THE INFLUENCE OF pH ON THE CATION EXCHANGE CAPACITY (CEC) AND EXCHANGEABLE CATIONS OF CLAYS.

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A RESEARCH PROJECT PRESENTED TO THE DEPARTMENT OF CHEMISTRY, FACULTY OF PHYSICAL SCIENCES, UNIVERSITY OF BENIN, BENIN CITY, IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF M.sc DEGREE IN CHEMISRY.

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CERTIFICATION

This is to certify that, this project was carried out by EBOH ANTHAR ABOYOWA, in the Department of chemistry, Faculty of Physical Science, University of Benin city, Nigeria.

Dr. E.E.I. IRABOR Date

(Project supervisor)

Prof. J.U. IYASELE Date

(Head of Department

DEDICATION

I dedicate this project work to the Almighty God, for His protection, direction and grace, throughout my academic pursuit.

ACKNOWLEDGEMENT

My profound gratitude goes to my supervisor, Dr Irabor, for his supervisor and guidance throughout the course of this work.

My sincere appreciation goes to everyone who has made this program as hitch-free, as possible, I say may God richly bless you all, Amen.

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ABSTRACT

This study determined and compared the values of exchangeable cations Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, and cation exchange capacity (CEC) of clay soil samples in Nigeria, using different pH media (4,5,7,8). Two different clay soil were analysed. Ammonium acetate displacement method was used for the analysis. The chemical analysis were performed using Atomic Absorption Spectrophotometry (AAS), to determine the Mg^{2+}, Ca^{2+} content; Flame photometer to determine Na^{+}, K^{+}, content and Colorimeter; used to determine ammonium nitrogen content.

The result showed that Sample 1, Exchangeable cations (E.C) for Mg^{2+}, had its highest at pH 7(0.198±0.03) and its lowest value at pH 4(0.142±0.04), Ca^{2+} had its highest at pH 7(2.692±0.08) and its lowest value at pH 5 (1.188±0.16), Na^{+} had its highest value at pH 8 (1.884±0.05) and its lowest value at pH 5 (0.409±0.03), and K^{+} had its highest value at pH 7 (0.926±0.09) and its lowest value at pH 8 (0.415±0.03)

The result showed that Sample 2, Exchangeable cations (E.C) for Mg^{2+}, had its highest at pH 5(0.047±0.002) and its lowest value at pH 8(0.032±0.003), Ca^{2+} had its highest at pH 8(1.339±0.08) and its lowest value at pH 4 (0.349±0.06), Na^{+} had its highest value at pH 8 (2.185±0.04) and its lowest value at pH 4 (1.598±0.08), and K^{+} had its highest value at pH 8 (0.693±0.06) and its lowest value at pH 5 (0.415±0.07).

Generally there was a decrease in CEC as the pH increased in the acidic media from pH 4 to 5 and an increase in the CEC as the pH approached neutral, and also a decrease when the pH was increased to 8 (basic medium).

From the results obtained, it is evident that pH is an important soil property, because when the clay sample was treated at different pH, the values of the cations as well as their exchange capacity was greatly was affected i.e they had different pH values when subjected to different pH medium.

CHAPTER ONE

1.0 INTRODUCTON

The determination of CEC is an important test in the evaluation of the quality of commercial clays, for example, Bentonite. It is important to note that cation exchange affects the physical and mechanical properties of clays (Guggeheim et al 2011). CEC is an index of the dispersibility of the formation shales which may affect the properties of drilling fluids and borehole stability (Burrafato et al., 1993).

The ability of soils to hold these cations is a function of the abundance of clay minerals and organic matter it contains (Martel *et al.,* 1978; Emmanuel *et al.,* 2018). It is important to note that all minerals of extremely small size have a very small CEC as a result of broken bonds around their edges.

The CEC of clays is susceptible to change depending on the type of saturating and extracting solutions used in the measurement of CEC. This change can only occur through the variable CEC, because it depends on the soil's pH, which might change when saturating or extracting solution is added to the natural soil. The less the change in the clay pH after treatment with extraction or a saturation solution is, the lower the error in the CEC measurement (Summer 1996, Laird and Fleming 2008.

The ability of soils to hold these cations is a function of the abundance of clay minerals and organic matter it contains (Martel *et al.,* 1978; Emmanuel *et al.,* 2018)

Across the globe, naturally occurring expansive soils have been found in various regions. (Chen 2012). Soils susceptible to swelling and shrinkage includes those with higher percentage of clay minerals like montmorillonite, expandable illite and vermiculite.

Clay minerals are abundant naturally occurring fine-grained, earthy materials which become plastic at appropriate water content and har when fired or dried (Akhirevbulu *et al.,* 2010). Chemically, they are composed of hydrous aluminum phyllosilicates arranged in either an octahedral and/or a tetrahedral geometry to form individual layers or sheets interlayered with cations such as potassium, sodium, calcium magnesium or iron (Lainé *et al.,* 2017).

Clay is a type of soil particle that is characterized by its small size and high surface area. It is an important component of soil, playing a key role in various soil processes, including nutrient cycling, water retention, and soil structure formation.

Several studies have focused on understanding the properties and functions of clay in soil systems. For example, studies have shown that clay can help to improve soil fertility by increasing nutrient retention and availability (Sposito, 1989; Haynes, 2005). It has also been shown that clay can help to improve soil structure by promoting soil aggregation, which in turn can improve soil aeration and water infiltration (Six et al., 2002).

In addition to its positive effects on soil fertility and structure, clay has also been found to play a role in the retention and transport of contaminants in soil systems. For example, studies have shown that clay can help to reduce the mobility of heavy metals in soil, thereby reducing the risk of contamination of groundwater and surface water resources (Nduwimana et al., 2016; Lai et al., 2017).

Recent research has also focused on the use of clay as a material for various applications beyond soil systems. For example, clay has been used in the development of drug delivery systems, as it has the ability to adsorb and release molecules in a controlled manner (Lvov et al., 2008; Xu et al., 2021). Clay has also been used in the development of novel nanocomposites with improved mechanical and thermal properties (Chen et al., 2019).

Clay minerals have the property of absorbing certain ions and retaining tem in an exchangeable state; except for vermiculites and smectites, exchangeable ions are held onto the surface of the mineral, and the exchange reaction does not affect its structure. Some of the common clay minerals are kaolinite, montmorillonite, illite, nontronite, muscovite, etc. (Peng et al, 2006). However, for engineering purpose kaolinite, montmorillonite and illite have particular importance in geotechnical engineering (Hwang, 2002).

1.1 AIM OF THE STUDY

Investigating the effect of pH on the cation exchange capacity and exchangeable cations of clay: This research aims to study how the pH affects the CEC and EC of clay. The study will involve measuring the CEC and EC of clays under different pH conditions to determine how pH affects the exchange capacity of different cations.

Evaluating the relationship between soil pH and the release of exchangeable cations: This research aims to investigate how soil pH influences the release of exchangeable cations in clay. The study will involve measuring the EC of clay under different pH conditions to determine how pH affects the release of different cations.

1.2 OBJECTIVES OF THE STUDY

To achieve the aim, the following objectives are stated,

Determination of exchangeable cations using Atomic Absorption spectrophotometer (AAS) and Flame Emission Photometer.

Determination of exchangeable acidity.

Determination of CEC using Colorimeter.

Determination of the above parameters in the clay mineral subjected to both different acidic, alkaline, and neutral media.

1.3 RELEVANCE OF THE STUDY

This study is relevant for several reasons, which includes;

CLAY MINERALOGY: Understanding factors that influence CEC and EC, for example pH is essential for predicting the behavior of clay minerals such as clay mineralogy and reactivity in natural environments. As stated by Stucki (1991), An important factor in controlling the reactivity and stability of clay minerals, is the influence of pH on CEC and EC.

SOIL FERTILITY: The influence of pH on CEC and EC of clays is important for soil fertility and nutrient availability. affects the availability of nutrients in soil systems. According to sumner and Miller (1996); Soil pH affects the CEC of soils and the exchangeable cations that are available to plants. A change in soil pH can have an adverse effect on soil fertility and crop productivity. Therefore understanding the influence of pH on CEC is essential for sustainable agriculture.

SOIL MANAGEMENT: Management of soils pH is an important component of soil fertility and crop management. Knowledge of the influence of pH on CEC and EC of clays is important for developing strategies to optimize nutrient availability for plant growth. According to Brady and Well (2016); Soil pH, affects the types amounts of exchangeable cations, available to plants, therefore the types and amounts of fertilizers needed to provide nutrients essential for crops growth.

ENVIRONMENTAL IMPACTS: Soil pH affects the retention and transport of pollutants in the soil. Lindsay and Norwell (1978). Therefore a change in the pH of the soil can affect the availability of exchangeable cations that retain and adsorb pollutants, affecting their mobility and potential for groundwater contamination.

1.4 LITERATURE REVIEW

Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange. (Bradi 2004, Sajiidu 2008). Some studies have been conducted on clay material in Nigeria where the study of the chemical and mineralogical characteristics has been in focus. Clay is a vastly distributed, abundant, mineral resource of major industrial importance for an enormous variety of uses. In both value and amount of annual production, it is one of the foremost leading minerals worldwide.

They cause numerous costly damages to the roadways, buildings, bridges and other civil engineering infrastructures. Also, clay soils are generally hard in dry state but when become saturated, they lose their hardness.

Soft clays are characterized by excessive compressibility and low compressive strength. The reduction in bearing capacity of soft clays results in compressive failure and excessive settlement, leading to severe damage to buildings and foundations (Mc Dowell 1959, Bell 1996, Venkaramuthyalu 2012). Clay minerals expand when moisture is introduced and shrink upon drying. It is important to note that clay minerals and cations come in various forms and that it is the relative quantities of each type of these minerals that are important factors contributing to the swell/shrink behavior along with the dry density, soil structure, and loading conditions present (Al-Rawas et al 2006).

1.5 CLAY STRUCTURE

Clays are composed of micro-crystalline particles of a group of minerals. Generally, clays are naturally occurring material primarily composed of fine-grained minerals, which shows plasticity when mixed with appropriate amount of moisture and become stiff when dried or fired (Sirivitamatrie et al 2011, Das B 2015).

Important characteristics of clay, includes;

a) Small particle size (usually smaller than 0.002 mm)

b) Net negative charge

c) Show plasticity when mixed with moisture (Das B, 2015)

Although, clays are fine grained, they in fact very different from other fine-grained soils by differences in their size and mineralogy. Silts, which are fine-grained soils that do not contain clay minerals, have particle sizes larger than clays, but there are some similarities in both particle size and other physical properties, and there are many naturally occurring deposits which contain both silts and clays. The difference between clay and silt varies according to different discipline. Geologists and soil scientists usually consider the separation to occur at a particle size of 2 micrometres (clays being finer than silts), sedimentologists often use 4-5 micrometres and colloid chemists use 1 micrometre. Geotechnical engineers distinguish between silts and clays based on the plasticity properties of the soil, as measured by the soils (Guggenheim et al 1995).

1.5.1 TYPES OF CLAY

In Nigeria, there are two types of clay, namely;

Primary or residual clay; Primary clays consists of weathered particles that remain close to their parent rock; they are not carried away by water, wind or glaciers. They have relatively large particles and are largely impurities free.

Secondary or sedimentary clays; Secondary clays are transported from their origin by eroding forces (Coiler, 1976). As the clay is transported, especially by running water, some large particles are left on the way while others are carried further and is ground finer by the water on the eroding force. As a result, the particles of secondary clays are smaller than those of primary clay. During their transportation, secondary clays become mixed with other substances such as Iron, Quartz, Mica and Organic residue, they come in contact with; which explains why they contain more impurities than the primary clays and are usually very plastic.

