

ANALYSIS OF SOME NIGERIAN SOILS

A THESIS PRESENTED IN PARTIAL
FULFILMENT FOR THE DEGREE OF
MASTER OF SCIENCE (ANALYTICAL
CHEMISTRY) OF AHMADU BELLO
UNIVERSITY

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DEDICATION

In memory of my parents and in thankfulness to Professor Frank Stansfield for his Unique support, encouragement and interest.

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I wish to express my appreciation and thanks to my supervisor Dr. U. J. Ibok for his interest, inspiring guidance, patience and useful suggestions throughout the course of this investigation.

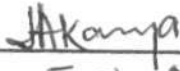
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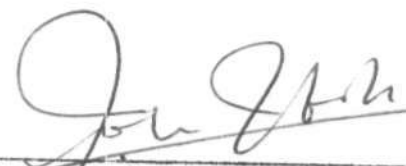
Finally, I wish to thank Erii Amdi, Musa Akanya, Mr & Mrs. Aileku and all those who have in one way or the other contributed to the successful completion of this work.

DECLARATION


This is to certify that this work has been carried out by
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ABSTRACT

The problems encountered in the analysis of soils, decomposition of refractory materials and methods of determination of elements are revealed in a literature survey. On the basis of previously reported work, Differential Thermal Analysis, X-Ray, Cation Exchange Capacity, glycol retention properties and chemical analyses have been employed to identify and quantify the clay minerals and elements present in each soil sample.

The decomposition of the samples was by sodium peroxide fusion and the different methods used in estimating the concentration of the elements in solution are described.

Some Nigerian soils were collected and separately analysed to determine their elemental and mineralogical constituent.

From the results of Differential Thermal Analysis, montmorillonite and kaolinite are the dominant clay minerals. This was confirmed by the results of X-ray analysis. The percentages of montmorillonite for all the samples lie between (6.1 - 83.4%) while kaolinite was (50.6 - 100%). Illite was present in four samples Bakura, Wase, Kongo and Suleiman Hall soils, although its concentration in each was relatively low (1.9 - 16.3%).

The constituent elements were determined using Atomic Absorption Spectrophotometer and chemical methods. Generally, the

major constituents for all samples are silica, and aluminium.

The concentration of silica and aluminium in all the samples **are relatively high**, SiO₂ (43.10 - 51.25%) **and** Al (4.89 - 10.05%).

The concentrations of Fe are greater in the latcritic and the Area E soil samples. All such soil samples have low Fe (16.89 - 22.59%) contents. The Maiduguri black cotton soil has greater amounts of SiO₂ (51.25%) and Al (10.05%). The concentrations of elements in all other samples follow similar trends.

These results indicate that the kaolinite containing soil samples could be used for construction works, but because of the low iron contents of the samples, modifications may be needed when used for the production of clay products. These soils cannot however be economically exploited as sources of iron and aluminium in the foreseeable future.

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CHAPTER I

1. INTRODUCTION

The properties of any soil depend mainly on the mineralogical and chemical composition, the texture and arrangement of particles and the effects of environment(1). Civil engineering embraces the analysis, design and construction of a diversity of structures and systems. All of these facilities, for example, buildings, dams, tunnels, highways, airfields, bridges, clay bricks etc., are built on, in or with soil or rock. Thus the behaviour of the soil and rock at the locations of any project and the interaction of the facility have a major influence on the success, economy and safety of the work. The mineralogy of soils can be considered fundamental to the understanding of the geotechnical properties, even though mineralogical determination are not made for many geotechnical investigations.

Mineralogy controls the sizes, shapes and surface characteristics of the particles in a soil, these features together with the interactions with the fluid phases determine plasticity, swelling, compression, strength and hydraulic conductivity behaviour. Mineralogy is related to soil properties in much the same way as the composition and structure of cement and aggregates are to concrete or as the component and crystal structure of steel are to its strength and deformability.

Most of the developed countries like Israel and Romania have placed much emphasis on clay brick industry in the last two decades. Nigeria is beginning to appreciate the enormous potentials of clay bricks as an alternative or at least a supplement to cement in the building industry. It is therefore not surprising that efforts are being made for the establishment, at least, of a brick industry in every state in the Federation. For an effective implementation of such a programme, a knowledge of the mineralogical composition of the potential soils, through a careful analysis is a necessary prerequisite.

A survey of work done on Nigerian soils has shown that not much attention has been given to the analysis of clay and other minerals by her soil scientists and engineers except perhaps the little efforts made by the mines division of the Federal Ministry of Mines and Power. This division is preoccupied with government bureaucracies and is not in any position to readily provide the much needed reliable information on our mineralogical and other soil properties. These coupled with the number of samples sent to the Department for analysis, and the enormous amount of some Nigerian soils from different locations in the Department of Civil Engineering, prompted the present investigation into the analysis of Nigerian soils.

The constituent particles of soils are grouped on the basis

of size unit - clay, silt, sand and gravel etc. Each size fraction contributes different properties to the soil. The behaviour of soils consisting of larger particles can be classified using the methods of mechanics but most of the problems in soil engineering practice are posed by clay soils whose behaviour cannot be successfully described by the methods of mechanics. Two clay soils with the same grain size distribution can have very different colloidal properties depending on their mineralogical nature. These varying characteristics will lead to differences in engineering behaviour, so a knowledge of the mineralogical composition and probably non-crystalline chemical composition of a soil can be of great value for understanding engineering properties and aid in evaluating soils in relation to classification and agronomic properties (2). Evaluating soil minerals can be achieved by careful analysis with the aid of selected analytical techniques.

In evaluating analytical techniques with respect to their relative utility for a given problem, the principal factors generally considered are selectivity, sensitivity and speed. Selectivity is the ability to detect and determine one substance in the presence of others which are associated with the desired constituent and which might be expected to interfere with its identification and determination. Sensitivity generally depends on the concentration of the constituents present in the sample. The degree

of accuracy required depends on the intended use of the analytical data, the availability of relevant facilities and experienced manpower. It is the desire of the analyst to strike a reasonable balance between these factors, which will result in low overall cost in time and material with a minimum of chemical processing and separation of the constituent elements before making the final estimation. In analytical chemistry, researchers have continued to direct their efforts towards the discovery, development and improvement of methods for obtaining rapid and reliable results. Recent instrumental methods are playing important roles in chemical analysis today.

Analysing for soil clay minerals is a difficult exercise. This is because soil clay minerals do not display the well defined properties of pure specimen minerals. Presence of other components to a high degree of interstratification lead to distortion, poor crystallinity and also different surface charge properties. Techniques for selective dissolution of selected minerals do not distinguish what in effect, are large balancing cations according to the mineralogical nature of the materials with which they are associated (3). Such procedures also bring about the solution of discrete amorphous and other crystalline minerals (4).

Analysis of elemental composition also pose some problems due to the presence of different mineral species and quantitative estimation of their proportion in such polycomponent system usually require the application of

several complementary qualitative and quantitative or at least semi-quantitative analyses.

Some of the most useful methods that may be employed for the determination of mineralogical composition of soils are cation-exchange capacity test (CEC), glycol or glycerol adsorption measurements, X-ray diffraction analysis, thermal analysis technique, total elemental analyses, differential dissolution technique and chemical analysis (5). All except total elemental analysis and differential dissolution technique were employed in this investigation.

The principles of some of the methods of analysis are discussed in detail below.

1.1 Ethylene Glycol Retention

The ability to interact with polar liquids is one of the most fundamental properties of clays. Data on this interaction should aid in understanding the adsorption characteristics of soil clays and in identifying mixed layer clay minerals in soils (6).

Retention of ethylene glycol by clays which have been heated so as to prevent interlayer swelling serves as a measure of external surface area while retention by unheated samples permit estimation of total surface area. In any case, the ethylene glycol retained by unheated clay in excess of that obtained by a correspondingly heated sample is probably a useful index of inter layer swelling. The above method is only applicable provided minerals

which absorb glycol between the structural units are not present. Vermiculite and endelite (the hydrated form of halloysite) are minerals which adsorb only one layer of ethylene glycol between the structural units. The presence of these minerals in samples causes values obtained to be low. Use of the method as an index for total surface area, therefore, requires prior knowledge of the absence of vermiculite and endelite. For practical application of the method it would be of great advantage if a procedure suitable for quantitative estimation of various clay minerals occurring in mixtures both with and without interstratification is available.

Dyal and Hendricks (7) proposed a simple gravimetric method which makes use of two layer solvate formed by glycol retention for the determination of internal swelling, and in a later paper Dyal and Hendricks (8) presented evidence that glycol retention is more reliable than X-ray reflection intensities even where a sample is dominantly montmorillonoid.

Improvements of the Dyal and Hendricks methods have been made in recent years. Martin (6), and Bower and Geschwind (9) have described methods with some modifications of the Dyal and Hendricks method (7). Briefly, the methods consists of wetting a dried, weighed sample of clay soil with glycol, and the subsequent removal of excess glycol by vacuum distillation with anhydrous Calcium

Chloride as absorbent until as indicated by a low rate of loss of glycol only a monolayer remains. The amount of ethylene glycol retained or adsorbed by soils and clays can be determined gravimetrically or by titration (10). Gravimetric method involves a simple difference in weight whereas the titration method consists of titrating the ethylene glycol retained against standard sodium thio-sulphate solution. Some data obtained by these methods for some clay minerals are shown on Appendix A.

2. Cation Exchange Capacity (CEC)

The cation exchange capacity is a measure of the degree of substitution of one cation by another in the crystal lattice and it can also be an aid in determining quantitatively the mineralogical composition of clays (11). Three sources of exchange capacity in clays have been identified (12):-

- (i) Isomorphous substitution - Al^{3+} for Si^{4+} in the silicate sheet and Mg^{2+} for Al^{3+} in the tetrahedral sheet are most common forms. Balancing cations are attracted to cleavage surfaces. This is the major source of exchange except possibly for Kaolin minerals.
- (ii) Broken bonds - the charge deficiencies owing to broken bonds are compensated by exchangeable ions located on the broken edges and non-cleavage surfaces. The importance of this contribution increases with decreasing size. It may be the

major cause in Kaolin and contributes 20 per cent of the total smectite.

- (iii) Replacement of the hydrogen of an exposed hydroxyl by an exchange cation.

Many methods have been established for the determination of CEC. Among those reported are the ammonium chloride method (13, 14, 15). Pratt and Chapman (16) have also reported the barium chloride method. These methods involve saturating the soil with the cations of these salts and determining their adsorption by chemical methods such as titration. Methods applied depends upon the considerations of the analyst, as each method has its own associated problems. This investigation employed the barium chloride method of Mehlich (13) reported by Pratt and Chapman (16). The principle is very simple. The soil is leached with a measured amount of triethanolamine containing barium chloride. The barium saturated soil is used for the determination of the cation-exchange capacity. The excess barium chloride is removed with distilled water and the adsorbed barium is replaced by calcium chloride and determined colorimetrically using potassium chromate.

The CEC is equivalent to total charge of the clay and identical with the excess cations in the double layer at very low electrolyte concentrations (5). The smaller the particles of a mineral the higher is the CEC. Particle size has no effect on the CEC of

montmorillonite and vermiculite but has on those of kaolinite, halysite and micas (5).

Because the amount of exchange capacity depends on the aforementioned factors a given clay mineral does not have a fixed single value of exchange capacity. Typical ranges of exchange capacity are summarised in Appendix B.

X-Ray Diffraction Method

X-ray diffraction analysis is one of the most useful methods of soil analysis. Hadding (17) and Rinne (18) were the first to apply X-rays to the study of clay minerals, and Hendricks and Fry (19) and Keldy et al (20) were the first to demonstrate that soil clays contain crystalline mineral components that yield X-ray diffraction patterns. Investigations of the structure, properties, and occurrence of soil clay minerals by X-ray diffraction methods have become a major technique in soil science.

A systematic and periodic arrangement of atoms in a three-dimensional array is one of the characteristics of crystal structure. The diffraction involves the scattering of the X-ray by the atoms of a crystal and reinforcement of scattered rays in definite direction away from the crystal. Quantitatively the reinforcement of the scattered rays is related to the distance of separation of the atomic planes as defined by the Bragg equation,

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

where θ = critical angle at which the rays are scattered
 d = interplaner spacing
 λ = wavelength of rays
and n = an interger.

θ is a distinctive characteristic of a particular mineral (5, 12, 21), and the method is particularly suited for identification of clay minerals because the first order reflection spacing $d(001)$ is characteristic for each mineral group (5, 12).

Continued improvements in X-ray identification, techniques of sample preparation and definition of criteria for identification and characterisation of clay mineral species in recent years have advanced the field of clay mineralogy to a point where mineralogical analysis yields a wealth of information relative to the properties and genesis of soils. X-ray diffraction has contributed more to mineralogical characterisation of clay fraction of soil than has any other single method of analysis. Despite these facts, however, methods of quantification are still facing many problems (22).

Clark and Reynolds (23) were among the first people to attempt to determine the percentages of minerals in natural mixtures. However, the report of Johns, Grin and Bradley (24), provided the basis for many of the semi-quantitative determinations later reported in the geologic literature and is the standard generally for which other modified methods have developed.

Among the modifications of the calculation techniques of these workers (24), are those of Schutz (25), Griffen and Goldberg (26), Biscaye (27), Meade (28), Neihaisai and Weaver (29). Other works dealing with the same topics have appeared in international geological literature and many others treating such methodology appear in soil science publications (30, 31). It is obvious from this brief appraisal that a confused situation exists because there is no standard method being used in the calculation of the quantitative or semi-quantitative amounts of clay minerals in sediments and sedimentary rocks.

