

Characterization of Ajebo Kaolinite Clay for Production of Natural Pozzolan

Gbenga M. Ayininuola, Olasunkanmi A. Adekitan

Abstract—Calcined kaolinite clay (CKC) is a pozzolanic material that is current drawing research attention. This work investigates the conditions for the best performance of a CKC from a kaolinite clay source in Ajebo, Abeokuta (southwest Nigeria) known for its commercial availability. Samples from this source were subjected to X-ray diffractometry (XRD) and differential scanning calorimetry (DSC). XRD shows that kaolinite is the main mineral in the clay source. This mineral is responsible for the pozzolanic behavior of CKC. DSC indicates that the transformation from the clay to CKC occurred between 550 and 750 °C. Using this temperature range, clay samples were milled and different CKC samples were produced in an electric muffle furnace using temperatures of 550, 600, 650, 700, 750 and 800 °C respectively for 1 hour each. This was also repeated for 2 hours. The degree of de-hydroxylation (d_{tg}) and strength activity index (SAI) were also determined for each of the CKC samples. The d_{tg} and SAI tests were repeated two more times for each sample and averages were taken. Results showed that peak d_{tg} occurred at 750 °C for 1 hour calcining combination (94.27%) whereas marginal differences were recorded at some lower temperatures (90.97% for 650 °C for 2 hours; 91.05% for 700 °C for 1 hour and 92.77% for 700 °C for 2 hours). Optimum SAI was reported at 700 °C for 1 hour (99.05%). Rating SAI as a better parameter than d_{tg} , 700 °C for 1 hour combination was adopted as the best calcining condition. The paper recommends the adoption of this clay source for pozzolan production by adopting the calcining conditions established in this work.

Keywords—Calcined kaolinite clay, calcination, optimum-calcining conditions, pozzolanity.

I. INTRODUCTION

CEMENT is one of the most-used materials in civil engineering works. The price and the convenience in handling have consistently driven its production and usage globally. However, this has given rise to a negative effect on the environment. Each metric tonne of cement emits about the same amount of CO₂ and this has an adverse effect on the climate, being a Green House Gas (GHG) [1]-[3]. Thus, any effort targeted at reducing CO₂ emission from cement production is considered crucial in sustaining environmental health. In this regard, attempts have been made to find suitable replacements for cement. The emergence of substances such as fly ash, silica fume, various biomass ash, and geopolymers among others are responses to this drive [4]-[6].

G. M. Ayininuola is with the Civil Engineering Department, University of Ibadan, Ibadan, Nigeria (e-mail: ayigbenga@gmail.com).

O. A. Adekitan is with the Civil Engineering Department, Moshood Abiola Polytechnic, Abeokuta, Nigeria and a PhD candidate at the Civil Engineering Department, University of Ibadan, Ibadan, Nigeria (phone: +2348020613643; e-mail: adekitan.olasunkanmi@mapoly.edu.ng).

The consideration for the cement replacement materials stems from the fact that they exhibit pozzolanic tendencies in various degrees. They are compounds of silicates or aluminosilicates, which react with calcium hydroxide (Ca(OH)₂) to form cementitious compound [4]-[6].

CKC is a material that has produced excellent results as a pozzolan. It has proven to be a replacement for cement up to 10% in cement concrete works [5], [7], [8]. Though more investigations are still underway, the results obtained so far signify that the use of CKC presents a potential for reduction of CO₂ emissions from the cement industry.

CKC (or metakaolin) is produced by treating kaolinite clay (hydrated aluminum silicate, Al₂Si₂O₅(OH)₄) in heat. The heat treatment or calcining is done under controlled temperature with the target temperature ranging between 650 and 900 °C [5], [9], [10]. The calcining alters the structure of the kaolinite rocks, removing the attached hydroxyl ions (OH⁻) in the process [5], [9], [11].

A number of factors affect the calcining process. Calcining temperature and calcining time is among these. These determine the reactivity of the resulting calcined kaolinite-rich clay. At low temperatures (below 700 °C), calcination produces residual kaolinite clays which make the product less reactive, whereas at higher temperatures (above 850 °C), re-crystallization occurs leading to the formation of non-pozzolanic materials such as spinel, silica, and mullite [5], [7].

The calcining rate can also influence the pozzolanic outcome of CKC. Reference [12] highlighted that fast heating rates and rise in ambient pressure makes the calcining to be more rapidly, leading to conservation of energy (since a smaller amount of energy is utilized eventually). However, the heating rate should not be extremely high so as not to produce CKC with large amount of residual/raw kaolinite clay [13]. In addition, the cooling rate also affects the performance of CKC. A gradual cooling enhances crystallization [14], [15] and reduces the amorphous content. Reference [14] suggested a sudden cooling or “quenching” of the CKC to discourage crystallization. Reference [12] had highlighted that the amorphous phase enhances the pozzolanic power of CKC. Moreover, the mineral constituent of the parent clay is also a factor affecting calcining. Kaolinite clays consist predominantly of kaolinite and quartz [7], [12], [16]. The amorphous content in the resulting CKC increases with increasing kaolinite mineral content. The amorphous phase in the CKC is responsible for the pozzolanic tendency [7], [12], [17]. Quartz, on the other hand, is only responsible for grittiness of kaolinite clays [18], [19]. It is inert and not contributory to the pozzolanic properties of the resultant CKC

[18], [20]. Thus, the performance of CKC increases with increasing kaolinite mineral in the parent clay [17].