1.5.2 CHEMISTRY OF CLAY

Different fields have different explanations of the term ’Clay’, while the potter refers to clay as a medium of many properties, the chemist defines clay as a complex mixture and combination of minerals. The chemist analyzes clay in two ways; One way separates the oxides, lists them and states their amounts while the other, expresses some idea of the clay’s properties by grouping the oxides, as clay content, feldspar, mica etc. For example, Frank (1975) analyzed clay as: Clay content - 50% Feldspar - 15% Free silica - 29% Plus Iron Oxide - 1% Limestone - 5%. He reiterated that the clay content, which was based upon the clay crystal structure have the formula: Al_2O_3. $2SiO_2.2H_2O$ and this gives it a composition of: alumina 39.5%, silica 46.5%, water 14.0%. From the aforementioned, it would be noticed that there is 14% of water in the form of hydroxyl groups (OH) in the gibbsite layer and therefore, many chemists prefer to describe the clay crystal by the formula $Al_2\ Si_2\ O_3\ (OH)_4$. They also call it hydrated aluminium silicate.

Clay contains water in the crystal structure called bound water; water in the holes between the particles called pore water; and water to allow the particles to slide through one another called water of plasticity. In dry state, clay contains bound water. During firing, this water becomes steam, which escapes slowly over a period 400^0C to 600^0C. The bound water would escape as steam without causing trouble because the pores of the clay are open at this temperature. Dry clay also contains pore water. This remains in the pores and does not dry out because there is water in the atmosphere. Plastic clay contains more water still.

This is the water of plasticity. In extreme cases, this water of plasticity could account for 30% of the weight of plastic clay but 20 to 25% is more normal.

1.5.3 THE PROPERTIES OF CLAY

One of the commonest processes of clay formation is the chemical decomposition of feldspar. Clay consists of sheets of interconnected silicates combined with a second sheet-like grouping of metallic atoms, oxygen and hydroxyl, forming a two-layer mineral such as kaolinite. Sometimes, the latter sheet like structure is found sandwiched between two silica sheets, forming a three-layer mineral such as vermiculite (Hillier, 2003). In the lithification process, compacted clay layers could be transformed into shale. Under the intense heat and pressure that may develop in the layers, the shale could be metamorphosed into slate.

Prominent properties of clay minerals include plasticity, shrinkage, under firing and air drying, fineness of grain, color after firing, hardness, cohesion, and capacity of the surface to take decoration. On the basis of such qualities, clays are variously divided into classes or groups. Individual clay particles are always smaller than 0.004mm. Clays often form colloidal suspensions when immersed in water, but the clay particles flocculate (clump) and settle quickly in saline water.

Clays are easily molded into a form that they retain when dry, and they become hard and lose their plasticity when subjected to heat. Clays are divided into two classes:

Residual clay –: Found in the place of origin; residual clays are most commonly formed by surface weathering, which gives rise to clay in three ways:

- Chemical decomposition of rocks, such as granite, containing silica and alumina.
- Solutions of rocks, such as limestone, clayey impurities, which being insoluble, are deposited as clay.
- Disintegration and solution of shale (Ehlers et al 1982).

Transported clay-: These clays are also known as sedimentary clay, removed from the place of origin by an agent of erosion and deposited in a new and possibly distant position.

1.5.4 THE COLOR OF CLAY

The color of clay is influenced by a variety of factors, including the mineral composition of the clay, the presence of organic matter, and the environmental conditions in which the clay was formed.

In general, clay minerals are white to light gray in color when they are pure and free of impurities. However, the presence of iron oxides, manganese oxides, and other mineral impurities can give clay a range of colors, including red, yellow, brown, green, and blue-gray (Singh and Gilkes, 1992).

For example, the red color of some clays is due to the presence of iron oxide minerals such as hematite and goethite, while the yellow and brown colors of other clays are due to the presence of iron oxide minerals such as limonite and ochre. The green color of some clays is due to the presence of iron-magnesium-aluminum silicate minerals such as chlorite, and the blue-gray color of some clays is due to the presence of iron-manganese oxide minerals such as birnessite (Churchman et al., 2017).

The color of clay can also be influenced by the environmental conditions in which it was formed. For example, clays that form in reducing environments (where oxygen is scarce) may be gray or black due to the presence of organic matter, while clays that form in oxidizing environments (where oxygen is abundant) may be red or yellow due to the presence of iron oxide minerals (Singh and Gilkes, 1992).

Understanding the color of clay is important for identifying different types of clay and for using clay in various applications, such as ceramics, construction, and environmental remediation.

1.6 CLAY MINERALOGY

Clay minerals are naturally inorganic compounds with definite physical, chemical and crystalline properties and are classified as primary or secondary, silicates or non-silicates and crystalline or amorphous (Karathanasis, 2006). Primary minerals form at elevated temperatures and pressures, and are usually derived from igneous or metamorphic rocks, while secondary minerals are the culmination of either alteration of the primary mineral structure or neoformation through precipitation or recrystallization of dissolved constituents into a more stable structure (Barton and Karanthanasis 2002, Wilson 1999). Common primary minerals in soil environments include silicates, oxides of Fe and Al, Zr and Ti, and phosphates, while typical secondary minerals found in soil environments include alumino-silicates, oxides and hydroxides, carbonates, sulphates and amorphous minerals (Karathanasis, 2006). Secondary minerals are mainly found in the clay-sized and fine-silt-sized fractions, and form the most reactive inorganic materials in soils (Churchman and Lowe 2012), thereby influencing availability of nutrient elements through various mechanisms.

Clay rocks could be identified by their very fine grain size of < 0.002mm, and have different properties depending on which particular clay minerals they contain. There are three main groups of clay minerals, each with its own particular properties; they include,

- Kaolinite

- Illite
- Montmorillonite

Clay rocks may contain a mixture of these minerals, so they have very variable properties, giving rise to a number of different uses. The most abundant use of clay is in brick-making. Granite is made up of quartz, mica, and feldspar. As quartz is resistant to chemical weathering, it may be removed only as mineral grains of quartz, feldspars and micas are susceptible to chemical weathering and break down to form clay minerals. Some of the original elements contained in the micas and feldspars are carried away in solution as irons (Na+, Ca+, and K+), and so the clays formed are relatively enriched in aluminium and silicon. The main groups of clay minerals are kaolinite, illite and montmorillonite. The layers of kaolinite are held together by fairly weak bonds, whereas there is strong bonding in illite and montmorillonite because of the presence of positively charged metal ions; potassium in the case of illite, and calcium and sodium in the case of montmorillonite. Generally, potassium feldspar breaks down to form kaolinite; micas weather to give illite and ferromagnesian minerals break down to form montmorillonite. (Odubiyi, 2004).

Clay minerals have a sheet-like, crystalline structure, which consist of hydrous alumino-silicates and metallic ions. The two fundamental crystal units of clay minerals, are tetrahedral and octahedral. A tetrahedral unit belongs to four oxygen enclosing silicon, while an octahedral unit composes of six oxygen or hydroxyls at corners surrounding aluminum, magnesium, iron or other ions. The pictorial representation of basic tetrahedral and octahedral unit is presented below, respectively. Figure 1: Single unit of tetrahedral mineral, Figure 2: Single unit of octahedral mineral (Mitchell.J. 2005).

Soil clay minerals are grouped into 1:1 and 2:1 clay minerals, depending on the ratio of silica tetrahedral sheet to alumina octahedral sheet. The 1:1 clay minerals, primarily kaolinite, are found in most soils, but predominate in highly weathered soils of humid tropical regions. In tropical environments, sesquioxide minerals rich in Fe and Al dominate. The 2:1 swelling or expandable clays include the smectite and vermiculite groups, which have large surface areas and high cation exchange capacities (CEC).

These clay minerals play a significant role in dictating the suitability and behaviour of soil for various land uses. Clay mineralogy-soil fertility relationship is an imperative component in understanding and managing soil fertility for sustaining crop production, especially in the tropics (Mandiringana et al 2005, Abe et al 2006). Clay mineralogy appears to be one of the most important indicators of soil quality (Blanco-Canqui and Lai 2008), and proper knowledge of the clay mineralogy of a soil has significant practical implications on the use of fertilizers, on application and management (Yerima and Van Ranst 2005, Scherer et al 2014, Li et al 2015, Moterle 2016), and on the bioavailability of heavy metals in soil (Kim et al 2015).

Most of these properties are influenced to a large extent by the mineralogical composition of the soil. Particle size distribution results from the physical degradation of soil minerals due to imperfect lattice energy distributions in the silicate layers causing strains in the mineral structure (Karanthanasis 1985). Soil strength, aggregation and plasticity are affected by the various attractive and repulsive forces exerted by the various minerals. The overall structure of the soil is the product of the arrangement and bonding of individual soil particles into aggregates caused by ionic, organic, water and clay mineral surface interactions (Nagy and Konia 2010). According to (Schulten and Leinweber 2000), clay mineralogical properties that influence aggregation are surface area, CEC, charge density, dispersity and expandability. Non-crystalline clay minerals, such as allophane and imogolite, have high surface areas, and highly variable and pH-dependant charge properties that generally increase aggregation (Powers and Schlesinger 2002). Non-expanding variable-charge crystalline clays, such as kaolinite (1:1), have low CEC and low surface area, which tend to decrease aggregate stability, while high activity clays such as smectites (Ca-smectites) and other 2:1 clays, which are associated with high CEC and large surface area, tend to increase aggregation (Schulten and Leinweber 2000)

Phyllosilicates with a permanent charge (e.g. vermiculite and smectite) offer exchange sites that hold a number of essential nutrients in their cationic form (cation exchange capacity), such as Ca2+, Mg2+, K+, and Na+ (Sollins et al 1988).

1.6.1 INDUSTRIAL APPLICATION OF CLAY AND CLAY MINERALS

Clay and clay minerals have numerous industrial applications in various sectors such as construction, ceramics, pharmaceuticals, cosmetics, agriculture, and environmental remediation. Here are some examples of their industrial applications:

- Construction: Clay and clay minerals are widely used in construction materials such as bricks, tiles, and cement. The addition of clay minerals in cement enhances the mechanical properties and durability of the final product (Ismail et al., 2019). Clay-based ceramics are also used in the construction of refractory materials, such as crucibles, furnace linings, and kiln furniture (Takahashi et al., 2019).
- Pharmaceuticals: Clay minerals are used as active ingredients in several pharmaceutical formulations, including antacids, laxatives, and anti-diarrheal agents (Majumder et al., 2020). Clay minerals such as montmorillonite and kaolinite have excellent adsorption properties, making them useful for drug delivery systems (Lu et al., 2020).
- Cosmetics: Clay minerals are used in cosmetic products for their absorbent and adsorbent properties. For example, bentonite clay is a popular ingredient in facial masks and scrubs due to its ability to absorb

excess oil and impurities from the skin (Kumar et al., 2020). Other clay minerals such as kaolinite and illite are also used in cosmetics as fillers and thickeners (Chaudhary et al., 2021).

- Agriculture: Clay minerals are used in agriculture as soil conditioners and fertilizers. The high cation exchange capacity of clay minerals such as montmorillonite makes them useful for improving soil fertility and water retention (Kumar et al., 2018). Clay minerals are also used as animal feed additives to improve digestion and reduce the risk of mycotoxin contamination (Oladimeji et al., 2020).
- Environmental remediation: Clay minerals have been extensively studied for their ability to remove pollutants from contaminated soil and water. For example, kaolinite has been used to remove heavy metals from wastewater, while bentonite clay has been used to remove organic pollutants such as dyes and pesticides (Mao et al., 2021).
- Petroleum industry: Clay minerals such as montmorillonite and bentonite are used in the petroleum industry as drilling muds to control fluid loss, lubricate drill bits, and provide support to the borehole walls. (Bourg, 2018).