It must be noted, however, that although calculation methods differ and give significantly different results if used with the same diffractograms, each method is internally consistent for a given study and can give results that suggest geological trends. A major problem arises, however when attempts are made to compare trends from different areas, based on the semi-quantitative amounts which are calculated using dissimilar methods. ~~The question then~~
~~is not the trends or differences in trends geologically meaning-~~
~~ful or the way in which they reflect geological variations.~~

In this investigation calculations of the relative amounts (semi-quantitative) of clay minerals in each of the samples based on the diffractograms obtained were made using four different methods as described by Pierce and Siggel (22). Selection of dif-

ferent methods used does not imply that these methods are better than others proposed, or that any one of the four methods is better than the others. Each is similar in that hydromica is used as an internal standard, the relative amounts of the clay minerals are weighted to hydromica, summed up and the total is equated to 100 per cent. No attempt was made to separate Kaolinite from non-expansible minerals with a unit 14\AA basal spacing. The methods used are summarised below:-

- (i) The integrated peak areas of the 17\AA and 10\AA reflections of the glycolated slides are determined. The relative values of montmorillonite (17\AA) and hydromica (10\AA) are obtained by multiplying the area of the 10\AA peak by a factor of four.
- (ii) The untreated 3.3\AA (003 hydromica) peak area is compared to that at 3.5\AA (002 kaolinite, 004 chlorite plus montmorillonite). A reduction in area of the 3.5\AA peak after glycolation is assumed due to montmorillonite and the remainder is due to kaolinite plus chlorite. This value is assumed equivalent to the 3.3\AA hydromica reflection on a one-to-one basis. The relative amounts of the minerals are assumed and the total is equated to 100 per cent.
- (iii) The integrated intensity of the 17\AA glycolated peak is equal to the relative amount of montmorillonite. The area of the 10\AA peak (glycolated peak) multiplied by four, is

equivalent to the amount of hydromica. The $7A^{\circ}$ area is multiplied by two for the relative amount of kaolinite plus chlorite.

- (iii) The intensity of the $10A^{\circ}$ reflection before heat treatment is compared to the intensity after heating. Illite and the expanding minerals were assumed to reflect X-rays with equal intensity at $10A^{\circ}$. The intensity of the $7A^{\circ}$ peak is compared directly with the reflection at $10A^{\circ}$ for comparison of hydromica to chlorite plus kaolinite.
- (iv) This is essentially the same procedure as that of the first method. The multiplying factor to compare hydromica to non-tmorillonite is 3 rather than 4.

A table for X-ray for some common minerals is shown in Appendix C (2).

1.4 Thermal Method of Analysis

This method of analysis can be grouped into three classes (5).

- (i) those that measure weight losses or gain during heating due to gaseous substance i.e. thermogravimetric analysis
- (ii) those that measure energy changes during heating i.e. differential thermal analysis (DTA)
- (iii) those that measure changes in the solid phase, that is, changes in crystallinity, volume, colour and various physical strength properties.

1.4.1 The DTA

This thermal technique is convenient for identifying or characterising, and quantifying certain mineralogical components of soils. The measurement of thermal changes in soils dates back to Le Chatelier who in 1887 (32), published thermal data on halloysite, allophane, kaolinite, pyrophyllite and montmorillonite. Le Chatelier used a single platinum-platinum and 10 per cent rhodium thermocouple for his work and Roberts-Austen (33) was the first to use the differential thermocouple for thermal analysis. Among other workers in this field who propounded theories on the principle and application of the method to mineralogical analysis include Kracek (34), Agafonoff (35), Spiel (36), Kerr and Kulp (37), and Gieseking (38). Since then continuous improvements have been advanced on its application.

The analysis often demonstrates water loss and energy changes during heating of the sample by the accompanying thermal effects. It involves the simultaneous heating of a test sample and ~~an~~^a ~~ther-~~
~~mally inert~~ reference substance from room temperature to any desired temperature between the sample and the inert substance which undergoes no thermal changes. The difference in temperatures between it and the sample is a measure of the thermal reactions which occur in the sample.

Many minerals undergo several reactions on heating. At low

temperature evaporation of imbibed water occurs, while oxidation of organic constituents and metallic ions in a reduced state occurs at intermediate temperatures. At high temperatures loss of crystal lattice hydroxyl ion, water and carbonate ion as carbon dioxide takes place; therefore the temperature of the sample during a test depends on the reaction taking place in the unknown sample and since different minerals react differently at different temperatures, this method of analysis serves conveniently for qualitative analysis.

The analytical results are presented as a curve called thermograms and since the area under the peak is related to the amount of energy evolved or absorbed and therefore to the amount of sample (38, 39, 40), the method has also gained useful application in quantitative estimation of clay mineral components of soils.

The DTA analysis of the samples were carried out on the Derivatograph. The Derivatograph used for this investigation was that of the Geology Department of Ahmadu Bello University. It is made by MDM-Budapest, Hungary. The instrument is capable, simultaneously to give information about how to:-

- (i) measure the temperature within the sample (or reference material)
- (ii) determine weight changes
- (iii) determine the rate of weight changes and

9iv) determine the energy changes in the sample, all by a graphical method described fully by Paulik et al (41). The curves obtained were also compared with the curves of known minerals (1, 5, 12). See Appendices A and C.

4.5 Chemical Analysis

For further information on the soil samples, chemical analysis can be used to determine the amounts of elements present.

Chemical methods involve the conventional methods of analysis and include gravimetry, titrimetry, spectrophotometry, atomic absorption and electrochemical methods.

When concentration of the constituent of interest lies within a fairly reasonable range in the sample, gravimetric method is usually capable of giving reasonable degree of accuracy. Within a range of 10 - 100 per cent, a precision better than one part in 1000 may be obtained. However, gravimetry is not very often selective and may require complete separation of the metal or compound of interest; it is time consuming and at the same time tedious, though generally cheap, since no sophisticated equipment are often involved.

Titrimetry is usually designed to be specific although in many cases separation may be necessary. It is capable of giving a precision of about three parts per 1000 or better in some cases if carefully performed. Although the method is not versatile, it is inexpensive.

Atomic absorption covers a large range of concentrations (from fractions of a part per million of many elements in solution to tens of per cent of constituent elements in the sample) whereas spectrophotometry usually covers a slightly smaller concentration range but has the advantage that its calibration curves shift less, and as the contents in the cells are static; its precision and accuracy depend critically upon the sensitivity of the instrument, chemical separation and the preparation of the sample which may be time consuming. The chemical separation can be avoided by adequate treatment of the solution such as adjustment of pH, formation of complexes, oxidation-reduction, selection of reagent, selection of wavelength used etc.

Electrochemical methods may compare favourably with atomic absorption when preliminary separations are not required.

Generally, the instrumental methods are faster than the classical titrimetric and gravimetric methods, especially as only one solution prepared may be required for the estimation of several or all elements present in the original sample. In addition, they are highly sensitive and therefore find useful application for trace analysis. On the other hand, titrimetric and gravimetric methods are more precise and accurate for major constituent analysis. The high cost of complicated and complex equipments in instrumental methods is more than offset by multiple number of

estimating various elements from one solution prepared and the time and labour saved.

Originally, all chemical analysis were to be carried out using a Unicam SP 1900 Atomic Absorption Spectrophotometer available in the Department. In the event, this technique was not used for all the elements of interest because of the lack of appropriate hollow cathode lamps and nitrous oxide gas which are required for specific elements. Consequently, other methods such as gravimetry, titrimetry and spectroscopy were used when these could have served as a check on the results obtained by atomic absorption techniques.

The chemical treatment of a clay as a sequence in the recognition of the mineral constituents is not very suitable because of its effects on the various components present. It may even attack some of the fine grained silicates so that results eventually obtained may differ somehow from the minerals of untreated materials. If the mineral assemblage is already known, chemical analysis may enable the mineralogical composition to be estimated. However, both identification and estimation of minerals on the basis of bulk chemical analysis are very uncertain because of the prevalence of isomorphous substitutions in mineral structures (1).

Since the determination of the constituent elements present in the soil samples depends upon effective dissolution of the samples and since the major analytical technique used extensively in this work is atomic absorption spectroscopy, the decomposition

procedures and an outline of atomic Absorption Spectroscopy techniques are discussed below.

.6 Decomposition Of The Samples

In analysing for elements in refractory substances such as rocks and silicate materials, the first consideration of the analyst is the best method for decomposing the sample since these materials are generally very resistant to attack by common solvents. The decomposition procedure sets the course of subsequent analytical work and can save many unnecessary steps.

There is no general rule regarding the advantages to be gained in employing a particular method since the latter is governed by both the nature of the work to follow. Obviously, the method should effectively decompose the sample. In dealing with a rock sample, however, it must be remembered that it is a mixture of minerals and, depending upon the ultimate goal of the analysis, effective decomposition does not necessarily imply complete decomposition, although a careful analyst would be happy when the two are synonymous.

The decomposition of silicates and similar materials have been extensively covered by Maxwell (21), Jeffrey (42) and more recently by Ojonuba (43). A review of problems associated with decomposition procedures in inorganic analysis was also fully reviewed by Šulcek et al (44) and would not be discussed here.

Suffice it to say that sodium peroxide fusion was employed

for the decomposition of the samples not because it is better than all other methods mentioned (21, 42, 43, 44), but because it was found that all the samples were got into solution and was most handy for the equipment available at the time of this work.

.7 Atomic Absorption Spectrophotometry

As far as rock and soil mineral analysis is concerned, atomic absorption is one of the popular and most used technique in recent years. The technique was first introduced by Walsh (45), and is based on the absorption of radiation by free atoms of elements particularly those of metallic elements.

The method involves the spraying of a solution into a flame, in which a portion of the solute is reduced to free atoms of its constituent elements. These free atoms can be raised to an excited state by the absorption of light of the energy corresponding to the difference in energy between the ground and excited states at certain discrete wavelengths known as "resonant wavelengths". Thus if light of a resonant wavelength of a particular element is passed through a flame into which a solution of a compound of that element is being sprayed, a fraction of that light will be absorbed by the atoms of the element and the extent of absorption is a measure of the concentration of the species of the incident light.

The source of the incident light is a "hollow cathode" lamp,

designed to emit characteristic spectrum lines, including the resonant wavelength, reduced in intensity after passing through the flame, are isolated by means of a grating or prism monochromator, and their intensities measured by a photomultiplier tube. Selectivity is achieved by the narrowness of the band of incident energy provided by the hollow cathode lamp, the effect of continuous radiation from the flame being eliminated by means of a mechanical interrupter, or an alternating power supply current detector circuit in the receiver.

Atomic absorption spectroscopy, the technique and application which are subject of continuous research (46, 27, 48, 49), has several attractive advantages over other techniques. For example it has high selectivity, low limits of detection and many elements can be determined from one solution.

CHAPTER II

2. EXPERIMENTAL

2.1 Materials

The major soil samples used in this work were supplied by the Department of Civil Engineering, Ahmadu Bello University, (A.B.U.) Zaria. Some of the soil samples were collected along trial roads, construction sites etc., and at different depths as indicated in Section 2.2. A test clay brick sample was sent by an industrialist proposing to undertake a brick industry. The location of the different soil samples are described in section 2.2. below. (See Appendix for map of Nigeria showing location of samples).

2.2 Location And Collection Of Soil Samples

2.2.1 Maiduguri Black Cotton Soil

Maiduguri black cotton soils cover the sufficiently large poorly drained areas of Lake Chad basin in Northern Nigeria and North Cameroun. Maiduguri is in Borno State, north-eastern part of Nigeria. The sample was collected at the 'heart' of the Maiduguri deposits at a distance of 112.6km (70 miles) on the Maiduguri Gaboru road in the North-eastern part of Borno State. The collection was done along the trial road at a distance of 20 metres away from the central line on both sides of the one-mile trial test road so as to obtain good representative sample. The sample was taken at a depth of about 91.4cm at every 500 metres along the road.

2.2.2 Bakura Swelling Soils

The swelling soils cover most part of the poorly-drained area of Bakura. Bakura is a small village some 90Km away from Sokoto, capital of Sokoto State in the North-west part of Nigeria. The sample was collected from a bore hole at a depth of 3.0 - 3.66 metres.

2.2.3 Wase Gidan Shehu Yelwa Road (Jos) Soil

Wase Gidan Shehu Yelwa road is a road in Jos, capital of Plateau State which is in the South-east part of Northern Nigeria. The sample was collected at the investigation site along the road at a depth of about 0.5 metres.

2.2.4 Kaduna Arewa Textile Limited Soil

The Arewa textile company is a textile industry located in the southern part of Kaduna, capital of Kaduna State in northern Nigeria. The sample was collected at a construction site within the industrial compound at a depth between 0 - 46cm.

2.2.5 Akure Concretionary Lateritic Soil

Akure is the capital of Ondo state in the Western region of Nigeria. The soil was collected from the Ministry of Works (M.O.W) yard at a depth of about 0.5m.

2.2.6 Institute of Administration Kongo Soil

Institute of Administration (Ahmadu Bello University) is based in Kongo, an area in the South-east part of Zaria. The sample was collected at the site of the proposed new students hostel in bore-

hole number 5 at a depth between 30 - 51cm.

2.2.7 Zaria Concretionary Lateritic Soil

Zaria is a town in the north-east part of Kaduna State. The sample was collected at the ground surface of the construction site of the new Ahmadu Bello University Teaching Hospital on Samaru-Funtua road.

2.2.8 Amina Hall, Suleiman Hall, Ahmadu Bello University Hospital (Tudun Wada), Area E, Proposed Conference Centre, Student Centre and Islamic Centre Soil Samples

These are all located in Zaria and are soil samples collected at bore holes at about 51 cm deep at the sites and proposed sites of buildings of Ahmadu Bello University authority.

2.2.9 Ilorin Test Clay Brick Sample

Ilorin is the capital of Kwara State. It is located in the central-west region of Nigeria, west of the river Niger. The sample was sent as a clay brick sample by an industrialist proposing a brick industry in that state.

2.3 Preparation Of The Samples

All the samples used were ground to a fine powder, grinding proceeding until all the samples pass through 200 B.S. mesh sieve, using an agate mortar. No pretreatments were performed before grinding but in some cases during the course of the analysis special treatments e.g. treatment with hydrogen peroxide etc were required to suit the experimental conditions.

2.3.1 Ethylene Glycol Retention Determination

Reagents and apparatus

Ethylene glycol, analar grade was redistilled, discarding the first and last 10 per cent.

Calcium chloride, the anhydrous salt was further dried at 200° for 24 hours.

