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Investigating durability potentials of selected kaolin clays in Edo state, south–south region of Nigeria

Paul Olaoluwa Ologunye[1]

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Abstract

The production of cementious material as a result of inorganic binders (geopolymer) being produced from aluminosilicate involving synthesized reaction with strong alkali solutions such as sodium silicates admixture by a poly-condensation reaction (geopolymerisation) between alumina and silica materials had greatly contributed to its use as alternative material and reduction in overdependence of Portland cement in Nigeria. The study aimed at the importance of reducing pressure on mining of non-renewable clay by concentrating on the qualities and grades of geopolymer produced using kaolin clays from Afor-okpella, Aforwa, Ossiomo and Ugbine kaolin clays in Edo state after subjecting each of them to optimal calcination process parameter (temperature): Afor-okpella: 600 °C,700 °C,800 °C,Aforwa: 600 °C,700 °C,800 °C, Ossiomo: 600 °C, 700 °C, 800 °C and Ugbine:600 °C, 700 °C,800 °C for which nearly complete dehydroxylation of the material and the durability properties the local material (kaolin clays) from Edo State geopolymer concrete will exhibit than normal concrete. By grounding Edo kaolin clays used, sieved to 212 µm and calcined at a temperature of 600 °C, 700 °C and 800 °C for six (6) hours. The geopolymers were synthesized using sodium silicate was ($Na_2SiO_{3)}$ as the activating solution. The setting time, compressive strength (for 7 and 28 days), bulk density, water absorption capacity and apparent porosity test at the 28 day of curing was determined. The results for compressive strength of synthesized geopolymers for 7 days of curing were between 10.0N/mm^2 to 19.0 N/mm^2 and 13.8 N/mm^2 to 25.6 N/mm^2 for 28 days of curing high enough to be a useful Portland cement alternative. Meanwhile, the results of water absorption capacity was as low as 10.0% for 28 days of curing.Comparing the values with ASTM standards C6918-12, C216, C902 and C90 confirmed their suitability and durability for use as geopolymer materials and applicability to making geopolymer bricks and load bearing concrete masonry units.

Keywords Aluminosilicate · Treatments · Compressive strength · Geopolymer durability

1 Introduction

The existence of geopolymer cement based on the curing properties more rapidly than portland cements in nature cannot be ignored. Geopolymer hardens at room temperature as a result of inorganic binding are more environmentally friendly as alternative to conventional Portland cements.

Activators (used in the production of geopolymer cement) are halide salts and alkali activators mainly chlorides, fluorides and salicates, which reactions with metallic components form metal halides and alkalides involving vapour pressure. Amongst the major activators, investigation shows that alkali activators like halide salts activators exhibits relative high CO_2 production because of the processes undergone by most oxides result in carbonates calcination. The

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✉ Paul Olaoluwa Ologunye, paulologunye@gmail.com | [1]Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

traces of CO_2 in the alkali activators concrete partly depend on the dosage concentration of the alkali activators. Nature of the hydrates formed is predominantly influenced by the activator; take for instance, sodium carbonate influences the production of brucite. Geopolymer cement is differentiated from geopolymer concrete by the fact that cement is a binder, unlike concrete which is composite materials formed by admixture and hardening of cement with water. Duxson et al., [1] simplified geopolymerisation mechanisms for key process occurring in the transformation of solid aluminosilicate source into a synthetic alkali aluminosilicates. The water content, curing as well as calcining conditions for kaolinite clays, effects on the final properties of a geopolymer and the influence of mild curing effect that seemed to improve physical properties, with rapid curing that may occur at too high temperatures followed by cracking could lead to negative effect on physical properties. As such, investigation from the extensive research on kaolin based geopolymers in recent years in comparison with scanty information is available on the characteristics of Nigerian clays as precursors for geopolymer synthesis [2]. Keppert et al. [3] investigation described red ceramic powders as geopolymer precursors with the consideration of amorphous portion and CaO content while Sa Riberiro et al. [4] amazonian metakaolin reactivity for geopolymer synthesis (2019) determined the viability of using a local material for the synthesis of geopolymer using metakaolin made from clay which results showed less unreacted material whereby increasing the mixing intensity and duration, the amount of residual unreacted material was found to be substantially reduced and mechanical properties considerably improved.

Poulesquen et al. [5] described rheological behaviour of alkali-activated metakaolin during geopolymerisation; the Journal of non-crystalline solids explained how inorganic materials synthesized by activation of aluminosilicate source with alkaline solution. And the results showing the nature of silica which has little influence on the viscous and elasticity module when the geopolymer is activated by KOH compared with NAOH; as preparation and properties of Alkali Activated metakaolin-based geopolymer further described in Chen et al., [6].

Moreover, the compressive strength of a material is determined by the total amount of tensile load at which the material may be subjected to and the property for the identification of fields of application of the material; this is because of the relationship between its structural property, strength ability and performance, Angelo et al. [7] which has to do with the geopolymerization processes based on the nature of precursor material in determining the compressive strength of a geopolymer product.

2 Review of empirical literature

The process of geopolymerisation proposed by Duxson et al., was divided into three stages which are concurrently reversible by Xu and Van Deventer [8]. It includes:

a. Dissolution of aluminosilicates source material resulting in reactive precursor e.g. $Si(OH)_4$ and $Al(OH)_4$
b. Restructuring and rearrangement of aluminosilicate precursors to a more stable state and
c. Condensation of mono silicates and mono aluminates to form Si–O-Si and Si–O-Al linkage.