1.7 EXCHANGEABLE CATIONS

The clay mineral and organic matter components of the soil have negatively charged sites on their surface which adsorb and hold positively cations by electrostatic force. The electrical charge is critical to the supply of nutrients to plants because many nutrients exist as cations (for example, Magnesium, Potassium and Calcium). In general term, soil with large quantity of negative charge are more fertile because they retain more cations (McKenzie et al 2004).

1.8 CATION EXCHANGE CAPACITY (CEC)

Cation exchange capacity (CEC) is a measure of the ability of a soil to hold and exchange cations (Positively charged ions) (Saidi, 2012). It is a very important soil property influencing soil structure stability, nutrient availability, soil pH and the soil's reaction to fertilizers and other ameliorants (Hazelton and Murphy 2007). It refers to the total capacity of soil to hold, absorb and exchange cations. CEC represents the amount of negative charges in soil existing on the surfaces of clay and organic matter. The ability of sediment to bind with cations often measured by CEC which could relate to migration of metals in soil (McLean and Bledsoe, 1992). Difference abilities for cation in exchanging cation process may be varied due to several factors such as pH, particle size and organic matter content in soil or sediment. It is important to note that the ability of soils and clays to hold onto and exchange cations has significant implications in agriculture, environmental remediation, and industrial applications.

In agriculture, the determination of soil CEC and EC is essential for soil fertility management. In acidic soils, the CEC is typically low due to the high concentration of hydrogen ions, which occupy the exchange sites on the soil particles. However, the application of lime or other alkaline materials can raise the soil pH, reducing the number of hydrogen ions, and increasing the availability of exchange sites for essential plant nutrients.

In environmental remediation, the measurement of CEC and EC is important for understanding the behavior of contaminants in soils and sediments. For example, heavy metals can bind to exchange sites on clay particles, reducing their mobility and bioavailability in the environment.

The main ions associated with CEC in soils are the exchangeable Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^{+}), and Potassium (K^{+}), (Rayment and Higginson 1992), and are reffered to as the base cation. In most cases, summing the analysed base cations gives an adequate measure of CEC, however as soils become more acidic these cations are replaced by H^{+}, Al^{2+}, and Mn^{2+}, and common methods would produce CEC values much higher than what occurs in the field (McKenzie et al 2004). This Exchange acidity needs to be included when summing the base cations and tis measurement is referred to as effective CEC (ECEC).

`1.8.1 MEASURING CEC

Cation exchange capacity is commonly measured on the fine earth fraction (soil particles less than 2 mm in size). Measuring CEC involves washing the soil to remove excess salts and using an ‘index ion’ to determine the total positive charge in relation to original soil mass. This involves bringing the soil to a predetermined pH before analysis. Methods, including pre-treatment, for measuring CEC and exchangeable cations are presented by (Rengasamy and Churchman 1999) and described in detail by (Rayment and Higginson 1992).

1.8.2 PRINCIPLE OF CEC MEASUREMENT

CEC is measured by displacing all the bound cations with a concentrated solution of another cation and then measuring either the cation or the amount of added cations that is retained. (Brady et al.,2008). Barium and Ammonium are frequently used as exchanger cations, although many other methods are available (Schaetzl et al., 2015).

CEC measurements depends on pH and therefore are often made with a buffer solution at a particular pH value. If this pH value differs from the natural pH of the soil, the measurement will not reflect the true CEC under normal conditions. Such CEC measurements are called potential CEC. Alternatively, measurement at the native soil pH is called effective CEC which more closely reflects the real value, but can make comparison between soils more difficult. (Pansu et al., 2006)

1.8.3 UNITS

CEC is conventionally expressed in meq/100 g (Rengasamy and Churchman 1999) which is numerically equal to centimoles of charge per kilogram of exchanger (cmol(+)/kg).

1.8.4 SIGNIFICANCE OF CEC

A soil CEC affects fertilization and liming practices. For example, soils (clay) with high CEC retain more nutrients than low CEC soils. With large quantities of fertilizers applied in a single application to sandy soils with low CEC, loss of nutrients is more likely to occur via leaching. In contrast, these nutrients are much less susceptible to losses in clay soils. Therefore, soils with a high cation exchange capacity are generally more fertile because;

1. They have little or no acid cation e.g Al^{3+} that is toxic to plant growth.
2. They contain greater amounts of the essential plant nutrient cations K^{+}, Ca^{2+}, and Mg^{2+} for use by plants. (Leticia et al., 2000)

1.8.5 WHY DO CLAY MINERALS HAVE CEC?

There are three possible causes of cation exchange capacity of clay minerals.

1. Broken bonds around the edges of the clay minerals gives rise to the unsatisfied charges, which could be balanced by absorbed cations. The number of broken bonds increases as particle size decreases and therefore the exchange capacity is due to this cause.
2. Isomorphic substitution: This refers to the replacement of silica by aaluminiumin the clay mineral structure. Isomorhic substitution within the tetrahedral sheet of ions of lower valence, especially Mg^{2} , Al^{3+} results in unbalanced charges in structural minerals. Clays have a net negative charge because of the substitution of silica (Si^{4+}) by aluminium (Al^{3+}) in the mineral structure of the clay and the result is clays with negative surface charge.

The relationship between CEC and EC is crucial in understanding the nutrient availability of soils and clays. Soils and clays with high CECs and high levels of exchangeable cations are generally more fertile and able to hold onto nutrients for longer periods, while soils and clays with low CECs and low levels of exchangeable cations may require more frequent applications of fertilizers to maintain soil fertility.

1.9 MANAGEMENT IMPLICATION

1.9.1 SOIL TYPE AND CEC

The CEC of soils varies according the clay %, the type of clay, soil pH and amount of organic matter. Pure sand has a very low CEC, less than 2 meq/100 g, and the CEC of the sand and silt size fractions (2 μm/2 mm) of most soils is negligible. Clayey sandy soils for managing water repellence increases the CEC of the surface layers by a small amount depending on type and amount of clay added. Typically CEC is increased by less than 1 meq/100 g. Organic matter has a very high CEC ranging from 250 to 400 meq/100 g (Moore 1998). Because a higher CEC usually indicates more clay and organic matter is present in the soil, high CEC soils generally have greater water holding capacity than low CEC soils.

1.9.2 SOIL PH AND CEC

Soils dominated by clays with variable surface charge are typically strongly weathered. The fertility of these soils decreases with decreasing pH which can be induced by acidifying nitrogen fertilizer, nitrate leaching and by clearing and agricultural practices (McKenzie *et al.* 2004). Soil pH change can also be caused by natural processes such as decomposition of organic matter and leaching of cations. The lower the CEC of a soil, the faster the soil pH will decrease with time. Liming soills to higher than pH 5 ($CaCl_2$) will maintain exchangeable plant nutrient cations.

1.9.3 Nutrient availability and CEC

Soils with a low CEC are more likely to develop deficiencies in potassium (K^+), magnesium (Mg^2+) and other cations while high CEC soils are less susceptible to leaching of these cations (CUCE 2007). Several factors may restrict the release of nutrients to plants. Some groups promote the controversial idea of managing cation ratios, claiming ideal ratios for Ca:Mg or Ca:K. For plant nutrition, a more critical factor is whether the net amount of Ca or K in the soil is adequate for plant growth. The addition of organic matter will increase the CEC of a soil but requires many years to take effect.

Figure 1 illustrates how CEC can change with depth. The sum of the base cations provides an estimate of the CEC of each soil layer. The surface 10 cm has a CEC of 4.6 meq/100 g because of a high organic content. At 10 – 30 cm depth, the organic content of the sand is very low, hence the low CEC. The CEC of the subsoil layers are governed by clay content, 61 %, 51 % and 34 % respectively. The dominant clay in this soil is kaolinite so CEC values remain low.

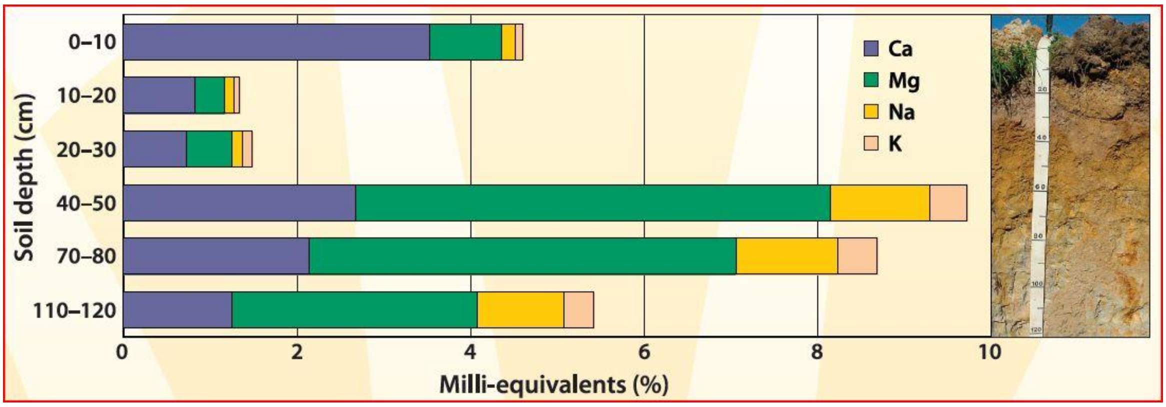

Figure 1: *Sandy duplex soil, with clay at 40 cm. Note the high CEC of the clay below 40 cm, and the impact of organic matter on the sand's CEC.*

1.9.4 THE ROLE OF CLAYS IN CEC AND EC

Clay minerals play a crucial role in determining the cation exchange capacity (CEC) and exchangeable cation (EC) properties of soils and sediments. Clays are the most significant component of soil colloids and have high surface area and high negative charges on their surfaces. These negative charges attract positively charged ions, known as cations, to the surface of the clay minerals, forming exchangeable cations that can be released to the soil solution.

The CEC of a soil or sediment depends on the type and amount of clay minerals present in the soil. Different types of clay minerals have different CECs due to differences in their mineral structure and chemical composition. For example, montmorillonite has a higher CEC than kaolinite due to its greater surface area and more significant number of exchangeable cations.

The EC of clays also depends on the type and amount of clay minerals present. The most common exchangeable cations in soils and clays are calcium (Ca2+), magnesium (Mg2+), potassium (K+), sodium (Na+), and hydrogen (H+). The EC of clays is affected by factors such as pH, soil moisture content, and the presence of competing cations.

The pH of the soil or sediment affects the EC of clays by influencing the amount of exchangeable cations present. At low pH, H+ ions displace the exchangeable cations from the clay minerals, leading to an increase in H+ concentration in the soil solution. In contrast, at high pH, Ca2+ and Mg2+ ions become more dominant in the soil solution, displacing the other exchangeable cations.

The organic matter content of the soil also affects the CEC and EC of clays. Organic matter has a high negative charge and can form complexes with the exchangeable cations, reducing their availability for plant uptake.

In industrial applications, the CEC and EC of clays are essential for understanding their adsorption properties. Clays are widely used in the manufacturing of ceramics, paper, and other materials due to their adsorption properties. Clays can adsorb a variety of molecules, including dyes, heavy metals, and organic compounds, making them useful in wastewater treatment and pollution remediation.

1.9.4 THE INFLUENCE OF PH ON CEC AND EC OF CLAYS

The pH of soil or sediment plays a crucial role in the cation exchange capacity (CEC) and exchangeable cation (EC) properties of clays. The pH affects the availability and exchange of cations on clay surfaces, which ultimately affects the nutrient and water holding capacity of soils.

At low pH levels, hydrogen ions (H^+) are abundant in the soil solution and compete with other cations for binding sites on clay surfaces. This results in an increase in H+ concentration in the soil solution and a reduction in the number of exchangeable cations on clay surfaces. As a result, the CEC of clays decreases, and the soil becomes less fertile. For example, in acidic soils, the exchangeable cation Ca^{2+} is often replaced by H^+ ions, resulting in a decrease in soil fertility.

