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ORIGINAL ARTICLE

An assessment of the pozzolanic potential and mechanical properties of Nigerian calcined clays for sustainable ternary cement blends

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Abstract: This study investigates the potential of calcined clays from Nigerian deposits as supplementary cementitious materials. Clay materials were obtained from three sites namely: Ikpeshi, Okpilla and Uzebba. The raw clay samples were then calcined at 700 ℃ and 800 ℃. Chemical and mineralogical compositions were determined for the raw and calcined clay samples using XRF and XRD respectively. The chemical composition by XRF confirmed these clays as potential pozzolans with SiO_2, Al_2O_3, and Fe_2O_3 collectively exceeding 70%. XRD analysis identified kaolinite and quartz as major mineral phases in the raw clays, which transformed into metakaolin upon calcination. Thermo Gravimetric Analysis (TGA) indicated varying lime consumption levels among the clays, with Ikpeshi clay displaying the highest pozzolanic reactivity and Uzebba clay the least. Compressive strength investigation on mortar cubes prepared with 50% substitution of Portland cement with the calcined clay and limestone, showed that Ikpeshi clay at 800 ℃ had the best strength performance, with strength activity index of 0.92 (at age 28 days), demonstrating superior pozzolanic potential. Strength development was more significant between 7 and 28 days, indicating the pozzolanic reaction's contribution to long-term strength. However, initial strength at 3 days was lower than the reference Portland cement due to a delayed pozzolanic reaction. XRD analysis of blended pastes revealed typical phases of hydration like portlandite, calcium silicate hydrate phase, strätlingite, and ettringite, with the calcined clay blends showing reduced portlandite content, indicating absorption by the pozzolan's alumina phase.

Keywords: Calcined clay; limestone; supplementary cementitious materials; pozzolanic reaction; portland cement; nigerian clays

1 Introduction

The global demand for concrete in the 21st century follows the growth of the middle class, thus, the concrete industry is faced with the challenge of developing systems to increase the availability of concrete while at the same time reduce its environmental footprint. In order to make a substantial global impact, developed solutions have to be abundant, affordable, and adapted to the users, especially in the developing world, where most growth is expected.

Supplementary cementitious materials [1] are soluble siliceous, aluminosiliceous, or calcium aluminosiliceous powders that are used to partially replace clinker in cements or to partially replace Portland cement in concrete mixtures. The main sources of SCMs are waste from industrial processes, among others, pulverized fly ash, granulated blast furnace slag, natural pozzolans (including agriculture

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ashes and silica fume), artificial pozzolans and limestone [2]. The term “natural pozzolan” covers a diverse group of materials. While some of these materials exhibit pozzolanic properties in their natural state, most require some form of processing to enhance their pozzolanic reactivity. They include calcined clay, calcined shale, diatomaceous earth, opaline shales, metakaolin and volcanic materials [3].

Cement hydration produces various reaction products, including alite, belite, calcium monosulfoaluminate, ettringite, aluminaferric oxide trisulfate (AFt) and aluminaferric oxide monoslfate (AFm). The main product of hydration is calcium silicate hydrate (C-S-H), which constites approximately 50 to 60% of the total mass. Lime accounts for 20 to 25%, ettringite for 15 to 20%, with the remaining 5 to 6% occupied by capillary voids and entrapped air. Altho-gh calcium hydroxide (CH) has a beneficial role in maintaining high pH levels that protect steel reinforcement from corrosion, it can also be a source of weakness due to its high solubil-y and susceptibility to acid attack. CH is also the most unstable phase concerning carbonate-n [4]. Furthermore, the presence of unreacted lime serves as a catalyst for the pozzolanic reation.

The pozzolanic reaction encompasses all interactions between lime (or calcium hydroxide), the reactive phases of pozzolana, and water [5]. The chemical composition of the product is crucial for selecting natural pozzolans. According to [6], the combined content of aluminum, silicon, and iron oxide should exceed 70%. Additionally, to qualify clay as metakaolin, its loss on ignition (LOI) value must be below 4% [7]. The mineralogy of the clay is a key factor influencing its pozzolanic reactivity, particularly in the long term [8,9]. Research indicates that pozzolanic reactivity is closely related to the type of clay minerals present, with reactivity typically following the order: kaolinite > montmorillonite > illite [10–12].

The chemical and mineralogy configuration of clay significantly affect the optimal calcination temperature. If the temperature is insufficiently high, there would be incomplete dehydroxylation of clay minerals, leaving the structure partially unchanged. Conversely, calcination temperatures exceeding 900 ℃ can cause high-temperature phases recrystallization with additional sintering, which in turn diminishes the pozzolanic reactivity of the material.

Thermogravimetric Analysis (TGA) provides an initial indication of the optimal activation temperature for calcined clay by identifying the point of complete dehydroxylation without recrystallization. The bond strength and crystal structure of clay minerals determine their dehydroxylation temperature, but factors such as impurities and crystal defects can also influence this temperature [13]. Therefore, TGA can be used to study the impact of impurities on the dehydroxylation temperature in clay samples. Previous research [14] indicates that there exists a linear relationship between the amount of amorphous material in calcined clay and the weight loss observed in thermogravimetric (TGA). The researchers also noted that when weight loss becomes negligible, the highest degree of dehydroxylation is achieved. Thus, TGA is highly useful for estimating the optimal activation temperature.

Research conducted at École Polytechnique Fédérale de Lausanne (EPFL) [15,16] has shown including approximately 40% kaolinite in an LC3-50 mixture (consisting of 50% ground clinker, 30% calcined clay, 15% limestone, and 5% gypsum) yields mechanical properties comparable to plain Portland cement within about 7 days. These findings were observed in mortar bars with a water-to-cement ratio (w/c) of 0.5 and a sand-to-cement ratio of 3 [17]. These types of clays are abundant in equatorial to subtropical regions, which are home to many rapidly emerging countries where the cement demand is expected to grow significantly in the future.

