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COMPOSITIONAL AND WEATHERABILITY INDICES OF GETSO KAOLIN DEPOSITS FOR POZZOLANA PRODUCTION

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ABSTRACT

Kaolin is an aluminio-silicate mineral naturally distributed within the earth's crust formed from the weathering of rich feldspartic rocks. The compositional requirements of Getso kaolin deposits for pozzolana production have been carried out. The kaolin deposits were hosted by the rhyolitic rocks of the basement complex of North-Western Nigeria. Three samples from each five locations at different depths were collected and analysed using Free Swelling Ratio (FSR), Free Swelling Index (FSI), X-Ray Fluorescence Spectrometry (XRF) and Scanning Electron Microscopy/Electron Dispersive X-Ray spectroscopy (SEM/EDS). The FSI and FSR ranged between 0-6-0.9 and 16-36 revealing non-swelling and non-expansive Kaolinitic material. The XRF results showed the average concentration of SiO_2+ Al_2O_3+Fe_2O_3: point 1 (78.99 wt.%); point 2 (78.62 wt.%); point 3 (79.14 wt.%); point 4 (80.10 wt.%) and point 5 (80.0 wt.%) suggested to be classified as N pozzolana (ASTMC 618). The Fe_2O_3/MgO versus SiO_3 indicated the samples were products of the calc-alkaline series which is an indication of light colour kaolin deposits. The computed Chemical Index of Alteration (CIA: 91.34), Chemical Index of Weatheribility (CIW: 98.13), Index of compositional variability (CIV: 0.29), Silica Modulus Ratio (SM: 1.77), Lime Silica Ratio (LSR: 0.14) and Aluminum Iron Ratio (AIR: 30.0) indicated very strong weathering intensity high matured, high silica moderate aluminum and less ferrite. The studied kaolin could be utilized for the production of pozzolana after its being beneficiated to remove the TiO_2.

Keywords: Deposits, Feldspar, Major oxides, Weathering intensity

INTRODUCTION

Clay is one of the natural materials that have been used for building construction since the Egyptian and Roman ages (Fernandez *et al*., 2010). Its widespread application is due to the availability of the clay minerals in most of the world. The kaolin clay is commonly a complex mixture of different minerals composed of plate-like particles, and very fine-grained in texture formed from either primary (intense weathering, hydrothermal alteration of aluminosililcate, sedimentary, residual) or primary (erosion and transportation).

The grade of kaolin determines its price and suitability for industrial applications. The properties to be considered for high-grade quality depend on colour, softness, fine particle size and chemical inertness (Ekosse, 2010). The uses of kaolin depend on several factors including geological condition under which kaolin was formed, the total mineralogical composition of the kaolin deposits and the physical and chemical properties (Murray, 2006). The mechanical strength of the material for instance bricks depends largely on their mineralogical composition, physical properties porosity, bulk densities, specific gravity, plasticity and water absorption capacity (Bordia and Camacho-Montes, 2012).

The uses of kaolin in the building industries in the cement, bricks, ceramics, floor tiles, roofing sheets and pottery have been documented (Murray, 2006). The industrial demand for kaolin in Nigeria was estimated to be over 360,000 metric tons annually, this is partly achieved from local production and import, leaving a supply gap of over 250,000 metric tons annually (Murray, 2006). Kaolin deposits are widespread throughout Nigeria almost every state in the country has at least one known deposit of kaolin. In Kano state, it can be found in Shanono, Bichi, Karaye, Getso Dawakin Tofa, Rim Gado and Gests (Bello *et al*., 2017). However, few deposits were discovered to possess good quality (Murray, 2002). Hence, this study assessed the compositional and morphological requirements for the production of pozzolana kaolin clay in the study area by the objectives: to study the geology of the area; to determine the concentration of the major oxides; to determine the morphological characteristics; to measure the extent of the feldspar and silicate weathering activities of the kaolin of study area.