In contrast, at high pH levels, calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions become more abundant in the soil solution, competing with other cations for binding sites on clay surfaces. This results in an increase in the number of exchangeable cations on clay surfaces and an increase in the CEC of clays. However, at very high pH levels, some clays may lose their negative charge, which leads to a decrease in the CEC.

The EC of clays is also affected by the pH of the soil. At low pH levels, H^+ ions displace other exchangeable cations from clay surfaces, leading to an increase in the concentration of H^+ ions in the soil solution. In contrast, at high pH levels, Ca^{2+} and Mg^{2+} ions become more dominant in the soil solution, displacing other exchangeable cations from clay surfaces.

The pH of soil is also important in understanding the adsorption properties of clays. For example, at low pH levels, clays can adsorb toxic aluminum ions (Al^{3+}) that can be harmful to plant growth. At high pH levels, the adsorption of Al^{3+} is reduced, making the soil less toxic for plant growth.

Understanding the influence of pH on CEC and EC of clays is crucial for managing soil fertility and the availability of essential nutrients for plant growth. Agricultural practices such as liming can be used to raise the pH of acidic soils and increase the availability of exchangeable cations. Additionally, the influence of pH on the adsorption properties of clays is important in environmental remediation and industrial applications. For example, the pH can be adjusted to optimize the adsorption of pollutants onto clay surfaces for wastewater treatment or pollution remediation.

CHAPTER TWO

2.1 MATERIALS AND METHOD

The clay materials were collected from …………Sampling of the clay materials was based on color variation in line with Onyeobi et al.,1994.

2.1 SAMPLE PREPARATION

The samples were first air dried at room temperature, then pulverized using a pestle and a mortar afterwards it was sieved using a 2mm sieve and taken to the muffle furnace at 4000C for 3 hours.

2.3 EXPERIMENTATION

The activated clay samples were subjected to different acid at (pH 4 and pH 5) and alkaline media (at pH 8) for seventy-two hours, mechanically agitated for at least three hours day. pH Thereafter, the various properties were determined which includes, cation exchange capacity, exchangeable cations and exchangeable acidity using an Atomic Absorption Spectrometerr (Buck scientific 210 VGP model), Flame emission spectrometer Sherwood 410 model and calorimeter Jenway 6051 model .These experiments were was carried out three times and their mean and standard deviations were also determined.

2.4 MATERIALS

Beakers

Weighing balance

Cornical flask

Measuring cylinder

Spatula

Pestle

Mortar

Muffle furnace

Filter paper

Buchner funnel

Erlenmeyer flask

Vacuum flask

Sieve 2mm

Stirrer

Mechanical shaker

Aluminum Foil

pH meter (Jenway 3020 pH meter)

Flame photometer

Volumetric flask

Atomic Absorption spectrometer Buck scientific 210 VGP

Colorimeter (Jenway 6051 model)

2.5 CHEMICAL AND REAGENTS

Glacial Acetic acid

Ammonium hydroxide

Deionised water

Potassium chloride

Ethanol

Concentrated Hydrochloride acid

Disodium tetraborate borax

Sodium hydroxide

Sodium potassium Tartrate

Potassium hydrogen phthalate

Alkaline Phenate

Sodum Citrate

Sodium Hypochlorate

2.6 REAGENT PREPARATION FOR ANALYSIS

2.6.1 PREPARATION OF 1M AMMONIUM ACETATE

Glacial acetic acid (57.4 cm3) was diluted with deionised water 700ml in a 1L volumetric flask and concentrated Ammonium hydroxide 68ml was added. The pH meter was used to determine the pH and the pH was adjusted to 7 with Ammonium hydroxide if needed.

2.6.2 PREPARATION OF POTASSIUM CHLORIDE

KCL (74.5g) was dissolved in deioinised water 800ml and diluted to 1L.

2.6.3 PREPARATION OF 0.1M POTASSIUM HYDROGEN PHTALATE KHP

Potassium hydrogen phthalate (20.422g) was dissolved in deionized water 900ml and diluted to 1L.

2.6.4 PREPARATION OF 0.1M SODIUM HYDROXIDE (NaOH)

Sodium hydroxide 4g was dissolved in 700ml of deionised water and diluted to 1l.

2.6.4 PREPARATION OF 0.1M HYDROCHLORIC ACID HCL

Hydrochloric acid (8.3ml) was diluted in 900ml of deioised water and diluted to 1L

2.7 CHEMICAL ANALYSIS

2.7.1 EXCHANGEABLE CATIONS AND CATION EXCHANGE CAPACITY (C.E.C) DETERMINATION

The air dried, sieved and activated clay (25g) was laced in a 250ml beaker followed by the addition of Ammonium acetate (125ml). it was covered with an Aluminum foil and placed in a mechanical shaker for 3hours and allowed to stand for 24hours. Thereafter, a Buchner funnel was prepared by fitting a whatman filter paper which was wetted with a minimum amount of ammonium acetate, and the funnel was inserted into a 250ml suction flask. The soil NH4OAc (100ml) for each sample. The soil was gently washed down four times with the addition of the NH4OAc (25ml), allowing each addition to filter through but not allowing the soil to crack or dry. The leachate was transferred into a 250ml volumetric flask and brought to volume with a 1M NH4OAc. The solution was analyzed for Ca2 , Mg2+, K2+, and Na2+, using atomic absorption spectrometer and flame emission spectrophotometer. To remove excess NH4OAc in the soil, the soil was laced with 95% ethanol (25ml) six times for a total volume of about 150ml. To remove adsorbed NH4in the soil, the soil was leached with 1M KCL (25ML) five times for a total volume of 125ml. The to a 250ml volumetric flask and brought to volume using 1M KCL. The solution was analyzed using the Colorimetric method for NH4+ concentration (Chapman 1965 and Gilman 1979).

2.7.2 DETERMINATION OF BEFFFER SOLUTION AT pH 4 USED FOR EXCHANCHEABLE CATIONS AND CEC

0.1M HCL (2Ml) was added to 0.1M Potassium hydrogen phthalate (KHP) (100ml) was taken to the pH meter and read at pH of 4. Then made up to 200ml with deionised water (Robinson and Stokes, 1968). The clay samples (25g) were placed in a beaker and 125ml of the buffer solution was added and allowed to stand for 72 hours with mechanical agitation carried out for 3 hours daily, thereafter it was washed with (100ml) deionised water and the clay samples were further subjected to the procedures required for exchangeable cations and cation exchange capacity (C.E.C) determination. Three replicate determinations were done.

2.7.3 DETERMINATION OF BUFFER SOLUTION AT pH 5 USED FOR EXCHANCHEABLE CATIONS AND CEC

0.1M NaOH (45.2ML) 0.1M Potassium hydrogen phthalate (KHP) (100ml) was taken to the pH meter and read at pH of 5. Then made up to 200ml with deionised water (Robinson and Stokes, 1968). The clay samples (25g) were placed in a beaker and 125ml of the buffer solution was added and allowed to stand for 72 hours with mechanical agitation carried out for 3 hours daily, thereafter it was washed with (100ml) deionised water and the clay samples were further subjected to the procedures required for exchangeable cations and cation exchange capacity (C.E.C) determination. Three replicate determinations were done.

2.7.4 DETERMINATION OF BUFFER SOLUTION AT pH 8 USED FOR EXCHANCHEABLE CATIONS AND CEC

0.025M Borax (100ml) was added to 0.1M HCL (41.0ml) was taken to the pH meter and read at pH of 8. Then made up to 200ml with deionised water

(Robinson and Stokes, 1968). The clay samples (25g) were placed in a beaker and 125ml of the buffer solution was added and allowed to stand for 72 hours with mechanical agitation carried out for 3 hours daily, thereafter it was washed with (100ml) deionised water and the clay samples were further subjected to the procedures required for exchangeable cations and cation exchange capacity (C.E.C) determination. Three replicate determinations were done.

2.8 DETERMINATION OF AMMONIUM NITROGEN (NH4+-N)

2.8.1 REAGENTS

- Alkaline phenate: (200ml) phenol was diluted in (200ml) deionised water, (200g) was dissolved in (400ml). The phenol solution was gently added to the NaOH and made to 1L. This was used after 24 hours.
- Sodium potassium tartrate: 45g sodium potassium tartrate and 15g sodium citrate was dissolved in 100g deionized water and added to the solution to make it up to 300ml.
- Standard Ammonia stock, 100ppm: Pure dry Ammonium 0.3667g Sulphate was dissolved in 800ml deionized water and diluted to 1L.
- Sodium Hypochlorite

2.8.2 PROCEDURE USING A COLORIMETER

The KCl filtrate (5ml) was pipetted and placed in a 100ml standard flask, 2.5ml alkaline phenate, 1ml sodium tartrate, 2.5ml sodium hypochlorite were added to the flask and was shaken vigorously. Afterwards, it was taken to the colorimeter (Jenway 6051 model) and read at an absorbance of 636nm according to Baethgen 1989.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

Table 1: Results of exchangeable cations, cation exchange capacity (C.E.C), exchangeable acidity and percent base saturation of sample 1 obtained at different pH.

	pH 4	pH 5	pH 7	pH 8
Mg (Cmol/kg)	0.142±0.04	0.176±0.02	0.198±0.03	0.143±0.14
Ca (Cmol/kg)	2.528±0.08	1.188±0.16	2.692±0.08	1.558±0.12
Na (Cmol/kg)	0.938±0.06	0.409±0.03	0.783±0.12	1.884±0.05
K (Cmol/kg)	0.468±0.03	0.487±0.04	0.926±0.09	0.415±0.03
C.E.C (Cmol/kg)	4.958±0.03	2.715±0.03	6.531±0.02	4.698±0.01
Exchangeable Acidity (Cmol/kg)	0.883	0.456	1.933	0.698
% Base saturation	82.196	83.210	70.403	85.138

3.1 DISCUSSION

From the results in table 2, the following results were obtained for clay sample, treated at pH 4, the exchangeable cations Mg^{2+} 0.142±0.04cmol$_c$/kg, Ca^{2+} 2.528±0.08cmol$_c$/kg , Na^+ 0.938±0.06cmol$_c$/kg, K^+ 0.468±0.03cmol$_c$/kg, Cation exchange capacity, 4.958±0.03cmol$_c$/kg, exchangeable acidity 0.883cmol$_c$/kg, and percentage base saturation 82.196%

From the results in table 2, the following results were obtained for clay sample, treated at pH 5, the exchangeable cations Mg^{2+} 0.176±0.02cmol$_c$/kg, Ca^{2+}1.188±0.1cmol$_c$/kg $^+$, Na^+ 0.409±0.03cmol$_c$/kg, K^+ 0.487±0.04cmol$_c$/kg, Cation exchange capacity, 2.715±0.03cmol$_c$/kg, exchangeable acidity 0.456cmol$_c$/kg, and percentage base saturation 83.210%

From the results in table 2, the following results were obtained for clay sample, treated at pH 7, the exchangeable cations Mg^{2+}0.198±0.03cmol$_c$/kg, Ca^{2+} 2.692±0.08cmol$_c$/kg $^+$, Na^+ 0.783±0.12cmol$_c$/kg, K^+ 0.926±0.09cmol$_c$/kg, Cation exchange capacity, 6.531±0.02cmol$_c$/kg, exchangeable acidity 1.933cmol$_c$/kg, and percentage base saturation 70.403%.

From the results in table 2, the following results were obtained for clay sample, treated at pH 8, the exchangeable cations Mg^{2+}0.143±0.14cmol$_c$/kg, Ca^{2+} 1.558±0.12cmol$_c$/kg $^+$, Na^+ 1.884±0.05cmol$_c$/kg, K^+ 0.415±0.03cmol$_c$/kg, Cation exchange capacity, 4.698±0.01cmol$_c$/kg, exchangeable acidity 0.698cmol$_c$/kg, and percentage base saturation 85.138%.

