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Utilisation of Mining Waste Clays for the Production of Geopolymer Binders: Process Optimisation

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ABSTRACT

The replacement of Portland cement with geopolymer binder (GB) is gaining global attention due to reduced carbon footprint in compliance with the United Nations agenda on sustainable development goals. The major drawback to geopolymer technology is the cost and unavailability of its aluminosilicate precursors. Therefore, this study investigated the utilisation of mining waste clays (MWCs) as sustainable precursors for the production of GBs, with a particular focus on process optimisation. The MWCs samples collected from Nigerian mining sites, namely Ijero, Owode, Ibeshe and Awo, were pre-treated by screening, drying, and sieving. These were characterised using the DTA/TGA technique for their thermal properties. The MWCs were calcined at varying temperatures of 420 ^{0}C – 850 ^{0}C range, at a time range of 3 – 14 h, NaOH concentrations in the range 4 – 10 M, and with varying NaOH/Na_2SiO_3 activator ratios 1:1 - 1:2.5. The GBs produced at these varied parameters were tested for their respective compressive strength to establish optimal process conditions. The dehydroxylation of MWCs into the reactive amorphous phase occurred within the range of 420-740 ºC. Optimised process conditions for GBs production were 600-740ºC calcining temperature, 6hrs calcining time, 8M NaOH concentration and 1:1.5 NaOH/Na_2SiO_3 ratio. The compressive strength of the geopolymer binders ranged from 26.1 to 33.7 MPa, meeting the applicable ASTM strength requirements. Process conditions were optimised for the production of GBs from MWCs.

KEYWORDS: Mining waste clays, climate change, geopolymer binders, carbon-footprint reduction.

1. INTRODUCTION

High and excessive energy requirements have been found to be a flaw associated with the manufacture of Portland cement. According to report by [1], the energy requirement for the manufacturing of PLC is just next to that of steel and aluminium. In addition, in the course of production or manufacture of Portland cement, a huge amount of dust gets released into the environment, which constitutes a major health concern. Coupled with these problems, a major adverse impact from cement manufacture is the high quantity of carbon (iv) oxide (CO_2) being released into the atmosphere during production. Studies have been ongoing to find more sustainable environmentally friendly alternatives to Portland cement in compliance with the UN goals on a sustainable environment. Consequently, geopolymer binders have gained much attention in this regard, because they can utilise aluminosilicate materials as precursor and, in the presence of an alkaline activator, provide a mechanically and environmentally superior alternative to the conventional Portland cement binders [2, 3]. The production of geopolymer binders generally involves the alkaline activation of silica and alumina-rich solid precursors. During the geopolymerisation process, reactive Si and Al species are dissolved from the precursor by the activator under alkaline conditions and are subsequently polycondensed to form a three-dimensional aluminosilicate network. The resulting binder can exhibit high compressive strength and other favourable engineering properties. The use of waste materials as precursors is a form of waste valorisation [4, 5]. Geopolymer technology may not be considered more advantageous over Portland cement ultimately, until there is proper identification of suitable low-cost precursor, and well optimized process conditions; to achieve waste valorisation and green process advantage respectively [6]. So many precursors have been investigated, including fly ash, volcanic materials, blast furnace slag, agricultural waste, metakaolin, and some mineral wastes. However, the sustainability of most of these precursors can not be guaranteed, due to changing technological process pathways generating these materials as by-products. This has aroused interest in naturally occurring wastes, such as waste clays [3, 4].

Clay is no doubt an aluminosilicate material, but is less reactive without thermal treatment, due to the ordered structure of the crystalline raw form. Thermal activation is usually employed to modify the mineral structure, remove structural hydroxyl groups and increase the availability of reactive

aluminosilicate species. Studies have reported the use of thermally treated clays as effective precursors for low-carbon geopolymer binders, although the optimal calcining temperature varies based on clay mineralogy and chemical composition [4, 7]. This variability is important because excessive calcination may cause structural reorganisation or sintering, whereas inadequate calcination may leave substantial quantities of unreactive crystalline phases. Therefore, investigating the appropriate calcining temperature and duration for a particular clay resource is an essential aspect of determining the geopolymer process.