CKC with small particle size makes large surface areas available for pozzolanic activities. High surface of CKC makes cation exchange during pozzolanic reactions occur at a high rate [5], [10], [12]. Reference [21] revealed that clays with high kaolinite mineral content possess high surface area for pozzolanic reactions.

It is known that the properties of kaolinite clays vary across the globe [22]. As such, the optimal calcining conditions will possibly differ across sources. Therefore, for the best potential, it becomes important to establish the best calcining parameters for specific clay sources. The aim of this work is to establish a protocol for production of CKC from an available kaolinite clay source in Abeokuta, southwest Nigeria and investigate the best calcining parameters for production of CKC from this source.

Natural sources of kaolinite clays have been reported to exist in different locations across Nigeria [20], [22], [23]. Ajebo kaolinite clay in Abeokuta, southwest Nigeria, has been found to be a source abundant in high quality kaolin. Authors who reported on its suitability for refractory work have identified the clay source as abundant of the kaolinite mineral [22], [24]. The results of the analyses carried out on the Ajebo clay were used to characterize this source as raw material for production of CKC.

II. METHODOLOGY

The kaolinite clay was sourced from deposits along Abeokuta-Ajebo Road, Abeokuta, Ogun state (789400 mN, 548209 mE). The deposit was located at a depth ranging from about 10 meters from the ground level (Fig. 1). Samples were collected from the site and tested. Tests carried out on the samples of the kaolinite clay include XRD, DSC, and pozzolanity tests.



Fig. 1 Location and collection of the kaolinite clay at the site

A. XRD Analysis

This was carried out for structural and quantitative analysis of the mineral constituents of the clay. This was done at the

XRD Laboratory of Engineering Materials Development Institute (EMDI), Akure, southwest Nigeria. The natural clay sample was crushed and milled into fine powder before it was prepared and placed into the diffractometer. The result of the XED was compared with International Card for Diffractometry Data (ICDD) and other similar patterns of kaolinite clay across the globe. Of particular interest is the content of the kaolinite mineral in the clay. This affects pozzolanity of the resultant calcined kaolinite-rich clay.

B. DSC (TG) Analysis

This was carried to determine the behaviour of the clay on exposure to heat. The analysis gives the losses in mass of the kaolin clay with increasing temperature and the phases in its conversion to CKC. More importantly, the test helps to determine the range of temperatures over which the de-hydroxylation or the formation of the CKC took place.

The DSC was carried out at the DSC laboratory of the Centre for Engineering Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, southwest Nigeria. About 15 grams of the clay sample was prepared and placed in the NETZSCH DTA 404 DSC analyser and subjected to temperature increase from ambient (32 °C) to 1250 °C.

C. Tests of Pozzolanity

Three tests were carried out to establish pozzolanity. Two of the tests were carried out in line with [12], [14], [15]. The DSC/TG analysis will only highlight the range of temperatures over which the CKC formation phase occurred. This does not clearly indicate the exact calcining temperature and time at which the CKC with the best pozzolanity is produced. These tests help identify the exact temperature. They are degree of de-hydroxylation/calcining and SAI.

The third test is chemical analysis of the CKC. While the first two tests particularly seek to determine the exact calcining temperature and time that produces the best/optimal pozzolanity, the third test was carried out on samples eventually prepared under these conditions. The results of the three tests are compared with the ASTM standard for calcined natural pozzolan [25] since this is an internationally accepted standard. The standard is summarized in Table I. Three samples were used for each of the three tests and their averages determined.

TABLE I
ASTM C618-12 REQUIREMENTS FOR CALCINED NATURAL POZZOLANS
(CLASS N POZZOLANS)

Constituents	ASTM C618-12 Requirement
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃	Minimum of 70%
SO ₃	Maximum of 4%
Moisture Content	Maximum of 3%
Available Alkalies (Na ₂ O, K ₂ O)	Maximum of 1.5%
Loss on Ignition, LOI	Maximum of 10%
Residue (percentage retained on 45µm sieve); measure of fineness	Maximum of 34%
Strength Activity of Cement	Minimum of 75%

1. Degree of De-Hydroxylation (d_{ig})

Fresh samples of natural kaolinite were collected as lumps, crushed and milled into powdery form. At various temperature-time combinations, samples were calcined and the corresponding degree of de-hydroxylation was determined for each combination. The calcining was done using an electric muffle furnace fitted with a temperature control device available at the Foundry of Mechanical Engineering Department, Moshood Abiola Polytechnic, Abeokuta, southwest Nigeria. The calcining time starts when the furnace's temperature gets to the target calcining temperature.

