



Base – Line Characterization of Unwana Ogwuta Cave (Iyi Ogo) New Site Clay in Afikpo, Ebonyi State

OBI, Chidi^{*1} & AGHA, Inya Inya²

¹Physical Chemistry Unit, Department of Pure and Industrial Chemistry, Faculty of Science,
University of Port Harcourt, Rivers State, Nigeria

²Chemistry Department, Ebonyi State College of Education, Ikwo

Corresponding Authors E – Mail: zarasexcom@yahoo.com

ABSTRACT

The physicochemical properties of the clay sample obtained from the underground Ogwuta (Isi Ogo) cave of Unwana New Site, Afikpo in Ebonyi State were evaluated. The following parameters such as pH, specific gravity, specific surface area, cation exchange capacity, pore volume, loss on ignition, metal oxide composition and the vibrational bands of the clay sample were examined. The results obtained showed that the physical properties of the clay sample are as follows: pH (2.8), specific surface area (133.4 m²/g), specific gravity (2.16 g/cm³), pore volume (0.45 m³/g), cation exchange capacity (18.8 meq/100 g) and loss on ignition (11.409 %). The metal oxide composition analysis showed that an alumina (32.6 %) and silica (47.3%) oxide was in major quantities. The low levels of magnesium, calcium and infinitesimal amount of phosphorus revealed limited mineral impurities. The Fourier Transform Infra-Red (FTIR) studies showed vibrational bands of Si-O, Al-OH and Al-O-Si in the clay interlayer. The results of the physicochemical properties of clay obtained from the Ogwuta cave of Unwana New Site have shown that it can be refined, modified and packaged for various industrial applications ranging from catalysis, paint production, building, and pottery to pollution control. It can also create employment opportunities and geometrically add value to our Gross Domestic Product.

Keywords: characterization, clay, Unwana, cave, economic importance

INTRODUCTION

Clay minerals sometimes maintain variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations found on earth surface (Sharma and Srivastava, 2006). Clay minerals occur extensively on earth but relatively rare in other planets. Its presence has however been detected in Mars (Wall, 2013). They are formed usually as by – product of chemical weathering of other silicate minerals, often found in shale's, the most common type of sedimentary rock. Clay minerals are usually ultrafine – grained.

Structurally, clay minerals like all phyllosilicates are characterized by two dimensional sheets of corner sharing SiO₄ tetrahedra and /or AlO₄ octahedra. The sheet units have the chemical composition (AlSi)₃O₄. Each silica tetrahedra shares three of its vertex oxygen atoms with other tetrahedral, forming a hexagonal array in two – dimensions. The fourth vertex is not shared with other tetrahedra and all of the tetrahedra points in the same direction, that is, all of the unshared vertices are on the same side of the sheet.

The octahedral layer is centered by with Al³⁺, Fe³⁺, Mg(OH)₂, but Zn²⁺, Li⁺ and Cr³⁺ can substitute as well. Si⁴⁺ is normally the center of tetrahedral layer. The cations of the octahedral sheets are coordinated by six oxygen atoms. The unshared vertex from the tetrahedral sheet also forms part of side of the octahedral sheet, but an additional oxygen atom is located above the gap in the tetrahedral sheet. This oxygen atom is bonded to hydrogen atom forming an OH group.

Different clays have different ways these layers of sheets are packed or arranged. Consequently clays are categorized depending on the tetrahedral – octahedral sheet arrangement. If there is only one tetrahedral and one octahedral in each layer, the clay is known as a 1:1 (T–O) clay. The alternative known as 2:1 (T–O–T) clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing toward each other and forming each side of the octahedral sheet. Bonding between the tetrahedral and octahedral sheets

requires that the tetrahedral sheet becomes twisted; causing ditrigonal distortion to the hexagonal array, and the octahedral sheet is flattened. This minimizes the overall valence bond distortion of the crystallite. Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge, or will have a net negative charge. If the layers are charged, it will be balanced by interlayer cations such as Na^+ or K^+ . In each case, the interlayer can also contain water. The crystal structure is formed from a stack of layers interspaced with the interlayer (Moore and Reynolds, 1997).

Based on their structures and chemical compositions, the clay minerals can be divided into four main classes of clays namely illites, smectites, chlorites and kaolinite.

