

Performance Evaluation of Groundnut Shell Ash-Modified Calcined Clay Geopolymers for Construction Applications

Olajumoke L. Oladele¹, Elijah D. Adesanya², Arantxa Arbe³, Amaia Iturrospe³, Mary B. Ogundiran^{4*}

¹ Department of Chemistry,
Adeyemi Federal University of Education, Ondo, Ondo State, NIGERIA

² Faculty of Technology, Fibre and Particle Engineering Research Unit,
University of Oulu, PO Box 4300, 90014 FINLAND

³ Centro de Física de Materiales (CSIC, UPV/EHU) and Materials Physics Center MPC,
Paseo Manuel de Lardizabal 5, E-20018 San Sebastián, SPAIN

⁴ Analytical/Environmental Chemistry Unit, Department of Chemistry,
University of Ibadan, Ibadan, NIGERIA

*Corresponding Author: mbogundiran@yahoo.com

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Abstract

The environmental impacts of Portland cement production, notably high carbon dioxide emissions and energy consumption, have accelerated the development of sustainable alternative binders for construction purposes. Geopolymers produced from aluminosilicate-rich materials present a viable low-carbon alternative. This study examined the influence of groundnut shell ash (GNA) on the performance of calcined clay (CC) geopolymer pastes and their application for building purposes. Groundnut shells sourced locally were thermally treated at 800 °C, and characterized using X-ray fluorescence (XRF), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray diffraction (XRD). Geopolymer pastes were produced by activating CC blended with 5-20 wt% GNA using sodium silicate solution only, followed by phase and properties evaluation. Based on 28-day compressive strength, the optimal CC/GNA paste was further modified with quarry dust to produce geopolymer mortars. A control geopolymer (RG) consisting of 100% CC activated with 8 M NaOH/Na₂SiO₃ was also prepared. All samples were cured at room temperature for 7 and 28 days. The results showed that the compressive strength of GNA geopolymer pastes and mortars at 28 days ranged from 23.8±0.3 to 63.5±0.1 MPa, and porosity values from 12.9 to 20.6%, outperforming the control geopolymer (18.1 ± 0.3 MPa; 49.5%). The results demonstrated that GNA enhances densification and strength development, supporting its effective use as a supplementary precursor in calcined clay geopolymers for sustainable construction applications and contributed new insights into the utilization of agricultural waste in geopolymer technology.

1. Introduction

Cement is one of the most essential materials in the construction sector; however, its production is associated with high energy consumption and significant environmental impacts. It has been reported that the cement industry account for about 7-9% of global CO₂ emissions [1,2]. More critically, cement manufacturing contributes substantially to global carbon dioxide (CO₂) emissions, primarily due to the decarbonization of limestone during clinker production. Consequently, the urgent need to reduce the environmental footprint of the construction industry has stimulated extensive research into environmentally friendly alternative binders, such as geopolymers.

Geopolymers are inorganic aluminosilicate materials formed through the reaction of solid precursors rich in reactive silica and alumina with alkaline activating solutions, followed by curing at ambient or elevated temperatures [3,4]. Common precursor materials used for geopolymer synthesis include fly ash and calcined kaolin clay (metakaolin), among others [5-8]. Structurally, geopolymers possess an amorphous to semi-crystalline three-dimensional Si-O-Al polymeric network, commonly referred to as a silicate framework, in which charge balance is maintained by alkali cations such as Na⁺, K⁺, or Li⁺ [9]. One of the notable advantages of geopolymers is their rapid early-age strength development [10], which has enabled their application in the production of sewer pipes, railway sleepers and other pre-stressed structural components [11], as well as in the immobilization of toxic heavy metals [12,13].

Compressive strength is a critical parameter for assessing the suitability of geopolymers as viable alternatives to Portland cement binders in construction applications. However, metakaolin-based geopolymers often exhibit relatively high porosity due to the large amount of water required for mixing (liquid-to-solid ratio $\approx$ 0.81), which can adversely affect their mechanical performance [14,15]. To address this limitation, various additive materials, including colemanite waste, silica fume, fly ash, slag, rice husk ash, wood ash, and other aluminosilicate sources, have been investigated to improve the microstructure and strength of metakaolin-based geopolymers. Nevertheless, the incorporation of sodium hydroxide in the activating solution has often been reported to result in reduced mechanical strength, and only limited studies have explored the use of sodium hydroxide-free systems, particularly those activated solely with sodium silicate solutions [16-20].

An earlier study reported the use of alkali-rich ash as an alternative activator in calcined clay-based geopolymers, enabling activation using only a sodium silicate solution [21]. Based on this premise, groundnut shell ash (GNA) is proposed in the present study to function simultaneously as a co-precursor and co-activator, with the potential to fill pores and enhance the mechanical strength of metakaolin-based geopolymers. Moreover, most agricultural waste remains under-utilized, and their conversion into value-added construction materials offers significant environmental and economic benefits while mitigating waste-related pollution [22].

Groundnut shells represent an abundant agricultural waste with promising potential for geopolymer production. Global groundnut production is estimated at approximately 47 million metric tons annually, with shells accounting for about 21-29% of the total weight [23]. Although groundnut shells are often used as biomass for energy generation [24], the resulting ash is typically disposed of indiscriminately, posing environmental concerns. Previous studies have demonstrated the beneficial use of groundnut shell ash in improving the properties of Portland cement-based materials. The reactive silica present in GNA has been shown to participate in pozzolanic reactions, leading to the formation of calcium silicate hydrate (C-S-H) phases. For instance, Ikumapayi et al. [25] reported that the incorporation of 8 wt.% GNA enhanced the mechanical strength of Portland cement concrete through improved C-S-H gel formation. Similarly, Buari et al. [26] observed improved durability performance when substituting 0-40 wt.% of Portland cement with GNA, with optimal strength, workability, and durability achieved at 30 wt.% replacement. Furthermore, Nemaleu et al. [27] produced lightweight geopolymers using GNA as an additive, while Bheel et al. [28] reported reduced porosity in fly ash-based geopolymers through the incorporation of metakaolin and GNA.

Despite these advancements, there remains limited information on the use of groundnut shell ash as a combined co-precursor and co-activator for reducing porosity and enhancing the compressive strength of metakaolin-based geopolymer pastes and mortars, particularly in systems activated solely with sodium silicate. Therefore, this study aims to develop calcined clay-based geopolymer pastes and mortars with reduced porosity and improved mechanical and performance-related properties by utilizing calcined kaolin clay and groundnut shell ash as precursor materials, activated exclusively with a sodium silicate solution. The chemical and structural characteristics of the source materials were examined, and the reactivity and optimal mix proportions of the clay-GNA blends were determined. Key properties, including setting time, compressive strength, efflorescence, porosity, density, and water absorption, were evaluated using standard test methods, while the structural evolution of the geopolymers was analyzed using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

2. Materials Preparation

The primary raw materials used in this study include kaolin clay, quarry dust (QD), periwinkle shells, and groundnut shells. All the materials were sourced from different locations in Nigeria. Before calcination, the raw clay was air dried, pulverized, and sieved to sizes below 212 μm , while the QD was air-dried to remove moisture and sieved to sizes below 212 μm as previously reported by Oladele et al. [21]. Kaolin clay was calcined at 700 °C for 6 h, while periwinkle shells, and the groundnut shells were calcined at 800 °C using a laboratory muffle furnace to obtain metakaolin, periwinkle shell ash (PSA) and groundnut shell ash (GNA) respectively.

2.1 Characterization of Raw Materials

Oxide composition of the materials was determined using X-Ray Fluorescence spectrophotometer/EDX (Sky Ray Instrument, EDX3600B). The oxide characteristics of the calcined clay, periwinkle shells ash and quarry dust is shown in Table 1. Thermogravimetric/differential thermal analyzer (Precisa Gravimetrics AG) was used to determine the ashing temperature of the groundnut shells. To measure the change in mass, crucible containing powdered sample of groundnut shells was heated at a rate of 10 °C/min from 23 to 1000 °C in an environment of inert nitrogen. The temperature at which the shells underwent certain mineralogy and phase changes were obtained.

