PHYSICO-CHEMICAL CHARACTERIZATION OF CLAY DEPOSITS FROM PUJE WARD WUKARI -TARABA STATE

Supported by tetfund TERTIARY EDUCATION TRUST FUND

J.T. Ugye*, S.P. Malu, P.A. Egwaikhide and T.M. Maigari
Department of Chemical Sciences, Federal University Wukari, PMB 1020, Taraba State, Nigeria
*Correspondingauthor:ugye@fuwukari.edu.ng

Received: April 10, 2017 **Accepted:** July 27, 2017

Abstract: Physico-chemical and X- Ray Fluorescence (XRF) analyses was used to characterize the clay deposits from Puje ward of Wukari, Taraba State with the view to establishing its suitability for industrial usage. The physical parameters considered were moisture content, bulk density, particle density. pH and loss on ignition. Chemical analysis was performed using X-ray fluorescence spectrometry. The result of the physical analysis showed a moderate moisture content of 4.08±02%, bulk density of 1.56±16 g/cm^3, pH of 7.68±01 and loss on ignition of 13.18±32%. The result of the chemical analysis showed an elemental composition in the clay samples of 54.68±12% (SiO_2) > 6.50±03% (Al_2O_3) > 1.896±01% (Fe_2O_3)> 0.98±22% (K_2O) as the major components while the minor components included P_2O_5, SO_2, CaO, TiO_2,V_2O_5,Cr_2O_3, MnO, CoO, CuO ,ZnO,PbO,WO_3,Au_2O_3, Rb_2O, Nb_2O_5, MoO_2, SnO,$Sb_2O_5$and ZrO_2.The results of the physical parameters were found to be within the acceptable limits in comparison with the results of WHO, APHA and US Geological Agency. Also due to the high silica content of the clay deposits as shown in the results it can be inferred that the Puje - Wukari clay deposits could be used as source of silica for the production of floor tiles, ceramics, building bricks and in the synthesis of zeolite, glass, cement, lubricants and paints.

Keywords: Characterization, clay, oxides, physcio-chemical, spectrometry, x-ray

Introduction

Clay is an earthly material that is plastic when moist but hard when fired or dried, it is composed mainly of fine particles of hydrous aluminium silicates and other minerals. Clay and its associated minerals have played major roles in anthropogenic activities.(Sidhu& Gosh, 1996). The low cost of clay and its relative abundance in nature, its high sorptive properties, high electric charges, ion exchange ability and its compatibility with materials gives it a wide range of applications in bricks, tiles and pottery etc. Clay materials are known for their distinctive properties such plasticity, shrinkage under firing and under air drying conditions, finest of grain, colour after firing, hardness, and cohesion and capacity of the surface to take decoration (Barbell and Kurnianwan, 2013; Costanzo, 2001).

Clay occurs most abundantly in nature in soils, sediments, sedimentary rocks and hydrothermal deposits (McGraw-Hill *et al.*, 1992). There are two general types of clay namely; expandable and non-expandable clay. The expandable clay swells up when water is added to it and can become liquid when enough water is added to it. While the non-expandable clay called Bentonite is used to make drilling mud in petroleum industry. It is also used in the ceramics industry to make bricks, tiles pottery and porcelains (Ahmed *et al.*, 1986). Clay materials present layer and sheet orientations and the several possible structural presentations of the elements in clay results in different classes of clay such as Kaolinite, Serpentine, pylophylite (talc), smectite (Bentonite /montroillonite, sepiolite) sepiolite and vermiculite (Shichi&Takaji, 2000). The particle size, surface area and high charge density of clay materials are some of the properties that accounts for the adsorption capacity of clays (Alkan*et al.*, 2004).