The first temperature used was the lowest temperature in the de-hydroxylation phase (CKC formation phase), as obtained from the DSC result. 300 grams of the powdered natural kaolinite were placed in high temperature resistant crucible and heated in the furnace at a constant temperature of 105 °C for 1 hour to drive out residual moisture. Thereafter, the sample with the crucible was cooled, weighed, re-placed again in the furnace, and calcined for 1 hour. Mass loss after calcining for 1 hour was determined. The same process was repeated again two more times and the average mass loss was determined. Another batch of three samples were also treated at the same temperature but now for a calcining time of 2 hours. The d_{ig} was determined as well. Subsequently, higher temperatures in steps of 50 °C were also used at calcining time of 1 hour and of 2 hours respectively. The d_{ig} was also determined for these temperature-time combinations.

The d_{ig} at each calcining temperature-time combination was determined as:

$$d_{ig} = (M/M_{max}) \quad (1)$$

where, M = average mass loss at temperature-time combination; M_{max} = maximum mass loss (Loss on ignition, LOI of the kaolinite clay)

The loss on ignition was determined in line with ASTM standard [26]. The standard recommends that the rate of calcining (rate of heating) should be such that the temperature in the oven rises from ambient to 950 °C within two hours. This process was also repeated two more times and the average was taken to give the LOI. The temperature-time combination that gave the highest d_{ig} is regarded that which will produce the CKC with the best pozzolanic tendency [12], [14].

2. SAI

The SAI of the samples of the calcined clay at the various temperature-time combinations were also determined to support the result of the d_{ig} . It has been suggested that these two tests can be combined [12]. The test was conducted in line with the requirements of [27], [28]. Three 50 mm cement mortar cubes were prepared using cement:sand ratio of 1:2.75 and water:binder ratio of 0.484. These served as control cubes. Thereafter, for each temperature-time combination, the CKC produced were sieved using 90 μ m sieve and combined with cement at 20% cement replacement. This was used with sand in the same ratio to produce its respective 50 mm mortar test

cubes. Water content required to produce a flow of 110% in the control mortar paste was used. Since there are three CKC samples per temperature-time combination, three samples of 50 mm mortar cubes are produced. Moreover, the portions of the CKC samples used for the SAI were of particle size 90 μ m and below. This ensures that the particle sizes of the cement and the CKC are in the similar range (maximum particle sizes of ordinary Portland cement have been reported to be about 100 μ m mostly [11], [29]).

The 28-day compressive strengths of the mortar cubes were determined using the Universal Testing Machine at the Civil Engineering Department of Federal University of Agriculture (FUNAAB), Abeokuta, southwest Nigeria. For each set of three cubes produced per temperature-time calcining parameter, average compressive strengths were determined. The average strength for each temperature-time combination was compared with that for control to give the SAI at each instance. The temperature-time combination that produces the highest SAI is taken as that which will produce CKC with the best pozzolanicity. Needless to say, this result should agree with the result of d_{ig} . Besides, the SAI for each temperature-time combination should satisfy the minimum of 75% as required for natural pozzolans [25].

3. Chemical Analysis (XRF Test)

This test was done at the analytical laboratory of Lafarge-WAPCO Cement Factory, Ewekoro, southwest Nigeria using the Thermo Fisher Model ARL 9900. The X-ray fluorescence, XRF helped to establish the chemical constituent of the CKC sample. The CKC sample that gave the highest SAI was assessed for its chemical constituents. The major oxides checked include SiO₂, Al₂O₃, Fe₂O₃, SO₃, CaO, Na₂O, and K₂O (Table I). The LOI was also determined. The result was compared with the requirements for classifying a material as a pozzolan as established by the American Society for Testing Materials (ASTM) [25].

III. RESULT

The collected clay samples were whitish/milky in colour. This was suggested to indicate that the samples are rich in kaolinite. Some reddish coloration is also noticed indicating the possibility of leached oxides of iron from the overlying soil. The results presented cover the earlier identified tests - XRD, DSC/TG, and pozzolanity tests.

A. XRD Analysis

The XRD trace was presented in Fig. 2. The diffraction pattern was obtained using Cu radiation ($\lambda = 1.54056 \text{ \AA}$) with 2θ ranging between 10° and 70°. The patterns were recorded at intervals of 0.025°.

The comparison of the diffraction pattern with International Card for Diffractometry Data [30] indicates that the clay sample consist mainly of kaolinite mineral (Table II). The peaks were predominantly of kaolinite and clearly reflect the orderly or crystalline nature peculiar to the kaolinite mineral. This result is in agreement with the pattern of previous authors [24] who had worked on the refractory properties of the same

Ajebo clay. The authors similarly reported that the kaolinite mineral was predominant (over 95%).