The clay sample used in this study was collected from the underground Ogwuta (Isi Ogo) cave in Unwana, Afikpo. Afikpo being noted as the centre of ancient Igbo tradition is also endowed with different kinds of clay minerals. Afikpo popularly called "Ehugbo" is a town and the second largest urban area in Ebonyi State, Nigeria. It is the headquarters of Afikpo North Local Government Area. It is situated in the southern part of Ebonyi State and is bordered to the north by the town of Akpoha, to the south by Unwana, to the south west by Edda in Afikpo South LGA, to the East by the Cross River and to the West by Amasiri. Afikpo covers an area approximately 164 square kilometers in size. Afikpo is a hilly area despite occupying a region low in altitude, which rises 350 feet above sea level. It is a transitional area between open grassland and tropical forest and has an average annual rainfall of seventy – seven inches (198 cm).

According to the work done by Nwabinele *et al.*, (2013), Unwana is found at the extreme north – east of Ebonyi State. There have been several refractory, physical and chemical investigations of clay minerals found along the outer surfaces of Unwana, Afikpo, Nkanu and Udi in Enugu State, Anambra State and some parts of Delta State. The results obtained showed that these clay minerals are good precursors for numerous industrial applications. However, since evidence of sedimentary formations in Unwana have been established (Nwabinele *et al.*, (2013), there are needs to investigate the characteristic properties of the underground clay minerals mostly especially the ones found inside the caves.

This base – line study will ultimately put the clay minerals obtained within this region on grades depending on their composition. This study will draw the attention of the federal Government on the need to refine and package these clay minerals for export and equally to reduce the cost of importing these materials as catalysts and adsorbents used by our petrochemical and allied industries. This will create employment opportunities that the Federal Government of Nigeria is looking for and geometrically add value to our Gross Domestic Product (GDP).

Therefore, the aim of this study is to investigate and characterize underground clay sample found in Ogwuta (Isi Ogo) cave of Unwana New Site in Afikpo, Ebonyi State and present economic values of the clay sample.

METHODOLOGY

Sample Collection and Preparation

The clay sample was collected from its natural deposit 12 cm below earth surface in the Ogwuta (Isi Ogo) cave of Unwana New Site, Afikpo North Local Government Area of Ebonyi State, Nigeria. The sample was sun – dried for 2 – 3 days. The impurities found on the clay sample were removed by hand. The sample was further oven – dried at 105°C for 2 hours, crushed with an iron roller to fine particle size of $63\mu\text{m}$. It was stored in a glass bottle for further use.

Characterization of Clay Sample

pH Determination

Deionized water (50 ml) was added to 10 g of clay ($63\mu\text{m}$) sample in a 250 ml beaker in the ratio of 1:5 of clay to water. The mixture was stirred with glass rod and allowed to stand for 30 minutes and the pH taken.

Surface Area Determination

The clay sample (1.5 g) passed through $63\mu\text{m}$ was agitated in 100 ml of dilute HCl, that had been diluted to pH of 3.0. Then 30 g of NaCl was added while stirring the suspension. The volume was made up to 150 ml with deionized water, resulting in the change of pH to 4.0. 0.1N NaOH was used to raise the pH

from 4.0 to 9.0 and the volume (**V**) of NaOH used was recorded. The surface area **s**, was calculated using the equation:

$$s = 32v - 25 \dots\dots\dots (1)$$

Specific Gravity Determination

This was determined using the Archimedes principle described by Dada et al., (2012). Briefly, the weight of an empty 50 ml specific bottle (**w₁**) was measured on a weighing balance. Then the bottle was filled with water and the weight (**w₂**) measured. Clay sample (10 g) passed through 63 – 150µm was added to an empty dry specific bottle and the weight (**w₃**) recorded. Finally, the bottle containing the sample was then filled with water and all air bubbles expelled before the weight (**w₄**) was measured. The specific gravity (**s.g**) of the clay was calculated as below:

$$s. g = \frac{\text{weight of sample}}{\text{weight of equal volume of water}} \dots\dots\dots(2)$$

$$s. g = \frac{w_3 - w_1}{(w_2 - w_1) - (w_4 - w_3)} \dots\dots\dots (3)$$

Total Pore Volume Determination

The total pore volume of the clay sample (63µm) was determined by boiling 20 g of the sample immersed in water. After the air in the sample had been displaced, the sample was superficially dried and weighed. The total pore volume was calculated as increase in weight divided by the density of the water (1 g/cm³).

