FUTY Journal of the Environment Vol. 14 No. 1 March, 2020

Physio-Chemical and Thermal Properties of Alkaleri Kaolin, Bauchi State, Nigeria for Ceramics Applications

*[a]Shaaibu, S., [a]Abdullahi A. U., [a]Sadiq, Y. O. and [b]Odey, O. A.
[a]Department of Industrial Design, Abubakar Tafawa Balewa University, Bauchi, Nigeria
[b]Department of Chemical Engineering, Abubakar Tafawa Balewa University, Bauchi, Nigeria
*Correspondence email: Suraj1ng@yahoo.com

Abstract

A kaolin deposit is of considerable economic potential and occurs in Alkaleri local government area in Bauchi state, Nigeria. It is well accepted that the mineralogical composition controls ceramics processing properties. The qualities of raw clays are evaluated merely by their chemical composition and grains size distribution. The kaolin investigated in this study was evaluated through multi-approach method. Atterberg limit: Liquid limit 50.4%; Plastic limit 24.3%; Plasticity index 26.1%; drying and firing shrinkage 5%. Chemical composition: XRF revealed SiO_2 *40.90%;* Al_2O_3 *38.90% and total fluxes content of 1.43%; LOI 13%. XRD revealed the present of quartz, hematite, kaolinite and illinite; DTA curve revealed the present of endothermic peak at* 600^oC *and exothermic peak at* 1000^oC*. SEM showed irregular particles shape and porous texture. The study elucidated properties of Alkaleri kaolin suitable for application in ceramics.*

Keywords: Alkaleri, Kaolin, Physio-Chemical quality, XRF, XRD, Differential Thermal Analysis

INTRODUCTION

Kaolinite forms as a residual weathering product, or by hydrothermal alteration of alumino silicates, especially of feldspars (Oberlin and Couty, 1970). Kaolinite occurs in soils and a sedimentary rock like kaolin, which contains minable amounts of kaolinite. The thickness of the unit layer is 7.15 Å. The charges in the ideal kaolinite structure are balanced. Thus, kaolinite has no layer charge. Talibudeen and Goulding (1983) reported kaolinite samples to have low percentages (0.1 to 10%) of vermiculitic, micaceous, or smectitic layers, which is probably the explanation for the negative layer charge of some kaolinites, resulting in a low shrink-swell capacity and a low cation exchange capacity (<15 meq/100 g).

It is well-accepted that the mineralogical composition controls ceramic processing related properties (Schmidt, 1981), but relations between components in mineralogical systems and properties taking into account the main components only (Schüller, 1980). As summarized by Kaufhold and Penner (2006), especially the amount and nature of swelling clay minerals, smectite and smectitic components in illite-smectite mixed-layer minerals exert a strong influence on workability, such as viscosity (Störr, 1983, Lagaly, 1989), making moisture content (Hofmann, 1962), plasticity (Kromer and Rose, 1994), dry bending strength (Wiegmann *et al*., 1978; Schüller, 1980), and shrinkage (Kromer and Schüller, 1973; Wiegmann *et al*., 1978; Störr and Schwerdtner, 1979).

Despite the known influence of mineral composition, the quality of raw clays for industrial application is often still evaluated merely by their chemical composition (Schejbal, 1978) and grain-size distribution (Winkler, 1954). The mineralogical composition of ceramic clays is characterized by varying amounts of finely dispersed quartz, feldspars (mostly K-feldspars, albite/oligoclase), micas (often referred to as sericite*, muscovite and biotite), illites, kaolinite, Fe-(oxy-hydr) oxides, and occasionally varying portions of mixedlayer minerals, as illite-smectite. In addition, several clays contain very fine organic matter and also lignite, which sometimes contains marcasite (Kromer, 1979; 1980).