The characterization of clay is done in order to know the composition or the elements present and the level in which they occur in a given sample. There are many methods of characterizing clay as reported in the literature. The commonest are atomic Absorption Spectrophotometry, X-ray Fluorescence, Fourier transform infrared, UV-visible analysis and X-ray diffraction methods. XRF technique has variously been used to determine the concentration of major metallic elements such as Na, Al, Si, K, Fe, Cu, Mg, Ca and toxic elements such as As, Pb, and Cd as well as other contaminants in the form of Ag and Hg. Many clay materials are used as fillers, pigments, and additives (Uribe, 2001). Although silica, aluminium and water are the basic components of clay, iron, alkalis, and alkaline earth metals may be present in good measures (Stevens & Anderson, 1996).

Clay is structured at an atomic, molecular and macro level and these structures interact to produce the variations in observed behaviour (Velde, 1995).The atomic lattice of clay minerals present two unique structural units of octahedral and tetrahedral conformations. The octahedral confirmation involves oxygen and hydroxyl groups that are linked to aluminium, iron and magnesium atoms at equidistance from six oxygen or hydroxyl species and the tetrahedral silica conformations, where the units are oriented into hexagonal network, which is repeated continuously, forming a sheet of silica. The different ratios of the basic components of clay and the several possible combinations of the orientations of layers sheets in conjunction with the particular metal present, determines the mineral type of clay (Holtz & Kovacs, 1981).

In view of this natural architectural design of clays, it is imperative to always characterize them before putting them into use. There is however paucity of literature reports on the characterization of the huge clay deposits in Taraba State of Nigeria. To the best of our knowledge the clay deposits at Puje-Wukari have not been characterized in spite of its local use for bricks and earthen pots. This study is therefore set to use standard methods to characterize the Puje-Wukari clay deposits with the view to providing a baseline for future studies and for ascertaining its industrial applications.

Materials and Methods

Sampling

The clay samples were collected based on the method of Malu*et al.* (2013) from northern and southern Puje ward of Wukari respectively in an area covering 200 m^2. The clay samples were obtained from the selected points using plastic shovel at a distance of 20 m apart, in a triangular fashion and a depth of 30 cm. into two different polythene bags. The samples were collected in such a way that contamination was minimized as far as possible by avoiding the use of metallic tools for sampling. On collection, stones and other particles were removed from the clay samples. Two composite samples coded Samples A and B representing samples taken

from northern and southern Puje ward of Wukari respectively were obtained for analysis. The origin, location and physical appearance and structure of the clay samples is as listed in Table 1.

Table 1: Description of the Clay Samples used in the Study

Sample	Origin	Location	Physical Appearance and structure
A	Puje-Ward Wukari	Puje-North	Dark in colour, very fine, smooth feel
B	Puje-Ward Wukari	Puje-South	Brownish – grey, very sticky

Sample preparation

The clay samples collected were sun dried separately and were grounded using mortar and pestle into powdered form. They were further sieved through a 30 µm mesh to remove the larger non-clay fractions from the finer particles. The essence of for grinding to this size was to bring the samples to a pulverized form in order to expose the clay to a greater surface area. The grounded and sieved portion of each sample was then used for analyses and characterization using EDX3600B X-ray fluorescence spectrometer. Standard methods and other procedures based on the methods of USAGS (2017) were used for the physico-chemical analysis.

Physical analyses

Moisture content, pH, bulk density, particles density, loss on ignition (L.O.I) were carried out on the prepared clay samples.

pH determination

The pH of the sample was determined by weighing 10g of each of the clay samples into 100 cm^3 beaker and was followed by addition of 20 cm^3 of distilled water. The mixture was stirred for 10 minutes and the volume made up to 50 cm^3. The sample pH was then measured with an electronic pH meter and the average values recorded (Foley, 1999).