Phosphorous pentoxide, anhydrous (P₂O₅)

Pyrex Vacuum dessicators

Hypervac Vacuum Pump

Petri dishes

Water bath, maintained at 25± 1°

Procedure: (Dyal and Hendricks method (1950) as described by Torrence Martin (6)

The soil sample (approximately 10g) was mixed with hydrogen peroxide solution (10 per cent) and air-dried to removed any organic matter.

The organic matter-free sample was accurately weighed (1g) in a 4cm-diameter petri-dish. The samples (six per dessicator) were placed in a vacuum dessicator containing P₂O₅ and then evacuated for 15 minutes. The samples were left in the dessicator for five hours to dry to constant weight. By means of a pipette having a tip drawn to a fine point, redistilled ethylene glycol (1ml) was distributed dropwise over the soil sample surface. The glycol was allowed to soak in contact with the soil samples for at least 12

hours. The glycol-treated samples and a dish containing pure glycol were placed in dessicator containing carefully dried calcium chloride and ~~the~~ evacuated for 15 minutes. The dessicator was placed in a large water bath, maintained at $25 \pm 1^\circ$ to eliminate excessive temperature fluctuations. The samples were removed and weighed after 16 hours and every 4 hours there after until equilibrium was reached; that is when 3 weighings agreed within $\pm 0.3\text{mg}$. The results are expressed as mg glycol per gramme soil sample by use of the average weight of glycol retained and the dry weight of clay was determined as the equilibrium weight obtained in an evacuated dessicator over P_2O_5 . Triplicate analysis were carried out.

2.3.2 Determination of Cation-Exchange Capacity

Barium Chloride-triethanolamine method

Reagents

Buffer Solution, barium chloride (0.5N) and triethanolamine (0.2N).
Triethanolamine, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, (100ml) [Sp gr 1.126, about 1N] was diluted with water (100ml) and partially neutralised with hydrochloric acid to adjust the pH to 8.1. About 2 litres were prepared and this was mixed with 2 litres of a solution containing $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (250g) and kept away from CO_2 from the air.

Replacement Solution, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (250g) was dissolved in distilled water (4 litres) and buffer solution (10ml) was added and mixed.

Calcium Chloride, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (50g) was dissolved in water and saturated solution of calcium hydroxide (10ml) was added and the

volume made up to 1 litre.

Saturated Solution of Barium Chromate

A small amount of barium chromate was saturated by adding potassium chromate solution (50ml) to 0.05N barium chloride solution (200ml). This was warmed on a steam bath for about 2 hours. It was then filtered and washed with water until it was free of barium and chromate ions. The washed precipitate was put into a litre flask and made up to the mark. This was shaken properly and left to settle. The supernatant liquid was used as the wash solution.

Hydrochloric Acid, dilute, one volume of concentrated hydrochloric acid to 4 volumes of water.

Barium Standard: 0, 1, 4, 6, 8 and 10ml portions of 0.1N barium chloride which was made by dissolving $BaCl_2 \cdot 2H_2O$ (2.22g) in water (1 litre) was measured into 50-ml volumetric flasks containing calcium chloride solutions (12.5ml). Portions of each of these solutions (10ml) were measured and mixed with potassium chromate (1ml) into a centrifuge tube and treatments as in the procedure below was followed. The reading on the spectrophotometer at 450nm were plotted as milliequivalents of barium ions.

3.2.1 Preliminary Experiments

Preliminary experiment was carried out first to determine the organic matter content of the soil samples and their respective pH

values in water. Organic carbon was determined on the samples (2g) by wet oxidation procedure of Walkey and Black as outlined by Jackson (50). The per cent organic matter was obtained by multiplying organic carbon value by a factor of 1.72.

The pH values were determined by the glass electrode on a 1:2.5 soil-water mixture after equilibrating the soil in water for 30 minutes.

Procedure

The soil sample (10g) was placed in a 400ml beaker, the buffer solution (25ml) was added and the flask was allowed to stand for 2 hours, mixing the contents occasionally by swirling. This was then filtered into another flask using another portion (25ml) of buffer to aid in the transfer of all the soil to the funnel. By adding small increments, the soil was leached with the replacement solution (100ml).

The barium saturated soil was then washed with distilled water (150ml) in small portions of 10-15ml, allowing the portions to leach through before the next was added. The washing was discarded and the soil was leached with calcium chloride solution (125ml). The calcium chloride leachate was then transferred into a 250ml flask, diluted to the mark and mixed. Aliquot of this (10ml) was transferred into a centrifuge tube and potassium chromate solution (1ml) was added and then placed in a beaker of water

and warmed for 30 minutes on a water bath to about 80^o - 90^o. After 2 hours of settling of the precipitate, the beaker was removed from the bath, cooled and then centrifuged for 15 minutes. The supernatant was decanted and allowed to drain. The sides of the tube were washed down with saturated barium chloride solution (5ml), mixed with a glass rod and recentrifuged. The precipitate left was dissolved in dilute hydrochloric acid (10ml) and the absorbance taken at 425nm, using water as blank. The cation exchange capacity was calculated in milliequivalents per 100g of soil from the standard curve.

2.2.3. X-Ray Diffraction Analysis

Procedure: Powdered samples were used for the X-ray diffraction analysis. The oriented aggregates were analysed and diffractograms obtained from the Philips X-ray instrument model PW1390 of the Department of Geology, using CuK α , Ni-filtered radiation at selected voltages and currents.

X-ray diffractograms were obtained for the following treatments of samples

- (i) Air-dried preferred orientation
- (ii) slides exposed to a saturated atmosphere of ethylene glycol at 60^o
- (iii) one heated at 600^o for one hour.

2.3.4 Differential Thermal Analysis Using the Derivatograph

The Derivatograph is a fairly sophisticated instrument and

would need some expertise for its proper handling. A full description of the procedure would therefore be very difficult here. The practice is fully described in the manual to the instrument (41).

2.3.5 Decomposition of Samples

Sodium Peroxide Fusion

Reagents and Apparatus

Sodium Peroxide, anhydrous powder

Nickel Crucibles

Nickel Spatula

Procedure: Finely ground dried soil sample (about 0.5g) whose percentage moisture has been pre-determined was accurately weighed into a nickel crucible and sodium peroxide (15g) was added. The crucible was first heated gently with low flame using Bunsen burner and then placed in the muffle furnace when the sodium peroxide has melted. The fusion was carried out at 700°. After about thirty minutes the content of the crucible was in a fused melt. This was allowed to cool to about 30° and then carefully disintegrated with warm water and then transferred into 1 litre volumetric flask and made to the mark, ready to be used for subsequent analyses.

2.3.6 Chemical Determination of Elements SiO₂, Fe, Al, Ti, Mg, Ca, Mn, Na and K

After preliminary qualitative analysis from the fusion solution, iron, aluminium, titanium, calcium and magnesium were deter-

mined. Manganese, sodium and potassium were determined separately. Calcium was precipitated at pH4 as the oxalate using Chapman method (51).

Reagents and apparatus

Chemicals used were all analar reagent grade.

Hydrochloric acid, concentrated

Hydrofluoric acid, concentrated

Sulphuric acid, concentrated

Hydrochloric acid, dilute. The concentrated hydrochloric acid (50ml) was diluted with water (950ml).

Oxalic acid, 5 per cent aqueous solution.

Acetic acid, 1.65N

Bromo Cresol Green, 0.04 per cent aqueous solution

Ammonium hydroxide, 1N

Sulphuric acid, 1N

Potassium permanganate, 0.05N standard solution

Ammonium chloride, 20g per 1 volume of solute

Quinoline reagent, 8-hydroxyquinoline was dissolved in ethanol (100ml) and then diluted to 1 litre with distilled water.

Nitric acid, concentrated

Sulphuric acid, dilute, 3.6N concentrated sulphuric acid (100ml) was added to water (about 800ml). When the solution had cooled to room temperature, this was diluted to 1000ml.

Ammonium persulphate, solution, 8 per cent

Ammonium hydroxide, approximately 7.5N concentrated ammonium hydroxide was diluted with an equal volume of distilled water.

Hydrogen peroxide, 30 per cent

Potassium pyrophosphate, dry powder

Hydrogen sulphide, generator

Potassium permanganate, 0.1N, standard solution

Hydrochloric acid, approximately 6N

Ammonium hydroxide, concentrated

Ammonium hydroxide, 40ml of concentrated ammonium hydroxide diluted to 1 litre with water.

Ethanol, 95 per cent.

Whatman filter paper, ashless

3.6.1 Silica

To the solution of the melt from the sodium peroxide fusion in a beaker was gently added concentrated hydrochloric acid (15ml). This was evaporated on the steam bath overnight so that the separated silica gel would be sufficiently dehydrated. The residue was taken up with concentrated hydrofluoric acid (15ml) and hot water (15ml). This was filtered, and washed with hot water until practically free from chlorides. The filtrate was again evaporated to dryness to precipitate any silica not retained in the first precipitate. The treatment was repeated for this precipitate and the two precipitates combined. The precipitate was ignited in

the crucible used for fusion. The ignition was carried out at 1200^o in the muffle furnace for 30 minutes. Blasting was continued for 10 minutes, and weighing to constant weight. The silica was then moistened with water and strong hydrofluoric acid (6 - 8ml) and a few drops of dilute sulphuric acid were added and cautiously evaporated to dryness in a fume cupboard. The crucible was then ignited for about 3 minutes at 1200^o, cooled and weighed.

The weightlost during the hydrofluoric acid treatment was equal to the weight of silica. The crucible and content were kept for the analysis of the iron group.

3.6.2 Iron Oxide, Aluminium and Titania

The filtrate from the silica determination was neutralised with a pure ammonium solution, using the precipitate as an indicator, made slightly acid with hydrochloric acid and heated to boiling. The group was precipitated with a slight excess of ammonia, diluted with the same volume of water. This was boiled for one minute, allowed to settle and then filtered into a 500 ml beaker. The filter paper with its content were transferred into the beaker in which the precipitate was made and dissolved in concentrated hydrochloric acid (10ml) and hot water. The filter paper was mercerated with glass rod and enough hot water was added to make the volume to 150ml. The iron group was precipitated as before, filtered and washed with hot water containing about

one per cent ammonium nitrate in the latter washings, until the washings were free from chlorides. The filter paper and precipitate were transferred into the crucible used for the silica determination and this was ignited to a constant weight at 500° , with the cover of the crucible so adjusted so as to allow free access of air.

To the ignited iron-group in the crucible was added potassium pyrosulphate (about 5g) and was heated very cautiously over a low flame of the Bunsen burner, keeping the crucible covered. At the completion of the fusion, it was cooled and concentrated sulphuric acid (4ml) was added and dissolved in water, keeping the volume under 150ml.

3.6.3 Reduction and Titration of the Iron

Hydrogen sulphide was passed into the solution of the iron group just obtained to reduce the iron. This was boiled for a few minutes to coagulate sulphur and then filtered into a 500ml beaker. The volume was made up to about 200ml and hydrogen sulphide was passed through the cold solution and was slowly brought to boiling with the hydrogen sulphide was still passing. This was cooled for about 10 minutes without interrupting the hydrogen sulphide stream. The stream was disconnected and the hydrogen sulphide was boiled off while carbon dioxide was passed into the solution when the hydrogen sulphide was indicated completely expelled by

means of lead acetate paper, the solution was cooled while carbon dioxide was still passing. The carbon dioxide stream was stopped and after about 30 minutes, the solution was titrated with standard permanganate solution. 1ml of 0.01N $\text{KMnO}_4 \equiv 0.005085 \text{g Fe}$.

2.3.6.4 Titania

The liquid from the iron titration was evaporated to reduce to about 75ml and concentrated sulphuric acid (10ml) and a few drops of strong hydrogen peroxide were added and the volume made up to 100ml. The titania was determined at 410nm and values obtained from a standard curve of titania prepared by heating potassium titanyle oxalate (3.68g), ammonium sulphate (8g) and sulphuric acid 100ml in a Kjeldah flask and then diluting to 1 litre in a volumetric flask; 1ml $\equiv 0.50\text{mgTi}$.

3.6.5 Alumina

From the total weight of the ignited oxides, the sum due to iron and titanium oxides was subtracted. The difference represents the weight due to aluminium oxide $\text{Al}_2\text{O}_3 \equiv 0.52913 \text{Al}$.

3.6.6. Precipitation of Ammonium Sulphide Group

The combined filtrate from the iron group was evaporated to less than 100ml, transferred to a 250ml volumetric flask and concentrated ammonia solution (3ml) was added. Hydrogen sulphide was passed in to saturation and another concentrated ammonia portion (3ml) was added. This was stoppered and left to stand overnight

Manganese, Zinc, Copper, Cobalt and Nickel were precipitated as sulphides. This was filtered and washed with ammonium hydroxide and ammonium sulphide solution, keeping the funnel covered and washing continuously to prevent oxidation and resolution of the manganous sulphide.

2.3.6.7 Precipitate of Calcium as Oxalate

To the filtrate in section 2.3.6.6 (at pH 4.0) was added oxalic acid (1g) in solution, 1.65N acetic acid (10ml) and 0.04 per cent bromo cresol green (10 drops). The volume was made to about 150ml. The solution was brought near boiling and 1N ammonium hydroxide solution was added until the colour changed from yellow, through yellowish-green to pure green. The solution was boiled gently for 10 minutes and on cooling the calcium oxalate precipitate as a coarse crystalline solid. The precipitate was allowed to stand on a steam bath for about 3 hours to ensure complete precipitation. The precipitate was filtered and then washed thoroughly with distilled water to free it from soluble oxalate.

The filter paper was pierced, the precipitate washed into a beaker and hot 1N sulphuric acid (75ml) was added. The volume was made to 200ml with water, heated to 90° and then titrated with standard potassium permanganate [one milliliter of 0.05N potassium permanganate is equal to 0.001g of calcium].

2.3.6.8 Determination of Magnesium; 8-hydroxyquinolate Method

Following the separation of calcium as oxalate, the magnesium is precipitated and weighed as the quinolate salt.