Table 1 Geopolymer paste and mortars mix ratio (first stage)

	Ref (g)	GNAG 5% (g)	GNAG 10% (g)	GNAG 15% (g)	GNAG 20% (g)
GNA	0	4	8	12	16
CC	80	76	72	68	64
Activator	65	62	60	59	56

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to identify the functional groups of the ash. Absorption spectrum was collected using ATR-FTIR spectrometer (FTIR-6300/ATR-6000). Spectra were obtained in the 4000-500 cm^{-1} range at 4 cm^{-1} resolution for each sample. The mineralogy phases were determined using X-ray diffractometer (Bruker X-ray diffractometer, D8 Advance, US). This diffractometer works in parallel beam geometry with $\text{CuK}\alpha$ transition photons of wavelength $\lambda = 1.54 \text{ \AA}$. The experiments were performed in reflection mode (θ -2 θ configuration), varying the scattering angle 2 θ from 10° to 90° with steps of 0.05°. The average measuring time was 50 s/point. The XRD patterns were analysed using Diffrac.EVA V2.1 software.

2.2 Geopolymer Paste / Mortar Production

The calcined clay was activated with 8M NaOH/ Na_2SiO_3 solution to produce control geopolymer, while the CC:GNA mixes were activated with sodium silicate solution only. Geopolymer paste and mortars were produced by dry mixing the starting materials in Tables 1 and 2 in a mixer for five minutes. The liquid activator was then added and mixed for five minutes to form a thixotropic paste. The resultant paste/mortar was vibrated to release trapped air before being cast into 40 x 40 x 40 x 40 mm cubic moulds. The geopolymers were maintained at room temperature and covered in polyethylene to cure. The samples were demoulded three days and placed in Ziploc bags for 7 and 28 days in the laboratory until further testing. The groundnut shell ash-based geopolymer (GNAG) paste exhibiting the highest compressive strength (GNAG 15%) was subsequently modified with 2% periwinkle shell ash (PSA), quarry dust to produce geopolymer mortars designated as GNQG as shown in Table 2. The PSA was added to improve the setting time of the geopolymers.

Table 2 Geopolymer paste and mortars mix ratio (second stage - optimizing GNAG 15%)

	GNQG 2.5% (g)	GNQG 5% (g)
GNA	12	12
CC	64.4	62.4
PSA	1.6	1.6
QD	2	4
Activator	62	65

2.3 Characterization of Geopolymer Pastes and Mortars

Calorimetric measurement, setting time, compressive strength, density, water absorption and porosity as well as efflorescence potential of the geopolymer pastes and mortars were determined.

2.3.1 Calorimetric Measurement

TAM Air Isothermal Calorimeter (TAM Air Isothermal Calorimeter) was used to measure the geopolymer mixes reactivity. The pastes were produced, and 7 g each of the pastes was deposited in the ampoule bottle and placed in the calorimeter. The measurement was carried out at 20 °C for 14 days.

2.3.2 Setting Time

In the absence of a Vicat needle, the setting time of the geopolymer was determined using the commercial needle penetration method following the procedure reported by Ogundiran et al. [13]. Freshly prepared geopolymer paste was poured into a square mould immediately after mixing, and the time of mixing was recorded as the initial time. The sample was maintained at room temperature and covered with polyethylene film to minimize moisture loss. A commercial steel needle (approximately 1 mm diameter) was manually inserted vertically into the paste surface at 10 minutes intervals using a fresh location for each penetration. The setting time of the geopolymers was defined as the time interval between moulding and when the paste completely resisted needle penetration.

2.3.3 Compressive Strength

Using an ADR-Touch 2000 Standard Compressive test Machine with a 100 kN maximum load, the compressive strength of the geopolymers was tested at 7 and 28 days. The failure of the load (kN) applied to break a test specimen was divided by the cross-sectional area (mm²) resisting the force and reported in unit of (MPa), to obtain the compressive strength values (Eq. 1).

$$CS = \frac{L}{A} \quad (1)$$

Where; CS represents the compressive strength in (N/mm²). L is the applied load (kN), A (mm²) is the cross-sectional area of the geopolymer. The average of the compressive strength value readings from two samples was used to calculate all values.

2.3.4 Density

The density of the geopolymers was measured after 28th day using the NEN 1170 – 6 methods [14]. The geopolymers were oven-dried at 105 °C to constant mass and cooled to room temperature in a desiccator. The dimensions (length, width and height) were measured using a vernier caliper and the volume was calculated from the average dimensions. The dry mass was measured using an electronic balance with an accuracy of ±0.01g. The density was calculated as the ratio of the mass to the volume of the geopolymer and expressed in g/cm³ (Eq. 2). The reported density represents the average value obtained from three replicate geopolymers.

$$Density = \frac{Mass\ of\ sample\ (g)}{Volume\ of\ sample\ (cm^3)} \quad (2)$$

2.3.5 Water Absorption and Porosity

The water absorption and porosity of the cured geopolymers at 28 days were determined in accordance with ASTM C642. The cured geopolymers were cleaned to eliminate any loose particles from the surface and oven dried at 105 °C until constant mass was achieved. After drying, the geopolymers were allowed to cool to room temperature in a desiccator to prevent moisture uptake from the atmosphere. The oven-dry mass was then measured and recorded as W_d (g). The dried samples were completely immersed in distilled water for 48 h. After, each sample was removed from water and excess surface moisture was wiped off using a damp cloth to obtain a saturated surface-dry condition. The saturated surface-dry mass after immersion was recorded as W_w (g).

Subsequently, the samples were placed in fresh distilled water and boiled continuously for 5 h. After boiling, the samples were allowed to cool naturally while remaining immersed in the water until they reached room temperature. The samples were removed, surface dried with a damp cloth, and weighed to obtain the saturated surface-dry mass after boiling, recorded as W_s (g). Each sample was finally suspended in water using a wire without touching the container, and its apparent immersed mass was measured and recorded as W_i (g). The water absorption and porosity were calculated using the equations below (Eq.3 and Eq. 4)

$$Water\ absorption\ (\%) = \frac{(W_w - W_d)}{W_d} \times 100 \quad (3)$$

$$\text{Porosity (\%)} = \frac{(W_s - W_d)}{(W_s - W_i)} \times 100 \quad (4)$$

Where; W_d = weight of dried sample, W_w = weight of wet samples, W_i = weight of suspended sample, and W_s = weight of saturated sample. Three samples were tested for each geopolymer mix composition, and the average values of water absorption and porosity values were reported.

2.3.6 Efflorescence Potential

The efflorescence potential of the samples was assessed by measuring 1.0 g of finely ground geopolymer, 20 mL of distilled water was added to it and covered. Following a 24-hour period, the mixture was decanted and transferred to the oven for the purpose of water evaporation, resulting in the retention of solely the leached soluble salts, which were subsequently measured in terms of weight. This was done in the understanding that the movement of alkali substances is the main factor that results in the occurrence of efflorescence [29].

3. Results and Discussion

3.1 Thermogravimetric and Differential Thermal Analyses of Groundnut Shells (TGA/DTA)

The result of the TGA/DTA of powdered groundnut shells before calcination is shown in Fig. 1. The analysis showed an initial minor mass loss below 150 °C due to moisture evaporation. A major decomposition peak occurred between 200 and 400 °C, accompanied by a pronounced endothermic DTA peak, indicating the breakdown of thermally unstable components such as hemicellulose, cellulose and lignin present in the groundnut shells [30]. Beyond 400 °C, the sample exhibited gradual mass loss with no significant thermal events [31], suggesting the formation of a stable inorganic residue up to 1000 °C. The groundnut shells were calcined at 800 °C to ensure complete removal of organic constituents and to obtain a thermally stable, silica-rich ash with high pozzolanic reactivity. This temperature was selected based on the thermal analysis, which indicated that major decomposition occurred below 500 °C. Calcining at lower temperatures may leave incompletely transformed phases, while excessively high temperatures (>900 °C) can cause crystallization and reduce reactivity.

From the TGA/DTA analysis of the raw clay as reported by Oladele et al. [21], it can be inferred that the dihydroxylation of kaolinite to form metakaolinite is expected at 650 °C. However, the clay was calcined at 700 °C to ensure total dihydroxylation.