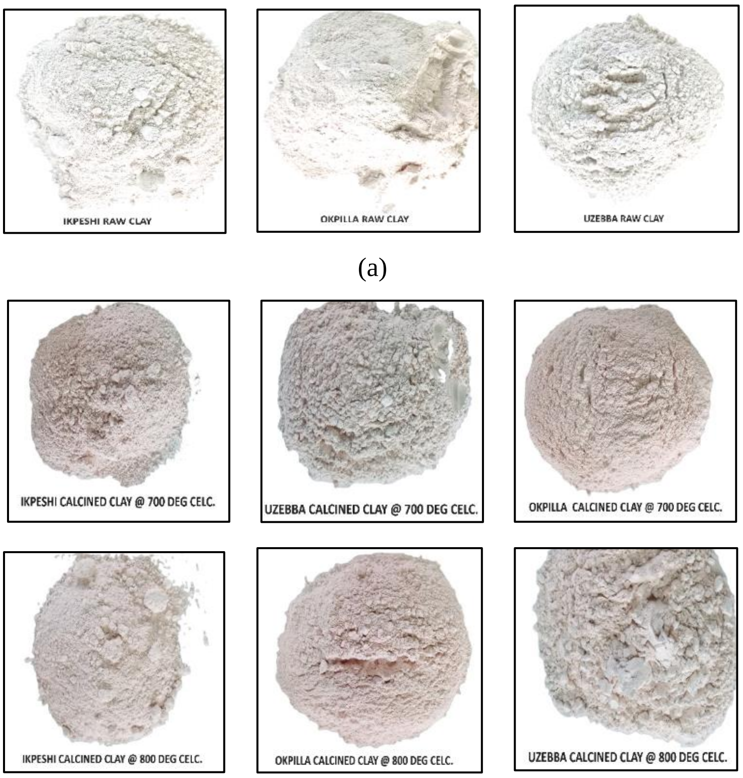
Clay is a complex material and there are no two kaolin that display the same properties. Research into the optimum calcination temperature of the Nigerian kaolinite clay for LC^3 applications is lacking. According to Rautureau et al. [18] the environmental formation influences kaolin properties and deposition conditions. Hence, this research aims to investigate the potential use of some clays obtained from Nigeria clay deposits in the production of ternary blends of cement, via assessment of its pozzolanicity and mechanical.

2 Materials and Method

2.1 Materials

2.1.1 Clay:

Clay material were obtained from Uzebba, a town in Owan West Local Government Area, Okpella in Etsako East Local Government Area and Ikpeshi in Akoko-Edo Local Government Area of Edo state, Nigeria. These areas are located in the warm-humid tropical climate, which is distinguished by a distinct dry and wet season. Generally, the vegetation of the areas is the Guinea Savannah type, with shrubs, dispersed trees and grass savannah. The three clay sources were chosen due to availability of kaolinite clay in this area and the establishment of some mining and cement industries in the region. The Uzebba area falls within the Eastern Dahomey Basin of southwestern Nigeria in which the underlying Upper Cretaceous sedimentary rocks belong to the Araromi Formation. This formation comprises of fine to medium grained fluvial sandstone and gritstone at the base, and is covered by shales and siltstones with interbedded marl, limestone and lignite [19]. The region of Okpella and Ikpeshi lies within the PreCambrian Basement Complex of the Southwestern Nigeria. Most parts of this region is underlain by the metasediments, referred to as the Igarra Schist Belt [20]. Raw clay samples were heated at temperatures of 700 ℃ and 800 ℃ in a fixed-bed furnace with a heating rate of 10 ℃/minute and a retention time of 2 hours, to produce calcined clay. The raw and calcined clay samples are depicted in **Fig. 1**.



(a)

(b)

Fig. 1. (a) Raw clay samples (b) Calcined clay samples

2.1.2 Limestone:

The limestone used in the study was obtained as a commercial product from Okpilla.

2.1.3 Portland cement (PC):

For this study, CEM II cement of grade 42.5N was utilized as the reference cement. Gypsum was incorporated into the limestone-calcined clay cement blends to maintain the system under-sulphated and enhance early-age strength.In this research, the gypsum concentration was consistently maintained at 5%.

2.1.4 Fine aggregate:

The fine aggregate employed for fabricating test specimens was natural silica sand, which complies with the specifications for graded standard sand [21].

2.1.5 Water:

Potable water obtained from the University's main supply was employed for the mixing of samples, adhering to standards [22].

2.2 Preparation of mortar and paste samples

Mortar samples were prepared using a mixture of 1 part cementitious material to 2.75 parts sand, with a 0.5 water/binder ratio. The Portland cement-limestone-calcined-clay blends were composed of 50% Portland cement, 30% calcined clay, 15% limestone, and 5% gypsum, as detailed in **Fig. 2.** Mortar sample cubes (50x50x50 mm)

Table 1. A total number of 63 mortar samples were cast for the strength test, using 50x50x50 mm cube moulds. Each batch of six cubes comprised 500g of binder (250g-OPC, 150g-calcined clay, 75g-limestone and 25g-gypsum for the blended mixes), 1375g of sand and 250g of water. A vibrating table was used to compact two-inch (50 mm) test cubes in layers (**Fig. 2**). The mortar samples prepared were covered with thin polythene sheets and left to cure under air for 24 hours. Thereafter, they were demoulded and placed in saturated limewater to cure till the day of testing.

Fig. 2. Mortar sample cubes (50x50x50 mm)

Table 1. Mixture proportioning for LC^3 systems

Sample	Clinker (% wt. binder)	Calcined clay (% wt. binder)	Limestone (% wt. binder)	Gypsum (% wt. binder)	w/b ratio
OPC	100.0	0	0	0	0.5
LC^3-50	50.0	30.0	15.0	5.0	0.5

Paste samples were prepared using calcined clay and slaked lime in a 40:60 proportion. The calcined clay and slaked lime were placed in a bowl, dry mixed; thereafter, water was added to the mixture in a 1:1 water to solid ratio. The resulting mixture was stirred thoroughly for one minute with a spoon. Thereafter, the paste was placed into four plastic bottles (each holding about 20ml), and sealed (**Fig. 3).** To avoid carbonation, it is crucial to move fast and effectively during this procedure. Also, the sample tubes were pressed as they were being filled up so as to help prevent the inclusion of air bubbles, which contain CO_2. In order to promote the hydration reaction over the carbonation reaction, the pastes were then kept in a fog room to cure.