Cation Exchange Capacity Determination

The cation exchange capacity of the clay was determined according to the method described by Kahr and Madsen, (1995). The clay sample (5 g) was transferred into a centrifuge tube and 35 ml of 1M NH₄OAC (ammonium acetate) added. The tube was shaken for 15minutes in a reciprocating shaker and centrifuged at 2000 revolutions per minute. The supernatant was poured off and another 30 ml of NH₄OAC added to residual clay, mixed, shook and centrifuged as before. The process was repeated until sample was treated 5 times. The sample was further washed 3 times using 30 ml of 95% ethanol. The washed clay was also treated 5 times with 45% KCl using 30 ml each. The volume of collected extract was made up to 200 ml using KCl solution. The above extract (10 ml) was transferred to a flask and mixed indicator of bromocresol green plus methyl red added and titrated to a faint pink end point using 0.01M HCl.

Metal oxide Composition Determination

The sample (1 g) was washed three times with a homoionic solution of 1M NH₄Cl and then with a 50% (v/v) mixture of ethanol and distilled water until the supernatant solution is free of Cl⁻ by the AgNO₃ method. The sample was oven – dried overnight at 105°C. The elemental composition of the sample was determined following digestion with analytical grade aqua regia and boric acid in an oven. The sodium and potassium contents were analyzed by flame emission spectrometry. All other elements including silicon, aluminum, iron, magnesium, manganese and titanium were determined by Atomic Absorption Spectrometry.

Fourier Transform Infra – Red (FTIR) Spectroscopy

Small amount of the sample was mixed with a little quantity of KBr in the ratio of 1:10 (1 mg: 10 mg) and finely pulverized in an agate mortar with pestle to homogenize the mixture. A little amount of the mixture was placed in a miniature press and compressed to form a disc or pellet of about 1mm thickness. This was placed in the appropriate sample holder, the holder, with sample, was mounted on the sample compartment of the FTIR spectrometer. The system was set to make 16 scans within 4000 cm⁻¹ to 400 cm⁻¹ and on completion of the scan, the spectrum was displayed on the ‘view’ window automatically. The individual peaks on the spectrum were labeled with their corresponding wavelengths and the spectrum printed out.

RESULTS AND DISSCUSION

Clay pH

The pH of the clay sample was 2.8 at 30°C. This acidic value can largely be accounted for by the composition of the parent rock – material from which it was formed and partly by environmental factors such as rainfall (Denis *et al.*, 2009), that is, clay samples from areas with lots of rainfall have pH values less than 3.5. The result agrees with the observation by Suedina and Carla, (2012) that clays have 0.67 units of negative charge per unit cell resulting from the isomorphous substitution of Al³⁺ by Mg²⁺ and Si⁴⁺ by Al³⁺. Consequently, they behave as weak acids with pH values less than 4. The acid level, more often than not is related to the cation exchange capacity (CEC) of the clay sample. High CEC indicates higher capacity to hold hydrogen ion (Gupta and Bhattacharyya, 2007).

Specific Surface Area

The specific surface area of the clay sample used in this study was 133.4 m²/g. The value depends on the size of the clay; finer particles of a given sample pose values that are higher than coarser particles. Specific surface area values range from 50 m²/g to as high as 736 m²/g in silica – bonded montmorillonite (Ahmet and Angel, 2010). Expectedly, adsorption capacity increases with increase in surface area if all other factors remain constant.

On the other hand, the result of the pore volume obtained show that the clay sample under study is micro – porous according to the classification proposed by Dubinin, (1989).

Specific Gravity

The specific gravity of the clay was 2.16 g/cm³. This value fell within the range of most clay. Generally, the specific gravity of clay ranges from a minimum of 1.8 to a maximum of 2.6 (Dominique and Francoise, 1996). The value was comparable to the clay from Ihitte Obama with value 2.14 (Obi, 2006) and those from Abakaliki area with values 2.23 and 2.28 (Nweke and Ugwu, 2007).