Bulk density determination

The bulk density of each of the clay samples was determined according to the procedure described by (Ahmedna*et al.,* 1997; Huerta-Pujol*et al.,* 2010) as follows: A known quantity of clay (100 g) was placed in a 100 cm^3 measuring cylinder and a little vibration was applied until no particle space and constant level of clay was observed in the cylinder and the volume recorded. Triplicate measurements were carried out and average readings recorded. The bulk density was calculated using the relation:

$$\text{Bulk density} = \frac{\text{Weight of clay}}{Volume} \quad \text{---------(1)}$$

Moisture content determination

A quantity of wet clay sample was weighed in a beaker of known weight and oven dried at a temperature of 110^{0}C for 2 h, removed and was cooled an reweighed following the procedure of Sreeramulu (2003). Triplicate measurements were performed and the average readings recorded. The percentage moisture content was calculated from the relation:

$$\text{Percentage moisture content} = \frac{\text{Wm - Wd) x 100}}{\text{Ws}} \quad \text{----(2)}$$

Where: Wm = weight of wet sample + beaker, Wd = weight of dry sample + beaker, Ws = weight of clay sample

Particle density

A quantity of oven dried clay sample (20 g) was placed into a measuring cylinder, the cylinder was gently tapped and the volume recorded as V_1. Then 50 cm^3 of distilled water were added slowly by the side of the cylinder to soak the clay completely and the final clay and water volume in the cylinder was noted as V_2. The particle density was then calculated according to the equation of Sreeramulu (2003).

$$\text{Particle density} = \frac{\text{Weight of clay}}{\text{Volume of clay taken}} = \frac{W}{\text{V2 - V1}} \quad \text{--(3)}$$

Determination of loss on ignition (L.O.I)

Some clay sample 1g was weighed into a clean dried crucible of known weight and was placed inside an oven at 110 ^{0}C for 1hr and the crucible was removed from the oven and allowed to cool in a desiccator and reweighed. The process was repeated until a constant weight was obtained (Malu, *et al*., 2013).

The percentage loss on ignition was calculated as follows:

$$\% \text{ loss on ignition} = \frac{\text{W1 - W2}}{\text{Ws}} \quad \text{-----(4)}$$

Where: W_1= Weight of crucible + sample, W_2= Weight of sample + crucible after ignition, Ws = Weight of sample

Table 2: Physical analyses of Puje Ward of Wukari clay samples

Samples	Bulk density (g/cm^3)	Particle density (g/cm^3)	pH	% Moisture	% LOI
A	1.51±02	0.45±05	7.71±16	3.94±07	12.95±08
B	1.55±04	0.47±02	7.65±23	4.21±13	13.40±12

XRF analysis

The XRF analysis was done following the procedure of Neuwirthová*et al.* (2012). X-ray fluorescence spectrometer applies XRF technique to conduct fast and accurate analysis of complex composition clay and other substances. Energy dispersive fluorescence spectrometer (XRFS) SPECTROXEPOS equipped with 50 Watt Pd X-ray tube was used to excite the samples. The target changer, with up to 8 polarization and secondary targets, offers many different excitation conditions ensuring optimum determination of all elements from sodium to uranium. Measurements were performed in helium atmosphere. The detector was a state-of-art silicon drift detector (SDD). A spectral resolution of less than 160 eV for Mn K-alpha was achieved. The maximum count rate was 120,000 cps. The analyser can handle samples with diameters up to 32 and 40 mm. A voltage of 40kv and a current of 350 mA were applied to generate the X-ray needed to irradiate the clay samples in this study for a pre-set period of 100 seconds for each sample. The system detected elements between samples were analysed and concentrations of the elements determined were expressed in percentage oxides as shown in Table 3- 4.

$$\text{Percentage element} = \frac{\text{\% Oxide x100}}{\text{Relative atomic mass}} \quad \text{--(5)}$$

Results and Discussion

Table 1 showed the physical appearance and structures of the clay samples A and B that were collected from northern and southern parts of Puje ward of Wukari. Sample A is dark-brown coloured while sample B is brownish - grey with smooth texture. The particle sizes of both samples passed through 30 µm mesh, indicating their fine nature. These are comparable to the acceptable properties of clays characterized by US Geological Agency (Foley, 1999).