Alkaleri clay is investigated in this study for ceramic application. Despite the known variations in properties of Alkaleri kaolin as reported by various authors due to the variability of mineralogical composition, from different location, ceramic clays similar in composition show different processing properties. Those differences can only be elucidated with a comprehensive mineralogical characterization by the advanced methods.

The different processing properties in terms of extrusion behavior and making moisture content could not be explained on the basis of the bulk material composition. As minor constituents exert a strong effect on processing properties (Schüller, 1980), a detailed characterization of the smectite layer content is required to understand and predict the behavior of ceramic masses in a forming process.

A kaolin deposit of considerable economic importance occurs in Alkaleri, a village north of Bauchi in Bauchi State of Nigeria. Alkaleri kaolin deposit is a sedimentary deposit formed most probably by the decomposition of some igneous rocks and later deposited in its present position or by an in situ kaolinization of a sedimentary rock .Contacts between the kaolin concentrations and the overlying laterite are sharp, suggesting transported rather than in situ decomposition. A sedimentary deposit of commercial magnitude may be produced where conditions are favourable for an adequate amount of the clay to be separated from associated non-clay material, deposited without appreciable dilution by other detritus or chemical precipitates and preserved from subsequent alteration or erosion (Bates, 1964,. Eze, 2015).

The deposit has well exposed sections along the Jalgalwa River bank. The Kaolin occurs as a continuous massive body overlain by a ferruginous Laterite top soil which constitutes the overburden .Generally, the Kaolin occurs as light gray to pale orange, with variable iron oxide staining which results in red coloration in some places .The deposit trends approximately in an east–west direction (Eze, 2015).

The Atterberg limits (liquid limit, plastic limit, and shrinkage limit) provide a useful indication of the properties of the tailings. They have been used in soil mechanics for over five decades, providing a measure of the moisture content at which a soil (tailings) changes from a liquid, to a plastic, to a semi solid to a solid state. Moisture content is defined as the mass of water divided by the mass of dry solids.) In particular, the arithmetic difference between the liquid limit and the plastic limit (plasticity index) is a particularly useful indicator of likely soil properties, including its potential to resist liquefaction. Kaolins for ceramics are assessed for their plasticity (determination of Atterberg limits), green strength, dry strength, volume and linear drying, firing shrinkage, and modulus of rupture. Chemical composition is also important for ceramic grades. Physical properties are determined on wet and dry test specimens with specific dimensions which are prepared from the raw materials (Christidis, 2013).

X-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles that are similar to an electron microprobe (EPMA). However, an XRF cannot generally make analyses at the small spot sizes typical of EPMA work (2-5 microns), so it is generally used for bulk analyses of larger fractions of geological materials. The relative ease and low cost of sample preparation, and the stability and ease of use of x-ray spectrometers make this one of the most widely used methods for analysis of major and trace elements in rocks, minerals, and sediment.

Powder X-ray diffraction (XRD) is the common standard technique of mineral identification and quantification (e.g., Chung and Smith, 2000). Clay minerals are very difficult to quantify, because of their variable chemical composition and structures. Due to their platy habit, clay mineral particles have a strong tendency for orientation, enhancing the (00l)-reflections and weakening the (hk)-reflections as compared with a sample of fully random orientation (Środoń, 2006). Information on the magnitude of analytical errors is available from recent worldwide contests and round-robins (e.g., the Reynolds Cup) in quantitative analysis of artificial rocks containing clay minerals. Out comings of these contests indicate that some XRD techniques are capable of providing very accurate results of below 10% of cumulative error from actual values (McCarty, 2002; Kleeberg, 2005).