The rocks underlying some parts of Edo State southern part of the nation undergone extensive alterations resulting in kaolin clay deposits over years. Meanwhile, the acid-resistant property of geopolymer cement, contrary to the Portland cement, do not rely on lime, but dissolved by acidic solutions by exposing the samples in 5% of sulfuric acid and chloric acid test, the stability of geopolymer cements were relatively found with the weight loss in the range of 5–8% while that of Portland cements were weathered and destroyed as the calcium alumina cement lost weight about 30–60%.

However, [9] reviewed the degradation in the compressive strength of test specimens after acid exposure and the rate of degradation which depends on the period of exposure. Davidovits 1994 and Bakharev, 2005 [10] further investigation on development of geopolymers disabilities which depends on the amount of silica-alumina composition in the geopolymer precursor as described in Table 1.This is a very crucial factor that needs to be considered since research has shown that not all the silica and alumina in the starting materials will eventually take part in the geopolymerisation reaction. The amount of silica and alumina that eventually take part in the geopolymerisation reaction is based on concentrations of the alkali hydroxides. The higher the concentrations of the alkali hydroxide the higher the dissolutions of the silica and alumina.

Table 1 Clay compositions in percentage by weight

Oxide	Weight % in sample			
	Afor-okpella	Aforwa	Ossiomo	Ugbine
Al_2O_3	40.1	35.6	29.7	30.9
SiO_2	53.1	56.4	55.1	53.9
P_2O_5	0.26	0.23	0.23	0.31
SO_3	0.51	0.45	0.84	0.79
K_2O	–	0.55	0.29	1.18
CaO	0.07	0.05	0.10	0.15
TiO_2	1.09	1.29	1.95	1.22
V_2O_5	–	0.02	0.04	0.01
Cr_2O_5	–	–	–	0.02
MnO	–	–	0.01	0.01
CoO	–	0.03	0.05	0.08
Fe_2O_3	1.01	2.37	7.00	6.22
NiO	0.07	0.05	0.08	0.11
CuO	0.04	0.02	0.06	0.06
ZnO	0.10	0.06	0.12	0.14
PbO_3	0.04	0.03	0.03	0.01
WO_3	–	0.01	0.01	0.07
Au_2O	–	0.07	–	0.04
Ag_2O	–	–	0.01	–
Rb_2O	–	–	–	0.01
Nb_2O_5	0.04	0.04	0.06	0.05
MoO_3	0.15	0.21	0.18	0.27
SnO_2	1.81	1.33	2.18	2.29
Sb_2O_3	1.62	1.11	1.94	2.15

The exploitation of non-clay minerals limit the applications of kaolinitic clays industrially; for the fact that high grade kaolinitic clays suitable for good performance calcination is found in such. This is well documented in Alujas and Fernando [11].

The secondary minerals of kaolin clays include quartz, dickite, halloysite and nacrite with different chemical reactions behavior; dehydrated halloysite, dickite, and nacrite have similar chemical composition like kaolinite but structurally characterized; kaolinite has a sheet structure as halloysite has a tubular structure; kaolinite has two out of the three hydroxyl groups contributing to the bond. Further studies have shown that various hydroxyl groups resulting in varying dehydroxylation behavior, which may impact the reactivity of kaolin clays with conclusion that the secondary minerals present in kaolin has the tendency to affect reaction processes and resulting properties of geopolymer. Investigation to include how secondary minerals content in kaolin affects the geopolymers due to various types, quantities and composition of mineral constituents in kaolin as this is important for the possible application of geopolymers in future which involves huge amount of kaolin from multiple types of clay deposits. Potential characteristics of kaolin-based geopolymers includes high bonding strength, low permeability and excellent thermal stability [12]. Moreover, there is tendency for the formation of thick gel that is instantaneously upon mixing source material and alkaline activator solutions [13].

In a model aluminosilicate mineral metakaolin has been used to study geopolymerisation potentials. This is produced by the dehydroxylation of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) when heating the kaolinite to 500–900 °C. Kaolin and metakaolin have been used relatively in various studies that had to do with determination of geopolymerisation characteristics of clay minerals. They have been utilized as a secondary source of soluble aluminosilicates for the synthesis of geopolymer. Only kaolin or metakaolin is used without any other aluminosilicate material, a weak structure is formed; and there is an increased effectiveness that is accomplished when two aluminosilicate materials are combined; Kim and Lee [14] by comparing the characteristics of metakaolin-based geopolymer and fast setting research determined the flexural strength of geopolymer.

Constantly, kaolinitic clay is kaolinite with the chemical formula ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Kaolinites are expected to lose most of their adsorbed water (100–200 °C) and become calcined by losing water through dehydroxilisation (500–800 °C). Kaolinite dehydroxilisation to metakaolin is an endothermic process that require large amount of energy to remove the chemically bonded hydroxyl ions; breaks down the crystal structure producing a transition phase (silica and amorphous alumina in reactive form) with high surface area.