2.3 Method

2.3.1 Chemical Analysis by XRF

The chemical composition of the clays sourced from the three different locations was analysed to assess their suitability as natural pozzolans. The Xenemetrix Genius-IF EDXRF spectrometer was utilized for this analysis. Approximately 5g of pulverized clay sample was filled into each cup, and the analysis was conducted to determine the chemical composition.

Fig. 3. Clay-lime paste samples

2.3.2 Mineralogical Analysis of Raw and Calcined Clay by X-ray Diffraction (XRD)

X-ray diffraction (XRD) was employed to study the mineralogical composition of the raw and calcined clay samples. Each powdered sample was prepared using a sample preparation block and compressed into a flat, smooth surface. The sample was mounted on the sample stage within the XRD cabinet and analysed using a reflection transmission spinner stage with specific two-theta settings. The X-ray wavelength employed was Cu-Kα (1.54060 Å). The X-ray tube operated at 40 mA and 45 V. The setup included a Programmable Divergent Slit with a 5mm width mask and utilized Gonio Scan.

During analysis, the intensity of diffracted X-rays was monitored as the sample and detector rotated. Peaks in intensity corresponded to lattice planes within the mineral structure. Results were presented as peak positions at $^{0}2\theta$ and X-ray counts (intensity), either in tabular form or as an x-y plot. Intensity was reported as peak height intensity or integrated intensity. Relative intensity was recorded as the ratio of the peak intensity to the most intense peak. Results were matched with libraries such as NIST and PubChem for chemical structure identification and physicochemical properties.

2.3.3 Calcium Hydroxide Quantification by Thermogravimetric Analysis

Previous investigations have shown that the ratio of calcined clay to slaked lime in the produced pastes varies between 20:80 and 50:50 [10,23,24]. In this research, a ratio of 40:60 was employed. The calcined clay and hydrated lime were dry-mixed in a bowl, and water was added to achieve a 1:1 water-to-solid ratio. The mixture was manually stirred in a cup with a spoon for one minute and then divided among four sealed bottles, each holding 20 mL. To avoid carbonation, it was crucial to work quickly and efficiently during this procedure. Additionally, the sample tubes were pressed as they were filled to prevent the inclusion of air bubbles, which contain CO_2. To promote the hydration reaction over the carbonation reaction, the pastes were stored in a fog room [25].

In order to halt the hydration process, the solvent exchange method was utilized. Two solvents were used – isopropanol and diethyl ether. The cured paste samples were crushed, grounded and soaked in isopropanol for 3 days and later in diethyl ether for a day. Thereafter, the ground samples were filtered and kept in an oven to dry at a temperature of 50 ℃.

Thermogravimetric analysis (TGA) was conducted to quantify the pozzolanic reactivity by measuring the residual portlandite in pozzolan-lime pastes. The calcium hydroxide consumption after 28 days was determined using a PerkinElmer thermal analysis machine with a temperature range from

28 ℃ to 950 ℃ at a heating rate of 10 ℃ per minute in a nitrogen atmosphere. At approximately 400 ℃, portlandite decomposes, resulting in loss of weight owing to the release of water, as shown in Equation 1;

$$Ca(OH)_{2(S)} \rightarrow CaO_{(S)} + H_2O_{(g)} \qquad (1)$$

The pozzolanic activity can be approximated by determining the weight loss of the residual calcium hydroxide within the range of 350 ℃ to 600 ℃ through linear extrapolation [26].

The amount of portlandite that is consumed on the calcined clay is estimated using the expression [27];

$$\%\ \text{portlandite consumed} = 100 \times \left(1 - \frac{Mm\left[Ca(OH)_2\right] \times \%H_2O}{Mm\left[H_2O\right] \times \%Ca(OH)_2} \right) \qquad (2)$$

where, Mm[$Ca(OH)_2$] = 74g/mol; Mm[H_2O] = 18g/mol; %H_2O = mass loss due to decomposition of portlandite; %$Ca(OH)_2$ = the quantity of portlandite in the initial mix when blended. This was 60% for the samples investigated.

2.3.5 Mortar Strength Test

Compressive strength test was performed on mortar samples at ages of 3, 7 and 28 days. At the day of the test, the mortar samples were brought out from the curing tank and left to dry under air before testing. The cubes were crushed using a Matest compression-testing machine loaded at the rate of 2000N/s. Three sample cubes of a particular mix proportion were crushed and the failure load was recorded using from the digital screen of the compression machine (**Fig. 4**). The failure strength can be calculated by dividing the failure load by the surface are of contact of the cubes (i.e 2500mm^2) or by simply taking the value from the screen as well.

Fig. 4. Strength test on mortar samples

Fig. 5. Grinding of hardened clay-lime paste sample

2.3.6 XRD Analysis on Ternary Blend Paste

The objective of this analysis was to identify immediate phase transformations during the process of hydration and potential alterations in the initial stages of hydration of pastes with varying proportions of calcined clay replacing cement. The cement-clay material were manually blended in a plastic cup for one minute with a spatula, using a 0.4 water/binder ratio, and then filled into the appropriate sample holders. The samples were cured in a fog room for 3 and 28 days to investigate both early and late hydration processes. After the curing period, the samples were grinded in a mortal (**Fig.** 5) to powder and further exposed to isopropanol and diethyl ether in order to stop the hydration process for three days. Thereafter, the sample was filtered and dried in a furnace at regulated temperature of 50 ^{0}C.

The hydration process and phase changes during hydration were monitored using the Rigaku MiniFlex 600 XRD Diffractometer, with settings consistent with those mentioned earlier.