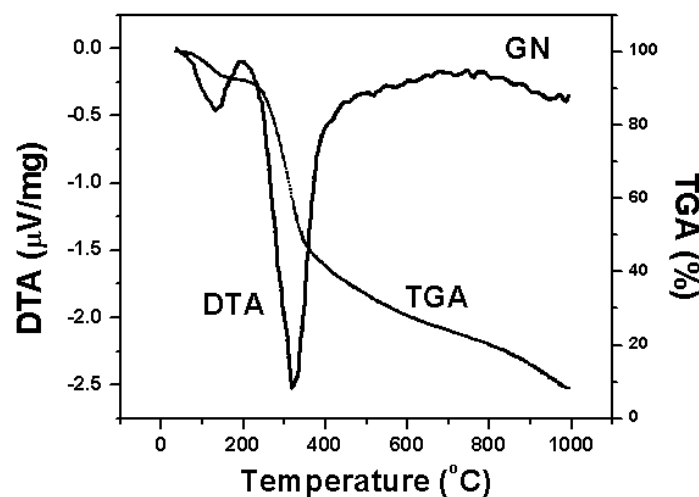


Fig. 1 TGA/DTA curves of groundnut shells

3.2 ATR-FTIR Spectrum of Groundnut Shells

In the groundnut shell ash (GNA) spectrum (Figure 2), the berlinite (AlPO_4) absorption peak was observed at 1027 cm^{-1} , and Si-O-Si asymmetric stretching vibrations of quartz appeared at 873 cm^{-1} [32], confirming that SiO_2 in the ash exists primarily as quartz. These FTIR features confirm the aluminosilicate nature of the raw materials and the presence of functional groups essential for geopolymerization, which underpin the mechanical and durability performance of the resulting geopolymers.

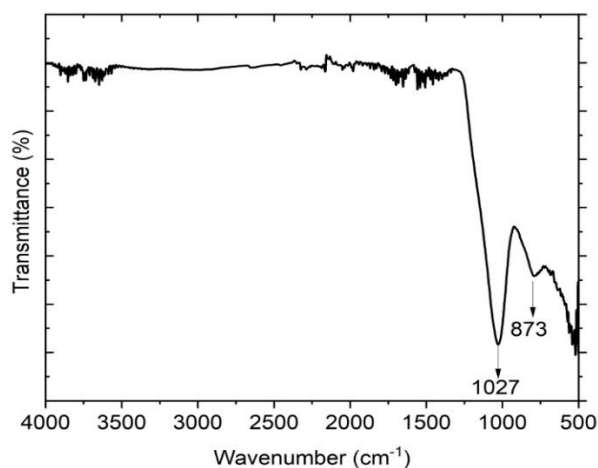


Fig. 2 FTIR spectrum of groundnut shells ash

3.3 Mineralogical Composition of Groundnut Shells

The XRD patterns of raw clay, calcined clay, periwinkle shells ash and quarry dust as reported previously by Oladele et al. [21] showed that the raw clay contained kaolinite and quartz as the main chemical phases. Periwinkle shell ash had calcite (CaCO_3), Al_2O_3 , hematite (Fe_2O_3), portlandite [$\text{Ca}(\text{OH})_2$] and albite ($\text{NaAlSi}_3\text{O}_8$) as its minerals. Quarry dust had Fe_2O_3 , SnO_2 , K_2O , and quartz [21].

The XRD pattern of groundnut shells ash is presented in (Fig. 3). The main mineral identified in the ash was quartz (SiO_2). Some small peaks that match those of hematite (Fe_2O_3) were also observed. These minerals are confirmed with the presence of their corresponding elements in the XRF data. As seen in Table 3, silicon dioxide (SiO_2) made up 59.4% of GNA as its dominant oxide, with appreciable amounts of Al_2O_3 . As revealed by the XRD results, this SiO_2 is essentially quartz, which likely served as strength enhancer in the geopolymers. The presence of the Al_2O_3 in the ash would lead to an increase in reactivity, while K_2O and CaO are alkaline in nature which enhanced the reactivity of sodium silicate solution in the preparation of geopolymer pastes and mortars.

Table 3 Oxide composition (Wt.%) of solid materials

Oxides	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Fe_2O_3
GNA	9.30	59.4	0.73	1.34	2.81	7.85	0.66	8.82
CC	41.4	46.7	0.21	0.44	0.10	0.08	1.37	2.32
PSA	0.65	1.10	0.57	1.62	-	94.7	-	0.24
QD	12.9	58.6	0.57	1.19	4.27	4.32	0.41	15.4

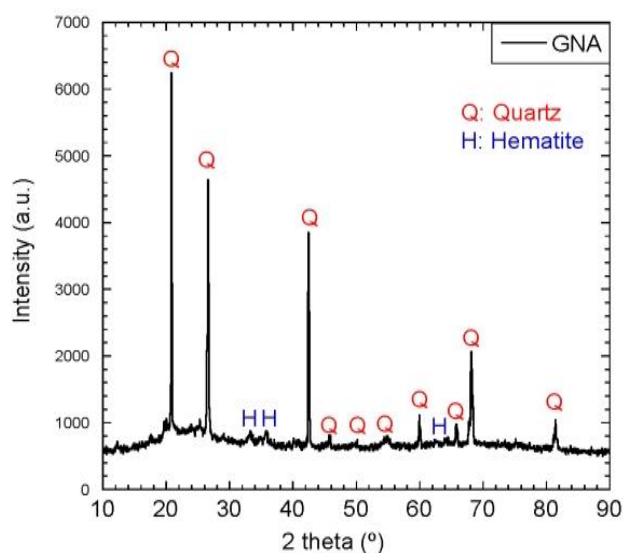


Fig. 3 XRD pattern of groundnut shells ash

3.4 Characterization of Geopolymers

The reaction kinetics, compressive strength, setting time, density, water absorption, porosity and efflorescence potential, FTIR and XRD spectra of the geopolymer pastes and mortars were discussed.

3.4.1 Reaction Kinetics of the Geopolymer Paste

The reactivity of a control geopolymer paste which was activated with 8 M NaOH/Na₂SiO₃ was compared with GNA-CC series of geopolymers activated with Na₂SiO₃ solution only. The heat evolution which is a function of reaction time of the geopolymers at room temperature is presented in Fig. 4. In contrast to the ash-containing geopolymer pastes, which showed three peaks after days of reaction, the control geopolymer (Ref GP) had just two unique peaks that might be attributed to dissolution/hydrolysis and geopolymerization stages of the reaction [6]. The reaction of silica, potassium and calcium present in the GNA may have caused the emergence of this third peak.

The control geopolymer (RG) demonstrated a greater rate of dissolution and higher heat release within the first 24 hours compared to the systems that contained ash. When compared to the control, the first and second exothermic peaks in GNA-containing pastes demonstrated that dissolution/hydrolysis began rather slowly after mixing with activator. This may be connected to the slow release of alkali/alkaline hydroxide stocked in the ash. This was further supported by the extended setting times recorded with CC/GNA geopolymers. Further dissolution of the chemicals in the ash in the alkaline environment probably resulted in the formation of the third peak. This is consistent with the strength development (see Fig. 5 later) when ash was co-precursor in the geopolymer. As the amount of ash increased, the rate of dissolution and heat release reduced, which was visible in the evolution of the peaks and the reaction time.