Description and Brief Geology of the Study Area

The study area lies within latitudes 11°58'25"Nand longitudes 7°58'32"E. It falls within the Gwarzo local government of Kano Southern senatorial district of northwestern Nigeria. It is a small rural area with mainly farming and fishing, local hand works, trades and very few kaolin miners as their occupation. The kaolin mining site is about 1.6 Km away from off Gwarzo-Getso-Karaye road. The study area is underlain by the basement rocks of northwestern Nigeria and particularly cross-cut rhyolitic suits (Obaje *et al*., 2009).

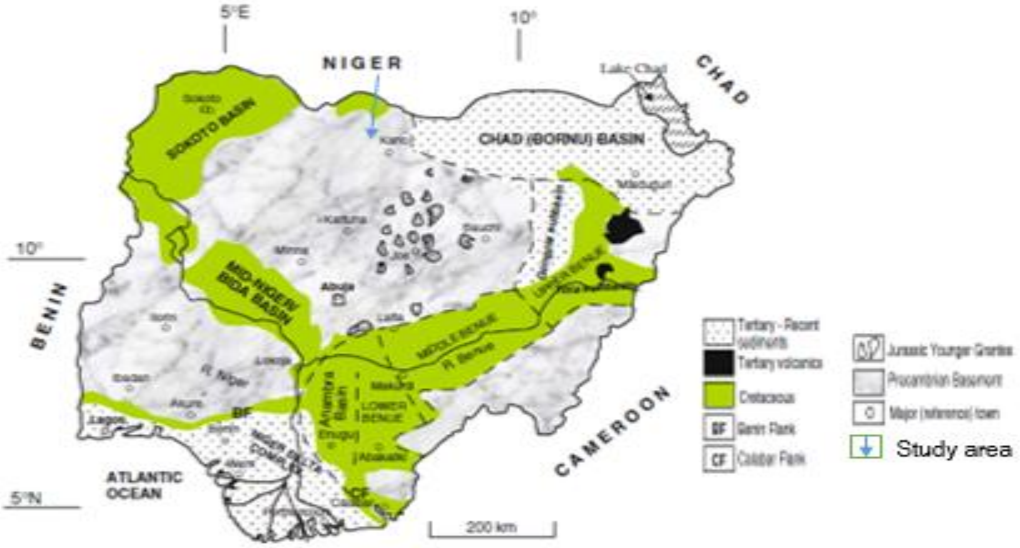

Figure 1: Location Map of the study area (After Obaje *et al*., 2009)

MATERIALS AND METHODS

Sample Collection

A total of about (15) Samples were collected from five (5) different points (Different depths) at the cardinal points and also center of the location with three different samples from each location at different depths (Table 1). The samples were carefully labeled and then transported to the Umaru Musa Yaradua University (UMYU), for laboratory analyses.

Free Swelling Index Test

Free swelling tests were carried out on the kaolin samples by the procedure described by Prakash and Sridhran (2004) in the NBRRI Kano office laboratory. About 10g sample of sieved (with 425μm) kaolin was weighed after oven drying and put in a graduated cylinder. Distilled water was then added to one of the cylinder and the other cylinder was added with Kerosene to make a liquid suspension and then mixed vigorously. The specimen was then placed on the flat table to allow the particle to settle at about 24 hrs to attain an equilibrium state. The volume of the specimen in each of the cylinder was recorded. The free swell index was then computed by the relation:

$$FSI = \frac{\mathrm{V}d - Vk}{\mathrm{Vk}} \times 100\% \qquad (1)$$

$$FSI = \frac{\mathrm{V}d}{\mathrm{Vk}} \qquad (2)$$

Where Vd =Volume of kaolin with distill water, Vk=Volume of kaolin with kerosene

Chemical Properties of the Kaolin

The major oxides (SiO_2, Al_2O_3, Fe_2O_3, K_2O, Na_2O, MnO_2, TiO_2 and CaO) were ascertained by employing the use of X-RayFluorescence (XRF) spectrometry. After the values of the major oxides were obtained, the extent of silicate weathering, the equations (3-8) shall be applied thus according to the method adopted by Bukalo *et al*. (2017).