B. DSC (TG) Analysis

The DSC result was presented in Fig. 3. The graph is typical of the de-hydroxylation process of kaolinite clays. The first endothermic peak occurred at about 130 °C. This peak occurred due to losses of adsorbed water in the kaolinite [5], [7], [30]. The second endothermic peak occurred at about 600 °C. This represents the peak of the de-hydroxylation of kaolinite clay [5], [12], [30]. This phase was observed to be between 500 °C and 750 °C. This is the temperature range over which the degree of de-hydroxylation test (d_{ig}) was conducted.

C. Tests of Pozzolanicity

The DSC/TG analysis highlighted that the kaolinite de-hydroxylation phase occurred across a range of temperatures (500 °C to 750 °C) without clearly stating the exact temperature at which the best pozzolanic performance occurred. Though the peak of this transition phase was at 600 °C, it will be erroneous to assume that this temperature will give optimum performance. The result of these tests presented the optimum calcining conditions.

1. Degree of De-hydroxylation, d_{ig} .

The result of this test (Table III) presents 550 °C as the lowest temperature adopted. Higher temperatures in steps of

50 °C were also adopted with calcining times of 1 hour and 2 hours respectively. Table III reveals that optimum de-hydroxylation occurred at 750 °C for 1 hour with the highest degree of de-hydroxylation of 94.27%. Other calcining combinations such as 650 °C for 2 hours, 700 °C for 1 hour, 700 °C for 2 hours, and 750 °C for 2 hours, can also serve as possible close alternatives having recorded 90.97%, 91.05%, 92.77%, and 93.41% respectively as degrees of de-hydroxylation. Moreover, the loss on ignition (LOI) of 13.96% falls within the range of 13.95-14% specified for kaolinites in literature [31]-[34].

2. SAI Test

The SAI result was used to corroborate the result of the de-hydroxylation test. The strength index provides the pozzolanic potential of the CKC. The 28-day strength (Table IV) shows that the CKC produced at 700 °C for 1 hour was found to have the highest level of pozzolanicity. The SAI was almost 100% (99.05%). This indicated that the pozzolan prepared at this temperature-time combination performs as much as the control. Calcining at 650 °C for both 1 hour and 2 hours and at 700 °C for 2 hours was also found to produce pozzolans of appreciable potential. The SAI values for these were at least 85%. These could also serve as possible alternatives for calcining parameters.

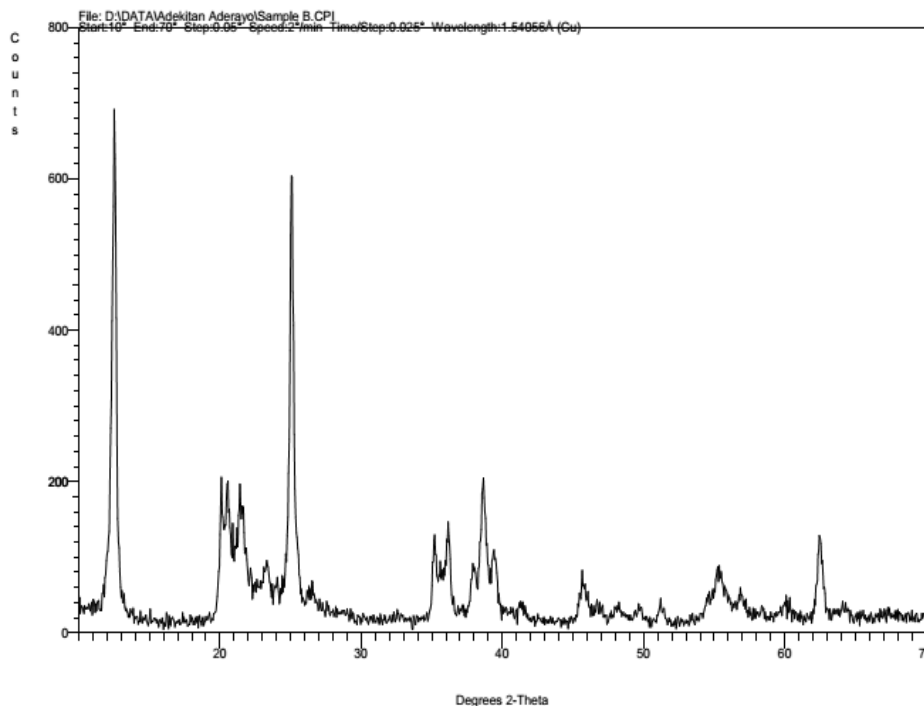


Fig. 2 XRD pattern of the kaolinite clay

Comparing this result with the earlier result on the degree of de-hydroxylation, adopting 700 °C for 1 hour will be quite adequate. The d_{ig} at this temperature-time combination is just marginally lower than the optimum. A similar scenario was

reported by [14] who worked on samples of Serbian kaolinite. The authors' degree of de-hydroxylation, d_{ig} showed 700 °C at 2 hours as the best calcining parameters whereas samples calcined at 650 °C for 1½ hours were reported as the best

pozzolan based on Chapelle tests. The lower temperature was however chosen rating the Chapelle test as a more preferred pozzolanic test than d_g [14], [16]. This explains why premium was also placed on the result of SAI test which presented 700 °C for 1 hour as the best. In any case, the degree of dehydroxylation, d_{tg} (91.05%) reported for this combination was not significantly different from 94.27% which was the highest d_g . Thus, calcining at 700 °C for 1 hour was adopted.