Procedure: The filtrate from the calcium oxalate precipitate was transferred to a 250ml beaker and evaporated to a small volume on the hot plate. This was heated to dryness with a small addition of nitric acid. Heating was continued until most of the oxalate residue had dissolved. When the residue was completely volatilized, the beaker was cooled and 6N hydrochloric acid (10ml) was added. Water was added to make up to about 25ml. The solution should be clear if not it should be filtered and washed with a few light rinses.

Quinolate reagent (30ml) was added to the solution along with concentrated ammonium hydroxide (5ml). This was heated on a hot plate to about 70°. The solution was stirred to initiate precipitation of the magnesium quinolate. The beaker was removed from the hot plate and kept in a dark place for about 5 hours. The precipitate was filtered through a weighed sintered glass funnel washed five times with hot dilute ammonium hydroxide and then washed with ethanol. This was placed in an oven at 105° and dried to constant weight. The weight obtained times 0.0697 gives the weight of magnesium in grams.

2.4 Determination of Manganese

Hydrofluoric Acid Extraction - Persulphate Method

In this method, the permanganate is formed using persulphate as the oxidising agent. The optical density of the permanganate is used as a quantitative estimation of manganese. The oxidation takes place at the boiling point in the presence of phosphoric and nitric acids and a small amount of silver nitrate.

Reagents

Acids, concentrated hydrofluoric, sulphuric and 85 per cent phosphoric.

Ammonium persulphate, dry salt

Special solution: Mercuric sulphate (75g), was dissolved in concentrated nitric acid (400ml) and water (200ml). To this mixture were added phosphoric acid (20ml) and silver nitrate (0.035g), cooled and diluted to one litre.

Standard Manganese Solution: Electrolytic manganese (0.10g) was dissolved in diluted nitric acid, boiled to drive out oxides of nitrogen and diluted to 1 litre. This is a 100 ppm solution.

Procedure: The ground soil sample (1.0g) was transferred into nickel crucible and hydrofluoric acid (4ml) and concentrated sulphuric acid (2ml) were added. This was placed on a hot plate and heated at low temperature initially and then the heat increased gradually until fumes of sulphuric acid were given off. This was

cooled, 6N sulphuric acid (3ml), a few drops of concentrated nitric acid were added and then evaporated. Water (10ml) was added to the hot solid to dissolve the soluble material and then filtered through acid-washed filter paper, keeping the total volume below 50ml.

To an aliquot of the filtrate was added concentrated phosphoric acid (1ml) and evaporated to a small volume. This was cooled, the special solution (section 2.4) (5ml) was added and then diluted to about 90ml. Ammonium persulphate (1g) was added and boiled on an adjusted flame so that it was brought to boiling in minutes. This was cooled and made up to 100ml volume in a volumetric flask and the absorbance determined at 525nm. The result was obtained from standards treated the same way.

5 Determination Of Sodium and Potassium

Ignition with Ammonium chloride and calcium carbonate mixture and Determination of Sodium by Uranyl Zinc Acetate

Sodium in soil is solubilised by ignition with ammonium chloride and calcium carbonate mixture, extracting with water and quantitative precipitation in aqueous solution of uranyl zinc acetate.

Reagents and Apparatus

Uranyl Zinc Acetate - A 30 per cent acetic acid (54g) was added to distilled water (486g). This was heated, uranyl acetate (60g) was added when these were dissolved, zinc acetate (180g) was added and heated until dissolved and then cooled, filtered and stored in a bottle.

Ammonium Chloride: Ammonium chloride was sublimed slowly, the crusts dissolved in water and evaporated on a steam bath while stirring constantly. The hot liquid was poured off, the precipitate filtered and the salt stored in a dessicator.

Calcium Carbonate: Calcite was dissolved in hydrochloric acid, precipitated with ammonium carbonate and ammonium hydroxide. The precipitate was washed thoroughly with hot water, dried and stored in a bottle.

Ammonium carbonate, 10 per cent solution

Ammonium hydroxide, concentrated

Glaced paper

Nickel Crucibles

Ethyl Alcohol, 95 per cent of A. R. alcohol saturated with, and containing a slight excess of the tripple salt sodium uranyl zinc acetate. This was always made fresh and filtered prior to use as a washing agent.

Anhydrous Ether, it is important that this reagent be anhydrous.

Procedure: The soil sample (1g) was weighed, transferred into a crucible; ammonium chloride (1g) and calcium carbonate (4g) were added and mixed thoroughly. This was covered and heated at low temperature until ammonia fumes no longer escaped. Heating was continued for about 45minutes at a dull red-heat and then cooled. The fused mass was loosened with a little water, washed into a

beaker with water (5ml) and digested on a steam bath. The precipitate was filtered and washed with hot water.

The filtrate contains the chlorides of sodium, potassium, calcium and some magnesium and calcium hydroxide. The calcium was precipitated by adding ammonium carbonate solution and ammonium hydroxide at a boiling temperature, filtered and washed with hot water and then redissolved with a little hydrochloric acid. The precipitation and filtration were repeated as before and the filtrate added to the first. The combined filtrate was evaporated to drive off the ammonium salts. The residue was dissolved in water, digested on a steam bath, filtered and made to a volume of 100ml in a volumetric flask. This solution contained sodium and potassium with perhaps traces of calcium, magnesium and other salts.

The filtrate (25ml) was evaporated to dryness and water (1ml) and uranyl zinc acetate reagent (10ml) were added and mixed properly. The precipitate was allowed to stand overnight and then filtered through a weighed sintered glass crucible. The precipitate was washed 5 to 10 times with portions of uranyl zinc acetate reagent (2ml). The excess was removed by washing 5 times with portions of 95 per cent alcohol (2ml) saturated with the tripple salt and then washed with anhydrous ether to remove the alcohol. The ether was evaporated by drawing air through the

the crucible. The crucible was wiped clean with an alcohol moistened cloth, placed in a desiccator and weighed after one hour. The weight of the precipitate times 0.01442 is equal to the weight of the sodium.

.6 Determination of Potassium as Cobaltinitrite

Reagents

Trisodium cobaltinitrite, made for each determination (1g per 5ml of water).

Nitric acid, 1N

Nitric acid, 0.01N

Ethyl alcohol, 95 per cent

Procedure: The decomposition procedure has been described in section 2.3.5. To the filtrate (10ml) obtained from section was added 1N Nitric acid (1ml) and the sodium cobaltinitrite solution (5ml), mixed thoroughly and then allowed to stand for 2 hours at a temperature of about 15 - 20°. The precipitate was filtered. 0.01N HNO_3 was used to wash and transfer the precipitate completely from the beaker to the filter paper. The precipitate was washed ten times with 2ml portions of ethyl alcohol. This was evacuated until dry. The precipitate was dried at 110° for 1 hour, cooled in a desiccator and weighed. The potassium is 17.21 per cent of the precipitate.

2.7 Determination of Elements by Atomic Absorption Spectrophotometer
SP 1900

Procedure: The decomposition procedure has been described in section 2.3.5. The filtrate obtained was used for the determination of the different elements.

With the Unicam SP 1900 Atomic Absorption Spectrophotometer, the graphical method of calibration may be eliminated depending upon the concentration of the elements in solution. This is because of the scale expansion and curve correlation facilities while the digital read out and auto zero system enable element concentration to be displayed directly. This method together with graphical method were used. The expansion method was applied to metals with reasonably low concentrations. In this method only two standards were required, one with a concentration of the element of interest significantly above the estimated maximum concentration (higher standard) in the sample and the second (lower standard) containing half the concentration of the element of interest.

Ionization interference during the estimation of calcium and magnesium was eliminated by the use of lanthanum chloride (0.1 per cent) in both sample and standard solutions.

CHAPTER 3

3. RESULTS AND DISCUSSION

3.1 Introduction

In this Chapter, the analytical results obtained from experiments performed using the different techniques discussed in Chapter 1 are compiled. They are used in semi-quantitative analysis for obtaining probable minerals present using only the X-ray diffraction technique and also in a more precise quantitative (and qualitative) analyses using the results of all the techniques employed in this investigations, that is, glycol retention measurement, cation exchange capacity, X-ray diffraction analysis DTA, and the results of chemical analysis. The analyses of all the materials provided are given and discussed.

Additionally, the results obtained by other workers on similar materials have been considered, and the few results of their tests have been presented for comparison and inferences.

The analytical data for the different samples are given in Tables 1 (ethylene glycol retention), 2 (cation exchange capacity), 3 (qualitative X-ray analysis), 4 (semi-quantitative X-ray analysis), 5 (qualitative DTA results), 6 (quantitative DTA results), and 7 (chemical analyses). The results of other workers on a few similar materials have been tabulated in Appendices A - G.

Detailed analysis of the results and discussion follow below.

5.2 Ethylene Glycol Retention

Many organic compounds with a dipole character are adsorbed on the layer surfaces and probably on the edges of a clay analogous with the behaviour of water. The adsorption of organic compounds leads to organo-complexes of the clay (11). Ethylene glycol is commonly used. Table 1 lists the ethylene glycol retention values of all the samples tested as determined by the Dyal and Hendricks method (7). A glance at the results reveals that the Maiduguri Black Cotton soil has the highest glycol retention value (78.7mg g^{-1}).

The retention of ethylene glycol by soil samples is to a large extent due to the presence of certain clay minerals. Soils with predominantly non-swelling clay minerals such as Kaolinite usually retain less amount of ethylene glycol than those containing such swelling clay minerals as montmorillonite. The result is therefore not surprising since it will be shown that the Maiduguri Black Cotton soil contains a high proportion of montmorillonite while the concretionary lateritic soils with low ethylene glycol retention values contain significant concentration of Kaolinite.

As different clay minerals have different values of specific surface area, the amount of glycol retained under controlled conditions is used to aid in the quantitative determination of clay minerals. The quantity of glycol retained can be used in the estimation of the surface area of clays (52, 53, 54). These methods have shown that the higher the amount of glycol retained, the greater

Table 1

Ethylene Glycol Retention mg/g^{-1}

Sample	mg/g Soil
Maiduguri Black Cotton Soil	78.7
Bakura Soil	53.2
Wase Gidan Shehu Soil	63.5
Kongo Institute of Administration Soil	60.8
Kaduna Arewa Textile Soil	49.3
Zaria Concretionary Lateritic Soil	22.5
Akure Lateritic Soil	23.1
ABU Suleiman Hall Soil	50.2
ABU Teaching Hospital Soil	24.2
ABU Amina Hall Soil	23.6
ABU Student Centre Soil	24.2
ABU Conference Centre Soil	62.7
ABU JIslamic Centre Soil	23.4
ABU House Unit Area E Soil	23.9
Ilorin Test Clay Brick Sample	60.4

the surface area of the soil. This implies that the Naidupuri Black Cotton soil has the largest surface area with the concretionsary lateritic soils having the least; others following accordingly. These results are in agreement with those of other workers (55).

Most of the differences between clay minerals in properties such as water retention, plasticity or cohesion can be explained by the different values of surface area. This can also explain the high swelling and liquid limit of montmorillonite.

Rapid but less accurate determination of surface areas of soils can be made using the method. The effects of temperature and erratic evaporation are removed by carrying out experiments at constant temperature and pressure. The presence of organic matter likely to interfere with adsorption was removed by treatment with hydrogen peroxide.

There appears to be no published work on any of the Nigerian Soils investigated, so it is impossible to compare results. The difference between values obtained for pure kaolinite (Appendix A) and soil samples estimated to contain 100 per cent kaolinite (see Tables 1 and 6) could be attributed to the fact that soil is a complex mixture and its behaviour may not be easily compared with a pure clay sample.

4.3. Cation Exchange Capacity

The amount of negative charge which is equal to the quantity of exchangeable cations held i.e. the cation exchange capacity of the

clay, has been used to aid the qualitative and quantitative determination of clay minerals. Each clay mineral has characteristic range of values of cation-exchange capacity that can be used or that can serve as a clue to its identification.

The kind and number of exchangeable cations have an important influence on the behaviour of soils. The exchangeable cations are not all held in a layer right at the clay surface, but are present at some average distance from the surface. This leads to the phenomenon of diffuse-ion-layers whose interaction with adjacent particles gives an explanation of such properties as swelling, plasticity and water retention of clays (2). Ion exchange reactions are important as far as the properties and stability control of drilling muds and slurries are concerned. Ground water quality, underground waste disposal and pollutant transport through soils are all influenced by the ion exchange properties of the soils. As the composition of the exchange complex relative to that of the pure water is influenced by both temperature and the composition of the free water and as the mechanical properties are influenced by the adsorbed ion type suitable controls on laboratory test conditions are needed if properties are to be correctly measured.

The results of the cation exchange capacities of the different soil samples are tabulated in Table 2. A preliminary study to investigate the amount of organic matter in the samples indicated that the percent organic matter was negligible (< 0.01 per cent).

Table 2
Cation - Exchange Capacity of Samples

Sample	pH (H ₂ O)	CEC (meq/100g Soil)
Maiduguri Black Cotton Soil	4.5	41.9
Bakura Soil	6.5	9.8
Wase Gidan Shehu Soil	5.8	16.8
Kongo Institute of Administration Soil	6.4	14.6
Kaduna Arewa Textile Soil	6.2	8.2
Zaria Concretionary Lateritic Soil	4.7	4.2
Akure Lateritic Soil	4.3	3.9
ABU Suleiman Hall Soil	5.6	11.5
ABU Teaching Hospital Soil	4.9	9.3
ABU Amina Hall Soil	5.2	12.4
ABU Student Centre Soil	4.8	13.6
ABU Conference Centre Soil	4.7	22.8
ABU Islamic Centre Soil	6.4	8.4
ABU House Unit Area E Soil	6.7	3.4
Ilorin Test Clay Brick Sample	5.8	23.2

The pH (H_2O) of all the samples varied between 4.3 and 6.4 (Table 2). The Maiduguri Black Cotton soil had the highest C.E.C. (41.9) with Akure soil having the lowest value of 3.9.