3 Results and Discussion

3.1 Mineralogical and chemical compositions of the raw and calcined clays

The result of the bulk chemical analysis of the raw clay and limestone is presented in **Table 2**. Summation of the components $SiO_2 + Al_2O_3 + Fe_2O_3$ is equal to or greater than seventy percent (70%), indicating that the three clays can be classified as potentially good pozzolans [6]. The clays from the three sources have high alumina (Al_2O_3) contents varying between 28 and 38 % and silica (SiO_2) content ranging from 39.35 to 60.87 %. The Fe_2O_3 content of the samples are between 1 and 2 % and that of TiO_2 varies between 2.74 and 5.28 %. There was a high CaO content of 24.60 % in the Ikpeshi raw clay. According to the French norm for metakaolin [7], the LOI value should not be more than 4 %. Determination of the LOI for the clay materials from the three locations revealed low values of 1.03, 2.05 and 2.29 % for the Ikpeshi, Okpilla and Uzebba clays respectively. A correlation between the alumina content and the LOI was observed.As the LOI value increased, there was a corresponding increase in the alumina content, which agrees with the findings of [28]. To be classified as a potential pozzolan for Portland cement substitution, the SO_3 content of the raw clay must not exceed 4% [6], and the SO_3 content of the activated clay must be below 1%. All samples met these criteria, with SO_3 values below 0.01%.

Table 2. Bulk chemical constituent of the raw clay samples

	Ikpeshi raw clay	Okpilla raw clay	Uzebba raw clay	Limestone
SiO_2 (%)	39.35	60.87	46.3	2.27
Al_2O_3 (%)	28.89	32.91	38.24	3.5
MgO (%)	0	0	0	5.9
TiO_2 (%)	4.3	2.74	5.28	1.02
Fe_2O_3 (%)	1.7	1.18	1.95	0.92
V_2O_5 (%)	0.2	0.11	0.26	0.03
CaO (%)	24.6	0.56	6.06	84.64
ZrO_2 (%)	0.15	0.41	0.53	0.03
BaO (%)	0	0.13	0.25	0
LOI (%)	1.03	2.05	2.29	1.96
SiO_2+Al_2O_3+Fe_2O_3 (%)	70.0	95.0	86.0	7.0

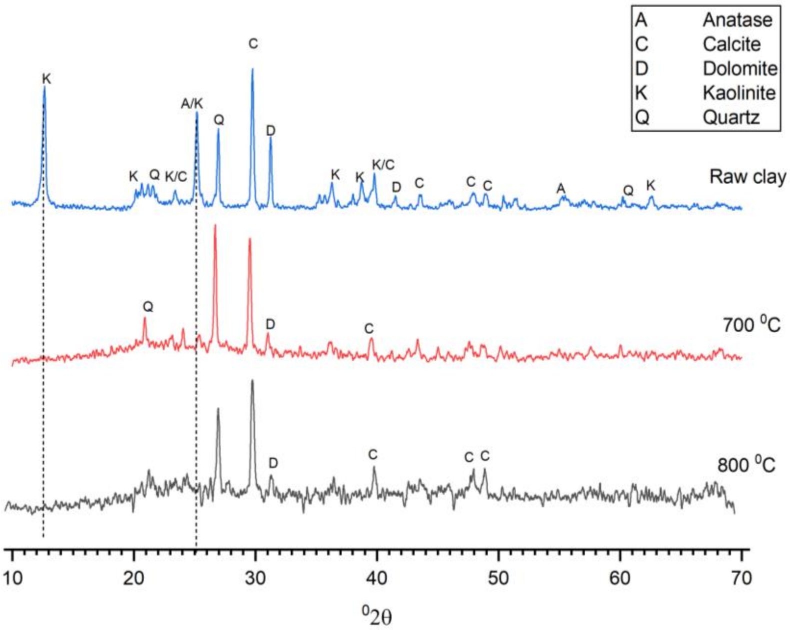


Fig. 6. XRD pattern of raw and Calcined clay (700 ^{0}C and 800 ^{0}C) from Ikpeshi

The XRD pattern of the raw as well as the calcinated clays from Ikpeshi, Okpilla and Uzebba are presented in **Fig. 6**, **Fig. 8** and **Fig. 8** respectively. The mineralogical composition of Ikpeshi clay is mainly kaolinite, associated with Calcite, Dollomite, Quartz and Anatase, this is similar to the mineral composition obtained by Mokwa *et. al* [29]. Okpilla and Uzebba clay diffraction pattern showed the presence of two major clay minerals, that is, kaolinite and quartz. Studies revealed the main components in Uzebba clay was kaolinite, sepiolite and chlorite [30]. Also Omang *et. al* studied three clay locations in Okpilla and discovered two major minerals, these are, kaolinite and quartz [31]. The XRD patterns of the raw clays from Ikpeshi and Uzebba showed two very high intensity reflection peaks around 12.5^0 2θ indicating the presence of kaolinite in the materials. The three clay samples displayed strong reflection peaks at around 27^0 2θ indicating the presence of quartz. This is a reflection of the silica content from the XRF result (**Table 2**). The presence of Anatase, Wollastonite and Dollomite are indicated by high peak reflections at around 25^0, 30^0 and 31^0 2θ respectively.

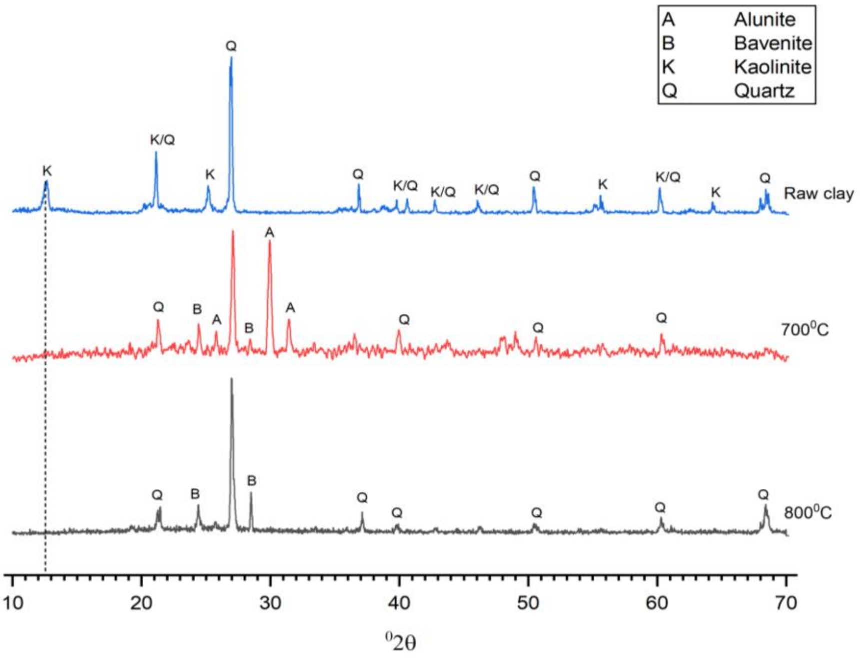


Fig. 7. XRD pattern of raw and Calcined clay (700 ^{0}C and 800 ^{0}C) from Okpilla