3. Chemical Analysis

The result of chemical analysis showed that the CKC passed the ASTM requirements [25] with the constituents of SiO_2 , Al_2O_3 , and Fe_2O_3 totaling 95.22%. This is more than the

required 70% minimum (Table V). Other conditions were seen to be satisfied as well signifying the suitability of the calcined clay as a pozzolan.

IV. CONCLUSION

It is obvious that the CKC obtained in this work has a high level of pozzolanity. The results serve as a reference for the adoption of Ajebo kaolinite clay in the production of a pozzolan that will have the best pozzolanity. The conditions that need to be met are quite clear from the result of this work. This serves as a reference for production of this pozzolan on a large or commercial scale.

TABLE II
ICDD REFERENCE FOR THE XRD ON AJEBO KAOLINITE SAMPLE

Status: Deleted	QM: Low-Precision (O)	Pressure/Temperature: Ambient															
Chemical Formula: $Al_2Si_2O_5(OH)_4$	Empirical Formula: $Al_2H_4O_9Si_2$																
Weight %: Al20.90 H1.56 O55.78 Si21.76	Atomic %: Al11.76 H23.53 O52.94 Si11.76																
Compound Name: Aluminum Silicate Hydroxide																	
Mineral Name: Kaolinite 1T																	
Radiation: CuK α	λ : 1.5418Å	d-Spacing: Guinier Intensity: Densitometer															
SYS: Anorthic																	
Author's Cell [AuthCell a: 5.14Å	AuthCell b: 8.93Å	AuthCell c: 6.9125Å															
AuthCell α: 91.8°	AuthCell β: 104.5°	AuthCell γ: 90.0°															
AuthCell Vol: 307.02Å ³]																	
Author's Cell Axial Ratio [c/a: 1.345 a/b: 0.576 c/b: 0.774]																	
SS/FOM: F(30) = 1.2(0.122, 197)																	
Molecular Weight: 258.16																	
Crystal Data [XtlCell a: 6.912Å	XtlCell b: 8.930Å	XtlCell c: 5.140Å															
XtlCell α: 90.00°	XtlCell β: 104.50°	XtlCell γ: 91.80°															
XtlCell Vol: 307.02Å ³]																	
Crystal Data Axial Ratio [c/a: 0.744 a/b: 0.774 c/b: 0.576]																	
Reduced Cell [RedCell a: 5.140Å	RedCell b: 6.912Å	RedCell c: 8.930Å															
RedCell α: 91.80°	RedCell β: 90.00°	RedCell γ: 104.50°															
RedCell Vol: 307.02Å ³]																	
Crystal (Symmetry Allowed): Centrosymmetric																	
Pearson: a??	Subfile(s): Mineral Related (Mineral , Natural), Deleted Pattern, Inorganic, Pharmaceutical (Excipient)																
Last Modification Date: 01/14/2012	Cross-Ref PDF #'s: 00-001-0527 (Deleted), 00-014-0164 (Primary)																
References:	Reference																
Type																	
Primary Reference	Melka, Slansky. Acta Univ. Carol., Geol. 3 (1959).																
Unit Cell	Mineral. Mag. 27, 242 (1946).																
Database Comments: Deleted Or Rejected By: Deleted by 00-014-0164. Sample Source or Locality: Specimen from Banska Bela, Czechoslovakia.																	
Unit Cell Data Source: Powder Diffraction.																	
d-Spacings (33) - 00-012-0447 (Fixed Slit Intensity) - Cu Ka1 1.54056Å																	
2 θ	d(Å)	I	h	k	l*	2 θ	d(Å)	I	H	k	l*	2 θ	d(Å)	I	h	k	l
12.369	7.15	50				35.1214	2.553	85	-1	2	2	47.9948	1.894	6	1	3	2
19.891	4.46	75	0	2	0	35.582	2.521	50	-1	-3	1	48.595	1.872	8	1	4	1
20.447	4.34	85	1	1	0	36.1301	2.484	85	2	0	0	49.6403	1.835	6	1	-1	3
21.341	4.16	65	-1	-1	1	37.8002	2.378	25	1	1	2	51.1908	1.783	4	0	5	0
21.604	4.11	40				38.575	2.332	95	1	-3	1	53.9549	1.698	8	-1	-1	4
23.205	3.83	50	0	-2	1	39.4189	2.284	65	-2	0	2	54.4403	1.684	20	1	-5	0
23.901	3.72	20				40.1702	2.243	20	0	4	0	55.2219	1.662	25	-3	0	2
24.992	3.56	50	1	0	1	41.3239	2.183	12	2	-2	0	56.9348	1.616	16	1	-5	1
26.426	3.37	12	1	-1	1	42.6954	2.116	6	2	-1	1	58.1938	1.584	4	-2	0	4
28.327	3.148	4	0	-1	2	45.6908	1.984	12	-1	2	3	60.1533	1.537	8	-1	5	2
32.704	2.736	4	0	-3	1	46.8904	1.936	6	-2	3	1	62.5849	1.483	100	-3	-3	1

© 2016 International Centre for Diffraction Data. All rights reserved.

