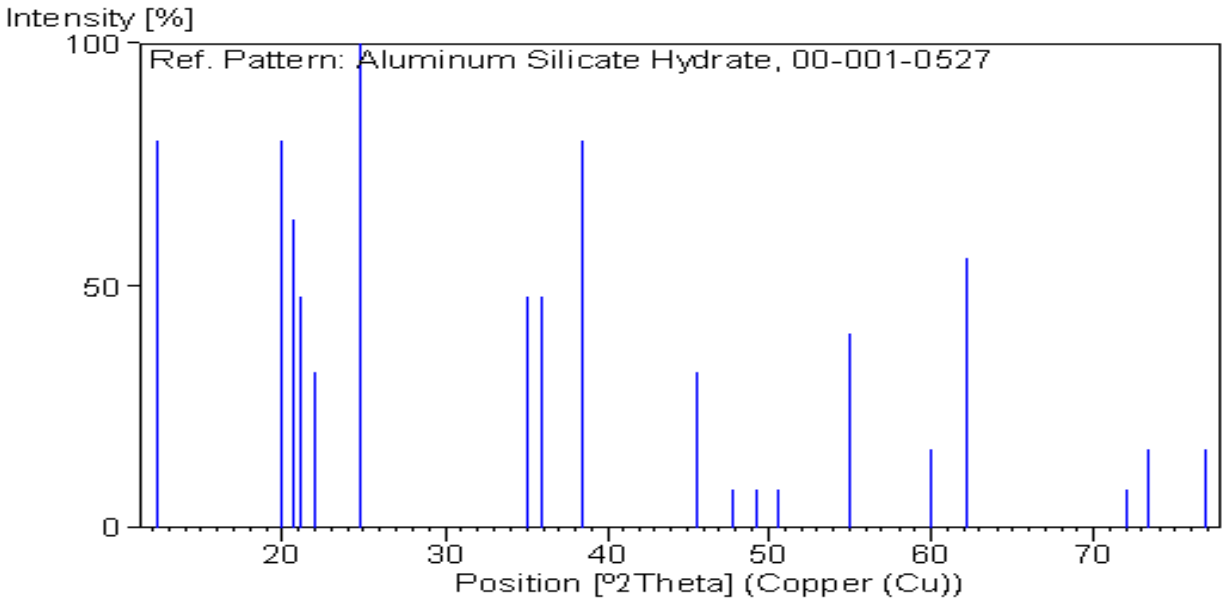
(b) Site 2 F



(c) Site2 R



(d) Site 3 FC


Intensity [%]
100
50
0
Ref. Pattern: Aluminum Silicate Hydrate, 00-001-0527
20
30
40
50
60
70
Position [°2Theta] (Copper (Cu))