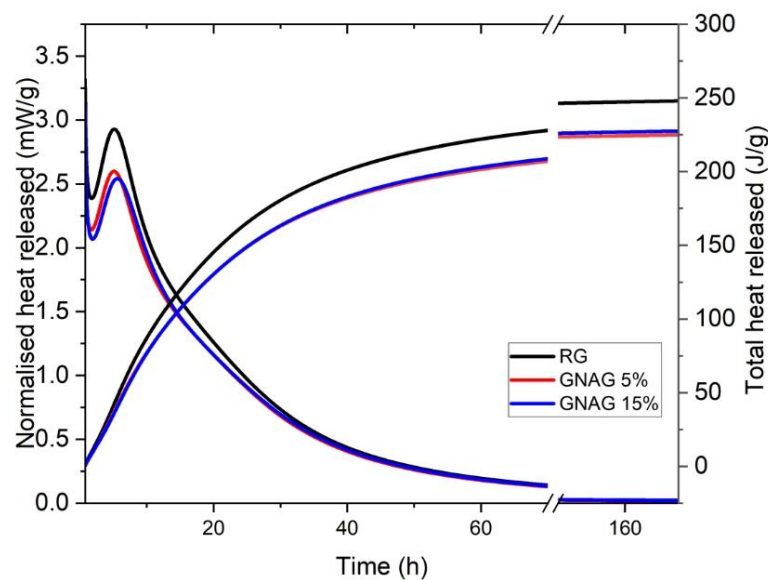


Fig. 4 Calorimetry curves showing heat release and cumulative heat release for the control and groundnut shell ash calcined clay geopolymers paste

3.4.2 Sub Section Headings

The compressive strength values of the geopolymer pastes (GNAG) and mortars (GNQG) are presented in Fig. 5. At 28 days, the control geopolymer exhibited a strength of 18.1 MPa, whereas the GNAG pastes showed strengths ranging from 25.8 to 63.5 MPa, with the highest value observed at 15% GNA replacement. The highest compressive strength observed at 15% replacement of calcined clay with groundnut shell ash can be attributed to an optimal balance between reactive aluminosilicate phases and available sodium and calcium for secondary reactions. At this level, the amorphous silica and alumina in groundnut shell ash actively participated in pozzolanic reactions with sodium/calcium hydroxide released during hydration, leading to the formation of additional binding phases such as sodium/calcium silicate hydrate and sodium/calcium aluminosilicate hydrate. These reaction products fill capillary pores, improve particle packing, and produce a dense, well-bonded microstructure with reduced porosity, thereby enhancing load transfer and compressive strength. This is consistent with the findings of Kannan and Ganesan [33], where composite geopolymer produced with rice-husk ash showed improved strength up to

15% replacement. The similarity in these results could be associated with the high amount of silica oxides present in rice-husk and groundnut shell ash.

In contrast, increasing the GSA replacement to 20% resulted in a sharp reduction in compressive strength due to over-dilution of the reactive calcined clay component. At this higher replacement level, the quantity of ash exceeded the amount that can effectively react with available sodium/calcium oxides, leaving a significant fraction of ash unreacted. This limits further gel formation and leads to a less compact microstructure characterized by unreacted particles, and weak interfacial zones. The resulting reduction in cohesive binding phases compromise the structural integrity of the matrix, explaining the observed decline in compressive strength at 20% replacement. This is similar to the observations of Kannan and Ganesan [33].

For the mortars, the optimum compressive strength of 46.8 ± 0.3 MPa was achieved at 2.5% QD addition, exceeding the minimum standard of 20.7 MPa required for construction materials such as paving blocks and masonry bricks under moderate weathering conditions [34]. However, further increase in QD content resulted in a reduction of compressive strength. This decrease can be attributed to the relatively high Fe_2O_3 content in the QD (15.4%, Table 1), which may interfere with the geopolymerization reaction, leading to a less connected aluminosilicate network. Similar observations have been reported by Choi and Lee [35], who found that Fe_2O_3 can negatively affect geopolymer strength.

Overall, all geopolymer pastes and mortars containing GNA exhibited superior compressive strength compared with the control geopolymer, demonstrating the effectiveness of GNA as a functional additive, while the impact of QD highlights the importance of chemical composition in optimizing geopolymer mechanical performance.

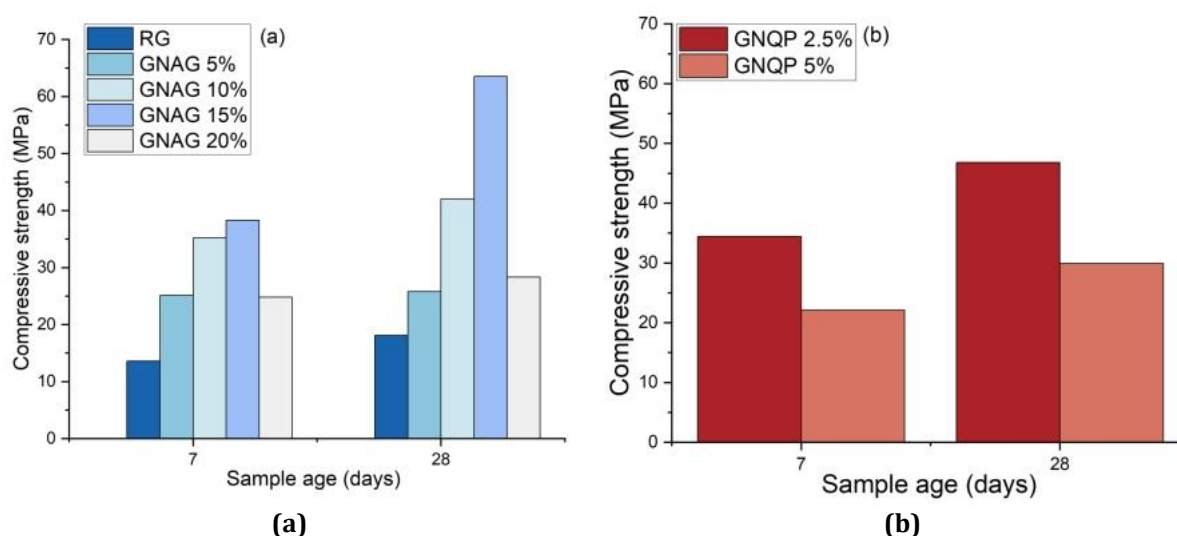


Fig. 5 Compressive strength of (a) Geopolymer pastes; and (b) Modified GNAG 15% mortars

3.4.3 Setting Time of Geopolymers

The setting time of the geopolymer pastes and mortars is presented in Fig. 6. The control geopolymer paste exhibited a relatively rapid setting time of approximately 4 h, whereas mixes containing groundnut shell ash (GNAG) showed markedly prolonged setting times, ranging from 15 to 17 h. Among the modified systems, the mixture containing 5% GNAG recorded the shortest setting time, while the 20% GNAG formulation exhibited the longest delay. This could be attributed to the availability of more soluble silica in the activating solution as reported by Ling et al. [36]. This progressive increase in setting time with rising GNA content is also consistent with observations reported by Babako and Apeh [37] for other biomass ash-modified geopolymer systems, where the incorporation of ash with lower intrinsic reactivity slows geopolymer gel formation. Consequently, the observed setting times exceeded the maximum 10 h limit stipulated by IS 4031 for certain construction applications, including paving blocks, indicating potential limitations for direct field deployment without further mix optimization.

In line with earlier findings by Oladele et al. [21], the incorporation of 2% Periwinkle Shell Ash (PSA) was effective in mitigating the delayed setting behaviour. In this study, 2% of PSA and between 2.5 and 5% of quarry dust were added to 15% GNAG to produce geopolymer mortar. The setting time of the geopolymer mortars was observed to be further shortened as the addition of sand to the paste also reduced the workability.