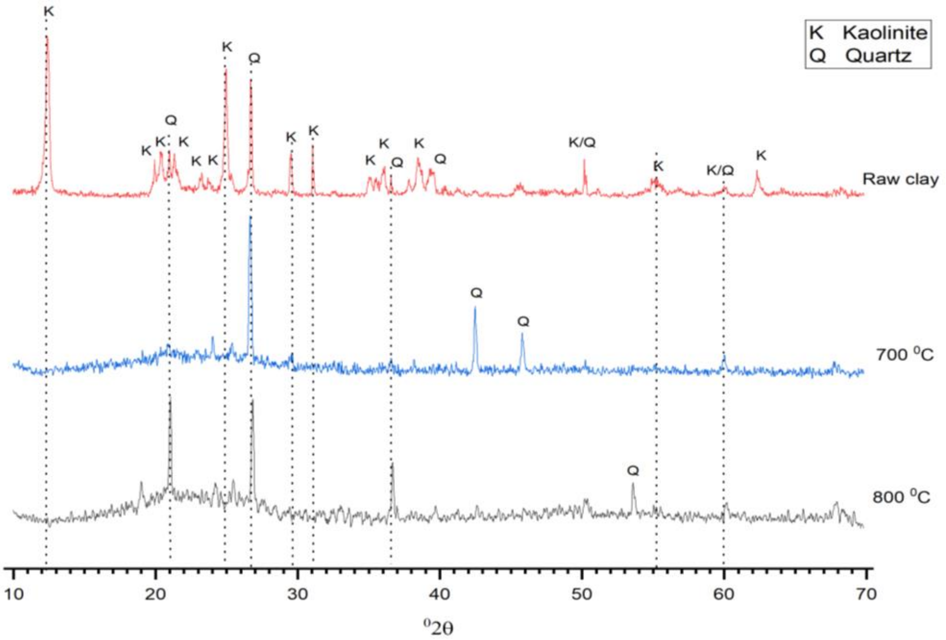


Fig. 8. XRD pattern of raw and Calcined clay (700 ^{0}C and 800 ^{0}C) from Uzebba

The Ikpeshi and Okpilla raw clay samples showed a lower Al_2O_3 concentration (28.89 wt. % and 32.91 wt. % respectively) than the Al_2O_3 content of pure kaolinite (39.49 wt. %), while the Al_2O_3 content (38.24 wt. %) of Uzebba clay compared well with that of pure kaolinite. Also, the SiO_2 content

(39.35 wt. %) of the Ikpeshi clay was lower than the SiO_2 content (46.3 wt. %) of pure kaolinite, while that of Okpilla (60.87 wt. %) is very much higher than for pure kaolinite and that of Uzebba (46.30 wt. %) is the same as that of pure kaolinite. The presence of other minerals such as dolomite and calcite confirms the high CaO content (24.60 wt. %) in the Ikpeshi clay.

Generally, it is observed from the three clay samples that at temperature of 700 and 800 ^{0}C, the kaolinite peaks disappeared, signifying the transformation of the crystalline mineral to metakaolin, which is amorphous. However, other minerals present such as calcite and quartz remain unaffected by the calcination processes, since their decomposition temperatures are much higher than that adopted in the calcination process.

3.2 Pozzolanic Reaction of the Calcined Clays Materials

Fig. 9 illustrates the consumed lime by the activated clays at different heating temperatures. The Ikpeshi calcined clay at 800 ℃ exhibited the highest lime consumption, with 89.2% consumed after 28 days, indicating significantly greater reactivity compared to the other clays. Conversely, the Uzebba calcined clay at 800 ℃ showed the lowest lime consumption at 10.4% after 28 days. Generally, clay calcined at 700 ℃ demonstrated higher consumption of lime compared to that calcined at 800 ℃, except for the Ikpeshi clay. Uzebba clay was observed to be the least reactive, with lime consumptions of 37.9% and 10.4% at 700 ℃ and 800 ℃, respectively.

In terms of pozzolanic potential, Ikpeshi calcined clay performed the best across both calcination temperatures among the three sources, indicating its superior pozzolanic activity. The pozzolanic potential order among the clays can be summarized as follows:

Ikpeshi > Okpilla > Uzebba.

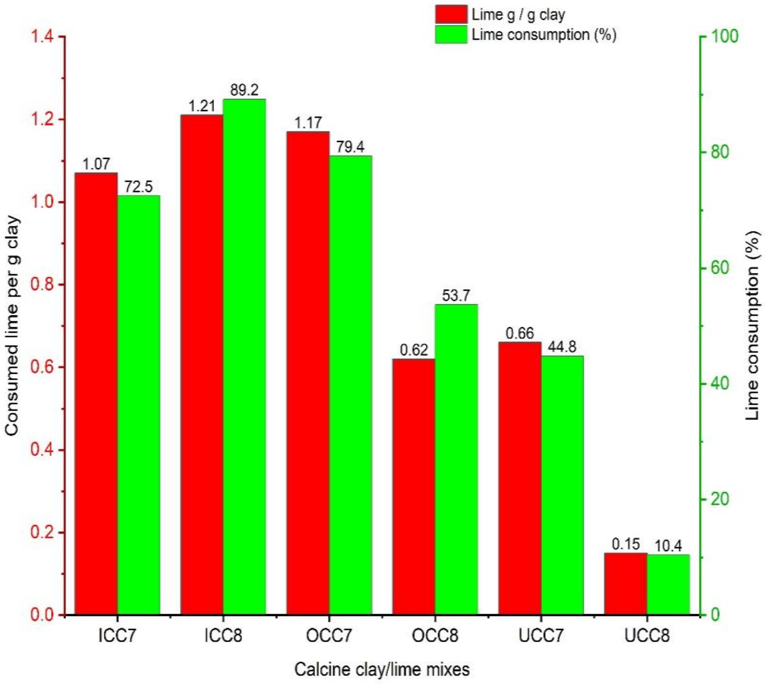


Fig. 9. Consumed Lime in calcined clay/Lime pastes at a ratio of 1/1.5, cured for 28 days in a fog room