From the results, obtained in table 3, for the exchangeable cations, it was observed that the highest values of Na^+, was obtained at pH 8, among the other pH used. At Ph7 Mg^{2+}, Ca^{2+}, and K^+, had their highest values. A gradual increase in values was observed in Mg^{2+}, Na^+, K^+, Ca^{2+}, values as the pH increased from acidic to neutral medium; Also a gradual increase in Na^+ value was also observed as the pH increased from neutral to basic medium; while, Mg^{2+}, Ca^{2+}, and K^+ value decreased from neutral to basic medium. There was also a decrease in Na^+, Ca^{2+}, the value as pH progressively increases in the acidic medium.

From the results, obtained in table 2, for the exchangeable cations, it was observed that at the highest values of Na^+ was obtained at pH 8, among the other pH used. At Ph7 Mg^{2+}, Ca^{2+}, and K^+, had their highest values. A gradual increase was observed in K^+, Mg^{2+}, as the pH is increased from acidic to neutral medium, while from neutral to alkaline media, Mg^{2+} ,Ca^{2+} and K^+ values decreased. There was also a decrease in the K^+, value as pH progressively increases in the acidic medium.

The properties of soil are greatly influenced when the ratio of exchangeable calcium ion to magnesium ion Ca:Mg is greater than or equal to 1. (Osemwota *et AL*., 2007; Salihaj and Bani, 2018). A few of these properties includes, soil drainage/water penetration, soil structures, root development and plant growth (Hazelton and Murphy, 2007; Osemwota *et al*., 2007; Ostrowska and Porebska, 2017).

A soil with a good structure, should have a calcium to magnesium ratio greater than 2:1 (Harzelton and Murphy 2007). In all the different pH used, the amount of Ca^{2+} measured, was significantly higher than twice than that of Mg^{2+}. It is evident that the sample is a well structured soil.

When Calcium to Magnesium ratio is higher than 4, Ca^{2+} is balanced, but if greater than 6, Magnesium is deficient (Rengasammy and Churchmann 1998). Judging from this fact, Magnesium is deficient in the clay sample for all the different pH worked on.

It is also important to take into consideration, the fact that, the tightness or looseness of a clay is determined by the Calcium to Magnesium ratio of the soil

(Astera 2014). Calcium content in soil determines the amount of oxygen in the soil, and also the drainage of the soil. The implications of more calcium in soil, is that calcium rich soil basically are loosed soils while more magnesium most likely implies a tight soil. The high calcium to magnesium ratio (Ca^{2+}: Mg^{2+}) in the sample makes it very susceptible to leaching.

Essential nutrients cations plants use in largest amounts inludes, Potassium K^+, Calcium Ca^{2+}, and Magnesium Mg^{2+} (Kissel and Sonons 1998). From the results stated above, the clay sample has sufficient amounts of Ca^{2+}, K^+ and Mg^+ for plants use. K^+ has substantial effects on enzyme activities on enzyme activation, photosynthesis, stomata movement, water retention and protein synthesis in plants (Marschner , 1995). It is evident that increased application of K^+ in different crops, enhances plant growth, plant yield, photosynthetic rate and drought resistance. (Sharma et al, 1996; Tiwari et al, 1998; Egilla et al, 2001).Therefore since the clay sample contains high K^+ content, it can be used to enhance yield of plants.

It is also important to note that the effect of Na on CEC can vary depending on the soil type, pH, and other factors. The effect of Na on soils can have a negative impact on CEC and plant growth, and careful management of Na levels is important for maintaining soil fertility and productivity. A study by (Yang et al. 2021) showed that the effect of Na on CEC is more visible in acidic soils compared to neutral or basic soils.

The highest C.E.C value of clay was obtained at pH 7 (5.613±0.04$cmol_c$/kg), Therefore, at pH 7, the soil is capable to hold more exchangeable bases or cations than other pH. Hence at pH 7, the clay can hold more cations (i.e no sufficient H^+ ions to push the cations away from the clay) than the other pH. It is visible that C.E.C slightly reduced with increasing pH in the acidic region and increased at pH 7(neutral region), but it greately reduced at the basic medium (pH 8).

The CEC of the clay sample showed great dependency on pH. CEC is an important tool in the studies of erosion, retention of pollutants and waste. The CEC is widely used in the characterization and study of soil fertility. The higher the CEC, the higher the fertility of that soil (Bergaya and Mayer, 1997). Hence soils with high CEC means more cationic nutrients (Ca^{2+}, K^{+}, Mg^{2+}) are held on the soil, decreasing their leachability and mobility. Low CEC indicates the presence of more cationic nutrients are in the soil solution, making them more available to plants but also increasing their leachability(Beaton, 2011).

Cation exchange capacity (C.E.C) is a measure of the cation holding capacity of a clay (Foth, 1990), and the highest CEC value was obtained at the neutral pH of 7 ($6.531 \pm 0.02 cmol_c/kg$), although the CEC values at all pH are sufficiently high enough to support plant growth. From Table 2, It is visible that CEC reduced drastically with increasing pH in the acidic region and increased at pH 7(neutral region), but it is significantly reduced at the basic medium.

It has been well established that soil fertility shows a direct proportionality to CEC values as it indicates the ability of the soil to hold cations, the high CEC values obtained at pH7 suggests that the desired plant nutrients (exchangeable cations) are more readily available for utilization plant at this pH. Thus, the relationship between CEC and the EA is very important to determine the best pH at which the exchangeable bases will be predominant in the clay.

The lowest percentage base saturation of 70.403% recorded at the neutral pH of 7 for the clay sample. The values for percent base saturation followed the order pH8> pH5 > pH4 >pH7. High percent base saturation implies that the negative sites of the clay material were occupied by exchangeable base cations. Thus, maintaining a soil blend with clay at a slightly acidic pH (pH5) or basic pH (8) will lead to maximum availability of plant nutrient. Moreso, at these pH values, the CEC levels are considerably high, therefore the clay fertility is guaranteed.

According to Moore (1998), values of C.E.C ranging from 0 to 10 Cmol/kg indicates a low value of CEC, and judging from its low C.E.C values it implies that the clay sample have low water holding capacity and also a very low nutrient holding capacity, as clay with high C.E.C also have a high water holding capacity (Quirrine Ketterings et al, 2007). Also, low C.E.C soils are more likely to develop more K^+ and increased Mg^{2+} deficiencies (CUCE 2007), which implies that the clay has a high K^+ content and a very low Mg^{2+}content.

The lower the C.E.C, the faster the soil pH decreases with time (Quirrine Ketterings et al, 2007), therefore the clay sample should be limed to increase the pH to the needed levels required for plants.

Exchangeable acidity includes Al^{3+}, and H^+ held on negatively charged sites on the clay. For strongly acidic soils, Al^{3+}, may become freely available to plants. At toxic levels when Al^{3+}, is greater than 5% of the C.E.C and when the clay is strongly acidic (pH less than 5.5 (Profit T. 2014). The highest exchangeable acidity was recorded at pH 7 (1.933$cmol_c$/kg) followed by pH 4 (0.883$cmol_c$/kg), which implies that other positive elements rather than H^+, Al^{3+} maybe present which was not accounted for.

Base saturation, is very similar to C.E.C, and it is the fraction of exchangeable cations that are base cations (Ca, Mg, K, and Na). The higher the exchangeable base cations, the more acidity can be neutralized in a short time. As expected, the low values of EA at pH 5, resulted in a very high percent base saturation of 83.210%. This confirms that at pH5, the negative sites of clay material are populated by more of the desired base cations (Mg^{2+}, Ca^{2+} Na^+, K^+).

The lowest percentage base saturation of 70.403% was recorded at the neutral pH of 7 for the clay sample. The values for percent base saturation followed the order pH8> pH5 > pH4 >pH7. High percent base saturation implies that the negative sites of the clay material were occupied by exchangeable base cations.

Thus, maintaining a soil blend with clay at a slightly acidic pH, of 5 or basic pH of 8 will lead to maximum availability of plant nutrient. Moreso, at these pH values, the CEC levels are considerably high, therefore the clay fertility is guaranteed.

Table 2: Results of exchangeable cations, cation exchange capacity (C.E.C), exchangeable acidity and percent base saturation of sample 2 obtained at different pH.

	pH 4	pH 5	pH 7	pH 8
Mg (Cmol/kg)	0.036±0.003	0.047±0.002	0.039±0.002	0.032±0.003
Ca (Cmol/kg)	0.349±0.06	0.837±0.08	1.297±0.17	1.339±0.08
Na (Cmol/kg)	1.598±0.08	2.043±0.09	1.906±0.16	2.185±0.04
K (Cmol/kg)	0.425±0.06	0.416±0.07	0.487±0.04	0.693±0.06
C.E.C (Cmol/kg)	4.919±0.03	4.901±0.04	5.613±0.04	4.813±0.04
Exchangeable Acidity (Cmol/kg)	2.511	1.558	1.884	0.564
% Base saturation	51.04	68.21	66.44	88.28

DISCUSSION

From the results in table 3, the following results were obtained for clay sample, treated at pH 4, the exchangeable cations Mg^{2+} 0.036±0.003cmol$_c$/kg, Ca^{2+} 0.349±0.06cmol$_c$/kg , Na^+ 1.598±0.08cmol$_c$/kg, K^+ 0.425±0.06cmol$_c$/kg, Cation exchange capacity, 4.919±0.03cmol$_c$/kg, exchangeable acidity 2.511cmol$_c$/kg, and percentage base saturation 51.04%.

From the results in table 3, the following results were obtained for clay sample, treated at pH 5, the exchangeable cations Mg^{2+} 0.047±0.002cmol$_c$/kg, Ca^{2+}0.837±0.08cmol$_c$/kg $^+$, Na^+ 2.043±0.09cmol$_c$/kg, K^+ 0.416±0.07cmol$_c$/kg, Cation exchange capacity, 4.901±0.04cmol$_c$/kg, exchangeable acidity 1.558cmol$_c$/kg, and percentage base saturation 68.21%.

From the results in table 3, the following results were obtained for clay sample, treated at pH 7, the exchangeable cations Mg^{2+}0.039±0.002cmol$_c$/kg, Ca^{2+} 1.297±0.17cmol$_c$/kg $^+$, Na^+ 1.906±0.16cmol$_c$/kg, K^+ 0.487±0.04cmol$_c$/kg, Cation exchange capacity, 5.613±0.04cmol$_c$/kg, exchangeable acidity 1.884cmol$_c$/kg, and percentage base saturation 66.44%.

From the results in table 3, the following results were obtained for clay sample, treated at pH 8, the exchangeable cations Mg^{2+}0.032±0.003cmol$_c$/kg, Ca^{2+} 1.339±0.08cmol$_c$/kg $^+$, Na^+ 2.185±0.04cmol$_c$/kg, K^+ 0.693±0.06cmol$_c$/kg, Cation exchange capacity, 4.813±0.04cmol$_c$/kg, exchangeable acidity 0.564cmol$_c$/kg, and percentage base saturation 88.28%.

From the results, obtained in table 3, for the exchangeable cations, it was observed that the highest values of Ca^{2+}, Na^+, K^+, was obtained at pH 8, among the other pH used. At pH 5 Mg^{2+} had its highest values. A gradual increase in values was observed in K^+, Ca^{2+}, values as the pH increased from acidic to neutral medium, while a gradual decrease in values was observed in Mg^{2+}, Na^+, as the pH increased from acidic to neutral medium. Also a gradual increase in Ca^{2+}, Na^+ values was also observed as the pH increased from neutral to basic medium; while, Mg^{2+} value decreased from neutral to basic medium. There was also a decrease in the K^+, value as pH progressively increases in the acidic medium.