Differential Thermal Analysis (DTA) DTA is a semi quantitative technique which is especially important in the study of short range order materials since it is applicable irrespective of the degree of crystallinity. The method determines the differences in temperature (T) between a sample and reference material as the two are heated at a controlled rate. When the sample undergoes a transformation, the heat effect causes a difference in temperature between the sample and reference materials. The difference in temperature (~T) is normally plotted against the temperature at which this difference occurs. Reviews of DTA and other related methods such as thermo-gravimetric analysis are contained in Mackenzie (1970), Mackenzie and Caillere (1975), and Tan and Hajek (1977)

A scanning electron microscope (SEM) is used to generate surface images of a specimen on a microscopic level. It does this by scanning a specimen with a beam of high energy electrons in an optical column. The electrons emitted by the beam then interact with the atomic structure of the specimen and generate topographic images. Different types of electrons are produced from the beam, secondary and backscattered, and are discussed in more detail below. If the microscope is also equipped with X-ray capabilities, the equipment can generate information about the elemental make-up of the structure as well as the specific location of those elements. The section serves to further discuss the processes occurring in the SEM optical column, the images produced by secondary and backscattered electrons, and complementary analyses using an energy dispersive X-ray spectroscope (EDS) (David, 1983)

Abel *et al.* (2012) evaluated Ikere Kaolinite using XRF, and physical: specific gravity and Atterberg limits the results found showed that the sample is predominantly kaolinite but high content of Fe_2O_3 and CaO content. Shehu *et al.* (2017) conducted study on chemical composition and particle size analysis of kaolin through XRD, XRF, LALLS and the results showed presents of eight element expressed in percentage in form of their oxide. Five crystalline structures revealed by XRD result; particle distribution showed that kaolin particles are mainly in the range of 25-

35um while few particle have size distribution varied between 0.4-0.75um. Aroke *et al.* (2013) subjected kaolin clay through XRF, XRD, Fourier transform infrared (FTIR); Thermo-grametric (TGA) and Differential thermal analysis (DTA) surface area, pore volume and pore size and found the techniques successful to analyze for conversion of raw Alkaleri kaolin clay to organo-clay for contaminated water treatment. Ozkan (2016) characterized ceramic properties of Turgutlu clay using XRD and plastic measurements, water absorption, linear shrinkage bulk density and Scanning Electro-Microscopy (SEM) based on the results the clay recommended for structural ceramics. Mohsen (2010) investigated Saudi clays by DTA, TGA, SEM and XRF and found them suitable for use in ceramics.

The aim of this study is to provide a consistent mineralogical characterization by a multi method approach that is able to detect processing-related differences of Alkaleri kaolin according to ceramic industrial assessment.

METHODOLOGY

The Kaolin material used for this research was sourced directly from the mine site in Alkaleri Local Governemtn Area (LGA) of Bauchi State, Nigeria. The lump were crushed in ceramics studio Abubakar Tafawa Balewa University (ATBU) Bauch, using Retsch BB 100-Mangan crusher machine. There after the material was soaked in plastic container for 48 hours. The slurry was plunged, Levigate and sieved through a 20mm mesh, there after the kaolin particle were allowed to settled down for 24 hours and the water decanted. The kaolin was placed into plaster of Paris mould (POP) and allowed to thoroughly dry. Liquid and plastic limits were conducted using Atterberg cone test (Matest S.P.A. Treviolo 24048 Model; 8057).Chemical composition was determined by x-ray fluorescence (XRF) using Manipal 4 panatical B. V. machine, as well as x-ray diffraction (XRD) analysis was conducted using the model. Scanning electron microscopy elucidated through PRO X Phenonm world, Model 800-7334 machine. Differential thermal analysis was observed using Nestch DTA/TGA thermal analyzer.

RESULTS AND DISCUSSION

Liquid Limit (LL) (table 1) is the moisture content in percentage at which the clay begins to behave as a liquid material and begins to flow. The liquid limit (50.4) shown on Table 1 is higher than the 49.54% computed from the liquid limit reported by Dondi *et al.*, (2008) for 20 ceramic kaolin samples. High liquid limit value corresponds to high clay content which is a desirable characteristic of kaolin in ceramic works.