Table 2 showed the mean values of the physical analyses of the two Puje clay samples A and B as follows: The moisture contents (3.94 and 4.21%), bulk density (1.51 and 1.55 g/cm^3), pH (7.71 and 7.65), Loss on ignition(12.95 and 13.40%). The results showed slightly higher values for sample B compared to sample A but correlates with the values obtained by Owabor*et al.* (2012) which were moisture content (4.25%), bulk density (1.15 g/cm^3), pH (7.10), respectively. The percentage loss on ignition values was also found to be

within the range specified by the British International Standard of clay specification. The percentage loss on ignition values also indicates that the clay samples have low carbonaceous matter and higher mineral matter contents (Malu*et al.*, 2013).

Tables 3 and 4 showed the XRF analyses values of the two Puje clay composites. The results revealed that the clay deposits contain mainly silica, alumina, iron and potassium oxides along with some important mineral elements in trace but appreciable quantities. The order of the major components is as follows: SiO_2, $>Al_2O_3>Fe_2O_3>K_2O$ while the minor mineral elements order is $ZrO_2>SnO>Sb_2O_5>SO_2>TiO_2>MoO_2>P_2O5>CaO>V_2O5>Zn$ O. Except for the observed higher values of silica (38.716±02%) in sample B against (26.899±07%) in sample A, the values of the percentage oxides in sample A have higher values than those of sample B in the results of the XRF analysis. This clearly shows that there exists a difference in soil formation along with mineral composition between these two locations within the sample area. The quantity of silica in the two different samples A and B is high and correspond to the result obtained for Arrirasho clay deposit as reported by Edah*et al.* (*2*012). The high content of silica in the two clay composite samples suggests the existence of quartz in the Puje - Wukari clay deposits and could be used as a source of silica for the production of floor tiles and as a binder in place of standard binders (Malu*et al.*, 2013). According to Breck (1974), clay samples containing high quantity of silica can be utilized in the synthesis of zeolite, a catalyst mostly used in the catalytic cracking of petroleum. The iron contents of the Puje clay deposits ranged (3.3090 - 8.1625%) and could give it a dark brown colour when pulverized(Edah*et al.*, 2012). Also the low quantity of alkali metal oxides in the clay samples showed that the clay deposits would not be suitable for making ceramic materials (Nnuka*et al.*, 2001). However, the presence of two of the minor mineral elemental oxides zirconium oxide and Zinc oxide found in the Puje clay deposits could make the puje deposits useful in ceramic industry after proper blending. These oxides are known to be of great industrial application in ceramics, plastics, glass, cement, lubricants, paints etc. It is reported that one of the reasons why interest in zirconium continues to grow is that, unlike many of the other metals in common usage; zirconium has a low toxicity and is classified as being non-hazardous to the environment and thus mostly used in ceramics industry for various applications (Cooper &Golledge, 2017). Zirconium is used in alloys as Zircaloy, which is used in nuclear applications since it does not readily absorb neutrons. It is also used in catalytic converters, percussion caps and bricks Beddeleyite an impure zirconium which has iron, titanium and silicon oxide impurities are used in lab crucibles. Zircon is also marketed as a natural gemstone used in jewelry. The metal also has many other uses, among them are in photographic flashbulbs and surgical instruments etc. (Cooper &Golledge, 2017).

Zinc oxide is an inorganic compound with the formula ZnO. It is a white powder that is insoluble in water and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes. It occurs naturally as the mineral zincite, but most zinc oxide is produced synthetically. Crude zinc oxide is a yellow-gray granular solid with no odour. It is insoluble in water, mild astringent and topical protectant with some antiseptic action. It is also used in bandages, pastes, ointments, dental cements, and as a sunblock.