The strength of geopolymers will depend on the nature of source materials, with geopolymers synthesized from calcined source materials, take for instance, fly ash, slag, and metakaolinite capable of higher compressive strength than those formed from non-calcined materials. The clay composition variables of the heat activation process complicate a general statement about the suitability of clay resources for the manufacture of geopolymers as defined in previous studies. However, there is no literature which discusses natural clay calcination on the properties of the post calcined geopolymers results.

Decision making as regards to the activator to be used; properties of importance such as durability (acid resistance, carbonation and silica-alkali reactions), fire resistance and dry shrinkage etc. [15]; Duxson et al. [1]; Abdullah et al. [16] need to be considered besides physical and mechanical strength.

Comparing the mechanical and microstructural properties of alkali-activated slag and slag + fly ash mortars exposed to high temperature investigated [17] with the investigation involving the use of stone—cutting wastes in geopolymer mortars that resulted into increased mechanical strength based on the XRD analyses performed on the microstructures of geopolymer mortars [18]. Thus, in some cases, the mechanical strength of geoplolymers is improved mainly by temperature and curing time. Also, it will improve the durability and limits efflorescence. Increase in temperature ranging from 550 °C to 800 °C transforms kaolinitic clay to an amorphous phase; meanwhile, initial curing will accelerate reaction rate of materials; as such, higher temperatures in Portland cement production may be beneficial as its adverse effect is on the mechanical strength development in geopolymer cements; the hydration products formed are generally amorphous while the elevated temperatures may lead to the formation of crystalline products occasionally [19].

The Curing temperature within 60–90 °C and curing time of 24 h -72 h seems to be optimal [20] while mild curing temperature improves physical properties as the curing under higher humidity will have adverse effects. Likewise, curing at higher temperatures will result in cracking with negative effect on physical properties of geopolymer. It is on this note that production of geopolymer products for specific applications requires careful consideration of process conditions such as curing temperature and humidity, in addition to the initial admixture design.

Factors such as nature of the precursor material, curing conditions, type of activators, etc. determine the mechanical properties of geopolymers. The behavior is of these properties are needed for the assessment and engineering of materials suitable for a specific application. Geopolymer is a cementitious material that needs considerable compressive strength as important factor for determining its mechanical properties. However, the compressive strength of geopolymers varies according to their raw materials and processing methods. A geopolymer with high compressive strength passed through formation high ratio of gel phases to non-polymeric phases. These factors relate directly to the type and molar ratios of oxides in the Al-Si source, type and pH of alkali solution and solubility of raw materials in the activators solution [21–24].

Moreover, the importance of the dissolutions of Al-Si species in alkali solution and polymerization reaction is for real with the characteristics of the alkali solution that directly inhibits the microstructural rearrangement of the calcined clay and the resultant mechanical properties of the geopolymer produced. There will be increase in flexural strength, compressive strength and apparent density of geopolymers as the concentration of NaOH solution increases.

3 Materials and methodology

3.1 Materials: materials to be used for the study are discussed as follows:

Sample A	Afor-Okpella kaolin clay
Sample B	Aforwa kaolin clay
Sample C	Ossiomo kaolin clay
Sample D	Ugbine kaolin clay

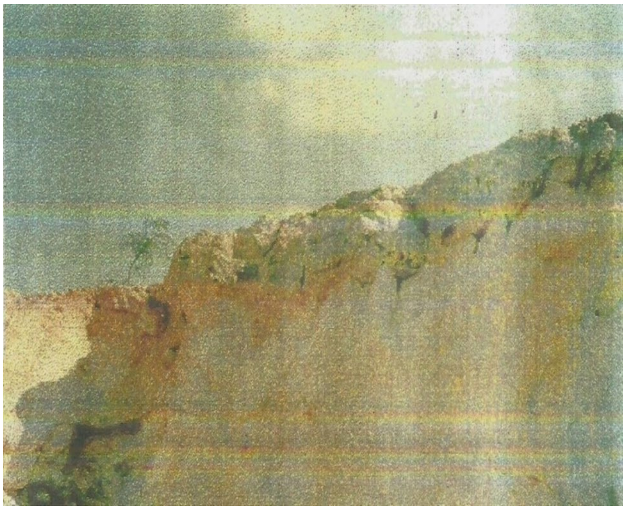

Fig. 1 Afor-okpella clay deposit

Fig. 2 Aforwa clay deposit

3.1.1 Kaolin clay

Grab Sampling of the samples are obtained from four(4) deposits located in Edo State, South-South region, Nigeria. The deposits include:

Afor-okpella clay deposit: This is located at Afor-okpella, a village in Okpella, Etsako East L.G.A., near Auchi, in the Northern part of Edo State. The coordinates of this deposit are 7°18′55.7″N 6°22′09.6″E and it is a hydrothermal clay formation.

Aforwa clay deposit: This is located at Aforwa near Jattu community, in Etsako West L.G.A. The coordinates are 7°06′16.0″N 6°18′39.0″E and it is a sedimentary clay formation.

Ossiomo kaolin clay deposit: This is located at the bank of the Ossiomo river near Abudu town, Orhiomwon Local Government Area. The coordinates are 6°17′09.8″N 6°01′55.1″E and it is a sedimentary clay formation like Aforwa.

Ugbine clay deposit: This is located at Ugbine, a small town in Ovia North-East Local Government Area. Latitudinal and longitudinal coordinates are 6°13′19.3″N 5°26′00.9″E and it is a sedimentary clay formation like Aforwa and Ossiomo.