Plastic limit is the minimum moisture content, in percent, at which the soil begins to crumble when rolled into a thin thread, approximately 3mm in diameter. The plastic limit of Alkaleri kaolin (24.3) corresponds to the plastic limit of 36 for Ca-kaolinite according to Worrall, (1986). The chemical composition is shown in table 2. This class of kaolin is particularly a good raw material for ceramics.

Clays may present a wide range of plasticity values. Plasticity is a fundamental property in the ceramic industry since it defines the necessary shape changes without rupture when a clay body with added water is submitted to an external force. Plasticity index (PI), is a measure of the range of moisture content over which the clay behaves plastically. Typical values of Atterberg's plasticity index for kaolinite clays range from 5 to 22 (Fernando *et al.*, 2010). The more plastic a clay, the more water it will tolerate without becoming fluid. Grimshaw and Searle (1971) recommended plasticity index of 10-30% for ceramic clays. The plasticity index of 26.1% obtained for Alkaleri kaolin fall within Grimshaw recommendation and presents the kaolin as excellent ceramic clay.

Table1. Atterberg Limits Test, colour, and shrinkage observation.

Alkaleri Kaolin	result	Raw		Fired 900^{o}C	
Liquid Limit	50.4	Very white gray		White	Colour
Plastic Limit	23.4	Dried	1%	4%	Shrinkage
Plasticity Index	26.1				

The lowest plasticity indices are generally obtained from hydrothermal kaolin deposits where the clay is both coarse and well crystallized. Secondary kaolin clays, formed by weathering and eventually carried into sedimentary deposits, are generally finer grained and less well crystallized, both features producing higher plasticity indices (Bain, 1971). The high plasticity index value of Alkaleri Kaolin is an evidence of it secondary origin.

Table2: chemical composition

Sio_2	Al_2o_3	TiO_2	F_2O_3	Cl	CaO	MgO	Na^2O	K2O	MnO	V2O5
40.90	38.80	2.93	1.25	1.61	0.039	0.020	.0.065	0.023	0.001	0.001

CrO3	CuO	ZnO	Ga2O3	AsO3	SrO	ZrO2	BaO	Pbo	LOI
0.043	0.028	0.011	0.021	ND	0.021	0.245	0.77	0.26	12.20

Shrinkage is a property of clay which makes it undergo structural changes and disintegration while being heated. High shrinkage values may result in warping and cracking in the finished products. The usually firing temperature range of commercial ceramic products is 1050^{o}C-1100^{o}C. The samples were fired to 900^{o}C. The average linear and volume shrinkage for the samples tested were 3.4%. Chester (1973) recommended linear shrinkage range of 7-10% for refractory clays. Alkaleri kaolin has a low linear shrinkage and consequently low volume shrinkage. Low shrinkage is beneficial in ceramic industry as it implies less cracking. Low linear shrinkage limits of less than 7% are obtained for kaolin of low feldspar or high quartz content. According to Correia (2004), kaolins which exhibit linear shrinkage limit as low as 3% are composed of as much as 65% quartz. The average quartz content of Alkaleri kaolin sample in work is however only 40.90%.

Different researchers have reported varying SiO2 content for clays used in the various products in the ceramic industry. This agrees with our X-ray Fluorescence (XRF) results (figure3). Chester (1973) reviewed the SiO2 content of clays from five different ceramic industry and gave a range of value of 47-48%. Abubakar *et al*., (2014) recommended clays from Dabagi clay deposit in Kebbi State, Nigeria with an average SiO2of 64.50% for ceramic works. The mean value obtained from the analysis sample of Alkaleri kaolin is 40.90% which is within the reported range of values of ceramic clays. The alumina content 38.90% of Alkaleri clay falls within the range of 25-44% recommended for ceramic by Chester (1973). A low iron content (<0.9%) is necessary in order to achieve fired brightness in excess of 83% at temperatures of 1000^{o}C and above (Highley, 1984). The iron oxide content of 1.25 may inhibit the kaolin from attaining brightness on firing. High level of iron oxide usually imparts reddish colour to clay when fired, and this is capable of making the final product attractive to some users. Where a red colouration is undesirable some form of beneficiation will be required to reduce the effect of high iron content in the final ceramic product. Firing behavior is mainly affected by the “fluxing oxides” (i.e.Fe_2O_3+MgO+CaO+N_2 O+K_2O).