Table 3: XRF elemental analysis of Puje-North clay deposits sample A, showing percentage elements and oxides present

Element	%Element	Oxide	% Oxides
Mg	0.000	MgO	0.000
Al	8.566± 06	Al_2O_3	8.734±21
Si	44.832±33	SiO_2	26.899±25
P	0.091±25	P_2O_5	0.123±23
S	0.334±24	SO_2	0.214±12
K	1.432±29	K_2O	1.346±03
Ca	0.563±28	CaO	0.316±08
Ti	0.411±09	TiO_2	0.329±10
V	0.010±23	V_2O_5	0.018±26
Cr	0.004±21	Cr_2O_3	0.006±21
Mn	0.127±16	MnO	0.090±22
Co	0.037±17	CoO	0.028± 27
Fe	5.102±20	Fe_2O_3	8.163±14
Ni	0.099±13	NiO	0.075±12
Cu	0.084±18	CuO	0.067±05
Zn	0.146±04	ZnO	0.119±13
As	0.000±06	As_2O_3	0.000
Pb	0.010±07	PbO	0.022±14
W	0.028±05	WO_3	0.069±12
Au	0.016±	Au_2O_3	0.069±
Ag	0.000±	Ag_2O	0.000±
Rb	0.011±	Rb_2O	0.020±
Nb	0.003±	Nb_2O_5	0.008±
Zr	1.100±	ZrO_2	1.350±
Mo	0.138±	MoO_2	0.004±
Cd	0.000	CdO	0.000
Sn	0.998±	SnO	1.348±
Sb	0.387±	Sb_2O_5	1.252±

Table 4: XRF elemental analysis of Puje south clay deposits sample B, showing percentage elements and oxides present

Element	%Element	Oxide	% Oxides
Mg	0.000	MgO	0.000
Al	8.039±04	Al_2O_3	8.734±15
Si	64.526±12	SiO_2	26.899±10
P	0.1382±09	P_2O_5	0.123±08
S	0.570±11	SO_2	0.214±11
K	1.502±05	K_2O	1.346±15
Ca	0.242±12	CaO	0.316±13
Ti	0.367±08	TiO_2	0.329±02
V	0.008±07	V_2O_5	0.018±01
Cr	0.003±06	Cr_2O_3	0.006±14
Mn	0.037±04	MnO	0.090±15
Co	0.014±06	CoO	0.028±07
Fe	2.068±19	Fe_2O_3	8.163±08
Ni	0.090±05	NiO	0.075±16
Cu	0.077±23	CuO	0.067±13
Zn	0.130±20	ZnO	0.119±08
As	0.000	As_2O_3	0.000
Pb	0.000	PbO	0.022±12
W	0.030±34	WO_3	0.069±14
Au	0.016±35	Au_2O_3	0.069±22
Ag	0.000	Ag_2O	0.000
Rb	0.006±23	Rb_2O	0.020±12
Nb	0.007±12	Nb_2O_5	0.008±08
Zr	1.100±14	ZrO_2	1.350±05
Mo	0.153±17	MoO_2	0.004±23
Cd	0.000	CdO	0.000
Sn	0.918±22	SnO	1.348±11
Sb	0.309±16	Sb_2O_5	1.252±01

Zinc oxide can be used in ointments, creams, and lotions to protect against sunburn and other damage to the skin caused by ultraviolet light. It is also widely used to treat a variety of other skin conditions, in products such as baby powder and barrier creams to treat diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments.The primary hazard is the threat posed to the environment. Immediate steps should be taken to limit its spread to the environment. Prolonged inhalation of the dust may result in metal fume fever with symptoms of chills, fever, muscular pain, nausea and vomiting (PubChem, 2015).

Conclusion

This study established that the characterized Puje clay deposits of Wukari, Taraba State-Nigeria are suitable for industrial usage particularly; they could be used as source of silica for ceramic industry. The characterized clay samples could also be used in the production of floor tiles and building bricks as zirconia gemstones and in the synthesis of zeolite.

Acknowledgements

We wish to appreciate the contributions of all the staff and students of the Department of Chemical Sciences, Federal University Wukari for their assistance and contributions in facilitating the conduct of the bench Chemistry of this study.

References

Ahmed KS &OnajiPB 1986.The effect of Beneficiation on the properties of some Nigerian Refractory Clays.*J. Nig. Soc. Chem. Engr.*, 6(2): 119-129.