Cation Exchange Capacity

The cation exchange capacity of the clay was determined to be 18.8 meq/100g of clay at pH 6. This property of clay arises from isomorphous substitution, a crystal lattice defect in which a given ionic series may be replaced by another in a crystal lattice, (Bergraya and Vayer, 2009). This makes their surfaces to be electrostatically charged and can attract and hold ions. The higher the CEC, the higher the negative charges and the more cations that can be held.

The ability of clay to hold on to the electrostatically attracted cations and exchange them with other cations thereby releasing these back into solutions measures its cation exchange capacity. By implication, the desorption of cations adsorbed on clays is easily achievable. Therefore, adsorbents can easily be regenerated and metals of interest recovered when metals contaminants are removed from industrial waste waters (Kubilay *et al.*, 2007).

Table 1: Physical properties of clay used in this study

pH	Surface Area	Specific gravity	Pore Volume	CEC
2.8	133.4 m ² /g	2.16 g/cm ³	0.45 m ³ /g	18.8 meq/100g

Metal Oxide Compositions

The metal oxide compositions showed that the alumina and silica oxide was in major quantity. The high oxide of iron content of about 2% is consistent with other local clays such as Oboro and Abakaliki clays (Nweke and Ugwu, 2007). The average loss on ignition value of 11.409% indicates that the clay is relatively high in carbonaceous matter (Pushpalettha *et al.*, 2005). The considerable amount of Fe and Ti suggests the presence of impurities which is commonly seen in clays formed from soils under tropical conditions, (Nnnuka and Enejo, 2001). However, with low levels of Mg, Ca and an infinitesimal amount of phosphorus, the clay shows limited mineral impurities.

Table 2: Metal oxide compositions of the clay used in this study

Element	Concentration (ppm)	% Oxide composition
Al	159.593	32.601
Si	232.431	47.380
Mg	14.320	2.919
Ca	5.902	1.203
Na	7.952	1.621
K	1.006	0.205
Fe	10.454	2.042
Ti	0.643	0.131
LOI	-	11.409

- LOI – Loss on Ignition

FTIR Spectrum

The Fourier Transform Infra – Red spectrum showed that peaks at 3695.61 cm⁻¹ and 3655.11 cm⁻¹ are due to Al-OH structural hydroxyl vibrations typical in Kaolinite and montmorillonite respectively (Alemayelu *et al.*, 2013). The inner surface hydroxyl group deformation band was observed at 904.61 cm⁻¹ and the bands associated with Si-O stretching were 790.81 cm⁻¹ and 1124.50 cm⁻¹ characteristic of quartz and montmorillonite respectively. The deformation band of Si-O was observed at 1006.84 cm⁻¹ (George – Ivo, 2005). In addition, observed bands at 3527.80 cm⁻¹ and 3392.79 cm⁻¹ arose from the stretching of water molecules (Madejova and Komadel, 2001). The difference in bands was as a result of the surrounding environment from clay type to another. The same reason accounts for the Al-O-Si stretching band observed at 694.37 cm⁻¹ and 559.26 cm⁻¹. The latter attributed to a hematite and the former consistent with quartz minerals (Bhaskar and Gopalakrishnareo, 2010).

Table 3: Vibrational bands of the clay used in this study

S/N	Band (cm ⁻¹)	Assignment
1	3695.61	Al—OH: Structural hydroxyl group of Kaolinite.
2	3655.11	Al—OH: Structural hydroxyl group stretching in Montmorillonite.
3	3620.39	Inter octahedral Al-OH stretching for kaolinite.
4	3527.80	H-O-H: Stretching from water molecule in Kaolinite.
5	3392.79	H-O-H: Stretching of water molecule from montmorillonite.
6	1647.21	OH: deformation of water.
7	1618.28	OH deformation in smectite.
8	1124.50	Si-O: stretching in smectite.
9	1006.84	Si-O: in-plane stretching characteristic of Kaolinite.
10	904.61	OH: deformation of inner surface hydroxyl group (Al-OH-Al)
11	790.81	Si-O: stretching in quartz.
12	694.37	Al--O—Si: stretching.
13	559.26	Al—O—Si: stretching in hematite.

CONCLUSION

The physicochemical evaluations of Unwana New Site clay in Afikpo North local government area of Ebonyi State have shown that the clay composition is useful for wide variety of industrial applications. It can create employment opportunities if refined, modified and packaged.