The properties of soil are greatly influenced when the ratio of exchangeable calcium ion to magnesium ion Ca:Mg is greater than or equal to 1. (Osemwota *et AL*., 2007; Salihaj and Bani, 2018). A few of these properties includes, soil drainage/water penetration, soil structures, root development and plant growth (Hazelton and Murphy, 2007; Osemwota *et al*., 2007; Ostrowska and Porebska, 2017).

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It is also important to take into consideration, the fact that, the tightness or looseness of a clay is determined by the Calcium to Magnesium ratio of the soil (Astera 2014). Calcium content in soil determines the amount of oxygen in the soil, and also the drainage of the soil. The implications of more calcium in soil, is that calcium rich soil basically are loosed soils while more magnesium most likely implies a tight soil. The high calcium to magnesium ratio (Ca^{2+}: Mg^{2+}) in the sample makes it very susceptible to leaching.

Essential nutrients cations plants use in largest amounts inludes, Potassium K^+, Calcium Ca^{2+}, and Magnesium Mg^{2+} (Kissel and Sonons 1998). From the results stated above, the clay sample has sufficient amounts of Ca^{2+}, K^+ and Mg^+ for plants use. K^+ has substantial effects on enzyme activities on enzyme activation, photosynthesis, stomata movement, water retention and protein synthesis in plants (Marschner , 1995). It is evident that increased application of K^+ in different crops, enhances plant growth, plant yield, photosynthetic rate and drought resistance. (Sharma et al, 1996; Tiwari et al, 1998; Egilla et al, 2001).Therefore since the clay sample contains high K^+ content, it can be used to enhance yield of plants.

It is also important to note that the effect of Na on CEC can vary depending on the soil type, pH, and other factors. The effect of Na on soils can have a negative impact on CEC and plant growth, and careful management of Na levels is important for maintaining soil fertility and productivity. A study by (Yang et al. 2021) showed that the effect of Na on CEC is more visible in acidic soils compared to neutral or basic soils.

The highest C.E.C value of clay was obtained at pH 7 (6.531±0.02cmol$_c$/kg), so at pH 7 it is capable to hold more exchangeable bases or cations than other pH. Hence at pH 7, the clay can hold more cations (i.e no sufficient H^+ ions to push the cations away from the clay) than the other pH. It is visible that C.E.C reduced drastically with increasing pH in the acidic region and increased at pH 7(neutral region), but it slightly reduced at the basic medium.

The CEC of the clay sample showed great dependency on pH. CEC is an important tool in the studies of erosion, retention of pollutants and waste. The CEC is widely used in the characterization and study of soil fertility. The higher the CEC, the higher the fertility of that soil (Bergaya and Mayer, 1997). Hence soils with high CEC means more cationic nutrients (Ca^{2+}, K^+, Mg^{2+}) are held on the soil, decreasing their leachability and mobility. Low CEC indicates the presence of more cationic nutrients are in the soil solution, making them more available to plants but also increasing their leachability(Beaton, 2011).

Cation exchange capacity (C.E.C) is a measure of the cation holding capacity of a clay (Foth, 1990), and the highest CEC value was obtained at the neutral pH of 7 (6.531±0.02cmol$_c$/kg), although the CEC values at all pH are sufficiently high enough to support plant growth. From Table 2, It is visible that CEC reduced drastically with increasing pH in the acidic region and increased at pH 7(neutral region), but it is significantly reduced at the basic medium.

It has been well established that soil fertility shows a direct proportionality to CEC values as it indicates the ability of the soil to hold cations, the high CEC values obtained at pH7 suggests that the desired plant nutrients (exchangeable cations) are more readily available for utilization plant at this pH. Thus, the relationship between CEC and the EA is very important to determine the best pH at which the exchangeable bases will be predominant in the clay.

The lowest percentage base saturation of 70.403% recorded at the neutral pH of 7 for the clay sample. The values for percent base saturation followed the order pH8> pH5 > pH4 >pH7. High percent base saturation implies that the negative sites of the clay material were occupied by exchangeable base cations. Thus, maintaining a soil blend with clay at a slightly acidic pH (pH5) or basic pH (8) will lead to maximum availability of plant nutrient. Moreso, at these pH values, the CEC levels are considerably high, therefore the clay fertility is guaranteed.

According to Moore (1998), values of C.E.C ranging from 0 to 10 Cmol/kg indicates a low value of CEC,and judging from its low C.E.C values it implies that the clay sample have low water holding capacity and also a very low nutrient holding capacity, as clay with high C.E.C also have a high water holding capacity (Quirrine Ketterings et al, 2007). Also, low C.E.C soils are more likely to develop more K^+ and increased Mg^{2+} deficiencies (CUCE 2007), which implies that the clay has a high K^+ content and a very low Mg^{2+}content.

The lower the C.E.C, the faster the soil pH decreases with time (Quirrine Ketterings et al, 2007), therefore the clay sample should be limed to increase the pH to the needed levels required for plants.

Exchangeable acidity includes Al^{3+}, and H^+ held on negatively charged sites on the clay. For strongly acidic soils, Al^{3+}, may become freely available to plants. At toxic levels when Al^{3+}, is greater than 5% of the C.E.C and when the clay is strongly acidic (pH less than 5.5 (Profit T. 2014). The highest exchangeable acidity was recorded at pH 4 (2.511cmol$_c$/kg) followed by pH 7 (1.884cmol$_c$/kg), which implies that other positive elements rather than H^+, Al^{3+} maybe present which was not accounted for.

Base saturation, is very similar to C.E.C, and it is the fraction of exchangeable cations that are base cations (Ca, Mg, K, and Na). The higher the exchangeable base cations, the more acidity can be neutralized in a short time. As expected, the low values of EA at pH 5, resulted in a very high percent base saturation of 68.21%. This confirms that at pH 5, the negative sites of clay material are populated by more of the desired base cations (Mg^{2+}, Ca^{2+} Na^+, K^+).

The lowest percentage base saturation of 51.04% was recorded at the neutral pH of 4 for the clay sample. The values for percent base saturation followed the order pH8> pH5 > pH7 >pH4. High percent base saturation implies that the negative sites of the clay material were occupied by exchangeable base cations. Thus, maintaining a soil blend with clay at a slightly acidic pH of 5 or basic pH of 8 will lead to maximum availability of plant nutrient.

REFERENCES

Abe, S.S., Masunaga, T., Yamamoto, S., Honna, T. and Wakatsuki, T. (2006) Comprehensive Assessment of the Clay Mineralogical Composition of Lowland Soils in West Africa. Soil Science and Plant Nutrition, 52, 479-488. https://doi.org/10.1111/j.1747-0765.2006.00060.x

Akhirevbulu, O.E., Amadasun, C.V., Ogunbajo, M.I., and Ujuanbi, O. (2010). The Geology and Mineralogy of Clay Occurrences Around Kutigi Central Bida Basin, Nigeria. *Ethiopian Journal of Environmental Studies and Management*3(3): 49–56.

Al-Rawas, A.A. and Goosen, M.F. (2006)"Expansive soils: recent advances in characterization and treatment", Taylor & Francis,.

Baethgen, W.E., and Alley, M.M. (1989). A manual colorimetric procedure for measuring ammonium nitrogen in soil and plant Kjeldahl digests. *Communications in Soil Science and Plant Analysis* 20(9-10): 961–969. Bamidele, F.F. (2018).

Barton, C.D. and Karathanasis, A.D. (2002) Clay Minerals. In: Lal, R., Ed., Encyclopedia of Soil Science, Marcel Dekker, New York, USA, 187-192.

Bell, F., (1996)."Lime stabilization of clay minerals and soils", Engineering geology, vol. 42(4): pp. 223-237,.

Blanco-Canqui, H. and Lal, R. (2008) Principles of Soil Conservation and Management. Springer, Berlin, 564.

Bourg, I. C. (2018). Clay minerals in petroleum geology. Clay Minerals, 53(1), 1-22.

Brady, Nyle C, Weil, Ray R. (2008). The nature and property of clay.

Chaudhary, P., Singh, P., Singh, D., & Kaur, I. (2021). Role of clay minerals in cosmetics: A review. Applied Clay Science, 207, 106067.

Chen, F.H., "Foundations on expansive soils", Elsevier, vol. 12. 2012.

Chen, X., Zhou, Y., & Zhang, L. (2019). Recent advances in clay-based nanocomposites for food packaging applications. Journal of Agricultural and Food Chemistry, 67(19), 5315-5326.

Churchman, G. J., Raven, M. D., Brown, G. K., & Fraser, A. R. (2017). Clay colors and their origins. Applied Clay Science, 146, 1-11.

Churchman, G.J. and Lowe, D.J. (2012) Alteration, Formation, and Occurrence of Minerals in Soils. In: Huang, P.M., Li, Y. and Sumner, M.E., Eds., Handbook of Soil Science. Properties and Processes, 2nd Edition, CRC Press, Taylor & Francis, Boca Raton, 172.

Coiler, B. (1976). Pottery step-by-step; New York: Macmillan Publishing Co. Inc.

Cornell University Cooperative Extension (CUCE) (2007) Cation Exchange Capacity (CEC). Agronomy Fact Sheet Series # 22, Department of Crop and Soil Sciences, College of Agriculture and Life Sciences, Cornell University.

Das, B. (, 2015). "Principles of foundation engineering", Cengage learning.

Egilla, J.N; Davies, F.T. Jr and Drew, MC. (2001). Effects of potassium on drought resistane of Hibiscus rosa-sinensis cv. Leprechaun: Plant growth, leaf micro and macronutrient content and root longetivity. Plant and Soil 229(2): 213224.

Ehlers, Ernest, G. and Blatt, Harvey. (1982). Petrology, igneous, sedimentary and metamorphic. San Francisco: W.H. Freeman and Company.

Emmanuel, A., Hitler, L., Udochukwu, A.O., Ayoola, A.O., and Tizhe, T.F.(2018). Assessment of Organic Carbon and Available Nitrogen in the Soil of Some Selected Farmlands Located at Modibbo Adama University of Technology, Adamawa State, Nigeria. *J. Environ. Anal. Chem*. 5(239): 2380–2391.

Frank, H. (1975). The potter's dictionary of materials and techniques; London: Pitman Publishing.

G. Burrafato and F. Miano (1993) Determination of the cation exchange capacity of clays by surface tension measurements clay minerals 28, 475 – 481

Guggenheim, S. and Martin, R.T. (1995). Definition of clay and clay mineral: Journal report of the AIPEA nomenclature and CMS nomenclature committees, Clays and clay minerals 43:255-256,doi:10,1346/CCMN,1995.0430213.http://www.clays.org/journal/archive/ volume %2043/43- 2-255.pdf. The Properties of Clay

Haynes, R. J. (2005). Labile organic matter fractions as central components of the quality of agricultural soils: an overview. Advances in Agronomy, 85, 221-268.

Hazelton PA, Murphy BW 2007 Interpreting soil tests results: What Do All The Numbers Mean? CSIRO Publishing: Melbourne.

Hillier, S. (2003). Clay Mineralogy in Middleton,

Hwang, C., "Determination of material functions for unsaturated flow", Ph. D. dissertation, University of Colorado, Boulder, Co, USA, 2002.

Ismail, H. A., El-Gamal, S. M., Ibrahim, M. A., & Shaban, M. E. (2019). Utilization of kaolin as additive in the production of cement. Journal of Materials Research and Technology, 8(1), 835-842.

Karathanasis, A.D (1985) Mineralogy and soil productivity. Agronomy notes, 18, 1-4.

Karathanasis, A.D.(2006) Soil Mineralogy. Land Use and Land Cover, from Encyclopedia of Life Support Systems (EOLSS), Developed under the Auspices of the UNESCO. EOLSS Publishers, Oxford, UK.