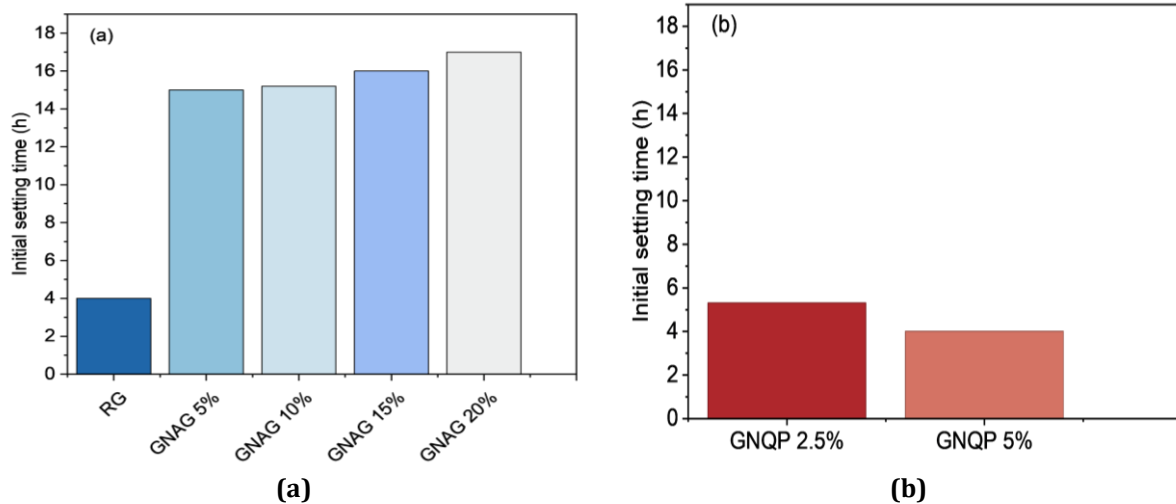


Fig. 6 Setting time of (a) Geopolymer pastes; and (b) Modified GNAG 15% mortars

3.4.4 Density of Geopolymer

The results of density of the geopolymer pastes and mortars at 28 days are shown in Fig. 7. The results varied from 1.95 to 3.40 g/cm³. The density of the control geopolymer was the lowest. This was found to be caused by an increased number of pores in its network, as confirmed by the porosity test (see Figure 8 later). An increase in the density of the geopolymers was also noted with the addition of quarry dust. This demonstrated that the QD and ash densified the geopolymer matrix by acting partly as fillers in the pores of the geopolymer system. These outcomes are consistent with previous results where the density of the geopolymers were reported to increase with the addition of quarry dust [21].

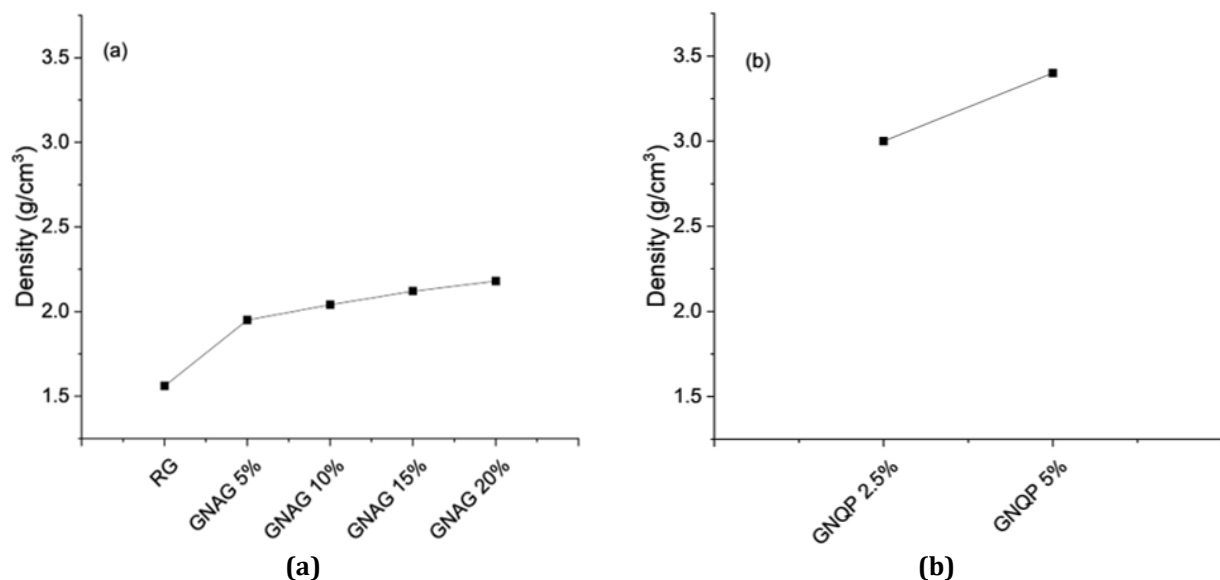


Fig. 7 Density of (a) Geopolymer pastes; and (b) Modified GNAG 15% mortars

3.4.5 Water Absorption and Porosity of Geopolymer

The water absorption and porosity of the geopolymers are presented in Fig. 8. Incorporation of groundnut shell ash (GNA) into the geopolymer matrix significantly influenced these properties. For GNA-containing geopolymer pastes and mortars, porosity ranged from 12.9 to 20.6%, while water absorption varied between 2.0 and 4.3%. In contrast, the control geopolymer, devoid of GNA, exhibited the highest porosity (49.5%) and water absorption (11.8%), indicating a more porous and less compact microstructure. The elevated porosity of the control sample facilitated extensive water ingress into the open pore network, thereby increasing water absorption. These results are consistent with findings by Srinivas et al. [38], who reported that geopolymers with reduced porosity,

achieved through the incorporation of ash or other fillers, demonstrate enhanced resistance to water penetration and associated deterioration. Kannan and Ganesan [33] also reported a decrease in water absorption for geopolymer composite produced with rice-husk ash, with 15% replacement documented as optimum. The reduction in porosity and water absorption observed in GNA-modified geopolymers is indicative of a denser microstructure, which is expected to improve durability and long-term engineering performance in construction applications.

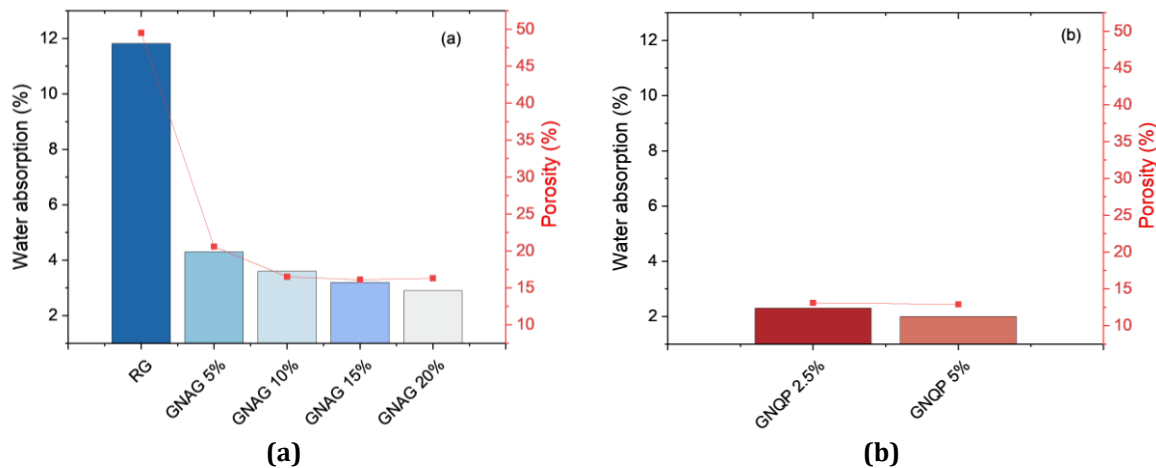


Fig. 8 Effect of GNA replacement on the water absorption and porosity of (a) Geopolymer pastes; and (b) Modified GNAG 15% mortars

3.4.6 Effect of Groundnut Shell Ash on Geopolymer Efflorescence

The efflorescence behavior of the geopolymer samples after 28 days is presented in Fig. 9. The control geopolymer exhibited the highest efflorescence (0.08 g), whereas samples containing groundnut shell ash (GNA) showed lower values, ranging from 0.01 to 0.05 g. This reduction correlates with the influence of GNA on both the chemical and microstructural properties of the geopolymer matrix. The lower efflorescence in GNA-modified geopolymers can be attributed to the reduced concentration of alkali metals in the system, which limits the formation of soluble salts capable of migrating to the surface [39]. Additionally, GNA contributes to a denser microstructure by filling voids and refining pore size distribution, thereby reducing pore connectivity and impeding salt transport. This densification is consistent with the observed decrease in total porosity and improved compressive strength of GNA-containing samples, suggesting a direct link between microstructural refinement and durability performance.