REFERENCES

- Ahmet, R.M and Angel, F.C. (2010). Baseline Studies of the Clay Mineral Society, Chemical Analysis of Major Elements. *Clays and Clay Minerals*, 51(5): 381-386.
- Alemayelu, K., Gholap, A and Giovanni, E (2013). Fourier Transform Infrared Spectroscopic Characterization of Clay Minerals from Rocks of Lalibela Churches, Ethiopia. *International Journal of Physical Sciences*, 8(3): 109-119.
- Bergraya, F and Vayer, M. (2009). CEC of Clays: Measurement by Adsorption of a Copper Ethylenediamine Complex. *Applied Clay Science*, 12: 275-280.
- Bhaskar, J.S and Gopalakrishnareo, P. (2010) Fourier Transform infrared spectroscopic characterization of Kaolinite from Assam and Meghalaya, Northern India. *Journal of Modern physics*, 1: 206-210.
- Dada, A., Olalekan, P., Olatunya, A and Dada, O. (2012). Isotherm Studies of Zn²⁺ into Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry*, 3(1): 38-45.
- Denis, L.G., Rubia, R.V and Claudio, A. (2009). Adsorption of Thorium (IV) on Chemically Modified Amazon Clay. *Journal of Brazilian Chemical Society*, 20(6): 1164-1174.
- Dominique, R and Francoise, E. (1996). Characterization of Soil Clay Minerals. *Clays and clay minerals*, 44(6): 791-800.
- Dubinini, M.M. (1989). Characterization of Porous Solids. *Society of Chemical Industries*, 38(2): 1135-1142.
- George – Ivo, E.E. (2005). Fourier Transform Infrared Spectrophotometry as a Complementary Technique in Characterizing Clay Size Fractions of Kaolin. *Journal of Applied Sciences and Environmental Management*, 9(2): 43-48.
- Gupta, S.S and Bhattacharyya, G.K. (2007). Influence of Acid Activation of Kaolinite and Montmorillonite on Adsorptive Removal of Cd (II) Ion from Water. *Industrial and Engineering Chemistry Research*, 46(11): 3734-3742.
- Kahr, G and Madsen, K (1995). Determination of the Cation Exchange Capacity of Bentonite, Illite and Kaolinite. *Applied Clay Science*, 9(5): 327-336.
- Kubilay, S., Gurkan, R., Savran, A and Sahan, T. (2007). Removal of Cu (II), Zn (II) and Co (II) Ions from Aqueous Solutions by Adsorption onto Natural Bentonite. *Adsorption*, 13(1): 41-51.
- Madejova, J and Komadel, P. (2001). Baseline Studies of the Clay Minerals Society Source Clays; Infrared Methods. *Clays and Clay Minerals*. 49(5): 410-432.
- Moore, D and Reynolds, R.C. (1997). X – Ray Diffraction and the Identification and Analysis of Clay Minerals. 2nd edition. New York, Oxford University Press.
- Nnuka, E.E and Enejo, C. (2001). Characterization of Nahuta Clay for Industrial and Commercial Application. *NJEM*, 2(3): 9 – 13.
- Nwabinehi, E.O., Otti, B.I and Okeugo, C.O. (2013). Economic potentials of clay deposit in Akanu Ibiam Federal Polytechnic Unwana, Afikpo North Ebonyi State. *International Journal of Innovative Research and Development*, 2(11): 461 – 463.
- Nweke, E.S and Ugwu, E.I. (2007). Analysis and Characterization of Clay Soil in Abakaliki, Nigeria. *The Pacific Journal of Science and Technology*, 8(2): 190-193.
- Obi, C. (2006). The adsorption studies of some local clay minerals in Imo State. An M.Sc. dissertation, University of Port Harcourt, Rivers State.
- Sharma, Y.C and Srivastava, V. (2006). Adsorption of Cadmium (II) from Aqueous Solutions by an Indigenous Clay Mineral. *Indian Journal of Chemical Technology*, 13: 218-221.
- Suedina, M.L and Carla, R.C. (2012). Application of Infrared Spectroscopy to Chitosan/Clay Nano Composites. *Infra – Red Spectroscopy - Material Science, Engineering and technology*. Theophanides Theophile (Ed). Shanghai. Intech Publishing.
- Wall, M. (2013). Mars could have Supported Life. Space.com.