Chemical Index of Alteration (CIA)

$$= \left\lfloor \frac{Al2O3}{Al2O3 + CaO* + Na2O + K2O} \right\rfloor \times 100 \qquad (3)$$

Chemical Index of Weathering (CIW) =

$$\left\lfloor \frac{Al2O3}{Al2O3 + CaO + Na2O} \right\rfloor \times 100 \qquad (4)$$

Index of Compositional Variability (ICV)

$$= \left\lfloor \frac{CaO + K2O + Na2O + Fe2O3(t) + MgO + MnO + Ti2O}{Al2O3} \right\rfloor \times 100 \qquad (5)$$

$$\text{Lime Silica Factor (LSF)} = \left\lfloor \frac{\mathrm{CaO}}{(2.8\ \mathrm{SiO2} + 1.2\mathrm{Al2O3} + 0.65\ \mathrm{Fe2O3}} \right\rfloor \qquad (6)$$

$$\text{Silica Mudolus (SM)} = \left\lfloor \frac{\mathrm{SiO2}}{\mathrm{Al2O3} + \mathrm{Fe2O3}} \right\rfloor \qquad (7)$$

$$\text{Aluminum Iron Ratio (AIR)} = \left\lfloor \frac{\mathrm{Al2O3}}{\mathrm{Fe2O3}} \right\rfloor \qquad (8)$$

RESULTS AND DISCUSSION

Clay Expansivity

There have been many available criteria for the characterization of soil expansivity and could be considered as one of the criteria in clay mineralogy (Sridharan and Prakash 2000). The expansivity of the samples fell within negligible expansivity (Table 1) which could be described as kaolinitic clay (Sridharan and Prakash, 2000).

The swelling index values were found to be within the range of 16-36%. This result indicates the quality of the kaolin samples own to possessing very low swelling properties which perhaps may qualify it to be highly pozzolanic.

The particle size distribution in a given kaolin deposit is very vital analyses in assessing its potential for pozzolana production this is because the kaolin porosity, roughness, pore sizes are considered to be among the function of the grain size particle distribution Hubadillah et al. (2016). The results revealed that all the samples were found to be compositionally of small-sized particles with a high proportion of silty/Clay content (Av. 87.91; 86.98; 90.4; 89.31; 90.92%) and low sand content (Av. 12.09; 13.1; 9.7; 10.69; 9.09%) for location 1-5 respectively.

Table 1: Swelling/expansivity of the studied kaolin of the study area

Sample No.	Point	Depth (m)	Clay w%	Av Clay w%	FSR	FRI (%)	Clay type	Degree of Expansivity	Dominant Mineral
BRRI 1a	Point 1	5	87.00	87.91	0.8	23	No-swelling	Negligible	Kaolinitic
BRRI 1b		8.6	87.90		0.8	32	No-swelling	Negligible	Kaolinitic
BRRI 1c		12	88.83		0.8	20	No-swelling	Negligible	Kaolinitic
BRRI 2a	Point 2	3.5	87.53	86.98	0.6	36	No-swelling	Negligible	Kaolinitic
BRRI 2b		6	86.63		0.9	16	No-swelling	Negligible	Kaolinitic
BRRI 2c		9.5	86.79		0.8	21	No-swelling	Negligible	Kaolinitic
BRRI 3a	Point 3	2.4	88.64	90.40	0.7	31	No-swelling	Negligible	Kaolinitic
BRRI 3b		5.3	90.58		0.8	18	No-swelling	Negligible	Kaolinitic
BRRI 3c		8	91.98		0.8	20	No-swelling	Negligible	Kaolinitic
BRRI 4a	Point 4	5	88.0	89.31	0.7	33	No-swelling	Negligible	Kaolinitic
BRRI 4b		10	89.49		0.8	20	No-swelling	Negligible	Kaolinitic
BRRI 4c		15.5	90.45		0.6	35	No-swelling	Negligible	Kaolinitic
BRRI 5a	Point 5	5	91.48	90.92	0.7	31	No-swelling	Negligible	Kaolinitic
BRRI 5b		8	91.38		0.7	35	No-swelling	Negligible	Kaolinitic
BRRI 5c		11.4	89.9		0.7	34	No-swelling	Negligible	Kaolinitic
	Range			86.98-90.92	0.6-0.9	16-36			