The discovery that soils have the ability of exchanging cation with solutions containing other cations was the result of careful observation (20). The stacking of silica, gibbsite and brucite sheet (see Appendix G) to form the basic clay mineral layer is such that a single plane of atoms is common to both the tetrahedral and octahedral sheets. Thus bonding between these sheets is very strong and of primary valence type. On the other hand, the bonds holding the unit cell layers together may be of several type and may be sufficiently weak that the physical and chemical behaviour of the clay may be influenced by the response of the bonds to changes in environmental conditions. Isomorphous substitution in all the clay minerals with the possible exception of the kaolinites, gives clay particles a net negative charge. To preserve electrical neutrality, cations are attracted and held on the clays between the unit cells.

From the results obtained, it followed that there is no single capacity value that is characteristic of a given group of clay minerals. These agreed with the conclusions of other workers (1, 11), that because of a wide variety of factors influencing cation exchange capacities of soils and clays, results are not always characteristic of any given group and therefore results are always

expressed in ranges.

However, the results obtained for the Bakura, Kongo, Kaduna, Zaria, Akure, Suleiman Hall, Teaching Hospital, Amina Hall, Student Centre, Islamic Centre and Area E soil samples are characteristic of kaolinite containing soils. The low C.E.C. value may be attributed to the structural composition of kaolinite. In kaolinite, there are opposing layers of oxygen and hydroxyl, or hydroxyl and hydroxyl. This gives rise to hydrogen bonding between layers, which provides a fairly strong bond that will not separate in the presence of water but can still provide good cleavage. Thus ions are not easily exchanged with environmental ions. The higher cation exchange capacity values in the montmorillonite containing samples, Maiduguri, Wase, Conference Centre soils, and the Ilorin test clay brick further confirms this. The higher values of C.E.C. in montmorillonite may be attributed to the structure of the mineral. The interlayer cations in montmorillonite hydrate and the hydration energy overcomes the attractive forces between unit layers so that ions are easily lost to the environment. This could be possible because the surface charge density in montmorillonite is moderate (1), so that the silicate layers may readily take up polar molecules from the environment and balancing cations may hydrate, resulting in a separation of layers. The expansion of montmorillonite may therefore be attributed to this effect.

The C.E.C. values obtained cannot be adequately used for quali-

tative determinations by comparing them with those of known pure minerals since each sample consists of many mineral groups which can influence each other. However, it appears that these values can be used in quantitative determinations. The results obtained cannot be readily compared, since C.E.C. for a given mineral type is influenced by several factors such as pH, organic matter content, temperature etc. (6, 12). Capacity values are only comparable when they have been obtained by similar standard procedures on some materials under comparable conditions.

5.4 X-Ray Analysis

Kaolinite has a first order basal spacing $d(001)$ of about 7.2\AA which is insensitive to drying or moderate heating. Kaolinite minerals are destroyed by heating to $500 - 600^\circ$. The other clay minerals are not. Hydrated Halloysite has a basal spacing of 10\AA , which collapses irreversibly to 7\AA on drying at 110°C . Dehydrated halloysite is similar to kaolinite and can be differentiated only by the use of electron microscope when dehydrated halloysite has a tubular morphology. All the kaolinite minerals retain their characteristic spacing $d(001)$ in the presence of polar liquid e.g. glycol. The illites are characterised by a basal spacing $d(001)$ of about 10\AA which remains fixed both in the presence of polar liquid and after drying.

The expensive character of smectite, (montmorillonoid group of minerals), provides the basis for their positive identification.

Table 3
Qualitative X-Ray Analysis Of The Samples

Sample/Treatments	Diffraction Spacing d (Å)	Minerals Inferred
<u>Malduguri Soil</u>		
1. ADPO	15.41, 7.19, 3.57 3.34	Montmorillonite and Kaolinite
2. GPO	17.49, 15.19, 7.49 3.56	Kaolinite and Montmorillonite
3. ADPO Heated to 600° for 1 hour	17.49, 9.96	Montmorillonite and Kaolinite
<u>Bokura Soil</u>		
1. ADPO	16.99, 9.83, 7.14 3.56, 3.33, 10.2	Montmorillonite Kaolinite, Illite
2. GPO	15.67, 17.49, 7.14, 10.2 3.14, 3.56, 3.34	Montmorillonite Kaolinite, Illite
3. ADPO Heated to 600° for 1 hour	9.61, 10.2	Montmorillonite Kaolinite
<u>Wase Gidan Shehu Soil</u>		
1. ADPO	15.78, 7.17, 4.27 3.57	Montmorillonite Kaolinite, Illite
2. GPO	17.33, 7.14, 3.57	Montmorillonite Kaolinite
3. ADPO (at 600° for 1 hour)	15.99, 9.94, 4.27, 3.36	Montmorillonite Kaolinite

table 3 contnd.

Sample/Treatments	Diffraction Spacing d (Å ⁰)	Minerals Inferred
<u>Kongo Soil</u>		
1. ADPO	15.78 10.28, 7.17, 3.57, 3.34	Montmorillonite Kaolinite, Illite and Quartz
2. GPO	17.33 9.94, 7.17, 3.57, 3.34	Montmorillonite, Illite Kaolinite and Quartz
3. ADPO (heated at 600° for 1 hour)	9.94, 3.57, 3.34	Montmorillonite, Kaolinite, Quartz
<u>Kaduna Arcwa Soil</u>		
1. ADPO	17.14, 3.57, 10.21	Montmorillonite, Kaolinite and Illite
2. GPO	17.33, 7.14, 3.57, 10.21	Montmorillonite, Kaolinite and Illite
3. ADPO (heated at 600° for 1 hour)	17.67, 9.94, 10.21	Montmorillonite, Kaolinite and Illite
<u>Zaria Concretionary Soil</u>		
1. ADPO	7.20, 4.16, 3.58	Kaolinite
2. GPO	7.20, 4.17, 3.57	Kaolinite
3. ADPO (heated at 600° for 1 hour)	All strong reflections disappeared. By comparison with reflections of known minerals only kaolinite is indicated present.	Kaolinite

Sample/Treatments	Diffraction Spacing d (Å)	Mineral Inferred
<u>Akure Soil</u>		
1. ADFO	7.17, 4.13, 3.58	Kaolinite
2. GPO	7.14, 4.13, 3.58	Kaolinite
3. ADFO (heated at 600° for 1 hour)	(As in the Zaria Soil above)	Kaolinite
<u>ABU Suleiman Hall Soil</u>		
1. ADFO	15.41, 10.21, 9.71, 7.19, 3.54	Montmorillonite Kaolinite, Illite
2. GPO	17.49, 7.19, 3.56	Montmorillonite, Illite Kaolinite
ADFO (heated at 600° for 1 hour)	15.41, 9.94, 3.56, 10.21	Montmorillonite, Illite Kaolinite
<u>ABU Teaching Hospital</u>		
1. ADFO	7.20, 4.61, 3.58	Kaolinite
2. GPO	7.20, 4.17, 3.57	Kaolinite
3. ADFO (heated at 600° for 1 hour)	(As in the Zaria sample)	Kaolinite
<u>ABU Amine Hall Soil</u>		
1. ADFO	7.20, 4.16, 3.58	Kaolinite
2. GPO	7.20, 4.12, 3.53,	Kaolinite
3. ADFO (heated at 600° for 1 hour)	(As in the Zaria sample)	Kaolinite

Sample/Treatments	Diffraction Spacing d (Å)	Minerals Inferred
<u>ABU Student Centre Soil</u>		
1. ADFO	7.20, 4.16, 3.58	Kaolinite
2. GPO	7.18, 4.15, 3.57	Kaolinite
3. ADFO (heated at 600° for 1 hour)	(As in the Zaria Sample)	Kaolinite
<u>ABU Conference Centre Soil</u>		
1. ADFO	15.13, 17.49, 7.19, 3.56 3.33	Montmorillonite
2. GPO	17.67, 9.94, 7.14, 3.33	Montmorillonite, Quartz, Kaolinite
3. ADFO (heated at 600° for 1 hour)	17.33, 9.94, 3.35, 3.33	Montmorillonite, Quartz, Kaolinite
<u>ABU Islamic Centre Soil</u>		
1. ADFO	7.21, 4.15, 3.57	Kaolinite
2. GPO	7.20, 4.15, 3.58	Kaolinite
3. ADFO (heated at 600° for 1 hour)	(As in the Zaria Sample)	Kaolinite
<u>ABU Area E Soil</u>		
1. ADFO	7.21, 4.15, 3.57	Kaolinite
2. GPO	9.94, 4.15, 3.58	Kaolinite
3. ADFO (heated at 600° for 1 hour)	(As in the Zaria Sample)	Kaolinite
<u>Ilorin Test Clay Brick</u>		
1. ADFO	16.94, 9.83, 7.14, 3.58	Montmorillonite Kaolinite
2. GPO	17.15, 9.94, 7.14, 3.56	Montmorillonite Kaolinite
3. ADFO (heated at 600° for 1 hour)	17.21, 9.94, 4.27	Montmorillonite Kaolinite

1. ADFO = Air Dried Preferred Orientation 2. GPO = Glycerol Preferred Orientation 60°
 2. ADFO = Air Dried Preferred Orientation Heated to 600° for 1 hour.

When air dried, those minerals may have a basal spacing of 12 to 15A⁰. After treatment with ethylene glycol or glycol, they expand to a d(001) value of 17 to 18A⁰, when heated to about 600⁰, the d(001) drops to about 10A⁰ as a result of the removal of interlayer water (1).

Chlorite minerals have a basal spacing fixed at 14A⁰ because of strong ordering of the interlayer complex. This reflection is often weak and since the higher orders coincide with the X-ray pattern for kaolinite, identification may be different. The fact that chlorite is destroyed when treated with warm acid and kaolinite is not affected, and that kaolinite is destroyed on heating to 600⁰ but chlorite may not be affected are useful for distinguishing the two clay mineral types (1).

In most soils, by far the most abundant non-clay mineral is quartz, with small amounts of feldspar and mica sometimes present. Quartz has a characteristic basal spacing of 4.26A⁰. It also has reflective spacings of 3.34A⁰, 2.46, 2.28A⁰, etc. The spacing remains fixed both in the presence of polar liquids and after drying.

The X-ray diffraction pattern of a powdered sample of the soils depends on the crystal structure of the clay as earlier mentioned. As noted above, the different clay minerals are characterised by first order basal reflections d(001) at 7, 10 or 14A⁰ (see Appendix C). For positive identification of specific mineral groups certain

pretreatments are ordinarily required and these had been discussed in section 2.3.3.

The results of the X-ray analyses is tabulated in Table 3, showing the different minerals present in the soil samples while Table 4 lists the result of the semi-quantitative analyses. The criteria for analyses are based on the data provided in Appendices C, D, E and F. The results obtained in Table 4 were calculated as discussed in section 1.3. Traces of quartz were found in three samples, namely Kongo, Kaduna Arewa and Ahmadu Bello University Conference Centre soils.

Results using the four sets of calculations on all the samples were corrected to two significant figures since this appears to be the common practice. As can be seen from Table 4, all the samples contain relatively high amounts of kaolinite excluding Maiduguri Black Cotton and Wase Gidan Shehu soils. In some samples, montmorillonite were present being exceedingly high in the Maiduguri Black Cotton soil whereas illite was present in only very few soils. Methods based on peak area measurement appear to give high percentages of kaolinite plus chlorite with no soil sample having less than 50 per cent. The use of multiplier 3 rather than 4 appeared to give lower values in all cases (Table 4).

Examination of the tabulated values (Table 4) shows that the different procedures revealed different trends between adjacent samples. In order to clearly reveal these changes, the results

may need a statistical analysis, ^{but} because the semi-quantitative results were supplemented by quantitative DTA determinations, ^{this} was not considered necessary.

Apart from lack of agreement of results due to methods of quantification employed, other variables which could have affected the results include, structural and chemical variations between mineral groups and within mineral species. Operator error and random errors in sub-sampling can also introduce discrepancies in the relative amounts of clay minerals present in a given soil sample. Slide preparation technique can also be critical in allowing segregation of the mineral species (56, 57, 58)

Because of the many variables affecting the results, there are some doubts as to the attainment of true quantification. It is however, hoped that with the use of four different methods of those presently in use for calculation of relative amounts of clay minerals from the same diffractograms, a fair estimation has been achieved.

5 DTA Analysis

The results of different thermal analyses are generally presented as a plot of the difference in temperature between sample and inert material (ΔT) versus temperature ($T^{\circ}C$). The analysis of test results is mainly the comparison of the sample curve with those of known materials so that each deflection can be accounted for. The shape, size and temperature of the thermal breaks are affected not only by the heats of reaction but also by various

Quantitative Result Of X-Ray Analysis

Method	1	2	3	4	Relative Amount of Quartz In Sample
Maiduguri Black Cotton Soil	M I K + C 30 - 20	M I K + C 73 - 27	M I K + C 71 - 29	M I K + C 70 - 22	-
Bakura Soil	15 12 73	13 6 71	8 4 88	13 11 76	-
Wase Gidan Shehu Soil	64 - 36	55 - 45	57 - 43	62 - 38	-
Kongo Institute of Administration Soil	3 10 87	7 3 90	5 7 88	2 15 83	tr
Kaduna Arewa Textile Ltd. Soil	5 12 83	6 15 79	4 5 91	3 10 87	M
Zaria Concretionary Lateritic Soil	- - 100	- - 100	- - 100	- - 100	-
Akure Lateritic Soil	- - 100	- - 100	- - 100	- - 100	-
ABU Suleiman Hall Soil	22 6 72	14 5 81	17 8 75	21 7 72	-
ABU Teaching Hospital Soil	- - 100	- - 100	- - 100	- - 100	-
ABU Amina Hall Soil	- - 100	- - 100	- - 100	- - 100	-
ABU Student Centre Soil	- - 100	- - 100	- - 100	- - 100	-
ABU Conference Centre Soil	45 - 55	38 - 62	42 - 59	43 - 57	tr
ABU Islamic Centre Soil	- - 100	- - 100	- - 100	- - 100	-
ABU House Unit Area E Soil	- - 100	- - 100	- - 100	- - 100	-
Ilorin Test Clay Brick Sample	48 - 52	36 - 64	38 - 62	44 - 56	-

tr = trace
M = Moderate

instrumental factors such as rate of heating, nature of thermocouple, size, shape and nature of sample holder and other details of the instrument itself (5). There may be some difficulty in selection of reference standards since the thermal behaviour of soils may differ from that of pure deposits.