The pictures of the deposits are shown in Figs. 1, 2, 3, 4. The clay samples were collected in clean-dry sacks. They were of varying colours: whitish, pinkish brown, light brown and grey for Afor-okpella, Aforwa, Ossiomo and Ugbine collected clays respectively.

Fig. 3 Ossiomo clay deposit

Fig. 4 Ugbine clay deposit

The clay samples collected were sun-dried to reduce moisture content and cohesiveness; the dried samples were then crushed into smaller bits using a mortar and pestle, ground to fine grained particles using a rolling rod and sieved using a < 2 mm sized sieve.

3.1.2 Mould

The mould used for this research was built to test the mechanical properties of the geopolymer formed which was synthesized before its final use for the production of paving tiles a wooden mould was built; constructed to have 20 holes each 40 mm × 40 mm × 40 mm in dimension with a carpet underneath to make the geopolymer formed to be smooth.

3.1.3 Alkaline activator

The nature of the alkaline is an important factor in the strength of the geopolymer. Thus, Sodium silicate hydrate which has proved to be the most effective alkaline activator was used. Sodium silicate acts as alkali activator, binder, plasticizer or dispersant while sodium hydroxide helps the dissolution of aluminosilicates sources. Sodium hydroxide in pellet form purchased from a local manufacturer was used for the purpose of this research. The sodium silicate used was commercially purchased from Kaob chemicals, Agbowo Ibadan. The chemical composition of the sodium silicate was 30.01% SiO_2, 9.4% of Na_2O and 60.5% of H_2O and the density of SiO_2/Na_2O at 20^0c is 3.2. 8 M sodium hydroxide solution was prepared by dissolving 320 g of sodium hydroxide pellets purchased with distilled water and made up to mark in a 1L standard flask. This generated a lot of heat as the dissolution of sodium hydroxide in water is exothermic. The solution which was allowed to attain room temperature. Then, the total weight of the 1L sodium hydroxide solution was taken using an analytical balance and the same weight of sodium silicate solution was added in a ratio of 1:1. The alkaline activator used was prepared 24 h before use.

3.2 Thermal activation

Kaolin clay samples were calcined in a muffle furnace (Carbolite AAF, 1100) for 6 h at suitable temperatures (determined from their DTA thermograms), converting the kaolin samples to metakaolin as profiled below. The four clay samples: Afor-okpella (A), Aforwa (B), Ossiomo (C) and Ugbine (D) were calcined at 600 °C, 700 °C and 800 °C each. The samples calcination colour change are shown in Fig. 5 after subjecting each sample to heat (@ 6 h), the samples were left to cool to avoid crystallization of the amorphous metakaolin. The Key Profile in Fig. 5 showed that the colour of uncalcined sample A (Afor-okpella), B(Aforwa), C(Ossiomo) and D(Ugbine) from left to right in plastic container changed after calcination as shown in samples A, B, C and D from left to right in aluminum steel plate respectively.

The indication is that uncalcined kaolin clay samples(A–D) subjected to temperatures (600°, 700 °C, 800 °C) for which nearly complete dehydroxylation of the material contents will bring about changes in colour and durability properties of each sample. Meanwhile, for each degree of temperature the uncalcined kaolin clay samples are subjected to; the colour change from whitish, pinkish brown, light brown and grey for Afor-okpella (A), Aforwa (B), Ossiomo (C) and Ugbine (D) collected clays respectively to whitish, light brown, light pink and peach respectively after calcination.As such, only sample A(Afor-okpella kaolin clay) colour remained unchanged after calcination.

3.3 Synthesis of geopolymer

The calcined kaolin clay sample which had been sieved to recommended mesh size (212 µm) was used for the synthesis. The solid material was homogenized before adding the alkaline activator gradually and then mixed for 5 min using a mixer. The mixing continued until a thioxtropic paste was obtained. The paste was then cast into the mould and vibrated thoroughly to remove any entrapped air. The mould was wrapped with nylon and cured at room temperature for three days. The samples were de-moulded after three days and kept in a Ziploc bag for curing and then for 7 and 28 days compressive strength. For the synthesis of the geopolymer brick, the mix ratio that gave the highest compressive strength after 28 days compressive strength was used for the production of geopolymer brick.

Fig. 5 Uncalcined and Calcined Kaolin clay samples A, B, C and D

3.3.1 Setting time

A needle was used to determine the setting time after the synthesis of the geopolymer, whereby the needle was made to penetrate the paste in the mould. Initially the needle would penetrate the whole mould but the time at which the needle could not go in totally was noted as the initial setting time and the time at which the needle could not penetrate the paste was noted as the final setting time.

3.4 Characterization of source materials

3.4.1 X-Ray fluorescence determination

The test was performed on the calcined clay samples to establish the chemical constituent of the metakaolin precursor. This was carried out at the Centre for Nanotechnology and Advanced Materials, National Agency for Science and Engineering Infrastructure, Akure, Ondo State, Nigeria. The samples were further grounded by using agate mortar and pestle, sieved through a 75 µm mesh sized sieve and mixed with small amounts of distilled water using a clean spatula. Samples were then pelletized using a cylindrical mould and dried in open air for 10 h to ensure loss of all water content.