(From Sridharan and Prakash, 2000**)**

Major Oxides

Major elements content is presented (Table 2). The total concentrations of SiO_2, Al_2O_3 and Fe_2O_3 in the studied samples revealed the average values based on the location as follows: point 1 (78.99 wt.%); point 2 (78.62 wt.%); point 3 (79.14 wt.%); point 4 (80.10 wt.%) and point 5 (80.0 wt.%). From the XRF results (Table 4.2) SIO_2 is the dominant oxide followed by $Al_2O_3$and the Fe_2O_3 while, there were minor oxides including K_2O, CaO, TiO, MnO among others present in the sample. All the tested kaolin samples are suggested to be classified as N pozzolan (ASTMC 618). The presence of minor oxides even in small quantity may affect the colour of the kaolin due to possible durability to heating at high temperature (Kraust, 1984). The values of Al_2O_3 content >30% could also increase the mechanical strength and refractory properties of the samples (Benea and Gorea, 2004).

Chemical Index of Alteration

The intensity of the weatheribility of the kaolin was estimated by equation (3) as adopted (Nesbitt & Young, 1982).The CIA always measures the state of chemical weathering by referring to the loss of alkaline (Na, K and Ca). Generally, CIA greater than 80 shows chemical weathering, 60-80 indicates moderate to high weathering, 55-60 shows moderate weathering, 45-55 indicates low weathering and below 55 reveals none to very low weathering (Singh *et al*., 2005; Amiputan, 2021).

The CIA measures the ratio of original/primary minerals and secondary products of clay minerals including kaolin (Eqn 1). The CIA values of completely weathered rock usually range from 50% and the fresh rock to 100% (Baiyegunhi *et al.* 2017). This pointed out to be that as the weathering intensity increases, the CIV increases. When the CIA is 100% the Na, K and Ca in the host rock had been totally leached from the weathered residue and the rock undergoes serious weathering releasing a large amount of gibbsite and/or kaolinite-rich rock (Alabi, 2015). As presented in (Table 1 & figure 2) the CIV of the samples were 90.86, 94.86, 89.97, 90.18, 90.86 and 91.34 for points 1,2,3,4, 5 and average respectively. This may infer that the source rock had undergone serious weathering resulting in the formation of kaolin deposits in the study area. The A-CN-K plot diagram describes the degree of weathering of the kaolin samples of the studied samples revealing that all the samples were exhibited to be within strong chemical weathering (Table 5). However, sample BRRI 2a possessed the maximum weathering intensity with a value of about 95.4 followed by BRR 2b and then BRRI 2c. Sample BRRI 5c showed the least of the CIA values followed by BRRI 4c. The order of weatheribility of the location: point 2>3>1>4>5.

The indication of relatively low content of CaO, NaO and K_2O could be an indication of loss of Ca^{2+}, Na^+ and K^+ during the degree of chemical weathering of K-feldspar (Bahlburg and Dobrzinski, 2009). Furthermore, Nebsitt and Young, (1982) used CIA to deduce the degree of weathering intensity of clay but Ratcliffe *et al.*(2007) went further to differentiate the environment of deposition where they adopted ternary plot of $Fe2O_3$ Versus MgO for either marine or non-marine.