Generally, as far as characteristic thermograms are concerned, the clay minerals show an endothermic reaction between 100° and 200° as the adsorbed water is lost - Dehydration, also between about 500° to 1000° as the crystal lattice water is being driven off in the form of hydroxy ions - Dehydroxylation, and an exothermic reaction between 800° and 1000° as new crystals are formed from amorphous materials or from old crystals destroyed - Crystallisation.

The common non-clay minerals in soils that give reactions with large thermal peaks are quartz, carbonates and free oxides such as gibbsite, brucite and goethite. Quartz has a phase change from α to β for (reversible) at 573° . The peak for the quartz phase change is sharp and the amplitude is almost directly proportional to the amount of quartz present. The carbonates give very large endothermic peak between 800° and 1000° and the oxides have an endothermic peak between about 250° and 450° . Some of these diagnostic data appear in Appendices A and C.

For the quantitative analysis, theoretically it had been shown that the area of the reaction peak can be taken as a measure of the

Table 5

Qualitative DTA Peaks Identified For The Samples

Sample	Endothermic Peaks °C	Exothermic Peaks °C	Minerals Inferred
Maiduguri Soil	135 - 160 540 - 620	930 - 982	Montmorillonite Kaolinite
Bakura Soil	548 - 620 125 - 152	930 - 982 876 - 920	Kaolinite Montmorillonite Illite
Wase Gidan Shehu Soil	120 - 148 540 - 623	930 - 982	Montmorillonite Kaolinite
Kongo Soil	120 - 146 541 - 620	928 - 980	Montmorillonite Kaolinite
Kaduna Arewa Soil	130 - 186 543 - 560	930 - 979	Montmorillonite Kaolinite
Zaria Concretionary Soil	492 - 622	948 983	Kaolinite
Akure Soil	492 - 621	946 - 979	Kaolinite
Suleiman Hall Soil	120 - 180 468 - 562	951 - 976	Montmorillonite Kaolinite
ABU Teaching Hospital Soil	472 - 590	942 - 979	Kaolinite
AMina Hall Soil	482 - 565	938 - 981	Kaolinite
Student Centre	482 - 564	942 - 981	Kaolinite
Conference Centre Soil	122 - 146 483 - 561	946 - 982	Montmorillonite Kaolinite
Islamic Centre Soil	483 - 562	946 - 982	Kaolinite
Area E Soil	490 - 563	943 - 983	Kaolinite
Ilorin Test Clay Brick	120 - 149 487 - 563	946 - 982	Montmorillonite Kaolinite

values, although their compositions are somehow different as shown by the DTA results. From the results it is observed that when kaolinite is present along with illite and montmorillonite, the ethylene glycol retention and exchange capacities are increased. This could be due to some structural differences. In illite, some of the aluminium is replaced in the silica sheets. The resulting charge deficiency is balanced in part by potassium ions between mineral layers (Appendix G). Since the size of the potassium ion is such that it fits into the holes formed by the bases of the silica tetrahedral in the silica sheet, it provides a strong bond between mica layers. It could then be that when illite, kaolinite and montmorillonite are present together these bonds are not so strong as in illite alone, present in a sample, due probably to some interaction, hence the high C.E.C values and high ethylene retention values.

A distinct advantage of the DTA method is the rapidity with which a curve can be obtained. A curve covering the range 0 to 1000° can be obtained in 100 minutes at a heating rate of 10° per minute - commonly used range. Many factors affect DTA results. The temperature range investigated, for example, may be too restricted to demonstrate distinct differences. This could have been the reason for the loss in amount of minerals detected in the Teaching Hospital and Area E samples. It is most probable that these samples contain some other minerals which cannot be detected under

Table 6
Quantitative DTA Analysis Of Minerals In Soil Samples

	Kaolinite Kaolinite	Per Cent		Chlorite Chlorite	Illite Illite	Relative Amount of Quartz
Maiduguri Black Cotton Soil	17.6	83.4	-	-	-	-
Bakure Soil	65.2	18.5	-	16.3	-	-
Wase Gidan Shehu Soil	32.8	67.2	-	-	-	-
Kongo Institute of Administration Soil	80.4	5.7	-	13.7	trace	trace
Kaduna Arewa Textile Ltd Soil	79.5	6.1	-	14.1	trace	trace
Zaria Concretionary Lateritic Soil	100	-	-	-	-	-
Akure Lateritic Soil	100	-	-	-	-	-
ABU Suleiman Hall Soil	74.8	23.3	-	1.9	-	-
ABU Teaching Hospital Soil	98.3	-	-	-	-	-
ABU Amine Hall Soil	100	-	-	-	-	-
ABU Student Centre Soil	100	-	-	-	-	-
ABU Conference Centre Soil	52.5	47.3	-	-	trace	trace
ABU Islamic Centre Soil	100	-	-	-	-	-
ABU House Unit Area E Soil	97.4	-	-	-	-	-
Ilorin Test Clay Brick Sample	50.6	49.4	-	-	-	-

Table 6
Quantitative DTA Analysis Of Minerals In Soil Samples

	Kaolinite Kaolinite	Per Cent		Chlorite Chlorite	Illite Illite	Relative Amount of Quartz
Maiduguri Black Cotton Soil	17.6	83.4	-	-	-	-
Bakure Soil	65.2	18.5	-	16.3	-	-
Wase Gidan Shehu Soil	32.8	67.2	-	-	-	-
Kongo Institute of Administration Soil	80.4	5.7	-	13.7	trace	trace
Kaduna Arewa Textile Ltd Soil	79.5	6.1	-	14.1	trace	trace
Zaria Concretionary Lateritic Soil	100	-	-	-	-	-
Akure Lateritic Soil	100	-	-	-	-	-
ABU Suleiman Hall Soil	74.8	23.3	-	1.9	-	-
ABU Teaching Hospital Soil	98.3	-	-	-	-	-
ABU Amine Hall Soil	100	-	-	-	-	-
ABU Student Centre Soil	100	-	-	-	-	-
ABU Conference Centre Soil	52.5	47.3	-	-	trace	trace
ABU Islamic Centre Soil	100	-	-	-	-	-
ABU House Unit Area E Soil	97.4	-	-	-	-	-
Ilorin Test Clay Brick Sample	50.6	49.4	-	-	-	-

the temperature range used. A wider temperature range may therefore be necessary in diagnostic work. The small loss in amount of clay mineral in other samples could be due to the presence of quartz since these were indicated in very small amounts.

The curve produced by DTA is also dependent on factors relating to equipment and other factors mentioned earlier. These factors could contribute to making results of two laboratories to exhibit marked differences, thus rendering identification difficult. Even with these difficulties, however, the technique has proved reliable within the limits of our experimental conditions, in providing a data which has agreed within the range 0 to 3.6 ± 1 per cent for kaolinite and montmorillonite and results of the X-ray semi-quantitative analyses.

Sensitivity coupled with simplicity of results and sophistication in their production have contributed to a successful diagnostic work.

6 Chemical Analysis

The results of chemical analysis of all the soil samples investigated are presented in Table 7, as determined by means of atomic absorption spectrophotometer available in the Department and other techniques as indicated. From these results, apart from silicon which has remained relatively high in all the soil samples, the concentrations of other elements, Na, Ca, Zn, Cu, Mn, etc. have been very small, being zero in some cases (Table 7). Aluminium is

Table 7

Fusion Analysis Of Soil Samples (Weight Per Cent)

Sample	Compound or Element	Weight Per Cent		
		Method 1	Method 2 Atomic Absorption Spectroscopy (AAS)	Mean
1. <u>Maiduquri Sample</u>	Ti	0.42	0.40	0.41
	Pb	-	0.24	0.24
	Al	10.49	11.21	10.85
	Cu	-	0.00	0.00
	Fe	0.00	0.00	0.00
	Mn	0.07	0.03	0.04
	Mg	0.48	0.52	0.50
	Zn	-	0.02	0.02
	Ca	1.35	1.35	1.35
	Na	0.21	0.17	0.19
	K	0.54	0.56	0.55
	Cr	-	0.11	0.11
	SiO ₂	51.8	50.7	51.25
2. <u>Bakura Sample</u>	Ti	0.31	0.32	0.32
	Pb	-	0.21	0.21
	Al	6.11	6.23	6.17
	Cu	-	0.00	0.00
	Fe	0.08	0.06	0.07
	Mn	0.11	0.15	0.09
	Mg	0.36	0.41	0.39
	Zn	-	0.00	0.00
	Ca	1.44	1.48	1.46
	Na	0.11	0.10	0.11
	K	0.22	0.24	0.23
	Cr	-	0.05	0.05
	SiO ₂	47.4	46.9	47.15
3. <u>Wase Gidan Shehu Sample</u>	Ti	0.11	0.14	0.13
	Pb	-	0.13	0.14
	Al	8.21	7.94	8.08
	Cu	-	0.00	0.00
	Fe	0.05	0.05	0.05
	Mn	0.51	0.54	0.53
	Mg	0.54	0.58	0.56
	Zn	-	0.00	0.00
	Ca	0.80	0.68	0.74
	Na	0.20	0.18	0.19
	K	0.42	0.46	0.44
	Cr	-	0.12	0.12
	SiO ₂	43.4	43.6	43.50

table 7 cont'd.

Sample	Compound or Element	Weight Per Cent		
		Method 1	Method 2 Atomic Absorption Spectroscopy (AAS)	Mean
4. <u>Kongo Sample</u>	Ti	1.06	1.11	1.09
	Pb	-	0.05	0.05
	Al	9.20	8.75	8.98
	Cu	-	0.01	0.01
	Fe	0.34	0.25	0.30
	Mn	0.01	0.02	0.02
	Mg	0.36	0.40	0.38
	Zn	-	0.01	0.01
	Ca	0.05	0.03	0.04
	Na	0.15	0.16	0.15
	K	0.45	0.48	0.47
	Cr	-	0.00	0.00
	SiO ₂	45.2	44.8	45.00
5. <u>Kaduna Arewa Sample</u>	Ti	0.51	0.49	0.50
	Pb	-	0.21	0.21
	Al	5.10	5.21	5.16
	Cu	-	0.02	0.02
	Fe	0.00	0.00	0.00
	Mn	0.05	0.05	0.05
	Mg	0.22	0.25	0.24
	Zn	-	0.04	0.04
	Ca	0.12	0.00	0.07
	Na	0.12	0.10	0.11
	K	0.38	0.40	0.39
	Cr	-	0.10	0.10
	SiO ₂	43.8	42.4	43.10
6. <u>Zaria Concre- tionary Sample</u>	Ti	0.13	0.15	0.14
	Pb	-	0.00	0.00
	Al	5.50	5.55	5.56
	Cu	-	0.01	0.01
	Fe	21.20	21.31	21.26
	Mn	0.02	0.04	0.03
	Mg	0.06	0.08	0.07
	Zn	-	0.01	0.01
	Ca	0.06	0.08	0.07
	Na	0.21	0.22	0.22
	K	0.21	0.23	0.22
	Cr	-	0.00	0.00
	SiO ₂	48.8	49.2	49.00

table 7 cont'd.

Sample	Compound or Element	Weight Per Cent		
		Method 1	Method 2 Atomic Absorption Spectroscopy (AAS)	Mean
7. Akure Sample	Ti	0.11	0.15	0.13
	Pb	-	0.02	0.02
	Al	4.90	4.87	4.89
	Cu	-	0.01	0.01
	Fe	16.48	17.30	16.89
	Mn	0.00	0.00	0.00
	Mg	0.21	0.23	0.22
	Zn	-	0.01	0.01
	Ca	0.11	0.09	0.10
	Na	0.18	0.16	0.17
	K	0.12	0.13	0.13
	Cr	-	0.00	0.00
	SiO ₂	46.9	45.3	46.10
8. ABU Suleiman Sample	Ti	0.15	0.18	0.17
	Pb	-	0.05	0.05
	Al	6.10	6.20	6.15
	Cu	0.00	0.00	0.00
	Fe	3.21	3.14	3.18
	Mn	0.14	0.12	0.13
	Mg	0.26	0.32	0.29
	Zn	-	0.03	0.03
	Ca	0.05	0.04	0.05
	Na	0.21	0.18	0.20
	K	0.25	0.28	0.27
	Cr	-	0.13	0.13
	SiO ₂	43.2	43.6	43.40
9. ABU Teaching Hospital Sample	Ti	1.15	1.30	1.23
	Pb	-	0.12	0.12
	Al	5.60	5.40	5.50
	Cu	-	0.02	0.02
	Fe	9.82	10.20	10.02
	Mn	0.05	0.03	0.04
	Mg	0.21	0.25	0.23
	Zn	-	0.00	0.00
	Ca	0.14	0.21	0.18
	Na	0.15	0.15	0.15
	K	0.23	0.25	0.24
	Cr	-	0.00	0.00
	SiO ₂	44.6	43.9	44.25

table 7 cont'd.

Sample	Compound or Element	Weight Per Cent		
		Method 1	Method 2 Atomic Absorption Spectroscopy (AAS)	Mean
1. <u>ABU Amine Hall Sample</u>	Ti	1.21	1.25	1.24
	Pb	-	0.20	0.20
	Al	6.34	6.24	6.29
	Cu	0.00	0.00	0.00
	Fe	3.14	4.22	3.68
	Mn	0.12	0.13	0.13
	Mg	0.19	0.22	0.21
	Zn	-	0.05	0.05
	Ca	0.21	0.21	0.21
	Na	0.20	0.18	0.19
	K	0.31	0.35	0.33
	Cr	-	0.11	0.11
	SiO ₂	46.2	46.7	46.45
1. <u>ABU Student Centre Sample</u>	Ti	0.92	1.02	0.97
	Pb	-	0.11	0.11
	Al	5.20	4.93	5.07
	Cu	-	0.12	0.12
	Fe	1.60	1.62	1.70
	Mn	0.00	0.00	0.00
	Mg	0.40	0.44	0.42
	Zn	-	0.002	0.002
	Ca	0.03	0.05	0.04
	Na	0.14	0.18	0.16
	K	0.34	0.36	0.35
	Cr	-	0.00	0.00
	SiO ₂	44.3	44.1	44.05
2. <u>ABU Conference Centre Sample</u>	Ti	1.31	1.21	1.25
	Pb	-	0.20	0.20
	Al	8.60	8.46	8.53
	Cu	-	0.11	0.11
	Fe	0.21	0.32	0.27
	Mn	0.16	0.18	0.17
	Mg	0.48	0.49	0.47
	Zn	-	0.05	0.05
	Ca	1.21	1.21	1.21
	Na	1.10	1.12	1.12
	K	0.40	0.42	0.41
	Cr	-	0.00	0.00
	SiO ₂	46.2	45.9	46.05

table 7 cont'd.