The fluxing oxides content in the kaolin is 1.424. The low flux value gives the clay a refractory behavior which is an advantage in ceramic products such as porous ceramic. High concentration of fluxing oxides impacts dark colour after firing and high shrinkage.

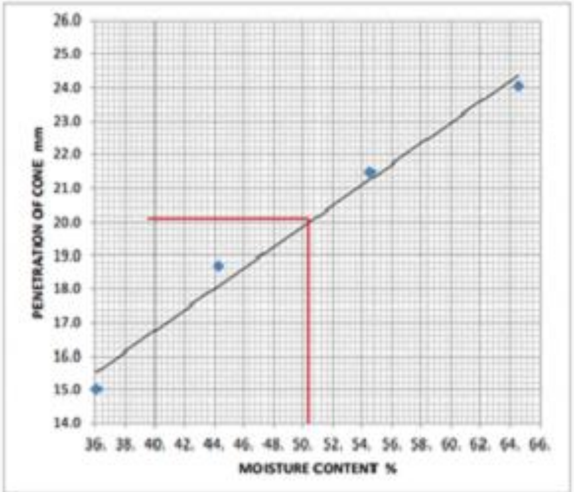

Figure1: Atterberg Limit Cone Test

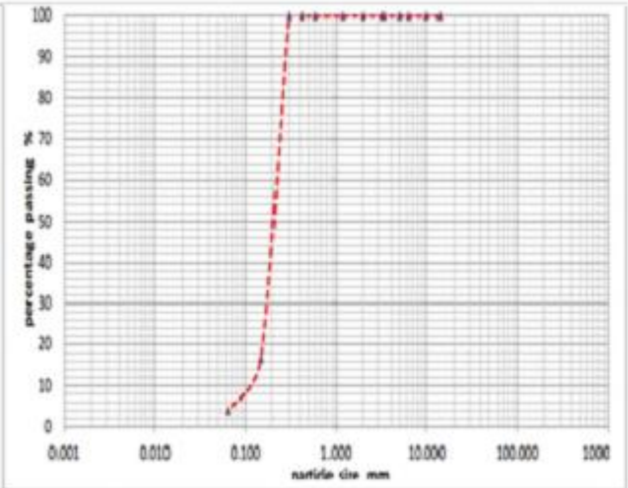

Figure2: Particle Size Distribution Sieves analysis

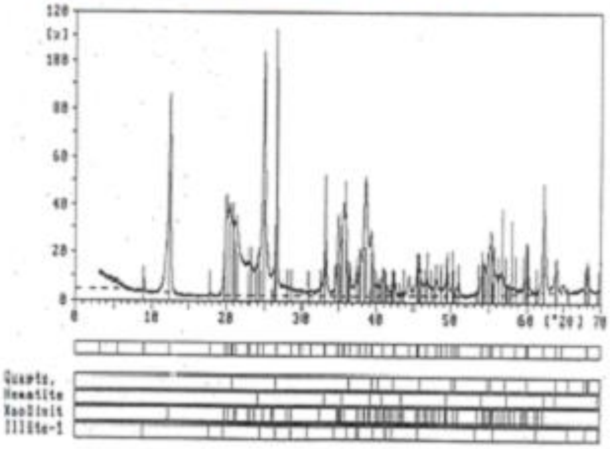

Figure3: X-ray diffraction Composition of Raw Alkaleri Kaolin

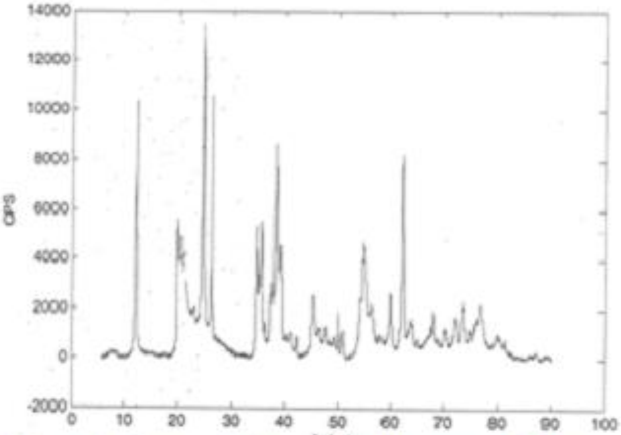

Figure4: X-ray Diffraction Pattern of Raw Alkaleri Kaolin

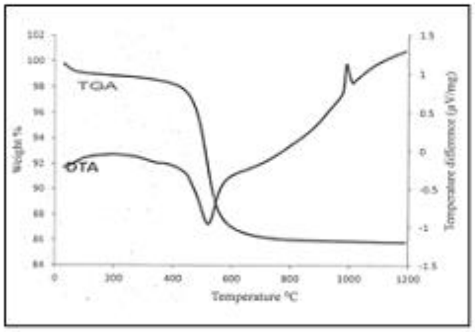

Figure5: TGA-DTA Thermo gram of Kaolin of Particle Fraction less than 63um.

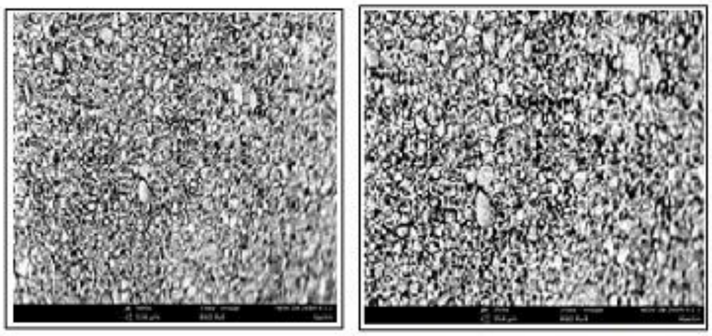

Figure6: Scanning electromagnetic results of Alkaleri kaolin sample.

Loss on ignition (LOI) is a commonly used method to determine the organic matter content of clay by oxidation at an elevated temperature in a muffle furnace by measuring the weight loss. It is a test designed to measure the amount of moisture or impurities lost when the sample is ignited under the

Conditions specified in the individual monograph. Organic matter is oxidized at 500-550°C to carbon dioxide and ash. Carbon dioxide is evolved of carbonate at 900-1000°C, leaving oxide (Heiri *et al*., 2001). The weight loss during the reactions is easily measured by weighing the samples before and after heating and is closely correlated to the organic matter and carbonate. The average loss on ignition recorded is 12.46±1.40% and this attested to the inorganic nature of the kaolin thereby making it a good ceramic raw material. Bloodworth *et al.* (1993) put the loss on ignition value of ceramic-grade kaolin as 13.20%, for the sample studied. The value obtained based on the LOI qualifies the Alkaleri kaolin as a ceramic-grade kaolin.

A well-known chemical reaction either gives off or takes on heat, at 200^0C the curve revealed the free water drove off adsorbed on the surface of the particles as shown in the Differential Thermal Analysis figure 5. At 400^0c -600^0C the revealed the endothermic peak the lost OH^-ion from the kaolin structure in form of water, at period the weight occurred and lost its plastic properties. The curve showed exothermic peak at 1000^oC and Meta kaolin layers condenses to form a new type of crystal structure called spinal with approximate composition $2Al_2O_3$ and $3SiO_2$ (Lawrence, 1972).