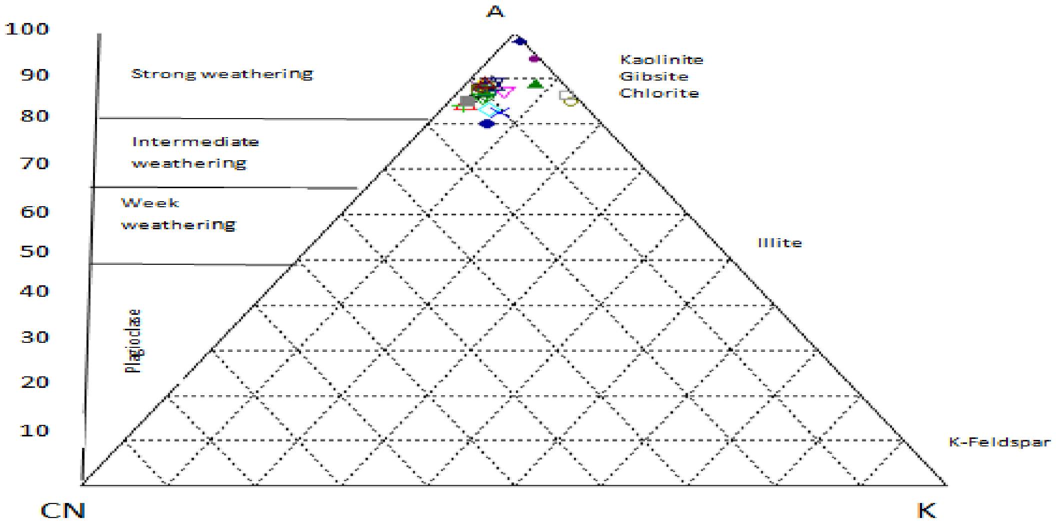

Figure 2: A-CN-K plot of weathering intensity of the Gesto Kaolin (adopted from Nebsitt and Young, 1982; Amiputan, 2021).

Chemical Index of Weatheribility (CIW)

The CIW values presented (Table) ranges between 97.08-99.05% computed from Eqn (4) with an overall average of 98.13% showing strong and intense chemical weathering and this is similar to the kaolin deposits obtained from Pugu, Capim Makoro, Ekon and Assin Fasso (Ekosse, 2000).

Index of Compositional Variability (ICV)

This was adopted (Eqn 5) to assess the level of maturity properties and climatic condition of the sediment (Cox *et al*., 1995). ICV values are high for the highly weathered and stable/low for less weathered minerals. The kaolinite group minerals should have ICV>1. From Table (2) the overall average of the ICV is 0.23, this could suggest that the kaolin deposits in the study area are compositionally matured and confirmed the evidence that kaolin deposits are formed from rhyolitic rock (Figure 3) and in conformity with the field rock identified in the field.

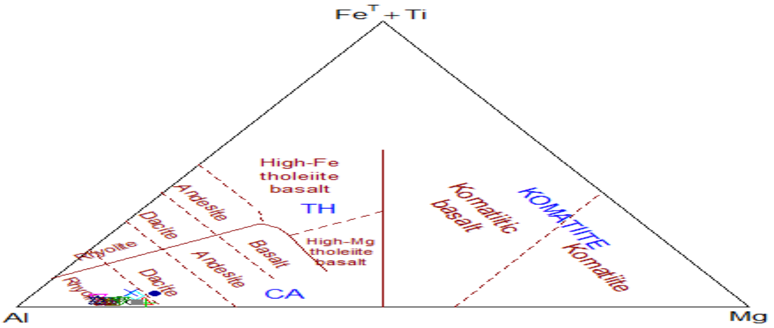

Figure 3: Ternary plot indicating Kaolin from rhyolitic rock (Jensen, 1976)

Lime Saturation Factor (LSF)

This is always employed to assess the quality of material in clinker (Eqn 6). The modern values regarded for LSF range between 0.92-0.98 and values above 1.0 showed the possibility of free lime present in the samples. In the present samples, the LSR (Table 2) falls between 0.41-0.05 which means that the CaO is very erratic. And hence required to be in uniform range for pozzolanic production (Roa *et al*., 2010).