Sample	Compound or Element	Weight Per Cent		
		Method 1	Method 2 Atomic Absorption Spectroscopy (AAS)	Mean
13. <u>ABU Islamic Centre</u>	Ti	0.46	0.48	0.47
	Pb	-	0.13	0.13
	Al	7.23	7.21	7.22
	Cu	-	0.05	0.05
	Fe	0.85	0.93	0.89
	Mn	0.05	0.12	0.09
	Mg	0.02	0.04	0.03
	Zn	-	0.002	0.002
	Ca	0.08	0.06	0.07
	Na	0.22	0.20	0.21
	K	0.46	0.50	0.48
	Cr	-	0.10	0.10
	SiO ₂	43.2	43.2	43.20
	14. <u>ABU Area E</u>	Ti	0.11	0.13
Pb		-	0.10	0.10
Al		5.58	5.47	5.53
Cu		-	0.00	0.00
Fe		22.52	22.66	22.59
Mn		0.03	0.02	0.03
Mg		0.02	0.04	0.03
Zn		-	0.00	0.00
Ca		0.05	0.07	0.06
Na		0.30	0.34	0.32
K		0.58	0.57	0.58
Cr		-	0.00	0.00
SiO ₂		47.3	47.2	47.25
15. <u>Ilorin Test Clay Brick</u>		Ti	0.20	0.21
	Pb	-	0.10	0.10
	Al	6.58	6.49	6.54
	Cu	-	0.02	0.02
	Fe	0.35	0.41	0.38
	Mn	0.00	0.00	0.00
	Mg	0.15	0.18	0.17
	Zn	-	0.01	0.01
	Ca	0.14	0.15	0.15
	Na	0.14	0.16	0.15
	K	0.38	0.40	0.39
	Cr	-	0.05	0.05
	SiO ₂	48.0	48.3	48.15

Method I

- (i) Gravimetric Method (Ti, Al, Fe, SiO₂)
- (ii) Periodate Method (Mn)
- (iii) Ammonium Phosphate Method (Mg)
- (iv) Oxalate Method (Ca)
- (v) Uranyl Zinc Acetate Method (Na)
- (vi) Cobaltinitrite Method (K)

also present to a reasonable level in all samples whereas there is a non existence of iron in the Maiduguri Black Cotton and Kaduna Arewa Textile Ltd., soils. The presence or absence of any particular element is of course dependent on the clay minerals present in a particular soil. For example, as could be expected, the lateritic soils (Zaria and Akure samples) have been seen to contain significant amounts of iron.

The fairly high aluminium contents of samples containing montmorillonite compared to soils containing kaolinite could be due to structural differences, where aluminium normally replaces silicon in the silica sheet of montmorillonite (1). The theoretical composition of montmorillonite in the absence of lattice substitution is $(OH)_4Si_6Al_4O_{20}^{2-}$ (interlayer) H_2O , hence it is not surprising that soils containing montmorillonite clay minerals have shown higher aluminium contents.

Magnesium appears to have been fairly constant except for the Zaria concretionary lateritic and Ahmadu Bello University House unit area E soils. This result is in agreement with the work reported by Ojunuba (43). The significant difference in the magnesium content observed compared to other samples somehow agrees with Lombin and co-workers (59) suggestions that the magnesium status of Nigerian soils is a function of parent materials and organic matter, the latter being governed by climate and vegetation. The Akure

lateritic soils thus contains a higher amount of magnesium than the Zaria lateritic soils since the former is located in the forest zones of Nigeria. The relatively higher concentrations of magnesium in the Kongo, Teaching Hospital and the Conference Centre soils could probably be attributed to constant burning of vegetation around the location of the samples.

Montmorillonite containing samples contain higher concentration of calcium. This is possibly due to the fact that calcium-bound montmorillonite is more stable than for example, monovalent ion (e.g. Na)-bound montmorillonite (60).

Since anhydrous mica (illite) minerals are the only minerals commonly found in clay size fractions of soils that contain potassium in their structure, a knowledge of the potassium, hence potassium oxide (K_2O) content can aid in both qualitative and quantitative determination of illite.

From the results obtained for potassium, it can be argued that none of the soil samples contains illite as earlier deduced from the results of other methods of analysis. It is however possible that illite might be present in the samples indicated (Table 6) but that there might have been interlayer cations other than potassium.

3.7 General Discussion

The present analytical study has tried to identify both clay mineral contents and elemental constituents of some Nigerian soils. The type of clay minerals present in a particular soil plays an important role in the determination of some behaviour in expansive and non-expansive soils. Of the three types of clay minerals - illite, kaolinite and montmorillonite detected in the samples, the latter possesses the ability to swell most. The swelling potential of expansive clay minerals is dependent upon the crystal lattice structure, the structure of the clay mass and the cation exchange capacity of the mineral (61).

The findings from these analyses could be of economic importance. As mentioned above, kaolinite minerals do not expand to any appreciable extent that could cause damage to different structural applications. (see Appendix G), due to the stable structural composition. Majority of the samples analysed showed high percentages of this mineral and the inference that may be drawn from this is that the 'status' of these soils in terms of stability, as a construction or foundation material is good (1) and would be of valuable economic importance to construction engineers and industrialists who are interested in clay brick industry. Although montmorillonite containing soils could nevertheless be used like the kaolinite, it poses some important economic problems. Such problems will be mentioned and suggestions would be made as to what

precautions would be taken in using such expansive soils as a construction material.

Documented evidence of the existence of problems associated with expansive clay soils is not isolated but world-wide, having occurred in such places as Africa, Australia, India, South America, United States, as well as regions of Canada (62). The problems with foundations on, and building with expansive soils have included heaving, cracking and break up of pavements, building foundations, slab-on-grade members, channel and reservoir linings. The costs of these damages in the United States alone amount to some \$2.3 billion annually, more than twice the damage from floods, tornadoes, hurricanes and earthquakes (62).

Structures constructed on expansive clays induce heave from a variety of reasons - shrinkage from the reduction of moisture caused by evaporation or evapo-transpiration of vegetation, and the subsequent increase in soil moisture. Environmental and local conditions of a particular area in which expansive soils are located play an important role in the behaviour of such soils. The local conditions include breakage of water drains and pipes, poor drainage of surface waters, local evaporation from heated areas such as fire places, boilers and furnaces. Environmental factors include frequency of rainfall, rate of evaporation along with the depth of expansive clay and the activity of clay under these conditions (63).

Previous construction procedures for small structures such as single family residential buildings in Nigeria were based primarily on observations and local experience, often without adequate consideration of the soil characteristics. Neglect of these characteristics and properties is reflected in the numerous structural damages in many parts of the country. Correlation between these damages with incidence of expansive soils and adverse climatic conditions is not too surprising. However, this should not pose a dreadful challenge since after careful analyses, and the mineralogical composition of the soil is known, steps can be taken to minimise occurrences of adverse damages to structures.

Swell potential leading to expansion and consequent heaving of foundation soils and structures depend on the following parameters (64).

1. thickness of the clay minerals strata
2. surcharge of load (overburden)
3. water table depth
4. soil moisture suction
5. air-entry characteristics
6. 6. horizontal or vertical stress in the soil
7. the amount of activity by clay (e.g. cation exchange)
8. depth and nature of seasonal moisture change
9. leakage of water from sewer lines
10. soil density
11. Time.

The composition of any particular soil sample can be used by a construction engineer for the determination of other factors. These factors can be determined using four tests - free swell index, Atteberg's limits, colloidal content and consolidation test. Of these four tests, the free swell index appears to be the most critical in determining swell potential, since its value depends on the mineral type and the amount present in the soil, which then accounts for all other factors (65); hence identification and quantification is a critical factor to the construction engineer.

After careful identification and quantification of the clay mineral type, decision can be taken regarding modifications of the soil before any construction work is carried out with or on the soil. Modifications generally involves stabilisation of the clay minerals if it is known to be expansive or mixture of expansive and non expansive type.

There are a number of technical operations which can be used to minimise heave in a particular expansive soil. These methods may include compaction control, prewetting, maintenance of constant water content and chemical and electro-osmotic stabilisation techniques. Any of these methods may be applicable depending on soil conditions, type of construction material and accessibility of equipment at the construction site. The success of any stabilisation

technique depends on a consideration of the applications and limits of that particular technique.

1. Prewetting - the purpose of prewetting is to allow desiccated foundation soils to swell prior to placement of a structure. One of the most common wetting methods is ponding or submerging an area in water (66).
2. Constant water content - most moisture control methods are applied around the perimeter of structures in an attempt to minimise edge wetting or drying foundations (67). One of the common methods of maintaining constant moisture is through the installation of impermeable barriers and adequate drainage system and control of vegetation coverage.
3. Chemical stabilisation - this is achieved by addition of chemical additives such as lime and cement (68). Organic chemicals such as 4-Tert-Butylpyrocatechol and arguard 2HT, fly ash and other compounds show some promise as agents that will reduce heave in expansive soils (69).
4. Electroosmosis - this stabilises expansive clay soils primarily primarily by dewatering and ion exchange processes, although some cost of electricity may dampen enthusiasm for the use of this method (70).

When all precautions are taken some structural modifications may be included as an aid to successful construction using expansive soils. The design of structures should be based on the sub-

soil and site conditions, and probably estimates of heave and accidents from existing and average environmental conditions. Apart from the amount and clay mineral type, a description to aid in the behaviour of the subsoil properties should also include such things as soil colour, origin, hardness, fissure, particle size, all of which are well known engineering properties, and special features as roots and lime nodules (71, 72, 73).

On the agronomical use of the samples analysed, the results of the analyses indicate that most of the soil contains the mineral elements essential for plant growth. This information, together with more details about the content of other inorganic constituents such as phosphorous and other trace elements etc., may be necessary to fully classify the soil. However, the results of the analytical studies have provided some informative data for some elemental content of the samples.

The accuracy and precision of each method were found to be good the errors and relative mean deviation rarely exceeding 3 per cent. The accuracy and reproducibility of methods were obtained by carrying out three or more replicate analyses on the samples. Again, methods exhibit an acceptable degree of accuracy.

On the decomposition procedure, a number of workers (21, 42, 43, 47, 48) have pointed out the high efficiency of anhydrous sodium peroxide fusion for soils and silicate materials. Any

errors which could have arisen from incomplete dissolution may be deemed minimal.

It would appear that the decomposition procedure adapted - sodium peroxide fusion, provides a rapid means of getting all the materials in a soil sample into solution. Analyses for metals and silicon can be carried out by making dilutions of the original stock solutions.

3.8 Summary Of Results

The materials were analysed using the different techniques discussed. Qualitative and quantitative results have been obtained and discussed. Chemical analysis has shown that the different soil samples contain at least the major elements present in clays identified in each soil sample. From the experimental results, the following quantitative and qualitative results have been obtained.

3.8.1 Maiduguri Black Cotton Soil

On the basis of Differential Thermal Analysis, montmorillonite and kaolinite are the dominant minerals. This is confirmed by the results of X-ray analysis. The values of cation exchange capacity and glycol retained when compared with standard (c.f. Table 1 and 2 and Appendices A and B) indicate the dominant influence of montmorillonite. The quantitative results or the percentage composition is selected from the results of semi-quantitative analysis on the basis of the afore mentioned results. Thus the soil can be said to contain about 83.4 per cent montmorillonite and 17.6 per cent kaolinite.

The major constituent element of this soil are silica (51.25%) and aluminium (10.85%) C.E.C = 41.9 meq per 100g soil and glycol retained 78.7 mg/g soil.

3.8.2 Bakura Soil

From the differential thermal analysis, montmorillonite, kaolinite and illite have been confirmed. The X-ray analysis confirms

the presence of all the three minerals. The values of C.E.C. and glycol retained compared with those for standard minerals (c.f. Tables 1 and 2 and Appendices A and B) also indicate that kaolinite is the largest quantity. In fact kaolinite constitute 65.2 per cent montmorillonite 18.5 and illite 16.3 per cent. The greatest single constituent is again silica 47.15 per cent followed by aluminium 6.17 per cent. The C.E.C. = 9.8 meq/100g soil and glycol retained 53.2 mg/g soil.

3.8.3 Wase Gidan Shehu Soil

The DTA confirms the presence of montmorillonite and kaolinite X-ray results also confirms the presence of these minerals. From the values of C.E.C and the glycol retained, montmorillonite can be inferred to be dominant. The most approximate percentage composition is selected from the semi-quantitative results to be montmorillonite 67.2 per cent while kaolinite was found to be 30.2 per cent. The silica content was found to be about 43.50 per cent. All other elements present were fairly low except aluminium which was found to be about 8.08 per cent. The C.E.C was 16.0 meq/100g soil and glycol retained 63.5 mg/g soil.

3.8/4 Institute of Administration Kongo Soil

The DTA analysis indicates montmorillonite, kaolinite, illite and a trace of quartz. This result has been confirmed by X-ray result The approximate composition of the soil is montmorillonite 5.7

per cent, illite 13.7 per cent and kaolinite 80.4 per cent. From the properties of the soil, montmorillonite is not indicated. Geologically the soil is lateritic and laterites contain no montmorillonite. The presence of this mineral is therefore very doubtful and might have probably existed as a trace. The silica content was 45.0 per cent while aluminium was 8.98 per cent
C.E.C = 14.6 meq/100g soil and glycol retained = 60.0 mg/g soil.