TABLE III
RESULT OF THE DE-HYDROXYLATION TESTS

	Mass loss (gms)			% mass loss= (mass loss*100/original mass)			Mean % mass loss (± standard deviation)	Degree of de- hydroxylation, dtg
	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3		
	LOI	42.03	42.58	41.90	14.01	13.91		
550@2hrs	22.64	22.90	22.43	7.55	7.63	7.48	7.55±0.06	54.08
600@1hr	20.84	20.44	21.75	6.95	6.81	7.25	7.00±0.18	50.14
600@2hrs	32.99	34.08	32.91	11.00	11.36	10.97	11.11±0.18	79.58
650@1hr	32.09	32.57	34.18	10.70	10.86	11.39	10.98±0.29	78.65
650@2hrs	38.11	37.63	38.53	12.70	12.54	12.84	12.69±0.12	90.97
700@1hr	38.13	37.17	39.09	12.71	12.39	13.03	12.71±0.26	91.05
700@2hrs	38.52	39.02	39.04	12.84	13.01	13.01	12.95±0.08	92.77
750@1hr	40.28	39.59	38.56	13.43	13.20	12.85	13.16±0.24	94.27
750@2hrs	39.15	39.10	39.11	13.05	13.03	13.04	13.04±0.01	93.41
800@1hr	36.33	37.05	36.34	12.11	12.35	12.11	12.19±0.11	87.32
800@2hrs	36.56	37.16	36.74	12.19	12.39	12.25	12.28±0.08	87.89

TABLE IV
SAI AT 28 DAYS OF CURING

Calcining parameters	Comp. stress 1 (N/mm ²)	Comp. stress 2 (N/mm ²)	Comp. stress 3 (N/mm ²)	Mean stress (N/mm ²)	Adopted mean stress (N/mm ²)*	SAI
550@2hrs	33.85	28.17	32.05	31.36	32.95	73.84
600@1hr	35.37	36.42	34.62	35.47	35.47	79.48
600@2hrs	31.67	37.7	36.02	35.13	36.86	82.60
650@1hr	32.77	39.1	36.87	36.25	37.99	85.12
650@2hrs	36.82	32.57	39.52	36.30	38.17	85.54
700@1hr	45.85	42.55	33.87	40.76	44.20	99.05
700@2hrs	37.22	37.2	39.85	38.42	38.09	85.36
750@1hr	32.95	38.75	36.32	36.01	37.54	84.11
750@2hrs	36.07	36.15	38.95	37.06	37.06	83.04
800@1hr	31.62	23.6	30.4	28.54	31.01	69.49
800@2hrs	33.22	32.42	28.12	31.25	32.82	73.55
Cement only	38.90	44.75	44.5	42.72	44.63	-

*ASTM 311 specifies that the range of the three compressive strengths should not be higher than 8.7% of their mean. Otherwise, the mean of the two closest compressive strengths is adopted, the range of which also must not be higher than 7.6% of their mean

TABLE V
RESULT OF CHEMICAL ANALYSIS ON THE CALCINED KAOLINITE-RICH CLAY

Chemical constituents	CKC (%)	ASTM C618-12 requirement for pozzolans
SiO ₂	41.08	SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃ ≥70%
Al ₂ O ₃	52.86	
FeO ₃	1.28	
CaO	3.00	
MgO	0.10	
K ₂ O	0.12	1.5% max
Na ₂ O	0.06	1.5% max
P ₂ O ₅	0.03	
SO ₃	0.12	4% max
LOI	1.16	10% max
Total	99.81	