These results indicate that the incorporation of GNA not only enhances the mechanical properties of calcined clay geopolymers but also mitigates efflorescence, improving their long-term durability and suitability for structural and construction applications.

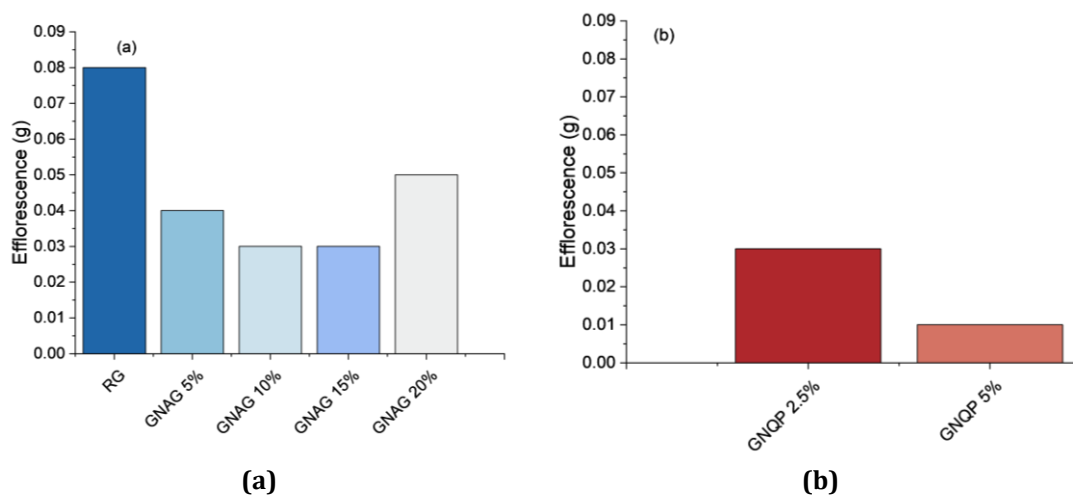


Fig. 9 Efflorescence of (a) Geopolymer pastes; and (b) Modified GNAG 15% mortars

3.4.7 FTIR Spectra of Geopolymer

The spectra of the geopolymer paste and mortars are presented in Fig. 10. The bands observed in the control geopolymer at approximately 3452 cm^{-1} and 1627 cm^{-1} were attributed to the stretching (-OH) and bending (H-O-H) vibrations of bound water molecules, which were either surface-adsorbed or trapped within the layer cavities of the polymeric framework, respectively. The poly-condensation of alternating Si-O and Al-O bonds caused the strong peak observed at 1068 cm^{-1} in CC to shift to 961 cm^{-1} in CC/GNA geopolymer paste [21]. This peak shift is consistent with the formation of reaction product during geopolymerization [40]. The control geopolymers also showed a similar shift. This similarity showed that geopolymer can be produced using only sodium silicate as activating solution and groundnut shell ash as pozzolanic additive [41].

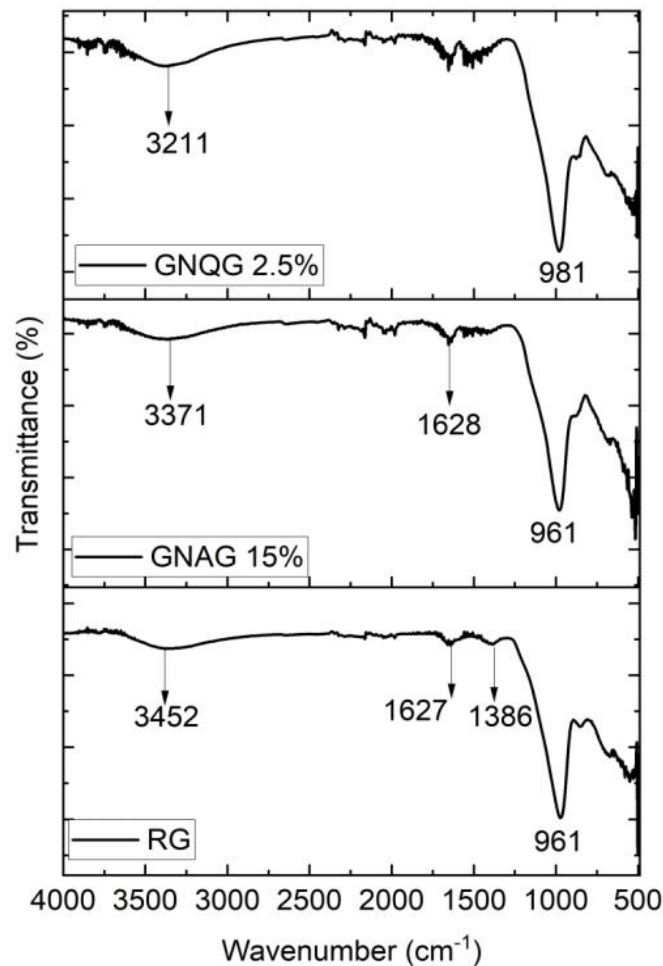


Fig. 10 ATR/FTIR spectra of geopolymer pastes and mortar

3.4.8 X-ray Diffraction of the Geopolymers

The XRD diffractograms of the geopolymers are shown in Fig. 11. A characteristic of the production of amorphous geopolymers is the diffuse halo peak that was seen between 20 and $30^\circ 2\theta$ in all the geopolymer paste and mortars. This is an indication that the addition of ash did not prevent geopolymerization reaction [42,43]. In addition to the amorphous phase, the control geopolymer had a few minor crystalline phases from CC and GNA, including quartz, anatase and illite. The ash-containing geopolymers also exhibit contributions from crystalline phases of undissolved minerals from the calcined clay and the groundnut shell ash. These minerals found in the ash and QD enhanced the properties of ash-containing paste and mortars [21].