Alkan M, Demirbas O &Celikeapa S 2004.Sorption of acid red 57from aqueous sodium into sepiorite.*Journal of Hazard Material*, 116-135.

Ahmedna M, Johnson M, Clarke SJ, Marshall WE & Reo RM 1997.*Potential* of *agricultural* by-*product-based activated* carbons for *use* in *raw* sugar decolourisation, pp. 1-17.

APHA 1993.Standard methods for the examination of water and waste water, 16th Edition, American Public Health Association, Washington DC 2005.

Barbell S &Kurnianwan TA 2013.*Journal of Hazardous Materials*, 97: 219.

BreckDW 1974. Zeolite Molecular Sieve Structure, chemistry and Uses. *Wiley Interscience (New York) USA*, 2: 19-22.

Costanzo PM 2001. Data and industrial minerals, including clay and clay mineral deposits.*Journal of Clay & Clay Materials*, 59**(**5): 372-373.

Cooper D &Golledge G (Eds). 2017. Zirconia-Royal society of chemistry. Retrieved 25-04-2017,pp. 1-20. http://media.rsc.org/Zinc%20and%20zirconia/Zirconia.pdf.

Edah AO, Kolawole JA, Solomon AO, Shamle N &Awode AU 2012. *J. Res. Envtal. Sci. &Techn.*, 1**(**2): 19-22.

Foley NK 1999. Environmental Characterization of Clays and clay mineral deposits.USGS Information handout September.US.Geoligical Survey. Vol. 954. National Center Reston, VA20192.

Holtz RD & Kovacs WD 1981.An introduction to Geochemical Engineering.Chapter 4. Prentice-Hall, pp. 30-36.

Huerta-Pujol O, Soliva M, Martinez-Farre FX, Valero J & .Lopez M 2010. Bulk density determination as a single and complementary tool in composting process control, pp. 205-209.

MaluSP, Andrew C &Malu FI 2013. Chemical characterization of clay deposit in Taavaan, North-Central Nigeria.*World Res. J. Chem.*, 1(2): 31-34.

McGraw Hill 1992.Encyclopaedia of Science and Technology.Mc-Graw-Hill Book Company.8th Edition, 3: 752-751.

Neuwirthová L, Matějka V, Kutlákováa K &Tomášek V 2012.X-Ray Fluorescence Spectrometry Analysis of Clay/Zno Composites.*NanoCom*· 23. - 25. 10. 2012, Brno, Czech Republic, EU, pp. 1-6.

Nnuka EE &Enejor C 2001.Characterization of Nahuta clay for industrial and commercial application.*Nig. J. Engr. & Materials*, 2(3): 9-12.

OwaborCN, Agarry SE &Jato D 2012. Removal of naphthalene from aqueous system using unripe orange peel as adsorbent: Effects of operating variables. *Desalination and Water Treatment*, 48(1): 315-319.

PubChem 2015. Open Chemistry data base. Zinc Oxide. Retrieved 2017-04-22; https://pubchem.ncbi.nlm.nih.gov/compound/zinc_oxide

Shichi T & Takagi K 2000.Photochem.Photobiol.C*Photochem. Rev.*, 1:113.

Sidhu& Gosh, 1996.*Clay Res*. 15.

Stevens J & Anderson S 1996. Clays. *Clay Miner*, 44: 132.

Sreeramulu US 2003. Principles in the quantitative analysis of water, fertilizer, plants and soils.*Scientific Publishers India*, 2: 230-237.

Uribe A 2001. Solidification, Stabilization of hazardous waste using organophilic clays.Master of Science Thesis.University of Cincinnati, Cincinnati, Ohio.

USAGS 2017. Data on industrial minerals, including clay and clay mineral deposits, are available from the USGS web site, http://minerals.er.usgs.gov/minerals/pubs/commodity

Velde B 1995. Composition and mineralogy of clay materials. In: Velde B (ed). Origin and Mineralogy of Clays. New York, Springer-Verlag, pp. 8-42.

WHO 1971. International Standards for Drinking Water, 3rd Edition, WHO, Geneva