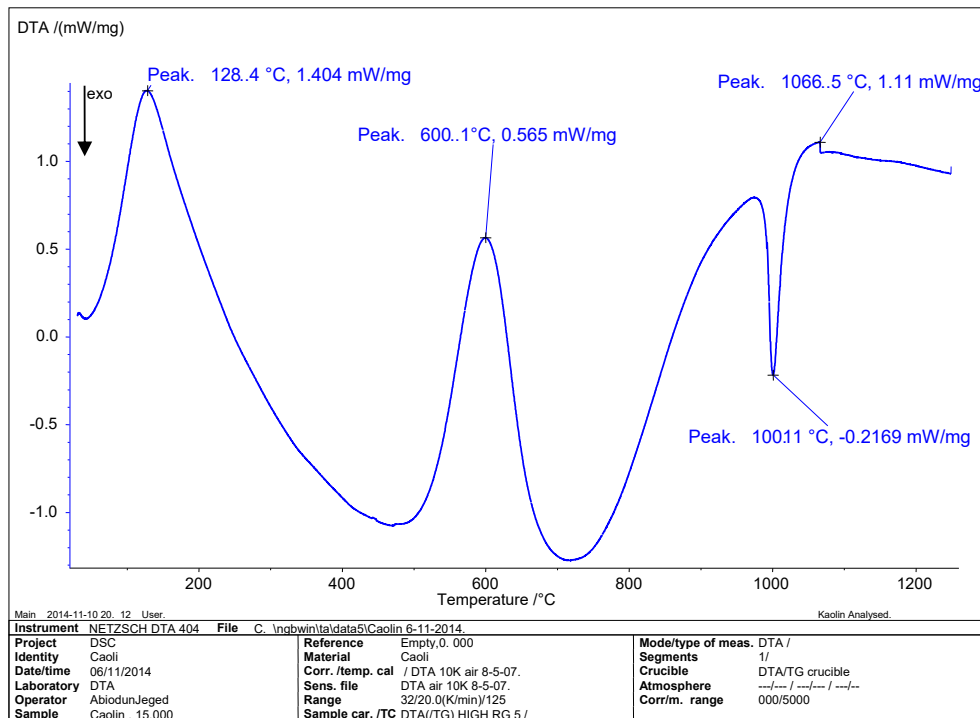


Fig. 3 DSC/TG result of the kaolinite clay

ACKNOWLEDGMENTS

O. A. Adekitan thanks the laboratories whose facilities were used in carrying out this work.

REFERENCES

- [1] L. Adeloye, "Cement: New investment yield 8.5million metric tones", Punch Newspapers feature article. Lagos Nigeria: Punch Newspapers, pp26, June 10, 2011.
- [2] J. Davidovits, "Geopolymer cement – a review". Saint-Quentin, France: Institut Géopolymère, 2008.
- [3] United States Department of Energy, USDoE, "Energy and Emission Reduction Opportunities for the Cement Industry", Technical Paper for Industrial Technologies Program. December 2003. Retrieved January 30th, 2013 from www.1.eere.energy.gov/industry/
- [4] O. O. Amu, S. A. Ogunniyi, and, O. O. Oladeji. "Geotechnical properties of lateritic soil stabilised with sugarcane straw ash", *American Journal of Scientific and Industrial Research*, vol.2, no. 2, 2011, pp.323-331.
- [5] J. M. Justice, "Evaluation of metakaolins for use as supplementary cementitious materials", *Unpublisshed M. Sc thesis, School of Material Science and Engineering, Georgia Institute of Technology*, 2005.
- [6] K. G. Kolovos, P. G. Asteris, D.M. Cotsovos, E. Badogiannis and, S. Tsvilivis, "Mechanical properties of soilcrete mixtures modified with metakaolin", *Construction and Building Materials*, vol. 47, 2013, pp. 1026–1036.
- [7] M. A. Aboubakar, E. Ganjian, H. Pouya, and, A. Akashi, "A study on the effect the addition of thermally treated Libyan natural pozzolan has on the mechanical properties of ordinary Portland cement mortar", *International Journal of Science and Technology*, vol. 3, no. 1, 2013, pp. 79-84.
- [8] O. Adekitan, A. O. Oyerinde and, M. B. Jaji, "Comparative compressive strength assessment of cement concretes blended with two locally produced natural pozzolans", *Proceedings of 7th Applied Research Conference in Africa*, Ibadan, Nigeria, August, 2015.
- [9] J. M. Justice, et al., "Comparison of two metakaolins and silica fume used as supplementary cementitious material" *Proceeding of the Seventh International Symposium on Utilization of High-Strength/High Performance Concrete*, Washington DC, June 20-24, 2005.
- [10] J. M. Justice, and K. E. Kurtis, "Influence of metakaolin surface area on properties of cement-based materials", *ASCE Journal of Materials in Civil Engineering*, vol. 19, no. 9, 2007, pp. 762 – 771.
- [11] R. Fernandez, F. Martirena and, K. L. Scrivener, "The origin of the pozzolanic activity of clay minerals: A comparison between kaolinite, illite and montmorillonite", *Cement and Concrete Research*, vol. 41, 2011, pp. 113-122.
- [12] T. Phung-Thi, "Metakaolin as an additive in composite cement". A *PhD Thesis submitted to the Faculty of Civil Engineering, Weimar Bauhaus University*, 2013.
- [13] B. B. K. Diffo, A. Elimbi, M. Cyrb, J. D. Mangac and, H. T. Kouamoa, "Effect of the rate of calcination of kaolin on the properties of metakaolin-based geopolymers", *Journal of Asian Ceramic Societies* vol. 3, 2015, pp. 130–138. <http://dx.doi.org/10.1016/j.jascer.2014.12.003>
- [14] B. R. Ilić, A. A. Mitrović and, L. R. Miličić, "Thermal treatment of kaolin clay to obtain metakaolin", *Hem. Ind.*, vol.64, no. 4, 2010, pp. 351–356. doi: 10.2298/HEMIND1003220141
- [15] F. Moodi, A. A. Ramezani-pour and, A. S. Safavizadeh, "Evaluation of the optimal process of thermal activation of kaolins", *Scientia Iranica* vol. 18, no. 4, 2011, pp. 906–912. doi:10.1016/j.scient.2011.07.011
- [16] M. A. Soleimani, R. Naghizadeh, A. R. Mirhabibi and, F. Golestanifard, "Effect of calcination temperature of the kaolin and molar Na₂O/SiO₂ activator ratio on physical and microstructural properties of metakaolin based geopolymers", *Iranian Journal of Materials Science & Engineering*, vol. 9, no. 4, 2012, pp. 43-51
- [17] G. Kakali, T. Perraki, S. Tsvilivis and E. Badogiannis, "Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity", *Applied Clay Science*, vol.20, 2001, pp. 73-80.
- [18] O. E. Akhirevbulu, C. V. O. Amadasun, M. I. Ogunbajo and, O. Ujuanbi, "The geology and mineralogy of clay occurrences around Kutigi Central, Bida Basin, Nigeria", *Ethiopian Journal of Environmental Studies and Management*, vol. 3, no. 3, 2010, 49-56.
- [19] T. U. S. Onyeobi, E. G. Imeokparia, O. A. Ilegiuno and, I. G. Egbuniwe, "Compositional, geotechnical and industrial characteristics of some clay bodies in Southern Nigeria", *Journal of Geography and Geology*, vol. 5, no. 2, 2013, 73-84.
- [20] B. S. Badmus, O. T. Olurin, S. A. Ganiyu and, O. T. Odulaye, "Evaluation of physical parameters of various solid minerals within