Activators are a major part of the process of geopolymerisation, which provide the alkaline environment and soluble silica needed for the dissolution of the aluminosilicate precursor's component species. Activators include calcium hydroxide, sodium hydroxide and sodium silicate, etc. However, variations in hydroxide concentration, silicate content and hydroxide-to-silicate ratio can substantially influence precursor dissolution, gel formation, setting behaviour and mechanical strength. Therefore, optimisation of the activator composition is essential for achieving adequate mechanical performance and also to avoid excessive activator consumption [6, 8].

Therefore, this study investigated the optimisation of processing conditions for the production of geopolymer binders from mining waste clays obtained from mining locations spread across four different states of Nigeria: Ekiti State (Ijero), Ogun State (Owode), Lagos State (Ibeshe) and Osun State (Awo). The chemical and thermal characteristics of the studied clays were determined. The effects of calcining temperature, and duration were studied. The NaOH/Na_2SiO_3 activator ratio on the compressive strength of the resulting geopolymer binders were determined; to establish suitable processing conditions for the different mining waste clays. The study therefore went beyond just the identification of mining waste clays as potential geopolymer precursors and sought to establish experimentally derived processing conditions for their effective conversion into mechanically effective geopolymer binders. The outcome is intended to provide a practical process basis for the valorisation of Nigerian mining waste clays as locally available precursors for sustainable, low-carbon construction materials.

2. MATERIALS AND METHODS

2.1 Materials

Samples of raw mining waste clays were randomly scooped from the mining grounds in each of the four selected mining locations: Ijero (Ekiti State), Ibeshe (Lagos State), Owode (Ogun State), and Awo (Osun State) mining sites. These were labelled EK, LA, OG and OS, respectively. Industrial-grade Na_2SiO_3 solution (26% wt SiO_2, 11 % wt Na_2O, and 63% wt SiO_2) and sodium hydroxide pellets were purchased from a credible chemical company.

Fig. 1: Map Showing Selected Mining Locations in the Southwest Region of Nigeria

The selected locations where sampling of the mining waste clays took place is represented on map in Fig. 1. Instruments used for this study included: Simultaneous thermal properties and mass loss analysers, which had Thermogravimetric analyser and Differential thermal analyser (TGA/DTA); NETZSCH STA 449 F3 Jupiter model, with temperature range set at 40 - 900 ^{0}C, heating rate of 10^{0}C per minute; Digital furnace (Vecstar furnaces 1100 series and Carbolite AAF, type 301 MC 16-GB-C 1.01), with a heating rate of 7.8 ^{0}C/minute was used; an oven and an analytical weighing balance, at the Department of Chemistry laboratories, University of Ibadan; Compression test machines: ELE

International, ADR Touch 2000 Standard Compression Machine, at Civil Engineering workshop, University of Ibadan.

2.2 Methods

2.2.1 Pre-treatment of mining waste clays

The collected MWC samples from Ijero (EK), Owode (OG), Ibeshe (LA) and Awo (OS) were initially screened manually to remove visible foreign materials, including stones, gravel, plant residues and other coarse impurities. The screened samples were oven-dried at 105 °C, pulverised and homogenised. The dried samples were subsequently passed through a 212-μm mesh sieve to obtain a relatively uniform particle-size fraction. The processed samples were stored in labelled airtight containers before thermal characterisation and calcination.

2.2.2 Preparation of activators

The activator mixture was composed of sodium hydroxide and sodium silicate. Pellets of sodium hydroxide were dissolved in cooled distilled water in plastic containers to achieve NaOH concentrations of 4, 6, 8, and 10 M. Sodium silicate solution was made available in a plastic container.