3.5 Mechanical test and characterization of geopolymer

3.5.1 Compressive strength determination

The compressive strength of the synthesized geopolymers was obtained at 7 and 28 days for each ratio using an automatic compression test machine (ADR Touch 2000 Standard Compressive Machine). Three samples were tested for each measurement and the mean value for the two closest were determined. This compressive strength determination was done using a compression test machine (ELE International, ADR Touch 2000 series).

$$\text{Compressive strength}\left(\text{N/mm}^2\right) = \frac{\text{Load (N)}}{\text{Area}\left(\text{mm}^2\right)}$$

Upon failure, the failure load was recorded in Kilonewton (KN). All values presented are the average of the strength result of two samples crushed, for 7 and 28 days of curing.

3.5.2 Dry bulk density and Water absorption of the geopolymer determination

The ASTM C642 (13) Standard Test for Density, Absorption and Voids in Hardened Concrete was used for the density and water absorption test. The method measures the water absorption rate and the maximum water absorption capacity. The samples were washed with distilled water and then dried in the oven at 105 °C for 24 1 h. The samples were weighed until the mass of the samples were constant. The samples were then placed in a container and covered with water until they are totally immersed with about 2 cm of water above them. Samples were taken out at interval, blot with damped cloth to remove surface water and the mass taken. The samples were then re-immersed in water and weighed at interval until a constant weight was obtained. The samples were taken out at this point and dried in the oven at 105 °C until they reached constant weight. The quantity of water absorbed with respect to the mass of the dry sample is expressed as:

$$\text{Mi}\,\% = 100 \times (\text{Mi} \cdot \text{Md})/\text{Md}$$

where Mi, weight of the wet sample at time ti; **Md**, weight of the dry sample; The water Absorption Capacity (WAC) is expressed as WAC = 100 × (Mmax·Md)/Md; Where Mmax, mass of the sample at maximum water absorption; Md, mass of the sample after re-drying at the end of the test; Bulk density is also expressed as; $p = M/V$; Where p is the density in g/cm^3 or kg/m^3; where m is the mass in Kg; V is the volume in cm^3 or m^3.

3.5.3 Dry bulk density and apparent porosity property of geopolymer determination

High bulk density is expected to correspond to low apparent porosity in relation to soil natural formation process.Typically, bulk density increases as the ratio of solids in a soil increases, that is, bulk density increases as the pore space tends to decrease.

The apparent porosity described the relationship between the volumes of the mass absorbed to the volume of the water absorbed which could be computed by dividing the weight of dry piece by the weight of the soaked piece and subtract the obtained value from the weight of the soaked piece. Again subtract the weight of the piece soaked and immersed from the resultant value. Multiply with 100 to get the result in percentage.

$$E = \left[(S - W)/(S - I)\right] \times 100$$

where, S, weight of piece soaked; W, weight of dry piece; I, weight of the piece soaked and immersed; E, apparent porosity; The molar ratio of the component samples was optimized to reach this favourable property together with a cost-cutting reduction of heat geopolymers. Bulk density is also expressed as; $p = M/V$; Where p is the density in g/cm^3 or kg/m^3.

4 Results and discussion

4.1 Thermal effects in calcined clay samples

The results showed that all four samples undergone calcination after which the kaolin clay materials felt finer and flaky to touch; the property which probably was as a result of changes in the clays morphological structure due to bond breakage during dehydration and dehydroxylation. Moreover, the observable colour changes from pinkish brown, light brown, greyish to light brown, light pink and peach in Aforwa, Ossiomo and Ugbine kaolin clays respectively, while Afor-okpella clay remained relatively unchanged. The colour change which may be attributed to changes in the oxidation state of chemical elements such as Fe, Ti and Mn, contained in inorganic impurities commonly present in clay minerals [25]. The colour of kaolinite materials is important to its market value, as non-conventional Portland cement colour (e.g. reddish and pinkish) are incorrectly misjudged as low quality materials [26].

4.2 Workability and setting time

Fernandez et al. Reviewed the origin of the pozzolanic activity of clay minerals described a comparison between kaolinite, illite and montmorillonite in relation to *Cement and Concrete research* [27]. *Meanwhile, the* suitable mix ratio (L/S) by weight (Table 1) of the geopolymer paste from mixing individual samples with activator and their setting time was determined in the course of this work. The parameters: mix ratio and setting time are both important in clay workability, as a large mix ratio is undesired from the economic point of view, while neither too short nor too long setting time is desired. Lowering the mix ratio improves the quality of geopolymers [27]. Thus, Afor-okpella calcined clay had the best performance in terms of workability due to its low activating solvent requirement and fast setting time (40 min @ 800 °C calcined) and highest compressive strength of 25.6 MPa compared to other calcined samples used to prepare the geopolymer paste. Moreover, the high setting time of the Aforwa clay calcined at 600 °C, compared to same clay treated at higher temperatures could be attributed to incomplete dehydroxylation, as some amount of –OH might still be trapped in the solid matrix. Thus, it displays lower reactivity.