Silica Modulus (SM)

This is the ratio of SiO2 to Al_2O_3 and Fe_2O_3 (Eqn 7). It has a great influence on the burning process and also on the production of cement of any kind. The high silica ratio reflects a higher concentration of calcium silicate and less aluminum and ferrite. The high amount of SM shows poor uniformity and changes in coating formation in the burning and it is more difficult to burn and may possess poor coating behaviour. Low silica modulus usually leads to the formation of rings in cement. The MR (Table 2) was noted to be within the normal range 1.5-2.1 (BRRI 2a & BRRI 4c) respectively.

Aluminum Iron Ratio (AIR)

The Al_2O_3/Fe_2O_3 was employed (Eqn 8) to define the industrial uses of kaolin samples. If the value of $Al_2O_3/Fe_2O_3 \geq 5.5$, it indicates that they are rich in aluminia and have a whitish colour (Garcia-vallies *et al*., 2020) and this is agreed with the field observation of the kaolin samples. This type of kaolin could be used for the production of pozzolana. If the $Al_2O_3/Fe_2O_3 \leq 5.5$, it means that they are rich in iron and have Reddish-brown coloration and this type of kaolin would not be suitable for the production of cement or pozzolana. The AIR for the studied samples shows overall values of 14.60, 41.48 and 30.0 minimum, maximum and average respectively.

Table 2: Major oxides composition of the Gesto kaolin and NBRRI Pozzolana Pilot plant

Sample No	**Sample Points**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**$SiO_2+Al_2O_3+Fe_2O_3$ (ASTMC-618-12)≥ 70**	**K_2O**	**K_2O (ASTMC-618-12) 1.5% Max**	**MgO**	**N_2O**	**N_2O (ASTMC-618-12) 1.5% Max**	**P_2O_5**	**P_2O_5 (ASTMC-618-12) 1.5% Max**	**TiO_2**	**CaO**	**MnO**
BRRI 1a	Point 1	48.82	26.41	0.72	79.0	2.44	2.46	3.73	0.1	0.21	0.12	0.13	0.1	0.17	0.65
BRRI 1b		51.19	27.73	0.77		2.55		4.47	0.31		0.11		0.09	0.09	0.47
BRRI 1c		50.77	29.83	0.74		2.39		4.95	0.21		0.15		0.09	0.17	0.37
BRRI 2a	Point 2	46.31	29.34	2.53	77.20	1.09	1.25	3.71	0.16	0.17	0.09	0.13	0.25	0.16	0.09
BRRI 2b		46.76	26.3	1.75		1.23		3.61	0.16		0.15		0.26	0.09	0.23
BRRI 2c		49.2	27.8	1.62		1.39		2.4	0.15		0.14		0.17	0.08	0.51
BRRI 3a	Point 3	49.98	29.13	0.78	79.14	2.42	2.49	2.97	0.27	0.25	0.13	0.13	0.1	0.71	0.14
BRRI 3b		48.75	26.81	0.83		2.49		2.46	0.22		0.13		0.09	0.17	0.05
BRRI 3c		51.92	28.38	0.84		2.56		3.14	0.26		0.13		0.11	0.31	0.07
BRRI 4a	Point 4	54.2	25.06	1.1	80.10	2.15	1.98	2.97	0.21	0.33	0.14	0.17	0.13	0.13	0.09
BRRI 4b		54.07	26.83	0.98		1.84		2.42	0.37		0.14		0.11	0.6	0.05
BRRI 4c		53.02	24.15	0.89		1.97		2.63	0.4		0.12		0.11	0.6	0.1
BRRI 5a	Point 5	53.17	28.37	0.62	80.03	2.17	2.30	3.19	0.2	0.43	0.13	0.11	0.13	0.15	0.1
BRRI 5b		49.62	29.83	0.74		2.2		3.45	0.21		0.11		0.11	0.25	0.14
BRRI 5c		49	28.02	0.73		2.52		4.26	0.87		0.09		0.09	0.1	0.27
NBRRI pilot Pozzolana plant	Ifenitedo	55.03	24.51	2.17	81.73		0.18	0.24		0.04					
	Immoto Yewa	63.36	16.36	5.44	85.16		0.1	0.4		0.58					
	Calcined Clay	65.45	19.07	6.38	90.84		0.85	0.6		0.85					