3.0.5 Kaduna Arewa Textile Limited Soil

DTA analysis suggest kaolinite, illite, montmorillonite and a trace amount of quartz. X-ray diffraction analysis confirms all the four minerals present. The percentage composition is kaolinite 79.5 per cent, montmorillonite 6.1 per cent and illite 14.1 per cent. The major elemental constituents were aluminium 5.16 per cent, and silica 43.10 per cent. C.E.C = 8.2 meq/100g soil and glycol retained = 49.3 mg/g soil.

3.0.6 Zaria Concretionary Laterite Soil

DTA and X-ray analyses confirm only kaolinite. The soil is lateritic so the presence of kaolinite is justified. The major constituent include iron 21.26 per cent, aluminium 5.56 per cent, silica 49.0 per cent and kaolinite 100 per cent. C.E.C. = 4.2 meq/100g soil and glycol retained = 22.5 mg/g.

3.8.7 Akure Lateritic Soil

This soil appears to be basically the same as the Zaria soil, though they are from two different places. The major constituents were iron 16.8g per cent, silica 46.10 per cent, aluminium 4.89 per cent and kaolinite 100 per cent. C.E. C. = 3.9 meq/100 g soil and glycol retained = 23.1 mg/g.

3.8.8 Suleiman Hall Soil

From the DTA and X-ray diffraction analyses results, this sample contained kaolinite, 74.8 per cent, montmorillonite 23.3 per cent and illite 1.9 per cent. The silica content was as usual high, about 43.4 per cent and aluminium 6.15 per cent. C.E.C = 11.5 meq/100g soil and glycol retained = 50.2 mg/g soil.

3.8.9 Teaching Hospital Soil

Both DTA and X-ray analyses suggest the presence of only kaolinite. The percentage of the mineral was about 90.3 per cent. Analysis shows the absence of montmorillonite. This does not imply that only kaolinite was present. There were other minerals probably present but these might have been just traces which could not be detected by the techniques employed.

The iron content was 9.82 per cent, aluminium 5.50 per cent and silica 44.25 per cent. C.E.C. = 9.3 meq/100g soil and glycol retained 24.2 mg/g soil.

3.8.10 Amina Hall Soil

Analysis of the sample showed the presence of only kaolinite (100 per cent). Both DTA and X-ray diffraction analyses gave 100 per cent kaolinite. Other major constituents include aluminium 6.29 and silica 46.42 per cent. C.E.C. = 12.6 meq/100g soil and glycol retained = 23.6 mg/g soil.

3.8.11 Student Centre Soil

This soil, like the Amina Hall sample was found to contain only kaolinite. The percentage composition of the soil was found to be kaolinite 100 per cent, silica 44.05 per cent and aluminium 5.07 per cent plus other minor constituent elements. C.E.C. = 13.6 meq/100g soil and glycol retained = 24.2 mg/g soil.

3.8.12 Conference Centre Soil

From the DTA, montmorillonite and kaolinite have been shown to be present and the quartz as a trace. X-ray diffraction analysis confirmed the presence of all three minerals. The percentages of the the clay minerals were kaolinite 52.5 per cent and montmorillonite 47.3 per cent. The silica content was found to be 46.05 per cent while aluminium was 8.53 per cent C.E.C. = 22.8 meq/100g soil and glycol retained = 67 mg/g soil.

3.8.13 Islamic Centre Soil

Analysis of this soil employing DTA and X-ray indicates the presence of a predominantly kaolinite mineral (100 per cent).

The silica content was 43.20 per cent and aluminium 7.22 per cent. C.E.C. = 8.4 meq/100g soil and glycol retained = 23.4 mg/g soil.

3.8.14 Area E Soil

This soil is similar to the Zaria concretionary lateritic soil, containing principally kaolinite, 97.4 per cent. There is the possibility of the presence of other clay minerals but these were not detected. The silica content was 47.25 per cent, aluminium 5.53 per cent and iron 22.59 per cent. C.E.C. = 3.4 meq/100g soil and glycol retained = 23.9 mg/g soil.

3.8.15 Ilorin Clay Brick

The presence of kaolinite and montmorillonite in this sample was detected by X-ray diffraction analysis and confirmed by DTA. The approximate mineralogical composition is of the order of, kaolinite 50.6 per cent and montmorillonite 49.4 per cent. The silica content was very high, about 48.15 per cent and aluminium content was 6.54 per cent. C.E.C. = 23.2 meq/100g soil and glycol retained = 68.4 mg/g soil.

The analysis of this sample has been of significance considering the recent interest in clay bricks and the fact that the results might provide some valuable data concerning mineralogical properties of clays suitable for clay manufacture.

Montmorillonite is one of the chief clay minerals in this brick sample. A montmorillonite clay is made up of numerous

flakes and requires much water to saturate the individual particles thereby giving the mixture a plasticity that is best for moulding. Montmorillonites also take considerable water into their expanding lattice layers especially those types with attached alkali (sodium ions).

The results of the chemical tests show that there are large amounts of refractory substances - SiO_2 and Al_2O_3 in the clay brick. The sample is correspondingly low in alkalines, magnesium and calcium oxides as well as other fluxes.

Because of the high ratio of silice and aluminium to fluxes, CaO , MgO , K_2O and Na_2O , the clay brick would require firing temperatures somewhat high above average to produce suitable burnt bricks. This in effect may inflate operation costs of non-vitrified clay products such as common bricks.

The absence of illite is unfortunate since the presence of this mineral could have increased the iron content of the sample, since illite has Fe, Mg, and K in its lattice structure. This is because iron oxide acts as pigment and sometimes as a fluxing agent. The most important quality of fired clay products is its colour, for largely upon colour depends its utilization; and iron, perhaps as the oxide, could produce all sort of colours depending upon its grain size and concentration.

3.9 Conclusion

The following conclusions have been drawn from the results of this analytical study.

- 3.9.1 Soil properties and mineralogy can be determined using the analytical methods employed. Soil properties and behaviour depend very much on the subsoil composition.
- 3.9.2. Most of the soil samples analysed were found to contain kaolinite and would be good for construction work. However, some of the soils contained montmorillonite and would pose some problems common to expansive soils. The Maiduguri Black Cotton soil would therefore need much engineering modification if it is to be used for any construction work since its montmorillonite content is high and would therefore be liable to expansion and heaving.
- 3.9.3 Samples from Jos and Ahmadu Bello University Conference Centre which contained mixed amounts of kaolinite and montmorillonite could be used for construction without the fear of cracking and heaving if some simple rules are observed. The suggestions outlined above could be considered along with some other engineering modifications of the soils.
- 3.9.4 The Ilorin clay brick sample contains mixed minerals mainly kaolinite and montmorillonite. It has significant amounts of refractory substances which are necessary for bricks but lacked sufficient iron to warrant production of fire clay products with different colours.

3.9.5 The decomposition of the soils by fusion with sodium peroxide is rapid, relatively easy and gives accurate results. It also has the advantage that all materials could be got into solution for subsequent estimation of the constituent elements by suitable common classical and instrumental analytical methods.

3.9.6 Results of the chemical analysis showed that all the soil samples contain varying but significant amount of silica and aluminium but low in the alkalines. The variation is probably due to the clay mineral contents of the soils. The presence or absence of iron in any soil is also thought to be due to the mineral type present and location of the sample.

3.10 Suggestions For Future Work

Some aspects of the analyses in this investigation would merit further work.

3.10.1 There is no analytical data on the amounts of trace elements and quartz contained in the samples. A more detailed composition could be obtained if these minerals can be analysed for, using some of the methods employed or other suitable methods.

3.10.2 Further work is also desirable on the mineralogical composition of soils from other localities and sites in Nigeria. Such analyses should not be restricted to clay and metallic elements alone but could be extended to include the non-metallic elements like phosphorous, sulphur and carbon.

- 3.10.3 The analytical data on the lateritic soils where iron was indicated to be high can be extended to include phosphorous and sulphur contents which are important factors in deciding the suitability of a particular iron ore to specific iron and steel making processes. It could also be desirable to estimate what percentage of the iron is FeO , Fe_2O_3 or limonite ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$).
- 3.10.4 Finally, investigation of two or more different methods of decomposition of soils could prove a useful exercise. This would enable comparison of results obtained using different methods possible.

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A P P E N D I X

APPENDIX A

Summary of Clay Mineral Identification Criteria Reference Data For
Clay Mineral Identification (-2 μ Fraction) Ref 1

Clay	X-Ray ^a d(001) A ^o	Glycol mg/g	CEC meq/100g	K ₂ O %	DTA ^b
Kaolinite	7	16	3 - 15	0	End. 500 - 660 ^o Exo. 900 - 975 ^o
Dehydrated Halloysite	7	35	5 - 12	0	Same as kaolinite but 600 ^o peak
Hydrated Halloysite	10	60	5 - 40	0	"
Clay mica (Illite)	10	60	8 - 10	0	End. 500 - 650 ^o (broad) End. 800 - 900 ^o (broad) Exo. 950
Vermiculite	10 - 14	200	100 - 150	0	
Smectite Montmorillonite	10 - 18	300	80 - 150	0	End. 600 - 750 ^o End. 900 ^o Exo. 950
Chlorite	14 ^a	30	10 - 40	0	End. 610 \pm 10 ^o or 720 \pm 20 ^o

Note (a) Heat treatment will accentuate 14A^o line and weaken 7A^o line.

(b) For clays prepared at same relative humidity the size of the 100 - 300^oC endothermic (adsorbed water removal) increase in the order kaolinite, illite, and smectite

CEC Of Some Known Minerals (Ref. 1)

Minerals	CEC (meq/100g)
Kaolinite	3 - 15
Halloysite (Dehydrated)	5 - 10
Halloysite (Hydrated)	5 - 40
Montmorillonite	80 - 150
Nontronite	110 - 150
Illite	10 - 40
Vermiculite	100 - 150
Chlorite	10 - 40

APPENDIX C

Diagnostic X-Ray and DTA Values For Some Minerals Found in Soils
(Ref. 2)

Mineral	Strongest X-Ray Peaks d(A°)	Strongest DTA Peaks. Endo-thermic °C	Strongest DTA peaks. Exothermic °C
Keolinite	7.15, 3.57, 2.33	550 - 600	950 - 980
Chlorite	14.0, 7.1, 4.7	600 - 650	840 - 900
Clay mica	10.0, 4.5, 3.3	550 - 600	about 900
Montmorillonite (air dry)	14 - 15, 4.5	150 - 200	-
Montmorillonite (Glycol saturated)	17.7, 8.9	-	-
Vermiculite	14.- 15, 3.5	150 - 200	-
Allophane		about 150	about 980
Quartz	3.2, 4.0, 1.8	-	-

APPENDIX D

Quantities Of Ethylene Glycol And Glycerol Adsorbed By The Different Clay Minerals (Ref. 1)

Quantity absorbed per gram of oven
- Dry Mineral of Indicated Particle
Diameter (g)

Mineral	Adsorbate	2 - 10 μm	2 μm	0. 1 μm
Kaolinite	Glycol	0.011	0.016	0.027
	Glycerol	0.014	0.023	0.033
Halloysite ⁹	Glycol	0.0209	0.0342	0.0476
	Glycerol	0.0255	0.0418	0.0580
Illite	Glycol	0.0430	0.0610	0.0790
	Glycerol	0.0500	0.0730	0.0960
Montmorillonite	Glycol ^(a)		0.03117	0.3117
	Glycerol ^(b)		0.4110	0.4110
Vermiculite	Glycol ^(c)		0.1951	0.2122
	Glycerol ^(c)		0.2294	0.2393
Allophane	Glycol	0.1200	0.1300	0.1400
	Glycerol	0.1470	0.1509	0.1700
Quartz	Glycol		0.0040	
	Glycerol		0.0033	

(a) $d(001) = 17.1\text{Å}^{\square}$

(b) $d(001) = 18.4\text{Å}^{\square}$

(c) $d(001) = 14.3\text{Å}^{\square}$

APPENDIX E

X-Ray Powder Data For Kaolinite (Ref. 74)

Spacing d(A ^o)	Relative Intensity
7.16	10
4.46	4
4.18	5
5.57	10
3.37	4
2.558	6
2.491	8
2.379	6
2.338	9

APPENDIX F

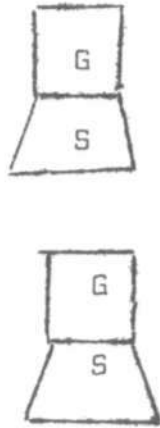
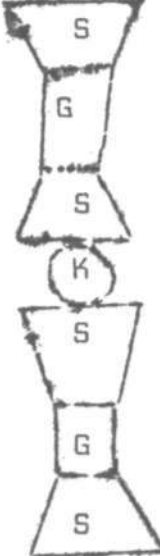
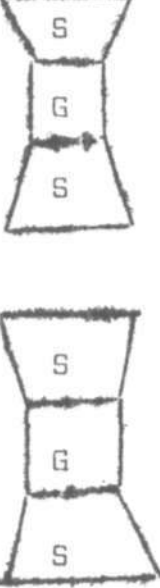
X-Ray Data For Quartz

(Ref. 74)

Spacing d(A ⁰)	Relative Intensity
4.26	35
3.343	100
2.458	12
2.282	12
2.237	6
2.123	9
1.980	6
1.917	17
1.901	1

APPENDIX G

Diagrams And Properties Of Clay Minerals (Ref. 73)

Property	MINERAL		
	Kaolinite	Illite	Montmorillonite
Schematic Structure (a)			
Particle thickness	0.5 μ - 2μ	0.003μ - 0.1μ	9.5A ⁰
Particle diameter, in microns	0.5 μ - 4μ	0.5μ - 10μ	0.5 μ - 10μ
Specific surface in Sq meter per gm	5 - 15	65 - 100	600 - 800
Cation Exchange capacity (meq per 100g of clay)	3 - 15	10 - 40	00 - 150
Maximum swelling as a percentage for surcharge load, in tons per square foot			
0.1	Negligible	350	1,500
0.2	Negligible	1,500	350

^aG = Gibbsit Sheet; S = Silica Sheet; K = Potassium Ion

SAMPLE LOCATIONS(in capital letters)

