International Journal of Recent Engineering Research and Development (IJRERD)
ISSN: 2455-8761
www.ijrerd.com || Volume 03 – Issue 05 || May 2018 || PP. 166-170

Stoichio - Chemical Characterization of Clay Samples from Ikere Ekiti, Ekiti State, Southwestern Nigeria

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Abstract: The need to further study the chemistry of the clay in Ikere Ekiti is crucial, being one of the common industrial minerals in Ekiti State. Four samples of the clay were collected from the site of the deposit at Ikere-Ise road from the depths of 0.6m,3.0m,3.5m and 4.5m respectively, below the lateritic overburden of about 2m thickness. The percentage concentrations of K_2O, Na_2O, MgO, CaO, Fe_2O_3, SiO_2 and Al_2O_3 in the Ikere clay samples were geochemically analyzed for by utilizing X - Ray Fluorescence. The stoichiochemical analysis of the percentage concentration of the oxides revealed that the Ikere clay is kaolinitic. Thus, the presence and high abundance of kaolinite in these samples indicated rigorous weathering of aluminium-rich source rocks with steep relief and exhaustive leaching of weathered materials under a warm, humid and acidic medium. High amount of kaolinite minerals also indicated continental setting. High occurrences of Al_2O_3 (19.2%) and SiO_2 (57.4wt %) could also be attributed to the effect of chemical weathering. As precipitation and weathering increases, kaolinitization is enhanced. The characterization revealed the presence of minor amount of Iron Oxide as impurity in the Clay. The presence of which could have been responsible for its reddish colouration.

Keywords: Characterization; Clay minerals; Kaolinite; Raw materials; X ray –Fluorescence; Geochemically, Stoichiometrically; Industrial application

1. Introduction

Clays are natural earthy, fine grained materials composed largely of group of crystalline materials that are known as clay minerals. These minerals are hydrous silicates composed of silica, alumina and water. According to Moore and Reynolds, (1997) clay minerals are among the most important structural materials on the Earth's surface, being major components in soils and sediments, and the rocks formed from these. Clays play an important role in environmental, agricultural and industrial processes such as nutrient cycling, plant growth, petroleum production, and contaminant migration (Stucki, 2006 and Stucki et al., 2002). Clay raw materials which include kaolin, are mined materials rich in kaolinite ($Al_2Si_2O_5(OH)_4$, and are generally formed by the intense weathering or hydrothermal alteration of aluminosilicate minerals, such as feldspars and mica. Most clay materials are also composed of appreciable quantities of iron, alkali and alkaline earth materials (Odeyemi, 1991). Clay deposit resulted from the tropical in-situ weathering that decomposes pre-existing hydrous aluminosilicate minerals and relics of former structures such as that of gneisses and mica flakes are commonly observed in some of the clay deposits. Clay deposit could also differ considerably with the type of constituent silicate minerals and admitted impurities such as quartz, feldspar, carbonate, organic matter and iron oxides. However, one basic and common characteristic of clay minerals are their extremely fine particle size of less than 2microns. The industrial uses of clays in pottery, ceramics, brickmaking and refractory cannot be overemphasized, hence the need to further study them, particularly, their chemistry. Various studies on solid mineral resources using geoscientific surveys and mineralogical characterization considered that the understanding of the nation's mineral potentials is critical for efficient exploration and exploitation towards promoting sustainable economic development (Adelabu, 2012). According to Tarbuck., et al., (1996), clay minerals are extremely important to humans and one of the most common clay minerals is kaolinite, which is used in the manufacture of fine chinaware and in the production of high-gloss paper. Adelabu (2012) discovered that it is noteworthy that clay minerals constitute over 50% of the non-metallic, earthy and naturally-occurring resources abounding throughout Nigeria's sedimentary basins. The abundance of clays of various kinds and grades has been discovered in Ekiti. According to Titiladunayo et al., (2010), the suitability of some local clay deposits in Ekiti State for the lining of furnace to be used to degrade woody biomass for fuel and chemical products was investigated. Four major sites in Ekiti State renowned for abundant clay deposits were selected, namely; Ikere Ekiti, Fagbohun Ekiti, Ishan Ekiti and Ara Ekiti. They discovered that the kaolin deposit at Ikere Ekiti was found to be the best material suitable for the lining of the furnace for the pyrolysis process as the expected furnace temperature is about 1400 degree celsius. The significance of solid mineral resources has been of profound value to man since time immemorial. Clay minerals appear not to be the most valuable among the minerals of the earth surface, yet they affect life on earth in far reaching ways. Nigeria in sub-Saharan Africa of surface area of 923,768 km^2 is a country with considerable wealth in natural resources, with a record of over 30 minerals of proven reserves. As far back as 1903 and 1904, geological survey in Nigeria evolved when the Mineral Surveys of the Southern and Northern Protectorates of Nigeria were established under the British colony. The Mineral Surveys carried out broad reconnaissance of mineral resources of the two Protectorates with the prospect of using the raw materials for industries in Britain. In course of these activities, such deposits as Tinstone, Columbite, Limestone, Bitumen, Lead-zinc Ores, Coal, Clays, Iron Ore, Gold, and Marble to mention a few were discovered in various parts of the country (Adelabu, 2012).