[ICC7: Ikpeshi calcined clay at 700 ^{0}C; ICC8: Ikpeshi calcined clay at 800 ^{0}C; OCC7: Okpilla calcined clay at 700 ^{0}C; OCC8: Okpilla calcined clay at 800 ^{0}C; UCC7: Uzebba calcined clay at 700 ^{0}C; UCC8: Uzebba calcined clay at 800 ^{0}C]

Upon calculating the consumed lime per gram of clay, it is evident that between 0.15 to 1.21 grams of lime were consumed per gram of clay across all mixes. This suggests that after 28 days of hydration, the remaining calcium hydroxide (CH) in the paste could potentially participate in further pozzolanic reactions.

3.3 Strength development of mortar samples

The compressive strength of the mortar samples prepared from the various limestone-calcined clay blends was determined after 3, 7 and 28 days of curing. The average compressive strength of each set of test is presented in **Fig. 10**.

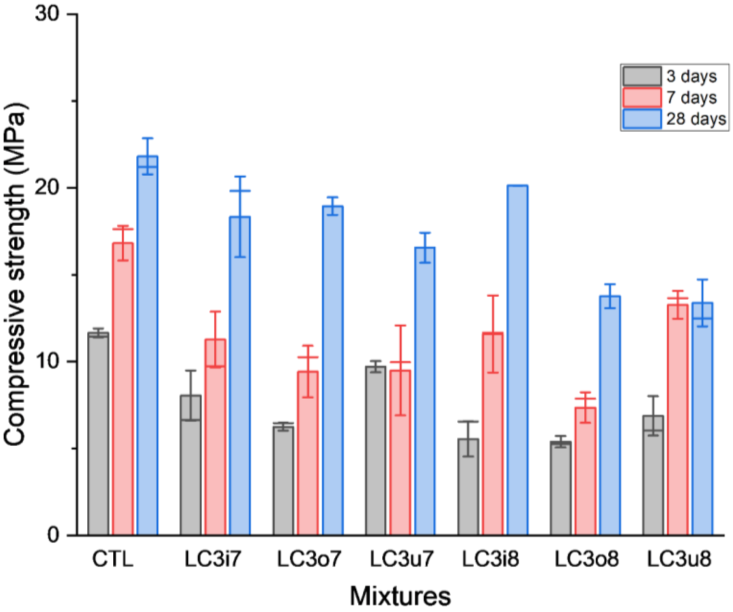


Fig. 10. Compressive strength of referenced OPC (CTL) and LC3 blends from various sources (i- Ikpeshi, o-Okpilla and u- Uzebba) at clay calcination temperatures of 700 and 800 ^{0}C

In general, the compressive strength of all cement blends at day 3 was lower compared to the reference sample, leading to an activity index below one. This limitation is crucial to consider for practical field applications. The phenomenon can be attributed to the dilution of the cement caused by substituting calcined clay-lime, as well as the delayed onset of the pozzolanic reaction [15,32,33]. The initial phase involves cement hydration, resulting in the formation of portlandite. Subsequently, calcined clay can react with portlandite to initiate the pozzolanic reaction [15]. Overall, the impact of the pozzolanic reaction from calcined kaolinites materials to strength development became more significant between the ages of 7 and 28 days. Hence, the compressive strength values at the age of 28 days are more indicative of the actual strength of the ternary cement blends.

Generally, the strength of the mortar decrease with increasing calcination temperature except for clay obtained from Ikpeshi, which displayed an increased strength upon increment in calcination temperature. The maximum compressive strength at 28 days (21.8 N/mm^2) was observed in the referenced OPC mix and the minimum value, 13.4 N/mm^2, was displayed by Uzebba calcined clay blend at 800 ^{0}C calcination temperature. Also there was a progressive strength growth from a period of 3 to 28 days for all the mortar samples except for Uzebba clay blend calcined at 800 ^{0}C, which shows no continuous strength gain after 7 days. The limestone-calcined clay blends from Okpilla and Uzebba (at calcination temperature of 800 ^{0}C) displayed the lowest strength development, while the mortars blends with calcined clay from Ikpeshi (at 700 and 800 ^{0}C), and Okpilla (at 700 ^{0}C), exhibited the highest strength development relative to the referenced OPC samples. At a 700 ℃ temperature of calcination, all calcined clay blends from the three sources, with the exception of Uzebba, exhibited their maximum reactivity in the mortar samples, achieving a 28-day strength comparable to the reference mortar. At this temperature, these clays demonstrated sufficient reactivity to function effectively as pozzolanic additives for cement and concrete.

The strength activity index (SAI) was also determined using the equation below [7];

$$\text{SAI}=\frac{\text{average compressive strength of the test mixture}}{\text{average compressive strength of the reference}} \tag{3}$$

Following the results of the strength of the various cement blends, calcined clay cement blend at calcination temperature of 800 ^{0}C from Ikpeshi can be classified as Type B [7] having a SAI of 0.92, while others have a SAI ranging from 0.61 – 0.87 (**Table 3**).

Table 3. SAI of mortar samples

Sample Mix	LC^3I_7	LC^3I_8	LC^3O_7	LC^3O_8	LC^3U_7	LC^3U_8
SAI	0.84	0.92	0.87	0.63	0.65	0.61

This strength performance correlates directly to the lime consumption (at 28 days) of the TGA test (**Fig. 9**). All clays consumed more CH at calcination temperature of 700 ^{0}C than at 800 ^{0}C after 28 days. The exception displayed by Ikpeshi clay calcined at 800 0C is also reflected in the lime consumption (89.2%).