4.3 Bulk density

Bulk density that determines the percentage of voids present in the aggregate material may affect the grading of the aggregates which is very important in high strength concrete. It is found to be the weight of soil for a given volume as used in the measure of its compaction. Particles of the same size can be packed to a limited extent but when the smaller particles are added, the voids get filled with them and the bulk density tends to increase. Coarse aggregate particle on the other hand has higher bulk density meaning that few are voids and to be filled by the fine aggregate and get cemented. Bulk density is noted to be highly depended upon the degree of packing; denser the sample; better the compressive

Table 2 Dry bulk density of geopolymers

Geopolymer bricks of calcined sample@6Hrs	Dry bulk density (g/cm^3)
Afor-okpella 600 °C	1.9
Afor-okpella 700 °C	1.7
Afor-okpella 800 °C	1.7
Aforwa 600 °C	1.8
Aforwa 700 °C	1.7
Aforwa 800 °C	1.6
Ossiomo 600 °C	2.0
Ossiomo 700 °C	1.8
Ossiomo 800 °C	1.4
Ugbine 600 °C	1.7
Ugbine 700 °C	1.6
Ugbine 800 °C	1.5

strength. In the course of the investigation; the results of the bulk density at 28 day geopolymer is shown in Table 2. A good value of dry density for saleable bricks should be between 1.6–2.4 g cm^{-3} [28]. All of the geopolymers produced are found within this range with the exception of Ossiomo and Ugbine calcined @ 800 °C with 1.4 and 1.5 respectively. The result of such showed that the degree of packing particles in such samples decreases as their calcined temperatures rises above 700 °C.

4.4 Compressive strength

Jamkar et al. [29], described the effect of fly ash fineness on workability and compressive strength of geopolymer concrete with emphasis on Indian Concrete. The compressive strength results of the geopolymers are shown in Table 3. It was observed that there was an increase in the compressive strength as curing time increases; compressive strength increases as the Si/Al ratio increases to about 4.0 but further increase in the Si/Al ratio more than 4.0 is known to cause a reduction in compressive strength [30]. Addition of superplatizer. The silicate content controls the dissolution and polymerization of Si and Al in aluminosilicate gel. It was found that at high silica content, the polymerization of aluminosilicate gel is not favored; instead, the dissolved precursor tends to form zeolites which are weaker in compressive strength. At 28th day compressive strength for Afor-okpella clay, it has the highest compressive strength of 25.6 MPa which showed that the water to solid ratio and the liquid to solid ratio has an effect on the compressive strength also. Here, the water refers to the total amount of water used during the preparation of the sodium hydroxide, water contained in the sodium silicate

Table 3 Compressive strength of geopolymers as calculated in mega pascals (MPa)

Sample (6 hours calcined) and synthesized	Day 7 MPa ± SD	Day 28 MPa ± SD
AFOR-OKPELLA 600 °C	18.9 ± 1.63	21.8 ± 1.49
AFOR-OKPELLA700 °C	19.0 ± 1.91	23.0 ± 5.45
AFOR-OKPELLA800 °C	15.3 ± 2.62	25.6 ± 5.22
AFORWA 600 °C	14.3. ± 1.49	17.1 ± 2.05
AFORWA 700 °C	13.4 ± 1.70	19.0 ± 2.62
AFORWA 800 °C	14.6 ± 1.56	18.6 ± 4.03
OSSIOMO 600 °C	13.1 ± 2.19	15.4 ± 1.70
OSSIOMO 700 °C	15.9 ± 0.85	16.4 ± 5.59
OSSIOMO 800 °C	18.6 ± 2.05	18.7 ± 1.20
UGBINE 600 °C	13.3 ± 2.05	16.5 ± 3.82
UGBINE700 °C	13.6 ± 1.84	14.7 ± 0.36
UGBINE 800 °C	10.0. ± 1.63	13.8 ± 1.27

and water that was added during the mixing of the paste. Water plays an important role as it aids the dissolution and polymerization of the aluminosilicate precursor. Water to solid ratio of 0.25 to 0.35 is most suitable for geopolymer binder as higher water to solid ratio gives segregated mix while lower ratio gives viscous and dry mix while lower water content greatly raises the viscosity of the liquid component reducing dispersal and ease of mixing. Likewise, activator to solid ratio also plays a very significant role on the compressive strength as fresh geopolymer paste with a high S/L ratio had a low viscosity while geopolymer paste with a low S/L ratio resulted in high viscosity. Thus, geopolymer with a low S/L ratio could speed up the rate of dissolution.

Although the water to solid ratio and solid to liquid ratio were not studied in this research, but the solid to liquid ratio was considered during the preparation of the geopolymer paste as the solid to liquid ratio can be the reason for the high compressive strength. A lower ratio contributes to low strength as a result of excessive OH^- left in the system (from the alkaline activator) which weakens the geopolymer structure. The Na_2SiO_3/NaOH ratio is also very important in the geopolymerisation reaction because at a higher ratio of 3.0, the workability of the paste is reduced which will lead to a lower strength.

A lower ratio of 1.0 and 1.2 is suitable for calcined clay based geopolymer. The use of Na_2SiO_3 helps to improve the geopolymerisation process by accelerating the dissolution of source material; by increasing the Na_2SiO_3/NaOH ratio, the geopolymerisation rate increased; but further increase tends to reduce the strength which may be due to excessive alkali content which retards the geopolymerisation process. Table 3 showed the compressive strength of synthesized geopolymer. Compressive strength which is the capacity of a material to withstand load is one of the most important and reliable parameters to measure the pozzolanic activity of a material. The mean ± SD of two geopolymers with closest results was recorded. However, few samples still had their coefficient of variation above 10%.