2.2.3 Thermal characterisation and calcining of the mining waste clay samples

The four mining waste clays were separately pulverised, sieved with a 212-micron mesh sieve, dried in the oven at 105 °C, and kept in appropriately labelled plastic buckets. These raw mining waste clays were characterised for their thermal properties using the thermogravimetry/differential thermal analysis method (TGA/DTA). The determination of the thermal properties of the samples was done to establish phase changes occurring during calcination and to determine the dehydroxylation temperatures of the clays. Hence, based on the values observed from the respective DTA curves of the clays, they were thereafter calcined in the furnace at varying temperatures in the 420 – 850 °C range.

2.2.4 Preparation of geopolymer binders and optimisation

The procedure used for the production of geopolymer binders included mixing of calcined mining waste clays and activator into paste or molten material, which was fed into moulds of 40 x 40 x 40 cm^3. These were kept for demoulding till after 3 days. Solid cubes of geopolymer binders resulted. Using this procedure, laboratory-scale experiments were performed, starting with the optimisation of calcination temperature by using clays calcined at the varied temperatures of the 420 – 850 °C range. At the same time, other parameters were kept at 6 hours calcining time, 8 M NaOH concentration and activator mixing ratio of 1:1($NaOH/Na_2SiO_3$), as observed in previous studies [9]. Replicate geopolymer samples were produced for all the temperatures selected for each of the four clays, respectively. The resulting geopolymers were subjected to compressive strength tests at 7, 14, 21, and 28 days of curing time. The temperature value that produced the geopolymer with the highest compressive strength was considered the optimum calcining temperature. This procedure was repeated to optimise other parameters; varying calcining time of 3, 6, 10, 14 and 20 hrs; varying NaOH concentration within the range 4, 6, 8 and 10 M; and varying activator ($NaOH/Na_2SiO_3$) mix ratios of 1:1, 1:1.5, 1:2, and 1:2.5 for all the clays respectively.

3. RESULTS AND DISCUSSION

3.1 Thermal Properties of the Clays by DTA/TGA technique

The thermograms resulting from thermal characterisation using DTA/TGA are represented in Fig. 2. The TGA/DTA results simultaneously monitored and presented the mass loss of clays with increasing temperature during dehydroxylation. According to [10], dehydroxylation, which has been understood to depend essentially on the clays' layered structures and the amount of hydroxyl groups, had been preceded by the removal of the interlayer water molecules and those absorbed from the atmosphere.