Source (present studies and Danladi, 2004)

Table 3: Chemical alteration of the Gesto Kaolin

Sample No	Points	CIA		CIW		ICV		LSR		SR		AIR	
BRRI 1a	1	90.69	90.86	98.99	98.77	0.30	0.31	0.100	0.08	1.79	1.75	36.68	37.67
BRRI 1b		90.38		98.59		0.32		0.051		1.79		36.01	
BRRI 1c		91.5		98.74		0.30		0.095		1.66		40.31	
BRRI 2a	2	95.41	94.86	98.92	99.05	0.27	0.27	0.096	0.07	1.45	1.60	11.60	14.60
BRRI 2b		94.67		99.06		0.28		0.055		1.67		15.03	
BRRI 2c		94.49		99.18		0.23		0.046		1.67		17.16	
BRRI 3a	3	89.55	89.97	96.75	97.78	0.25	0.34	0.41	0.23	1.67	1.74	37.35	34.47
BRRI 3b		90.3		98.57		0.24		0.10		1.76		32.30	
BRRI 3c		90.07		98.03		0.26		0.17		1.78		33.79	
BRRI 4a	4	90.96	90.18	98.66	97.06	0.27	0.26	0.071	0.24	2.07	2.04	22.78	25.76
BRRI 4b		90.52		96.51		0.24		0.33		1.94		27.38	
BRRI 4c		89.05		96.02		0.28		0.34		2.11		27.13	
BRRI 5a	5	91.84	90.86	98.78	97.97	0.23	0.26	0.081	0.09	1.83	1.72	45.76	41.48
BRRI 5b		91.81		98.48		0.24		0.14		1.62		40.31	
BRRI 5c		88.92		96.65		0.32		0.06		1.70		38.38	
Min			89.97		97.06		0.26	0.05	0.07		1.60		14.60
Max			94.86		99.05		0.34		0.24		2.04		41.48
Ave			91.34		98.13		0.29		0.14		1.77		30.0

CONCLUSION

The compositional and intensity kaolin clay deposits sourced from Getso for the production of pozzolana have been carried out. Kaolin is among the valuable natural resources used of industrial applications including cement pozzolana. The studied samples indicated the range of clay content (90.92-86.98%), FSI (0.9-0.6%) and FRI (36-16) describing the high amount of clay, non-swelling, negligible expansivity and Kaolinitic which could qualify it to be highly pozzolanic. The chemical compositions of the tested samples revealed $SiO_2+Al_2O_3+Fe_2O_3 \geq 70$, $N_2O \leq 1.5\%$, $P_2O_5 \leq 1.5\%$ fell within satisfied the requirement for cement pozzolana production excluding points 3 and 5 where K_2O values exceeded the required limits (ASTMC-618-12). The values of Al_2O_3 content >30% in the samples could increase the refractory and mechanical properties of the kaolin. The $Al_2O_3/Fe_2O_3 \geq 5.5$ could infer that they are rich in alumina and have a whitish colour which the kaolin could be satisfied to be used for the production of pozzolana. The kaolin deposits were confirmed to be very intensely weathered, and compositionally matured based on the computed values of CIA, CIW and ICV. This may be qualified for the kaolin to be sourced from the study area for the production of pozzolana but it may required for beneficiation to remove the excess TiO_2.

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