Kim, R.Y., Yoon, J.K., Kim, T.S., Yang, J.E., Owens, G. and Kim, K.R. (2015) Bioavailability of Heavy Metals in Soils: Definitions and Practical Implementation—A G. K. Kome et al. DOI: 10.4236/ojss.2019.99010 175 Open Journal of Soil Science Critical Review. Environmental Geochemistry and Health, 37, 1041-1061. https://doi.org/10.1007/s10653-015-9695-y

Kissel, D.E. and L. Sonon (Eds). (2008). Soil Test Handbook For Georgia.\ Osemwota, I.O., Omueti, J.A.I., and Ogboghodo, A.I. (2007). Effect of calcium/magnesium ratio in soil on magnesium availability, yield, and yield components of maize. *Communications in soil science and plant analysis* 38(19-20):2849–2860.

Krause, L., Rodionov, A., Schweizer, S.A., Siebers, N., Lehndorff, E., Klumpp, E. and Amelung, W. (2018) Micro aggregate Stability and Storage of Organic Carbon Is Affected by Clay

Kumar, A., Kumar, V., Yadav, D., & Singh, B. (2018). Role of clay minerals in soil fertility and plant growth—A review. International Journal of Agriculture and Biology, 20(4), 767-776.

Kumar, R., Patel, R. K., & Kumar, V. (2020). Applications of clay minerals in pharmaceutical formulations: A review. Journal of Drug Delivery Science and Technology, 57, 101657.

Lai, Y. J., Lu, X. T., & Xie, H. (2017). Sorption of heavy metals on clay minerals and its environmental significance. In Soil Heavy Metals (pp. 65-91). Springer, Singapore.

Lainé, M., Balan, E., Allard, T., Paineau, E., Jeunesse, P., Mostafavi, M., Robert, J.L., and Le Caër, S. (2017). Reaction mechanisms in swelling clays under ionizing radiation: influence of the water amount and of the nature of the clay mineral. *RSC advances* 7(1): 526–534.

Leticia S. Sonon, David E. Kissel, and Uttam Saha (2014) Cation Exchange Capacity and Base Saturation

Leticia S. Sonon, David E. Kissel, and Uttam Saha (2014) Cation Exchange Capacity and Base Saturation.

Li, T., Wang, H., Wang, J., Zhou, Z. and Zhou, J. (2015) Exploring the Potential of Phyllosilicate Minerals as Potassium Fertilizers Using Sodium Tetraphenylboron and Intensive Cropping with Perennial Ryegrass. Scientific Reports, 5, Article No. 9249. https://doi.org/10.1038/srep09249

Lu, Y., Zhang, X., Jiang, L., & Li, S. (2020). Applications of clay minerals in drug delivery. Journal of Materials Chemistry B, 8(45), 10351-10365.

Lvov, Y., de Villiers, M., & Fakhrullin, R. (2008). Clay nanotube encapsulation for functional biocomposites. Advanced Materials, 20(24), 4739-4743.

Majumder, A., Gupta, A., & Ali, M. (2020). Role of clay minerals in drug delivery: A review. Journal of Drug Delivery Science and Technology, 56, 101522.

Mandiringana, O.T., Mnkeni, P.N.S., Mkile, Z., van Averbeke, W., Van Ranst, E. and Verplancke, H. (2005) Mineralogy and Fertility Status of Selected Soils of the Eastern Cape Province, South Africa. Communications in Soil Science and Plant Analysis, 36, 2431-2446. https://doi.org/10.1080/00103620500253514

Marschner, H. (1995). Mineral Nutrition of Higher Plants. 2nd Ed. Academic Press, San Diego, California, USA.

Martel, Y.A., De Kimpe, C.R., and Laverdière, M.R. (1978). Cation-exchange Capacity of Clay-rich Soils in Relation to Organic Matter, Mineral Composition, and Surface Area. *Soil Science Society of America Journal* 42(5): 764–767. Ogeleka, D.F., Nmai, O.O., Okieimen,

Mc Dowell, C., (1959). “Stabilization of soils with lime, lime-fly ash, and other lime reactive materials”, Highway Research Board Bulletin, vol. 231.

McKenzie NJ, Jacquer DJ, Isbell RF, Brown KL (2004) Australian Soils and Landscapes: An Illustrated compendium. CSIRO Publishing: Collingwood, Victoria.

McLean JE, Bledsoe BE (1992) Behaviour of metals in soils. Groundwater Issue. United States Environmental Protection Agency (USEPA).

http://www.epa.gov/tio/tsp/download/issue14.pdf. Accessed 26 January 2012.

Mitchell, J., SOGAK, “Fundamentals of soil behavior”, New York: John Wiley & Sons,

Moterle, D.F., Kaminski, J., dos Santos, R.D., Caner, L. and Bortoluzzi, E.C. (2016) Impact of Potassium Fertilization and Potassium Uptake by Plants on Soil Clay Mineral Assemblage in South Brazil. Plant and Soil, 406, 157-172. https://doi.org/10.1007/s11104-016-2862-9

Nagy, N.M. and Konia, J. (2010) Interfacial Chemistry of Rocks and Soil. CRC Press, Taylor & Francis Group, Boca Raton, FL, 229.

Nduwimana, A., Chang, S. X., Wu, X. B., & Zhang, Z. (2016). Adsorption of heavy metals by clay minerals and variable charge soils. Advances in Agronomy, 136, 235-274.

Odubiyi, J.A. (2004). Clay, natures endowment for mankind. Multi-disciplinary Journal of Research Development. 3(1) Pp. 136 – 140.

Odubiyi, J.A. (2004). The potentials of clay for human development; Journal of Vocational Education. 5(1) Pp. 126 – 133

Onyeobi, T.U.S., Ujuji, E.R., and Okagbue, C.O. (1994). Geotechnical properties of Soils derived from the Udi and Mamu formations in the Enugu- Okigwe area of South eastern Nigeria and their relations to engineering problems. *Nigerian Journal of Mining and Geology* 30(1): 117-123.

Ostrowska, A., and Porębska, G. (2017). The content of calcium and magnesium and the Ca: Mg ratio in cultivated plants in the context of human and animal demand for nutrients. *Journal of Elementology*22(3): 995–1004.

Pansu, Marc, Gauntheyrou, Jacques (2006) Handbook of soil analysis, Berlin, springer verger.pp. 709-754)

Peng, X., Horn, R., Peth, S. & Smucker, A., “Quantification of soil shrinkage in 2D by digital image processing of soil surface”, Soil and Tillage Research, vol. 91(1): p. 173-180, 2006.

Powers, J.S. and Schlesinger, W.H. (2002) Relationships among Soil Carbon Distributions and Biophysical Factors at Nested Spatial Scales in Rain Forests of Northeastern Costa Rica. Geoderma, 109, 165-190. https://doi.org/10.1016/S0016-7061(02)00147-7

Rayment GE, Higginson FR (1992) Electrical conductivity. In ‘Australian Laboratory Handbook of Soil and Water Chemical Methods, ’Inkata Press: Melbourne.

Rengasamy P, Churchman GJ (1999) Cation Exchange Capacity, Exchangeable Cations and Sodicity. In Soil Analysis an Interpretation Manual. (Eds KI Peverill, LA Sparrow and DJ Reuter). CSIRO: Melbourne.

Saidi, D., 2012. Importance and role of cation exchange capacity on the physicals properties of the Cheliff saline soils (Algeria). Procedia Eng. 33, 435–449.

Salihaj, M. and Bani, A. (2018). Chemical Properties of Serpentine Soils from Kosovo. *Albanian Journal of Agricultural Science* 17(1): 78–83.

Schaetzl, Randal J, Thompson Michael L. (2015). Soils. Genesis and geomorphology (2nd edition).

Scherer, H.W., Feils, E. and Beuters, P. (2014) Ammonium Fixation and Release by Clay Minerals as Influenced by Potassium. Plant, Soil and Environment, 60, 325-331. https://doi.org/10.17221/202/2014-PSE

Schulten, H.R. and Leinweber, P. (2000) New Insights into Organic-Mineral Particles: Composition, Properties and Models of Molecular Structure. Biology and G. K. Kome et al. DOI: 10.4236/ojss.2019.99010 182 Open Journal of Soil Science Fertility of Soils, 30, 399-432. https://doi.org/10.1007/s003740050020

Sharma, K.D; Nandwal, A.S and Kuhad, M.S (1996). Potasium effects on Co_2 exchange, ARA and yield of clusterbean cultivars under water stress. Journal of Potassium Research 12: pp. 412-423.

Singh, B., & Gilkes, R. J. (1992). Factors influencing the color of soils and clays. Soil Research, 30(6), 763-801.

Sirivitmaitrie, C., Puppala, A. J., Saride, S. and Hoyos, L. (2204) “Combined lime-cement stabilization for longer life of lowvolume roads”, Transportation Research Record: Journal of the Transportation Research Board, vol. (1): pp. 140-147, 2011.

Six, J., Elliott, E. T., & Paustian, K. (2002). Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. Soil Biology and Biochemistry, 34(11), 1623-1637.

Sollins, P., Robertson, G.P. and Uehara, G. (1988) Nutrient Mobility in Variableand Permanent-Charge Soils. Biogeochemistry, 6, 181-199. https://doi.org/10.1007/BF02182995

Sposito, G. (1989). The chemistry of soils. Oxford University Press.

Stephen Guggeheim (2011) Introduction to the properties of clay yara – Technical Bulletin No.4 cation exchange capacity. Department of Geological Sciences, University of Illinois of Chicago page 371 – 388

Tiwari, H.S; Agarwal, R.M and Bhatt, R.K. (1998). Photosynthesis, stomatal resistance and related characters as influenced by potassium under normal conditions in rice (Oryza sativa L.). Indian Journal of plant Physiology 3(4): 314-316.

Venkaramuthyalu, P., K., Ramu, F. and Prasada, R. G., (2012). "Study on performance of chemically stabilized expansive soil", International Journal of Advances in Engineering and Technology, vol. 2: pp. 139-148,.

Wilson, M.J. (1999). The Origin and Formation of Clay Minerals in Soils: Past, Present and Future Perspectives. Clay Minerals, 34, 7-25. https://doi.org/10.1180/000985599545957

Yerima, B.P.K. and Van Ranst, E. (2005) Introduction to Soil Science: Soils of the Tropics. Trafford Publishing, Canada, 397.