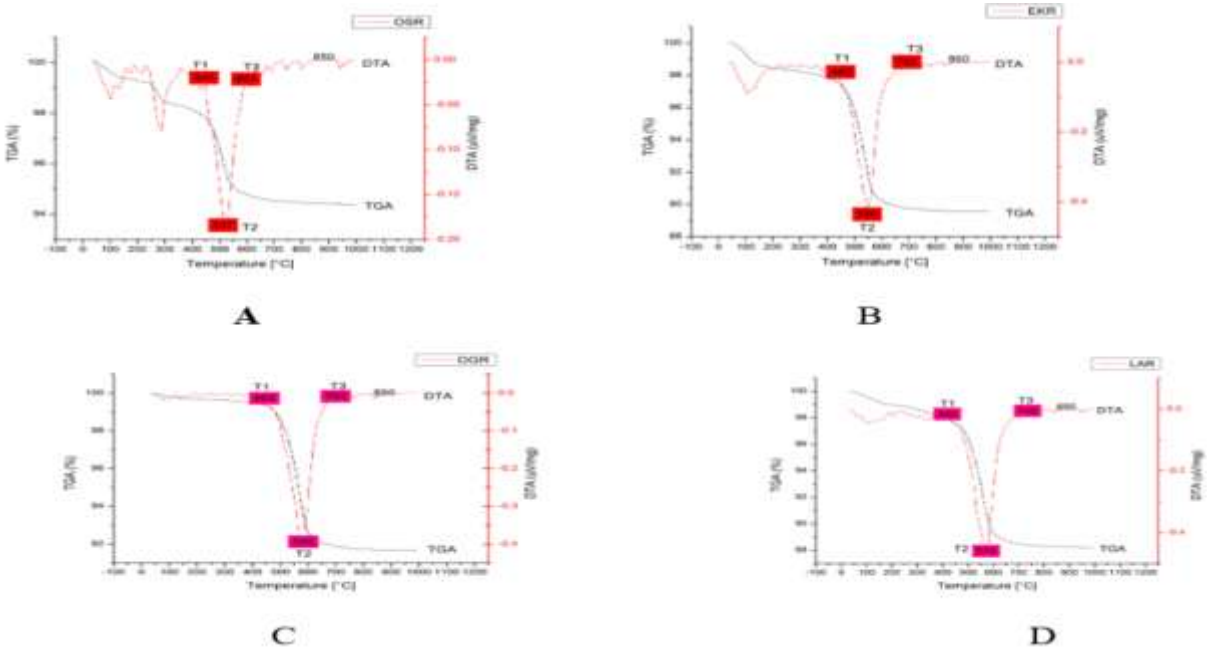

Fig.2 Thermograms of mining waste clays; A (OS); B (EK); C (OG); D (LA)

Dehydroxylation, however, requires more intense thermal treatment, leading to the loss of hydroxyl groups chemically bonded to the octahedral sheets. This causes a collapse of the crystalline structure, leading to the amorphisation of the clay. This phenomenon takes place at different temperatures for different clays, depending on the mineral composition. For the clays studied, the temperature range on DTA/TGA thermograms provided necessary information to predict the dehydroxylation temperature points for each clay source and also enhance identification of the constituent clay minerals.

There exist different groups of clay minerals, based on their silica-to-alumina ratio (SiO_2/Al_2O_3) and the way their structural sheets are layered. When the clay minerals consist of the tetrahedral-octahedral sheets, and the silica and alumina sheets form a layer by shared oxygen atoms, and these layers are held together by hydrogen bonding, this is referred to as a 1:1 clay mineral. An example of this type is the kaolinite clay mineral. However, when tetrahedral – octahedral- tetrahedral sheets are formed, and the silica, alumina, and silica sheets form a layer by shared oxygen atoms with an interlayer space, this is referred to as a 2:1 clay mineral type. The interlayer always contains adsorbed water molecules and other ions. Examples of this group of clay minerals include montmorillonite, illite, and chlorite [11]. The thermograms of the clay samples suggest the points of transformation of the kaolinite to metakaolinite, which is the reactive form of clay.

Generally, for all the clays, the temperature range for the dehydroxylation of kaolinite which occurred between 430^0C and 740^0C, had the most intense mass loss among the three peaks in the respective thermograms, suggesting a relatively large presence of kaolinite alongside the composition of the 2:1 clay types suggested by the XRF results. This assumption is further ascertained by the XRD results, revealing intense kaolinite peaks for the clays. At a temperature range above 800^0C, the occurrence here was the dehydroxylation of some 2:1 clay minerals; illite, montmorillonite, and mullite [12]. All the clays used in this study, as represented by the thermogrammes, exhibited all the dehydration and dehydroxylation phenomena

3.2 Optimisation of calcining temperature of the mining waste clays

The results of the compressive strength of the geopolymers produced from clays calcined at the varying temperatures are presented in Fig. 3. From the results, the optimal calcination temperatures for the clays are 700, 740, 600, and 700 (^{0}C) for OG, LA, OS, and EK, respectively. From these values, the clays can be calcined at temperatures within the range of 600 to 740 (^{0}C). Correlating the compressive strength test results with the thermograms (Fig. 2), it was observed that the calcination of clays at the T3 dehydroxylation (post-peak) temperatures gave the best geopolymer performance, across all the clays. This suggests that the thermal process of clay conversion to metakaolin continued after the peak and had only come to completion at the post-peak point. For all the investigated clays, strength generally

increased with curing age. The reduction in strength at 850 °C suggested that excessive calcination may be detrimental to geopolymer precursor reactivity.