- southwestern Nigeria using direct experimental laboratory methods”, *American International Journal of Contemporary Research* vol. 3, no. 3, 2013, pp. 152-161.
- [22] A. Tironi, M. A. Trezza, A. N. Scian and, E. F. Irassar, “Kaolinitic calcined clays: Factors affecting its performance as pozzolans”, *Construction and Building Materials*, vol. 28, 2012, pp. 276-281
- [23] B. S. Badmus and, O. B. Olatinsu, “Geophysical evaluation and chemical analysis of kaolinite rocks/clay rocks/clays deposit of Lakiri village, southwestern Nigeria”, *International Journal of Physical Sciences*, vol. 4, no. 10, 2009, pp. 592-606.
- [24] Raw Materials Research and Development Council (RMRDC), *Non-Metallic Mineral Endowments in Nigeria*. Abuja, Nigeria: Raw Materials Research and Development Council (RMRDC), 2010.
- [25] O. S. Olokode and, P. O. Aiyedun, “Mineralogical characteristics of natural kaolins from Abeokuta, South-West Nigeria”, *The Pacific Journal of Science and Technology*, vol. 12, no. 2, 2011, pp. 558-565.
- [26] ASTM C618-12, *Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete*. US: ASTM International, 1994.
- [27] ASTM D7348-13, *Standard test method for loss on ignition (LOI) of solid combustion residues*. US: ASTM International, 2013.
- [28] ASTM C311/C311M-13, *Standard test methods for sampling and testing fly ash or natural pozzolan for use in Portland-cement concrete*. US: ASTM International, 2013.
- [29] ASTM C109/C109M-13e1, *Standard test methods for compressive strength of hydraulic cement mortars (using 2-in. or [50-mm] cube specimens)*. US: ASTM International, 2013.
- [30] D. P. Bentz, E. J. Garboczi, C. J. Haecker and, O. M. Jensen, “Effects of cement particle size distribution on performance properties of Portland cement-based materials”, *Cement and Concrete Research*, vol. 29, no. 10, 1999, pp. 1663-1671
- [31] O. S. Olokode, P. O. Aiyedun, S. I. Kuye, N. O. Adekunle and, W. E. Lee, “Evaluation of a clay mineral deposit in Abeokuta, South-west Nigeria”, *Journal of Natural Sciences Engineering and Technology*, vol. 9, no. 1, 2010, pp. 132-136.
- [32] G. P. Souza, S. J. Sousa, L. A. Terrones and, J. N. Holanda, “Mineralogical analysis of Brazilian ceramic sedimentary clays used in red ceramic”, *Cerâmica*, vol. 51, no. 320, 2005.
- [33] E. Tiffo, A. Elimbi, J. D. Manga and, A. B. Tchamba, “Red ceramics produced from mixtures of kaolinite clay and waste glass”, *Brazilian Journal of Science and Technology*, vol. 2, no. 4, 2015, pp. 1-13. DOI 10.1186/s40552-015-0009-9