Fig. 11 illustrates the relationship between the relative compressive strength (at 28-day) of LC3 mortars and the consumed lime of various calcined clays (after a period of 28 days). A strong correlation is observed between the strength achieved and lime consumption, with an R-squared value of 0.86. The plot indicated that a slight increase in lime consumption resulted in a marginal enhancement in mortar strength. From the graph, it can be inferred that lime consumption exceeding 0.7 g lime per gram of clay led to significant further strength development in mortars. Conversely, lime consumption below this threshold did not contribute significantly to strength development.

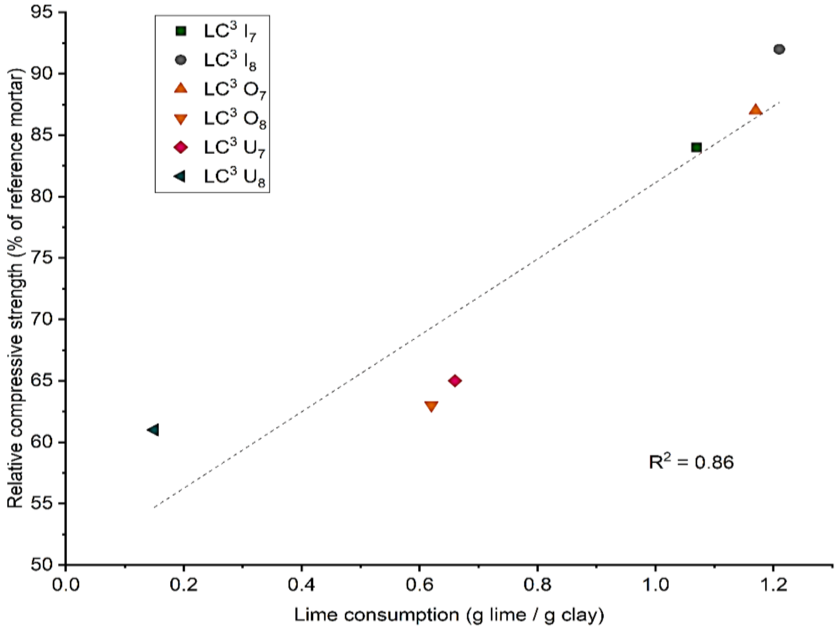
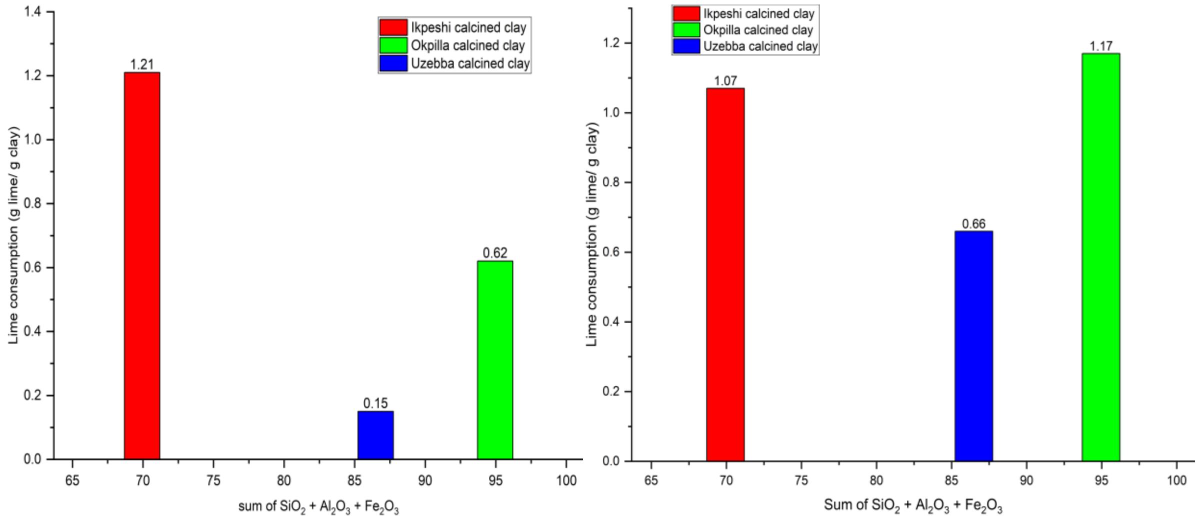


Fig. 11. Relative 28 days compressive strength of LC^3 mortars vs. Lime consumption after 28 days of different calcined clays.

In **Fig. 12**, the consumed lime by calcined clays after 28 days of hydration is plotted against the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ content of the clays. The ASTM manual [6] for pozzolanic materials states that, a material is considered as a good pozzolana if the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ is greater than 70% of its total chemistry. However, the figure indicates that the pozzolanic properties of natural calcined clays do not necessarily improve with increasing total $SiO_2 + Al_2O_3 + Fe_2O_3$ content. This is because natural pozzolans may contain minerals phases that are non-reactive such as quartz and feldspars that contribute to this sum but do not enhance pozzolanic activity.

Despite this, half of all calcined clays analysed in the study achieved a strength activity index of 75% or higher [6], indicating they qualify as good pozzolanic materials according to the standard.



(a) (b)

Fig. 12. (a) Lime consumption of calcined clays after hydration for 28 days versus the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ of the clays at 700 ^{0}C; (b) Lime consumption of calcined clays after hydration for 28 days versus the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ of the clays at 800 ^{0}C