This study on Ikere clay is aimed at analyzing samples of Ikere Clay for their metallic oxides. Jacob et al., (2004) was carried out X-ray fluorescence analysis on kaolinitic clay deposit at Beaconsfield, Grahamstown and revealed that there is a remarkable variation in the chemistry as Al_2O_3 content is generally near 20%, but may reach 29%. SiO_2 content varies between 55 and 70% or more. SiO_2 contents are highest in the layer occurring just below soil level. Fe_2O_3 content is high locally in the top part of the profile. K_2O and Na_2O are generally low, but increase towards the unweathered bedrock as the primary feldspar content increases. These compositional variations are compatible with residual concentrations of kaolinitic clays through deep weathering below the former African erosion surface. Lee et al., (2002) declared that a very low iron concentration in kaolin may result in a significant reduction in the whiteness of a ceramic product as any coloration is intensified by the firing process.

Kaolin is exploited for a wide range of industrial applications, such as the production of paper (as filler and/or a coating material), ceramics (to add strength, abrasion resistance, and rigidity), plastics (as filler) and paints (as a filler and thickening agent). Before kaolin products can be used by manufacturing industry, the raw kaolins have to be refined to meet commercial specifications (Hosseini et al., 2007 and Styriakova and Styriak, 2000).

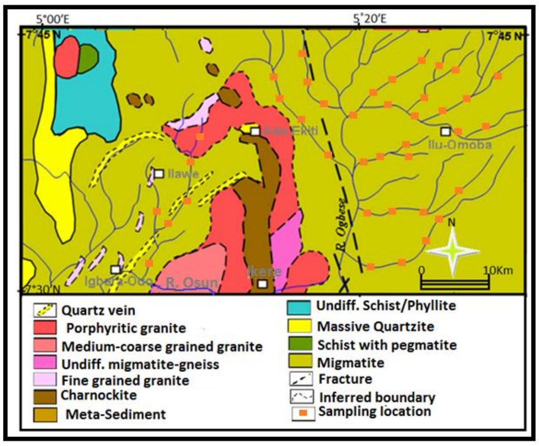

Fig. 1: Geologic Map of the Study area (Talabi et al., 2013)

2. Materials and Methods

Four samples of clay materials were collected from the Ikere clay deposit that is located at about 2.0 kilometers distance towards Ise-Ekiti from Ikere Ekiti. It lies within latitude No7^0 45^i429^{ii} and longitude E005^0 $22^i848^{ii}$by the Ikere-Ise, Road cut, at 523.5m elevation (Fig 2)

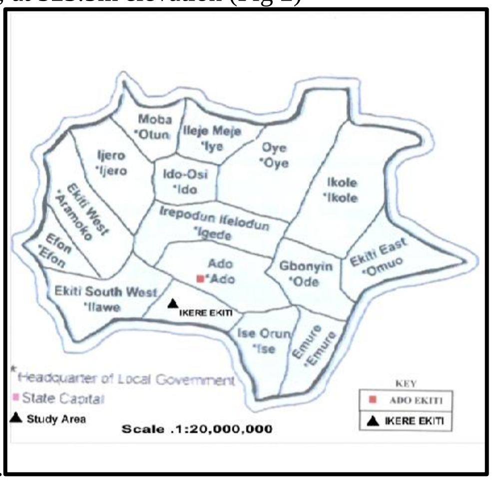

Fig 2: Map of Ekiti State Showing the Study Area in Ikere Ekiti

International Journal of Recent Engineering Research and Development (IJRERD)
ISSN: 2455-8761
www.ijrerd.com || Volume 03 – Issue 05 || May 2018 || PP. 166-170

The samples were taken at various depths of 0.6m, 3.0m, 5.0m and 7.0m respectively,with the aid of a digger and an auger drilling equipment all below the lateritic overburden of an average thickness of 2m.The samples were oven dried and then chemically analyzed by using energy dispersive X-Ray Fluorescence to determine the percentage concentrations of its constituent, K_20, Na_2O, MgO, CaO, Fe_2O_3, SiO_2 and Al_2O_3.The oxides were then determined stoichiometrically in order to chemically characterize the clay samples.

3. Results and Discussion

The results of the analyses conducted are as shown in Table 1- 4

Table -1: Chemical analysis of Ikere Clay at 0.6m depth

Sp 1	Wt. %	F wt.	Mp	Oc	Ac
Fe_2O_3	12.71	160	0.0794	0.4664[0.34]	Fe 0.93
Al_2O_3	20.97	102	0.2056	1.2077[0.64]	Al 2.42
CaO	0.07	56	0.0013	0.0076	Ca 0.01
MgO	0.11	40.31	0.0027	0.0159	Mg 0.02
Na_2O	0.08	62	0.0013	0.0076	Na 0.01
K_2O	0.08	94	0.0009	0.0050	K 0.01
SiO_2	67.80	60.09	1.1283	6.6278	Si 6.63
TOTAL:	95.82				