The results demonstrate that the strength of all the geopolymers increased with curing time, suggesting continuous chemical reactions by the geopolymers, giving rise to strength gain as the best performing clay in terms of compressive strength was determined, that is Afor-okpella clay as shown in Table 3 and further depicted in Fig. 6 for further illustration. This had previously shown excellent potential as it had the highest degree of dehydroxylation as shown by intense-broad peak; it had a shorter setting time and highest aluminosilicate composition as it is adjudged from the clay compositions in percentage by weight attributed to Table 1. Also, clays with alumina-silica ratio closer to 1 and lower ferric oxide content are expected to have good strength. Thus, the observed higher compressive strength at 28th day in Afor-okpella and Aforwa, compared to Ossiomo/Ugbine clay showed a stable increase from 600 °C to 800 °C (Afor-okpella) while thermal treatment at higher temperatures in Aforwa clay fluctuates between 700 °C and 800 °C (peak maxima and base end point) resulted in higher compressive strength than the temperature at which dehydroxylation began. At day 7, the compressive strength of the geopoloymer formed from kaolin clay calcined at 700 °C was higher than that calcined at 600 °C (for Afor-okpella/Ugbine) showing their stability at such temperature unlike Aforwa/Ossiomo which are more stable @ 800 °C. At day 28, the former and latter gained more strength.

The Fig. 6 showed the graphical representation of compressive strength results in Table 3 of samples A, B, C and D calcinated at three different temperatures: A1 = Afor-Okpella @ 600 °C, A2 = Afor-Okpella@ 700 °C, A3 = Afor-Okpella @

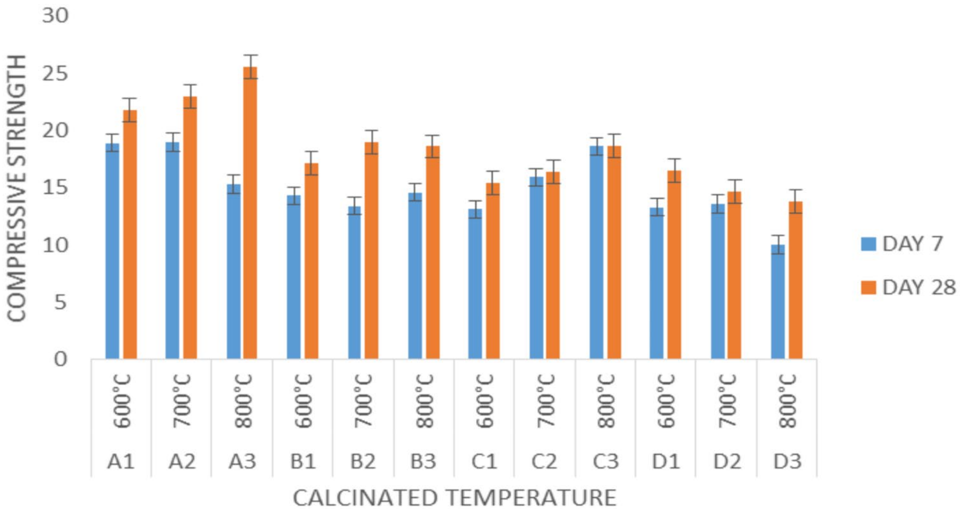

Fig. 6 Graph showing the results of temperature calcinations of selected kaolin clays @ (6) hours for 7 and 28 days

800 °C, B1 = Aforw @ 600 °C, B2 = Aforwa @ 700 °C, B3 = Aforwa @ 800 °C, C1 = Ossiomo @ 600 °C, C2 = Ossiomo @ 700 °C, C3 = Ossiomo @ 800 °C, D1 = Ugbine @ 600 °C, D2 = Ugbine @ 700 °C, D3 = Ugbine @ 800 °C for 7 days and 28 days.

The results for compressive strength of synthesized geopolymers for 7 days of curing were between 10.0 MPa to 19.0 MPa and 13.8 MPa to 25.6 MPa for 28 days of curing high enough to be a useful Portland cement alternative as the best performing clay in terms of compressive strength was determined, that is Afor-okpella clay with highest compressive strength (25.6 MPa) at 28 days being Calcined @ 800 °C (A3) as shown in Fig. 6.

4.5 Water absorption test

The water absorption capacities of the geopolymer as shown in Table 4 determines the durability of bricks as the absorption of water deteriorates concrete. The lower the water absorption the higher the resistance of the brick to water infiltration and to environmental damage [31]. The results of the water absorption for the entire geopolymer ratio are presented in Table 4, geopolymer sample with 100% kaolin clay shows highest water absorption while geopolymer with highest percentage of sand had the least in which the decrease could be attributed to the high silica content and sand. One of the main causes of deterioration is the interaction between water and the porous structure. Concrete can be viewed as a porous composite material due to the presence of pores and unfilled voids caused by improper grading of aggregates, inadequate cement paste, incomplete compaction, entraining of air if used and inadequate degree of hydration of cement. Sand does not involve in the geopolymerisation reaction but act as inactive filler filling the void in the geopolymer. This, by comparing the results with the American Society for Testing and Materials (ASTM C642 standard) [32] in Table 5, the different geopolymer ratio has an excellent water absorption capacity.

The summary of durability potentials is described and explained through the model—ASTM WAC American Society for Testing and Materials Water Absorption Capacity [33].