3.4 Limestone calcined clay Portland cement system

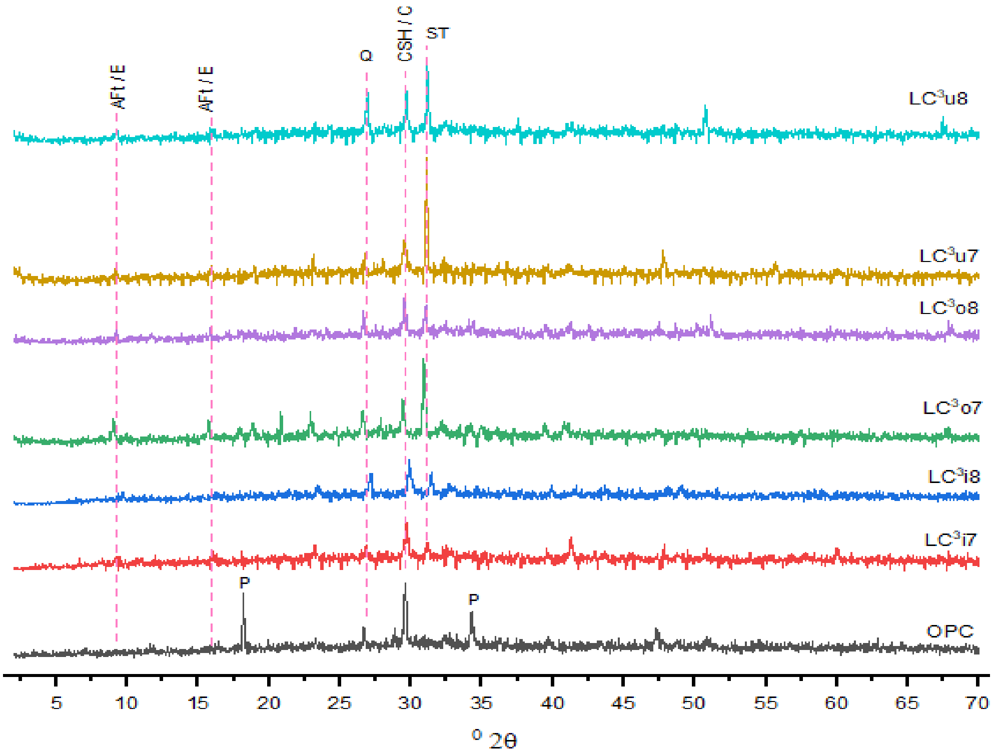


Fig. 13. XRD pattern of the pure OPC and of LC^3 pastes cured for 28 days. The present phases indicated as; P: Portlandite, St: Strätlingite, AFt: Alumina-ferric oxide trisulfate, C: Calcite, CSH: Calcium silicate hydrate, Q: Quartz, E: Ettringite

Generally, the hardened cement paste comprises of a combination of various reaction products [34]. **Fig. 13** presents the XRD pattern of pastes (at 28 days of curing), comparing pure Portland cement (PC) with LC^3 blends incorporating clays calcined at 700℃ and 800℃. The results revealed several hydration phases including portlandite, the C-S-H phase (calcium silicate hydrate), and strätlingite. Additionally, ettringite and AFt phases (Alumina-ferric oxide trisulfate) are predominantly formed in the blended pastes. The portlandite is crystalline, with relatively high intensity peaks at 18.12 ^{0}2θ and 34.24 ^{0}2θ. On the other hand, the C-S-H phase appeared microcrystalline and showed an amorphous response to X-rays, as typically observed [26,35]. At 28 days, the amount of portlandite in the various LC^3 blends has clearly reduced compared to that in the OPC paste, similar result was obtained by Shah *et al.* [32]. This signifies the absorption by the alumina phase in the pozzolan to produce other hydrated phases.

Higher alumina content promotes the precipitation of strätlingite [31,32], characterized by peaks typically observed around 31.18° 2θ in XRD patterns. At 7 days, strätlingite formation began, although the peaks are initially weak, indicating a low initial presence. By 28 days, the intensity of strätlingite peaks increased significantly, suggesting a more pronounced contribution from pozzolanic reactions. In contrast, no strätlingite formation was observed in the pure OPC paste at 28 days.

The aluminate phase reacted with gypsum and water to produce ettringite. It is noteworthy that aluminum in ettringite and monosulfate can be partly substituted by iron [33]. In the LC^3 blends, AFt phases (alumina-ferric oxide trisulfate), derived from ettringite with partial substitution of aluminum by iron and sulfate by other ions, were observed. These phases exhibited weak reflected peaks typically around 9.18° and 16.18° 2θ in XRD patterns . Other observed minerals in the samples include quartz and calcite with 26.68 ^{0}2θ and 29.7 ^{0}2θ respectively.

4 Conclusions

The study focused to assess the potential of calcined clays from Nigerian deposits as supplementary cementitious materials in the production of ternary blends of cement. Various analytical methods, including XRF, XRD, TGA, and compressive strength tests, were employed to assess the mineralogical, chemical, and pozzolanic properties of the clays.

- The chemical analysis revealed that the calcined clays from the three sources meet the criteria for potential pozzolans, with the sum of SiO_2, Al_2O_3, and Fe_2O_3 exceeding 70%. The XRD analysis confirmed the presence of kaolinite and quartz as the major mineral phases in the raw clays. Upon calcination at 700°C and 800°C, the kaolinite transformed into metakaolin, which has high pozzolanic potential.
- The TGA results demonstrated varying degrees of lime consumption, with Ikpeshi clay showing the highest reactivity and Uzebba clay exhibiting the least. This was corroborated by the compressive strength tests, where the mortar samples with Ikpeshi calcined clay at 800°C displayed the highest strength development, indicating its superior pozzolanic potential.
- The strength development of the ternary blends was found to be more pronounced between 7 and 28 days, suggesting that the pozzolanic reaction contributes significantly to the long-term strength of the blends. However, the initial strength at 3 days was lower than that of the reference Portland cement, indicating a delayed pozzolanic reaction.
- The XRD analysis of the blended pastes revealed typical hydration phases like portlandite, C-S-H phase, Strätlingite, and ettringite. The reduction in portlandite content in the LC^3 blends compared to OPC indicated the absorption by the alumina phase in the pozzolan, contributing to the formation of other hydrated phases.

This research underscores the potential of locally sourced calcined clays in sustainable cement production, particularly in regions with abundant clay deposits like Nigeria, offering a viable solution to meet the increasing demand for concrete while reducing its environmental footprint.

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Samuel Adesina Adegbemileke: Investigation, Formal analysis, Writing – original draft. **Sylvester Obinna Osuji**: Supervision, Investigation. **Okiemute Roland Ogirigbo**: Supervision, Investigation, Writing – review & editing.

Conflicts of Interest

The authors declare that they have no conflicts of interest to report regarding the present study.

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