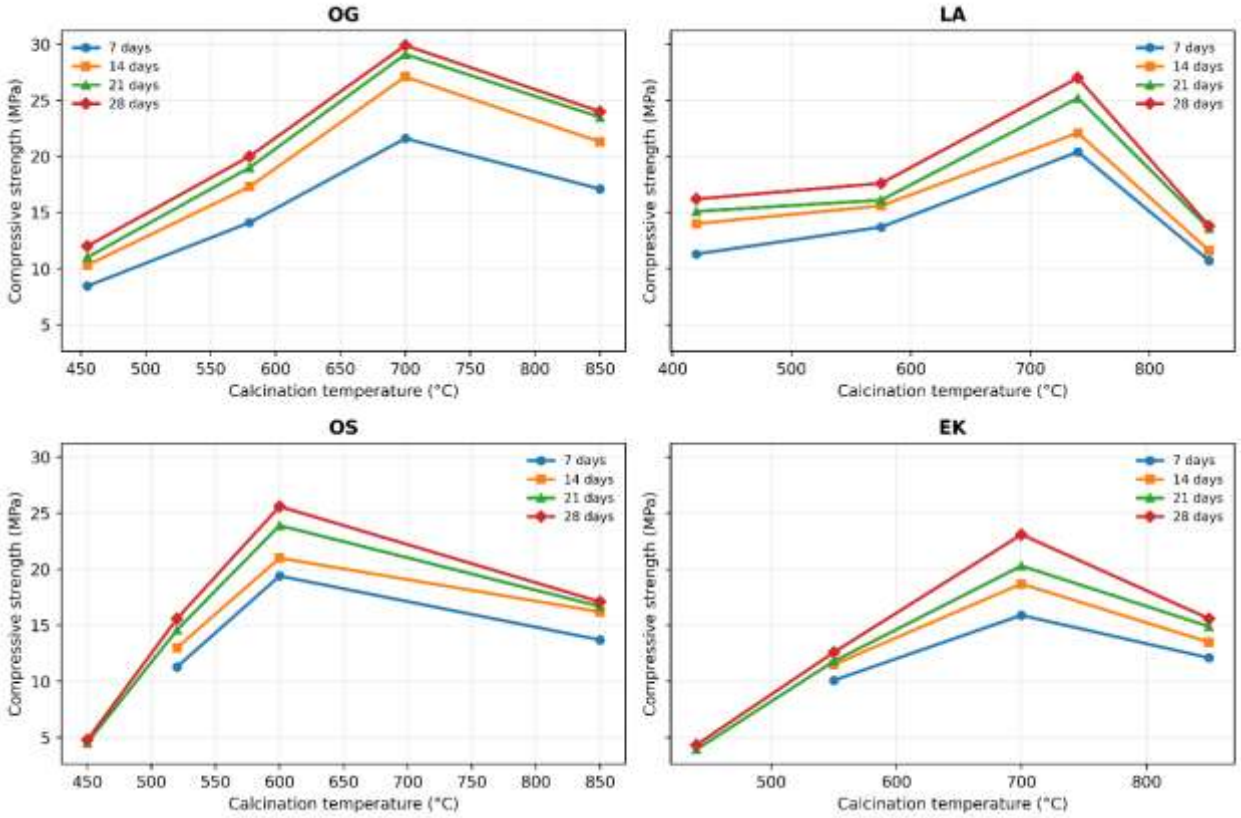

Fig. 3: Compressive Strength of Geopolymers at Varying Calcination Time

3.3 Optimisation of Calcination Time of the Mining Waste Clays

The results of the compressive strength of the geopolymers at varying calcining time duration are presented in Figure 4. The results suggest that the optimal calcination time for the clays is 6 hours at the optimised temperature. The decline in the compressive strength at higher temperatures suggests that at a calcination time longer than 6 hours, the clays experienced transformation to less reactive crystalline phase minerals.