4.6 Dry bulk density and apparent porosity

The rate of increase in bulk density corresponds to low porosity showing that natural soil-forming processes that increase aggregation reduce bulk density. Bulk density will increase as the ratio of solids in a soil increases. Likewise, bulk density increases as the pore space decreases. Meanwhile, apparent porosity described the relationship between the volumes of the mass absorbed to the volume of the water absorbed. This is computed by dividing the weight of dry piece by the weight of the soaked piece and subtract the obtained value from the weight of the soaked piece. Again subtract the weight of the piece soaked and immersed from the resultant value. Multiply with 100 to get the result in percentage.

The results from Table 6 showed that stability occurred only in Sample C (Ossiomo kaolin clay) while comparing relationship between the bulk density and apparent porosity of the four samples; whereas fluctuations occurred in other three samples which include sample A(Afor-okpella kaolin clay), sample B (Aforwa kaolin clay) and sample D (Ugbine kaolin clay).

Table 4 : Water absorption of synthesized geopolymer

Synthesized geopolymer	Water absorption capacity (WAC) % ± SD Day 28
AFOR-OKPELLA 600 °C	16.4 ± 3.4
AFOR-OKPELLA700 °C	16.3 ± 0.29
AFOR-OKPELLA 800 °C	10.0 ± 1.71
AFORWA 600 °C	18.8 ± 1.40
AFORWA 700 °C	18.3 ± 2.62
AFORWA 800 °C	17.4 4 ± 6.05
OSSIOMO 600 °C	20.8 ± 0.11
OSSIOMO 700 °C	20.9 ± 3.11
OSSIOMO 800 °C	20.0 ± 1.53
UGBINE 600 °C	20.7 ± 3.43
UGBINE 700 °C	19.9 ± 6.65
UGBINE 800 °C	18.7 ± 4.10

Table 5 Durability classification based on comparison with ASTM C642

Synthesized geopolymer	Water absorption capacity	ASTM WAC (% by weight)	ASTM C642 classification	Geopolymer WAC with ASTM WAC
AFOR-OKPELLA 600 °C	3.4	< 5	Excellent	Excellent
AFOR-OKPELLA 700 °C	0.29	5–6	Good	Excellent
AFOR-OKPELLA 800 °C	1.71	6–7	Normal	Excellent
AFORWA 600 °C	1.40	7–8	Marginal	Excellent
AFORWA 700 °C	2.62	> 8	Bad	Excellent
AFORWA 800 °C	6.05			Normal
OSSIOMO 600 °C	0.11			Excellent
OSSIOMO 700 °C	3.11			Excellent
OSSIOMO 800 °C	1.53			Excellent
UGBINE 600 °C	3.43			Excellent
UGBINE 700 °C	6.65			Normal
UGBINE 800 °C	4.10			Excellent

Table 6 Comparison of dry bulk density with apparent porosity

Sample (6 hours calcined) and synthesized	Dry bulk density (g/cm^3)	Apparent porosity (AP) %
AFOR-OKPELLA 600 °C	1.9	31.8
AFOR-OKPELLA700 °C	1.7	34.9
AFOR-OKPELLA800 °C	1.7	32.4
AFORWA 600 °C	1.8	47.5
AFORWA 700 °C	1.7	65.8
AFORWA 800 °C	1.6	16.3
OSSIOMO 600 °C	2.0	33.2
OSSIOMO 700 °C	1.8	39.8
OSSIOMO 800 °C	1.4	49.4
UGBINE 600 °C	1.7	42.7
UGBINE700 °C	1.9	41.5
UGBINE 800 °C	1.5	46.1

5 Conclusion

The main findings from the overall objective of this project led to the production of geopolymer paste which can be of great strength to be used for the production of geopolymer bricks. With a strength of 25.6 MPa, a geopolymer bricks that make for more eco-friendly binders and can be locally applied in construction activities, as this is determined to meet certain ASTM requirements. However, other mixing ratio that was adopted could also be used for other engineering and construction purposes e.g. building bricks, hollow bricks, ceramic faced facing brick, etc. as presented in Table 5, all the different geopolymer mix had a water absorption capacity below 3.5% which based on the ASTM C642 standard can be classified as having an excellent water absorption capacity.

Flowing from the above findings, the actual amount of soluble silica and alumina could not be ascertained because of the pattern of dissolution from the results. The setting time studied shows that there is an increase in the setting time as a result of the increase in the amount of silica giving rise to more of Si–O–Si bond in some samples as a result of thermal characterization of samples. Meanwhile, this is not a drawing back as it gives more time for the polycondensation reaction to occur. It is assumed that other compounds that are present in the calcined clays could be responsible for the increase in setting time.

6 Recommendations and limitations

To achieve a geopolymer of great strength, solid to liquid ratio is a very important factor to be considered. Futuristic works should focus on the different mixing ratio of calcined clays.

Studying the effect of solid to liquid ratio in relation to the different mixes will help understand the chemistry behind the process. For further use of each geopolymer mix, there is need for further studies on their durability and mechanical properties. Test like abrasion test, chloride resistance test, flexural strength, tensile strength, etc. should be carried out. This would give room for further application of each of the different mixes. There should be a focus on the funding and development of research in Nigeria by private individual, organization and the government at large. Studying the effect of solid to liquid ratio in relation to the different mixes will help understand the chemistry behind the process.

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Declarations

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