The X-ray diffracto gram of Alkaleri kaolin sample (figure 4) revealed the presence of quartz, hematite kaolinite and illinite. The semi quantitative mineralogical composition was based on determined relative peak intensities and reflects to a reasonable extent the mineralogical characteristic of kaolinite of about 70 %. Aroke (2014) citing Asmatulu (2002) recommended clay with high kaolinite content as basic raw material for ceramics.

In figure 6, Scanning electron microscopy (SEM) shows the kaolin particles that were irregular in shape and having porous texture. There is morphology which consists of big agglomeration of the particles surround by smaller particles measuring few micron sizes. Oscar (2016) reported the same morphology for natural kaolinite.

CONCLUSION

A comprehensive mineralogical investigation of Alkaleri kaolin for ceramic and its respective grain-size fractions was conducted to elucidate the processing properties. The study was aimed at contributing to the long-term objective of developing an assessment scheme for quality evaluation of Alkaleri kaolin for ceramic. The necessity of ceramic expert to evaluate special properties of Alkaleri kaolin to elucidate its suitability for single class of ceramic product is required in order to understand its bulk material properties. The deduction of a generally valid clay assessment scheme is additionally complicated by the high variability of clay systems and, thus, mineralogical composition, which have been shown to vary notably even in one single mining area. Nevertheless, decision-making for clay grade-classification on the basis of mineralogical phase analysis remains challenging due to the partial inconsistency of the quantification results obtained by XRD analysis based on Rietveld method. However, we conclude with the words of Galán *et al*. (1998), that "the industrial properties of kaolin cannot be predicted from other basic properties such as mineralogy because they are intricately related to one another." This means that the long-term objective of developing an assessment scheme for the quality evaluation of industrially used clays can only be reached by further efforts dedicated to a detailed determination of the quantitative phase content.

References

Abel, O. T. (2012). Compositional Features and Industrial Application of Ikere Kaolinite Sourthwestern Nigeria *J. of Engr. and Applied Sciences*. 1(5)327-333.

Aroke, U. O. (2014). Characterization, Synthesis and application of Organo-Kaolinite Alkaleri Clay for Removal of Oxynions from Contaminated Water. PhD Dissertation ATBU, Bauchi.

Bain, J. A. (1971). A plasticity Chart as an Aid to the Identification and Assessment of Industrial Clays. *Clay Minerals*. 9, 1-17.

Bates, T. F. (1964) Geology and Mineralogy of the Sedimentary Kaolin of the Southeastern United States - A Review. *Clays and Clay Minerals*, 12th Conference, Pergamon Press, New York: 177-194.

Bloodworth, A. J. Highley, D. E. and Mitchell, C. J. (1993). Industrial Mineral Laboratory manual:Kaolin. British Geological Survey Technical Report WG/93/1. *Mineralogy and Petrology Series.* Keyworth Nottingham, United Kingdom, 75pp

Chester, J.H. (1973). Refractories, Production and Properties. The Iron and Steel Institute: London, UK. 3-13: 295-314.

Dondi, M., Iglesias, C., Dominguez, E., Guarini, G., and Raimondo, M. (2008) The Effect of Kaolin Properties on Their Behaviour in Ceramic Processing as Illustrated by a Range of Kaolins from the Santa Cruz and Chubut Provinces, Patagonia, Argentina. *Applied Clay Science.* 40, 143-158.

Galán, E., Aparicio, P., González, I., and Miras, A. (1998) Contribution of Multivariate Analysis to the Correlation of Some Properties of Kaolin with its Mineralogical and Chemical Composition. *Clay Minerals*. 33, 65-75.

Grimshaw, R.W. and Searle, A. B. (1971). The Chemistry and Physics of Clays and Allied Ceramic Materials. *Wiley Interscience*, California, 1024pp.

Hofmann, U. (1962). Die Tonminerale und die Plastizität des Tons. *Keramische Zeitschrift*. 14, 14-19.