Possible Atomic Substitution in the Ikere Clay = $(Fe_{0.34} Al_{0.64}) Si_2O_5$

Note: Sp 1= Sample 1; Sp 2 = Sample 2; Sp 3 = Sample 3; Sp 4 = sample 4; Wt. % =Weight percentage; F. wt. = Formula weight; Mp = Molecular proportion; Oc = Oxide content per unit cell; Ac = Atoms content per unit cell

Table -2: Chemical analysis of Ikere Clay at 3.0m depth

Sp 2	Wt. %	F wt	Mp	Oc	Ac
Fe_2O_3	11.11	160	0.0694	0.4077 [0.24]	Fe 0.82
Al_2O_3	21.50	102	0.2108	1.2383 [0.74]	Al 2.48
CaO	0.23	56	0.0041	0.0241	Ca 0.02
MgO	0.15	40.31	0.0037	0.0217	Mg 0.02
Na_2O	0.08	62	0.0013	0.0076	Na 0.02
K_2O	0.15	94	0.0016	0.0094	K 0.02
SiO_2	66.09	60.09	1.0999	6.4610	Si 6.46
TOTAL:	99.31				

Possible Atomic Substitution in the Ikere Clay = $(Fe_{0.24}Al_{0.74}) Si_2O_5$

Table -3: Chemical analysis of Ikere Clay at 5.0m depth

Sp 3	Wt %	F. wt	Mp	Oc	Ac
Fe_2O_3	10.18	160	0.0636	0.3736 [0.22]	Fe 0.74
Al_2O_3	22.56	102	0.2212	1.2994 [0.76]	Al 2.60
CaO	0.15	56	0.0027	0.0159	Ca 0.02
MgO	0.13	40.31	0.0032	0.0188	Mg 0.02
Na_2O	0.06	62	0.0010	0.0059	Na 0.01
K_2O	0.10	94	0.0011	0.0065	K 0.01
SiO_2	65.39	60.09	1.0882	6.3922	Si 6.39
TOTAL:	98.57				

Possible Atomic Substitution in the Ikere Clay = $(Fe_{0.22}Al_{0.76}) Si_2O_5$

Table -4: Chemical analysis of Ikere Clay at 7.0m depth

Sp 4	**Wt %**	**F. wt**	**Mp**	**Oc**	**Ac**
Fe_2O_3	5.90	160	0.0369	0.22 [0.12]	Fe 0.44
Al_2O_3	27.08	102	0.2655	1.60 [0.86]	Al 3.20
CaO	0.08	56	0.0014	0.01	Ca 0.01
MgO	0.13	40.31	0.0032	0.02	Mg 0.02
Na_2O	0.04	62	0.0006	0.00	Na 0.00
K_2O	0.07	94	0.0008	0.00	K 0.00
SiO_2	65.87	60.09	1.0962	6.44	Si 6.44

TOTAL: 99.20

Possible Atomic Substitution in the Ikere Clay = $(Fe_{0.12}Al_{0.86})\ Si_2O_5$

Table -5: The Chemistry of Ikere Clay In Profile

Sample	**Depth Below The Lateritic Top Soil (m)**	**Stoichio- Chemical formulae of Ikere clay at various depths.**
1	0.6	$(Fe_{0.34}Al_{0.64})Si_2O_5$
2	3.0	$(Fe_{0.24}Al_{0.74})Si_2O_5$
3	5.0	$(Fe_{0.22}Al_{0.76})Si_2O_5$
4	7.0	$(Fe_{0.12}Al_{0.86})Si_2O_5$

3.1 Discussion

The colour of the clays varies from light reddish to whitish colouration as the depth increases as shown in table 5 (Rathinasamy and Saliha, 2017).The lateritic topsoil could have caused the red coloration. Plasticity also increases from the depth of 3.0m to 7. All the samples have minor and variable constituent of quartz, feldspar and Iron Stones. The analyses showed that the Ikere kaolinitic clay may be nearly pure due to the presence of minor amounts of Iron as indicated by the stoichio – chemical formulae of the kaolinitic clay samples in Table 5. The Ikere Ekiti clay could have been practically $Al_2O_3Si_2O_5$ (kaolin), in having some of the aluminium been replaced by Iron in minor variable amount as shown in Table 5. Grim (1968) also discussed the factors controlling properties of clay materials to include clay material composition, non-clay material composition, organic materials which also contain appreciable quantities of ions, alkalis and alkaline earth materials. Clay deposits differ considerably varying with the types of silicate materials contained as well as admitted ‘’impurities’’. Such impurities include minerals such as quartz, feldspar, carbonate, organic matter and iron oxide. High kaolinite with low non-clay mineral contents, in addition to high silica, low alumina, Fe, base metal and alkalis content could best appropriates the clay as ball clay (Jepson, 1984).

4. Conclusion

From the generated and analyzed data in this research work, it could be concluded that kaolinite is the dominant clay mineral present in the clay deposit in Ikere Ekiti and as the dominant clay mineral, kaolinite imparted plasticity on the clay which makes it easy for the clay to be shaped and moulded. The characterization revealed the presence of minor amount of Iron oxide as impurity in the clay.

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