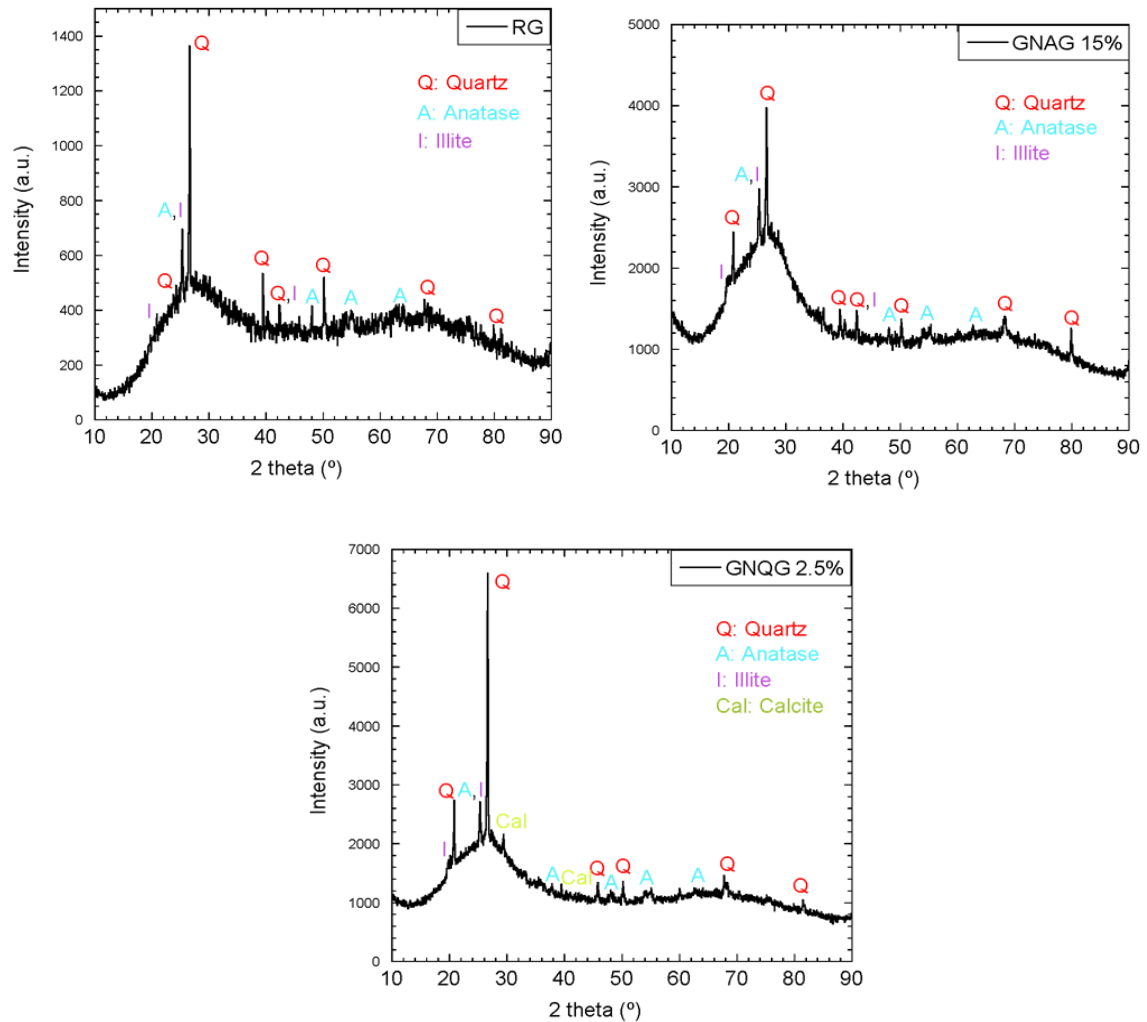


Fig. 11 XRD pattern of geopolymer pastes and mortars

4. Conclusion

This study evaluated the influence of groundnut shell ash (GNA) on the compressive strength, porosity, and overall performance of calcined clay-based geopolymer binders for construction applications. The results confirmed that GNA is rich in silica, with appreciable quantities of alumina, potassium, and calcium oxides, and that its contribution to geopolymer performance is primarily governed by chemical composition rather than amorphous content. Unlike highly amorphous aluminosilicate precursors, GNA functions predominantly as a co-activator and microstructural modifier, where potassium and calcium oxides enhance the alkalinity and activation efficiency of the sodium silicate system. The combined $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ content of 77.5% further supports the potential of GNA as a supplementary cementitious material.

The incorporation of GNA alongside calcined clay promoted more effective geopolymerization by facilitating aluminosilicate dissolution and gel formation, while calcium-bearing phases likely contributed to additional binding products. These mechanisms translated directly into the observed reduction in porosity and corresponding increase in compressive strength, indicating improved matrix densification and pore refinement. Optimization of the CC/GNA/PSA/QD blend ratios was therefore critical in achieving enhanced mechanical performance under a low-alkali activation approach.

In summary, the findings demonstrate that groundnut shell ash is a viable and sustainable additive for improving the engineering performance of calcined clay-based geopolymer binders. Its multifunctional role enables strength enhancement and microstructural refinement without reliance on highly alkaline activators, supporting the development of environmentally responsible construction materials and the valorization of agricultural waste in building applications.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: **study conception and design:** Mary B. Ogundiran; **data collection:** Olajumoke L. Oladele; **analysis and interpretation of results:** Olajumoke L. Oladele, Elijah D. Adesanya, Arantxa Arbe, Amaia Iturrospe, Mary B. Ogundiran; **draft manuscript preparation:** Olajumoke L. Oladele, Mary B. Ogundiran. All authors reviewed the results and approved the final version of the manuscript.

References

- [1] Cakmak, T., Ustabas, I., Kurt, Z., & Gurbuz, A. (2025). The importance of early strength in structural applications: Obsidian-based geopolymer mortars and silica fume substitution study. *Structural Concrete*, 26, 1578-1596. <https://doi.org/10.1002/suco.202400726>
- [2] Cakmak, T., Murat, C., & Ustabas, I. (2025). A novel study on dielectric aspect of mortars about multi-binder structures consisting of divergent binders. *Structures*, 77, 109066. <https://doi.org/10.1016/j.istruc.2025.109066>
- [3] Duxson, P., Fernández-Jiménez, A., & Provis, J. L. (2007). Geopolymer technology: The current state of the art. *Journal of Materials Science*, 42, 2917-2933. <https://doi.org/10.1007/s10853-006-0637-z>
- [4] Provis, J. L., & Bernal, S. A. (2014). Geopolymers and related alkali-activated materials. *Annual Review of Materials Research*, 44, 299-327. <https://doi.org/10.1146/annurev-matsci-070813-113515>
- [5] Cong, P., & Cheng, Y. (2021). Advances in geopolymer materials: A comprehensive review. *Journal of Traffic and Transportation Engineering (English Edition)*, 8(3), 283-314. <https://doi.org/10.1016/j.jtte.2021.03.004>
- [6] Ogundiran, M. B., & Kumar, S. (2015). Synthesis and characterization of geopolymer from Nigerian clay. *Applied Clay Science*, 108, 173-181. <https://doi.org/10.1016/j.clay.2015.02.022>
- [7] Shehata, N., Sayed, E. T., & Abdelkareem, M. A. (2021). Recent progress in environmentally friendly geopolymers: A review. *Science of the Total Environment*, 762, 143166. <https://doi.org/10.1016/j.scitotenv.2020.143166>
- [8] Jindal, B. B., Alomayri, T., Hasan, A., & Kaze, C. R. (2022). Geopolymer concrete with metakaolin for sustainability: A comprehensive review on raw material properties, synthesis, performance, and potential applications. *Environmental Science and Pollution Research*, 1-26. <https://doi.org/10.1007/s11356-021-17849-w>
- [9] Provis, J. L., Lukey, G. C., & van Deventer, J. S. J. (2005). Do geopolymers actually contain nanocrystalline zeolites? A re-examination of existing results. *Chemistry of Materials*, 17, 3075-3085. <https://doi.org/10.1021/cm050230i>
- [10] Alnadish, A. M. (2026). Geopolymer concrete: A comprehensive review of current research trends, challenges, and environmental-economic implications. *Archives of Computational Methods in Engineering*, 33, 1-38. <https://doi.org/10.1007/s11831-026-10515-9>
- [11] Khan, S. I. (2021). Mechanical performance of geopolymer pre-stressed railway sleepers. *Materials Today: Proceedings*, 47, 414-423. <https://doi.org/10.1016/j.matpr.2021.04.320>
- [12] Akar, T., Çınar, H., Sayın, F., Tunalı Akar, S., Kara, İ., Çelik, S., Yılmaz, A., Yılmaz, M., & Kara, F. (2026). A novel geopolymer supported biomass from immobilization design to applications for toxic cadmium uptake. *Biomass and Bioenergy*, 215, 109601. <https://doi.org/10.1016/j.biombioe.2026.109601>
- [13] Ogundiran, M. B., Nugteren, H. W., & Witkamp, G. J. (2013). Immobilisation of lead smelting slag within spent aluminate-fly ash based geopolymers. *Journal of Hazardous Materials*, 248-249, 29-36. <https://doi.org/10.1016/j.jhazmat.2012.12.061>