Heiri, O., Lotter, A. F. and Lemcke, G. (2001). Loss on Ignition as a Method for Estimating Organic and Carbonate Content in Sediments: Reproducibility and Comparability of Results. *Journal of Paleolimnology*. 25: 101–110.

Kaufhold, S. and Penner, D. (2006) Applicability of the SER Method for Quality Control of Clays from the German Westerwald. *Applied Clay Science*. 32, 53-63.

Kromer, H. and Rose, D. (1994) Der Einfluß des Stoffbestandes auf das Verflüssigungsverhalten von Tonen. Ber. DKG 71, 245-249.

Lagaly, G. (1989) Principles of Flow of Kaolin and Bentonite Dispersions. *Applied Clay Science.* 4, 105-123.

Lawrence, W. G. (1972) .Ceramic Science for the Potter. Chilton Book Company. Radnor Penneylvania.

McCarty, D. K. (2002) Quantitative Mineral Analysis of Clay-bearing Mixtures: The Reynolds Cup Contest. International Union of Crystallography. *CPD Newsletter.* 27, 12-15.

Oscar, R. (2016). Metallurgical characterization of kaolin from Atacama, Chile. REM, Int. Eng. Journal. Vol.69 N. 4.

Ozkan, I. (2016*)* Characteristics and Ceramic Properties of Tungutlu Clay. Special issue of the 6thIinternationational Congress & Exhibition-APMAS 2015. Maslak, Istanbul Turkey.

Galán, E., Aparicio, P., González, I., and Miras, A. (1998) Contribution of Multivariate Analysis to the Correlation of some Properties of Kaolin with its Mineralogical and Chemical Composition. *Clay Minerals*. 33, 65-75.

Kaufhold, S. and Penner, D. (2006). Applicability of the SER Method for Quality Control of Clays from the German-Westerwald. *Applied Clay Science*. 32, 53-63.

Oberlin, A. and Couty, R. (1970). Conditions of Kaolinite Formation during Alteration of some Silicates by Water at 200 °C. *Clays and Clay Minerals.* 18, 347-356.

Talibudeen, O. and Goulding, K. W. T. (1983). Apparent Charge Heterogeneity in Kaolins in Relation to Their 2:1 Phyllosilicate Content. *Clays and Clay Minerals.* 31, 137-142.

Schüller, K.-H. (1980) Die Bedeutung untergeordneter Bestandteile bei technologischen Prozessen. Fortschr. *Mineral*. 58, 79-105.

Środoń, J. (2006). Identification and Quantitative Analysis of Clay Minerals. In: Bergaya, F., Theng, B. K. G., and Lagaly, G. (Eds.), Handbook of Clay Science. *Elsevier*, Oxford pp. 765-787.

Störr, M. (1983) Die Kaolin in Deutsch Democratic Republic, Schriftenreihe for Geologist Wissenschaften. *Academics.* Verlag, Berlin, pp. 226.

Störr, M. and Schwerdtner, G. (1979) Geology, Mineralogy and Technology for the DDR. *Zeitschrift for Angewandte Geology*. 25, 505-514.

Wiegmann, J., Kranz, G., Horte, C.-H., Graul, J., and Doberenz, C. (1978) Beziehungenzwischen den petrologischen Charakteristika und den keramisch-technischen Eigenschaften von Kaolinen mit nennenswerten Gehalten an Illit-Smectit-Wechsellagerungsmineralen. *Silikattechnik* 29,263-267.

Winkler, H. G. F. (1954) Bedeutung der Korngrößenverteilung auf die stofflichen Eigenschaften grobkeramischer Erzeugnisse. Ber. Dtsch. Keram. Ges.31, 337-343. Worrall, W. E. (1986) Clays and Ceramic Raw Materials. Elsevier Applied Science Publishers Ltd, Barking, pp. 260.