APPENDIX

SAMPLE 1

Table 3: AT pH 4 AAS AND FLAME EMISSION

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	2.30	1.50	1.30
Ca^{2+}	49.40	52.30	50.00
Na^{+}	22.83	20.18	1.30
K^{+}	17.20	19.50	18.00

Mean Mg^{2+} = = 1.7 mg/l

Standard Deviation Mg^{2+}= 0.5292

Mean Ca^{2+} = = 50.567 mg/l

Standard Deviation Ca^{2+} = 1.5308

Mean Na^{+}= = 21.57mg/l

Standard Deviation Na^{+} = 1.3298

Mean K^{+}= = 18.233mg/l

Standard Deviation K^{+} =1.167

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 17 mg/Kg

Extractable Calcium (Ca) = = 505.67 mg/Kg

Extractable Sodium (Na) = = 215.7 mg/Kg

Extractable Potassium (K) = = 182.33 mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.1417 Cmol/Kg

Ca (Cmol/Kg) = = 2.5283 Cmol/Kg

Na (Cmol/Kg) = = 0.9378 Cmol/Kg

K (Cmol/Kg) = = 0.4675 Cmol/Kg

Table 4: AT pH 5 AAS AND FLAME EMISSION

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	2.44	1.90	1.98
Ca^{2+}	23.24	27.00	21.00
Na^{+}	10.20	8.70	9.30
K^{+}	19.00	20.60	17.40

Mean Mg^{2+} = = 2.11mg/l

Standard Deviation Mg^{2+}= 0.2915

Mean Ca^{2+} = = 23.75mg/l

Standard Deviation Ca^{2+} = 3.0319

Mean Na^{+}= = 9.40mg/l

Standard Deviation Na^{+} = 0.7550

Mean K^{+}= = 19.00mg/l

Standard Deviation K^+ =1.167

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 21.1mg/Kg

Extractable Calcium (Ca) = = 237.5mg/Kg

Extractable Sodium (Na) = = 94 mg/Kg

Extractable Potassium (K) = = 190 mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.1758 Cmol/Kg

Ca (Cmol/Kg) = = 1.1875 Cmol/Kg

Na (Cmol/Kg) = = 0.4087 Cmol/Kg

K (Cmol/Kg) = = 0.4872 Cmol/Kg

Table 5: AT pH 7 AAS AND FLAME EMISSION

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	2.01	2.50	2.60
Ca^{2+}	54.30	55.20	52.00
Na^{+}	16.00	17.00	21.00
K^{+}	32.44	37.00	38.90

Mean Mg^{2+} = = 2.37

Standard Deviation Mg^{2+}= 0.316

Mean Ca^{2+}= = 53.833

Standard Deviation Na^{+} = 1.650

Mean Na^{+} = = 18.00

Standard Deviation Ca^{2+} = 2.6456

Mean K^{+} = = 36.123

Standard Deviation K^{+} =3.388

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 23.7mg/Kg

Extractable Calcium (Ca) = = 538.33mg/Kg

Extractable Sodium (Na) = = 180 mg/Kg

Extractable Potassium (K) = = 361.23 mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.1975 Cmol/Kg

Ca (Cmol/Kg) = = 2.6917 Cmol/Kg

Na (Cmol/Kg) = = 0.7826 Cmol/Kg

K (Cmol/Kg) = = 0.9262 Cmol/Kg

Table 6: AT pH 8 AAS AND FLAME EMISSION

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	1.70	1.55	1.90
Ca^{2+}	34.00	30.00	29.50
Na^{+}	42.00	43.00	45.00
K^{+}	16.50	17.00	15.00

Mean Mg^{2+} = = 1.717

Standard Deviation Mg^{2+}= 0.200

Mean Na^{+} = = 43.33

Standard Deviation Na^{+} = 1.2472

Mean Ca^{2+}= = 31.1667

Standard Deviation Ca^{2+} = 2.4663

Mean K^+ = = 16.1667

Standard Deviation K^+ =1.0408

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 17.17mg/Kg

Extractable Calcium (Ca) = = 311.667mg/Kg

Extractable Sodium (Na) = = 433.33 mg/Kg

Extractable Potassium (K) = = 161.667mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.1431 Cmol/Kg

Ca (Cmol/Kg) = = 1.5583 Cmol/Kg

Na (Cmol/Kg) = = 1.8839 Cmol/Kg

K (Cmol/Kg) = = 0.4145 Cmol/Kg

TABLE 7: AMMONIUM NITROGEN (NH_4-N) RESULTS AT pH 4

NH_4-N	1st absorbance reading	2nd absorbance reading	3rd absorbance reading
	0.503	0.545	0.498

Mean = = 0.515

Standard Deviation = 0.03

CONVERSION OF ABSORBANCE TO mg/L

Mg/L =

Slope reciprocal = 13.754

Color volume = 100

Aliquot volume =10ml

Therefore absorbance = = 70.833mg/L

CONVERSION OF mg/L TO CEC (Cmol/kg)

(mg NH_4-N / L) × () × (1 Meq NH_4 / 14mg NH_4) × 100

70.833 × 0.01 × 0.07 ×100 = 4.958cmol/kg

CALCULATION OF EXCHANGEABLE ACIDITY

ACIDITY cmol / Kg = C.E.C – (Mg + Ca + Na + K)

= 4.958 – (0.1417 + 2.5283 + 0.4675 + 0.9378)

= 0.8827 CEC

CALCULATION OF PERCENTAGE BASE SATURATION

% BASE SATURATION =

=

= 82.196%

TABLE 8: AMMONIUM NITROGEN (NH_4-N) RESULTS AT pH 5

NH_4-N	1st absorbance reading	2nd absorbance reading	3rd absorbance reading
	0.243	0.298	0.304

Mean = = 0.282

Standard Deviation = 0.03

CONVERSION OF ABSORBANCE TO mg/L

Mg/L =

Slope reciprocal = 13.754

Color volume = 100

Aliquot volume =10ml

Therefore absorbance = = 38.786 mg/L

CONVERSION OF mg/L TO CEC (Cmol/kg)

(mg NH_4-N / L) × () × (1 Meq NH_4 / 14mg NH_4) × 100

38.786 × 0.01 × 0.07 ×100 = 2.7150cmol/kg

CALCULATION OF EXCHANGEABLE ACIDITY

ACIDITY cmol / Kg = C.E.C – (Mg + Ca + Na + K)

= 2.7150– (0.4087 + 0.4872 + 0.1758 + 1.1875)

= 0.4558$cmol_C$/Kg

CALCULATION OF PERCENTAGE BASE SATURATION

% BASE SATURATION =

=

= 83.21%

TABLE 9: AMMONIUM NITROGEN (NH_4-N) RESULTS AT pH 7

NH_4-N	1st absorbance reading	2nd absorbance reading	3rd absorbance reading
	0.680	0.653	0.702

Mean = = 0.678
Standard Deviation = 0.02

CONVERSION OF ABSORBANCE TO mg/L

Mg/L =

Slope reciprocal = 13.754

Color volume = 100

Aliquot volume =10ml

Therefore absorbance = = 73.298mg/L

CONVERSION OF mg/L TO CEC (Cmol/kg)

(mg NH_4-N / L) × () × (1 Meq NH_4 / 14mg NH_4) × 100

73.298× 0.01 × 0.07 ×100 = 6.531cmol/kg

CALCULATION OF EXCHANGEABLE ACIDITY

ACIDITY cmol / Kg = C.E.C – (Mg + Ca + Na + K)

= 6.531– 4.598

=1.933$cmol_C$/Kg

CALCULATION OF PERCENTAGE BASE SATURATION

% BASE SATURATION =

=

= 70.403%

TABLE 10: AMMONIUM NITROGEN (NH_4-N) RESULTS AT pH 8

NH_4-N	1st absorbance reading	2nd absorbance reading	3rd absorbance reading
	0.484	0.479	0.502

Mean = = 0.488

Standard Deviation = 0.012

CONVERSION OF ABSORBANCE TO mg/L

Mg/L =

Slope reciprocal = 13.754

Color volume = 100

Aliquot volume =10ml

Therefore absorbance = = 67.12mg/L

CONVERSION OF mg/L TO CEC (Cmol/kg)

(mg NH_4-N / L) × () × (1 Meq NH_4 / 14mg NH_4) × 100

67.12× 0.01 × 0.07 ×100 = 4.698cmol/kg

CALCULATION OF EXCHANGEABLE ACIDITY

ACIDITY cmol / Kg = C.E.C – (Mg + Ca + Na + K)

= 4.698-3.9998

=0.6982cmol$_C$/Kg

CALCULATION OF PERCENTAGE BASE SATURATION

% BASE SATURATION =

=

= 85.138%

SAMPLE 2

Table 11: AAS AND FLAME EMISSION AT pH 4

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	0.41	0.47	0.42
Ca^{2+}	8.39	6.54	6.00
Na^{+}	35.00	36.76	38.50
K^{+}	14.20	17.59	17.88

Mean Mg^{2+} = = 1.717

Standard Deviation Mg^{2+}= 0.433

Mean Na^{+} = = 36.7533

Standard Deviation Na^{+} =1.75

Mean Ca^{2+}= = 6.9767

Standard Deviation Ca^{2+} = 1.2534

Mean K^+ = = 16.5567

Standard Deviation K^+ =2.046

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 4.333mg/Kg

Extractable Calcium (Ca) = = 69.767mg/Kg

Extractable Sodium (Na) = =367.53 mg/Kg

Extractable Potassium (K) = = 165.567mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.0361Cmol/Kg

Ca (Cmol/Kg) = = 0.349 Cmol/Kg

Na (Cmol/Kg) = = 1.598Cmol/Kg

K (Cmol/Kg) = = 0.425Cmol/Kg

Table 11: AAS AND FLAME EMISSION AT pH 5

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	0.54	0.59	0.55
Ca^{2+}	15.78	18.54	16.00
Na^+	45.00	47.00	49.00
K^+	19.20	14.50	15.00

Mean Mg^{2+} = = 0.56

Standard Deviation Mg^{2+}= 0.026

Mean Na^+ = = 47

Standard Deviation Na^+ =2.00

Mean Ca^{2+}= = 16.7733

Standard Deviation Ca^{2+} = 1.534

Mean K^+ = = 16.233

Standard Deviation K^+ =2.5813

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 5.6mg/Kg

Extractable Calcium (Ca) = = 167.333mg/Kg

Extractable Sodium (Na) = = 470mg/Kg

Extractable Potassium (K) = = 162.33mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.047Cmol/Kg

Ca (Cmol/Kg) = = 0.837 Cmol/Kg

Na (Cmol/Kg) = = 2.043 Cmol/Kg

K (Cmol/Kg) = = 0.416 Cmol/Kg

Table 11: AAS AND FLAME EMISSION AT pH 7

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	0.49	0.47	0.45
Ca^{2+}	22.32	26.50	29.00
Na^{+}	48.00	40.72	42.81
K^{+}	17.52	19.00	20.45

Mean Mg^{2+} = = 0.47

Standard Deviation Mg^{2+}= 0.02

Mean Na^{+} = = 43.843

Standard Deviation Na^{+} =3.748

Mean Ca^{2+}= =25.94

Standard Deviation Ca^{2+} = 3.3750

Mean K^{+} = = 18.99

Standard Deviation K^{+} =1.4650

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 4.7mg/Kg

Extractable Calcium (Ca) = = 259.4mg/Kg

Extractable Sodium (Na) = = 438.43mg/Kg

Extractable Potassium (K) = = 189.9mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.039Cmol/Kg

Ca (Cmol/Kg) = = 1.297 Cmol/Kg

Na (Cmol/Kg) = = 1.906 Cmol/Kg

K (Cmol/Kg) = = 0.487 Cmol/Kg

Table 12: AAS AND FLAME EMISSION AT pH 8

CATIONS	1st reading (mg/L)	2nd reading (mg/L)	3rd reading (mg/L)
Mg^{2+}	0.34	0.42	0.38
Ca^{2+}	25.42	28.39	26.53
Na^{+}	50.20	51.09	49.47
K^{+}	22.58	28.53	30.00

Mean Mg^{2+} = = 0.38

Standard Deviation Mg^{2+}= 0.04

Mean Na^{+} = = 50.253

Standard Deviation Na^{+} =0.8113

Mean Ca^{2+}= =26.78

Standard Deviation Ca^{2+} = 1.50

Mean K^{+} = = 27.037

Standard Deviation K^{+} =2.1965

Conversion of mg/L to mg/kg

Extractable Magnesium (Mg) = = 3.8mg/Kg

Extractable Calcium (Ca) = = 267.8mg/Kg

Extractable Sodium (Na) = = 502.53mg/Kg

Extractable Potassium (K) = =270.37mg/Kg

Exchangeable Bases (Mg, Ca, Na, K)

Mg (Cmol/Kg) = = 0.032 Cmol/Kg

Ca (Cmol/Kg) = = 1.339 Cmol/Kg

Na (Cmol/Kg) = = 2.1849 Cmol/Kg

K (Cmol/Kg) = = 0.6933Cmol/Kg