- [14] Singh, N. B., & Middendorf, B. (2020). Geopolymers as an alternative to Portland cement: An overview. *Construction and Building Materials*, 237, 117455. <https://doi.org/10.1016/j.conbuildmat.2019.117455>
- [15] Jaya, N. A., Yun-Ming, L., Cheng-Yong, H., Abdullah, M. M. A. B., & Hussin, K. (2020). Correlation between pore structure, compressive strength and thermal conductivity of porous metakaolin geopolymer. *Construction and Building Materials*, 247, 118641. <https://doi.org/10.1016/j.conbuildmat.2020.118641>
- [16] Degirmenci, N. (2017). Effect of sodium silicate to sodium hydroxide ratios on durability of geopolymer mortars containing natural and artificial pozzolans. *Ceramics – Silikáty*, 61, 1-9. <https://doi.org/10.13168/cs.2016.0044>
- [17] Supic, S., Malesev, M., Radonjanin, V., Bulatovic, V., & Milovic, T. (2021). Reactivity and pozzolanic properties of biomass ashes generated by wheat and soybean straw combustion. *Materials*, 14(4), 1004. <https://doi.org/10.3390/ma14041004>
- [18] Uysal, M., Dilbas, H., Coşgun, T., & Bendjilali, F. (2024). Red-mud additive geopolymer composites with eco-friendly aggregates. *Construction and Building Materials*, 425, 135915. <https://doi.org/10.1016/j.conbuildmat.2024.135915>
- [19] Zhao, J., Trindade, A. C. C., Liebscher, M., de Andrade Silva, F., & Mechtcherine, V. (2023). A review of the role of elevated temperatures on the mechanical properties of fiber-reinforced geopolymer (FRG) composites. *Cement and Concrete Composites*, 137, 104885. <https://doi.org/10.1016/j.cemconcomp.2023.104885>
- [20] Sharma, U., Gupta, N., Bahrami, A., Özkılıç, Y. O., Verma, M., Berwal, P., Althaqafi, E., Khan, M. A., & Islam, S. (2024). Behavior of fibers in geopolymer concrete: A comprehensive review. *Buildings*, 14(1), 136. <https://doi.org/10.3390/buildings14010136>
- [21] Oladele, O. L., Adesanya, E. D., Arbe, A., Iturrospe, A., & Ogundiran, M. B. (2023). Mitigation of efflorescence, drying shrinkage and water demand of calcined clay-based geopolymers with biological waste ashes as activator and hardener. *Applied Clay Science*, 243, 107050. <https://doi.org/10.1016/j.clay.2023.107050>
- [22] Athira, V., Charitha, V., Athira, G., & Bahurudeen, A. (2021). Agro-waste ash based alkali-activated binder: Cleaner production of zero cement concrete for construction. *Journal of Cleaner Production*, 286, 125429. <https://doi.org/10.1016/j.jclepro.2020.125429>
- [23] Fernando, P. R., Madushani, L. D., Praththana, M., & Nanayakkara, H. M. (2018). Synthesis and characterization of clay brick using waste groundnut shell ash. *Journal of Waste Resources Recycling*, 1(1), 101.
- [24] Duc, P. A., Dharanipriya, P., Velmurugan, B. K., & Shanmugavadivu, M. (2019). Groundnut shell-a beneficial bio-waste. *Biocatalysis and Agricultural Biotechnology*, 20, 101206. <https://doi.org/10.1016/j.bcab.2019.101206>
- [25] Ikumapayi, C. M., Arum, C., & Alaneme, K. K. (2021). Reactivity and hydration behavior in groundnut shell ash based pozzolanic concrete. *Materials Today: Proceedings*, 38, 508-513. <https://doi.org/10.1016/j.matpr.2020.08.292>
- [26] Buari, T. A., Ademola, S. A., & Ayegbokiki, S. T. (2013). Characteristics strength of groundnut shell ash (GSA) and Ordinary Portland Cement (OPC) blended concrete in Nigeria. *IOSR Journal of Engineering*, 3(7), 1-7.
- [27] Nemaleu, J. G. D., Bakaine Djaoyang, V., Bilkissou, A., Kaze, C. R., Boum, R. B. E., Djobo, J. N. Y., ... & Kamseu, E. (2022). Investigation of groundnut shell powder on development of lightweight Metakaolin based geopolymer composite: mechanical and microstructural properties. *Silicon*, 14(2), 449-461, <https://doi.org/10.1007/s12633-021-01115-4>
- [28] Bheel, N., Awoyera, P., Tafsirojjaman, T., & Sor, N. H. (2021). Synergic effect of metakaolin and groundnut shell ash on the behavior of fly ash-based self-compacting geopolymer concrete. *Construction and Building Materials*, 311, 125327, <https://doi.org/10.1016/j.conbuildmat.2021.125327>
- [29] Najafi, K., Allahverdi, A., & Provis, J. L. (2012). Efflorescence control in geopolymer binders based on natural pozzolan. *Cement and Concrete Composites*, 34(1), 25-33, <https://doi.org/10.1016/j.cemconcomp.2011.07.007>
- [30] Lu, A., Yu, X., Ji, Q., Chen, L., Yagoub, A. E. G., Olugbenga, F., & Zhou, C. (2023). Preparation and characterization of lignin-containing cellulose nanocrystals from peanut shells using a deep eutectic solvent containing lignin-derived phenol. *Industrial Crops and Products*, 195, 116415, <https://doi.org/10.1016/j.indcrop.2023.116415>

- [31] Katare, V. D., Madurwar, M. V., & Raut, S. (2019). Agro-industrial waste as a cementitious binder for sustainable concrete: an overview. *Sustainable Waste Management: Policies and Case Studies: 7th IconSWM—ISWMAW 2017, Volume 1*, 683-702.
- [32] Feng, D., Tan, H., & Van Deventer, J. S. J. (2004). Ultrasound enhanced geopolymerisation. *Journal of Materials Science*, 39, 571-580. <https://doi.org/10.1023/B:JMSC.0000024157.26531.1b>
- [33] Kannan, V., & Ganesan, K. (2014). Chloride and chemical resistance of self compacting concrete containing rice husk ash and metakaolin. *Construction and Building Materials*, 51, 225-234. <https://doi.org/10.1016/j.conbuildmat.2013.10.008>
- [34] Mashaly, A. O., El-Kaliouby, B. A., Shalaby, B. N., El-Gohary, A. M., & Rashwan, M. A. (2016). Effects of marble sludge incorporation on the properties of cement composites and concrete paving blocks. *Journal of Cleaner Production*, 112, 731-741, <https://doi.org/10.1016/j.jclepro.2015.08.001>
- [35] Choi, S. C., & Lee, W. K. (2012). Effect of Fe_2O_3 on the physical property of geopolymer paste. *Advanced Materials Research*, 586, 126-129. <https://doi.org/10.4028/www.scientific.net/AMR.586.126>
- [36] Ling, Y., Wang, K., Wang, X., & Hua, S. (2019). Effects of mix design parameters on heat of geopolymerization, set time, and compressive strength of high calcium fly ash geopolymer. *Construction and Building Materials*, 228, 116763. <https://doi.org/10.1016/j.conbuildmat.2019.116763>
- [37] Babako, M., & Apeh, J. A. (2020). Setting time and standard consistency of Portland cement binders blended with rice husk ash, calcium carbide and metakaolin admixtures. *IOP Conference Series: Materials Science and Engineering*, 805(1), 012031. <https://doi.org/10.1088/1757-899X/805/1/012031>
- [38] Srinivas, T., Rahul, V., & Rao, N. R. (2017). Studies on permeability and sorptivity of low calcium fly ash and slag-based geopolymer concrete. *Gokaraju Rangaraju Institute of Engineering and Technology*, 387.
- [39] Allahverdi, A., Najafi, K. E., & Shaverdi, B. (2017). Carbonation versus efflorescence in alkali-activated blast-furnace slag in relation with chemical composition of activator. *International Journal of Civil Engineering*, 15(4), 565-573, <https://doi.org/10.1007/s40999-016-0085-3>
- [40] Ogundiran, M. B., & Kumar, S. (2016). Fly ash-calcined clay geopolymers: reactivity, mechanical strength, structural and microstructural characteristics. *Construction and Building Materials*, 125, 450-457. <https://doi.org/10.1016/j.conbuildmat.2016.08.076>
- [41] Doménech-Carbó, A., Doménech-Carbó, M. T., Osete-Cortina, L., Gimeno-Adelantado, J. V., Bosch-Reig, F., & Mateo-Castro, R. (2002). Electrochemical identification of metal ions in archaeological ceramic glazes by stripping voltammetry at graphite/polyester composite electrodes. *Talanta*, 56(1), 161-174, [https://doi.org/10.1016/S0039-9140\(01\)00563-2](https://doi.org/10.1016/S0039-9140(01)00563-2)
- [42] Murta, J. F. (2024). *Production and characterization of diatomaceous earth-based geopolymers and geopolymeric mortars* (Doctoral dissertation).
- [43] Santos, G. Z., Melo Filho, J. A., Pinheiro, M., & Manzato, L. (2019). Synthesis of water treatment sludge ash-based geopolymers in an Amazonian context. *Journal of Environmental Management*, 249, 109328. <https://doi.org/10.1016/j.jenvman.2019.109328>