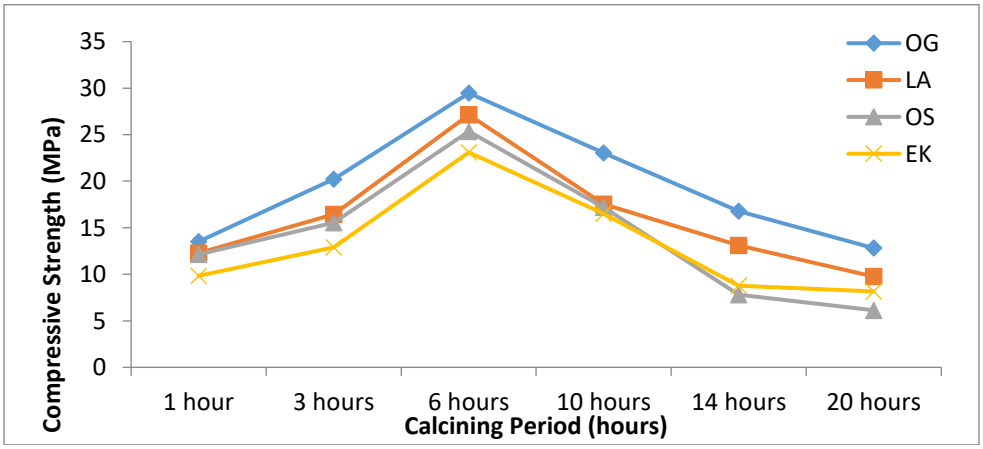

Fig. 4: Compressive Strength of Geopolymers of Different Clays at Varying Calcination Time

3.4 Optimisation of NaOH Concentration

The concentration of NaOH used in the making of the activator for geopolymer production was optimised to determine which concentration was most suitable. The results are presented in Figure 5.

It was observed from the results that the geopolymers produced with NaOH of 8 M concentration had the highest compressive strength across all the selected clays.

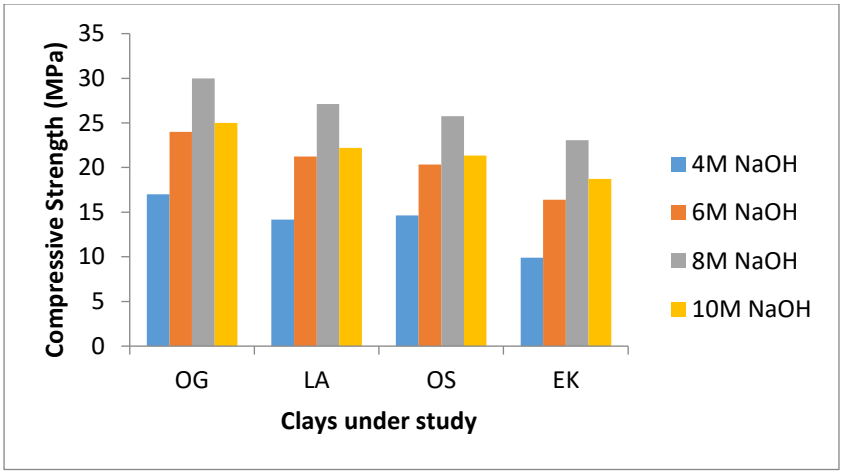

Fig. 5: Compressive Strength of Geopolymers of Different Clays with Varying Concentrations of NaOH

3.5 Optimisation of Activator Mixing Ratio ($NaOH/Na_2SiO_3$)

The results of the optimisation of the mixing ratio of activator consisting of Na_2SiO_3 and NaOH as presented in Fig. 6 suggested that a careful balance of the constituent species in these two activator components largely influenced the mechanical strength development of the geopolymers. This ratio may have provided the most favourable alkaline environment for the best strength development for geopolymer. The highest 28-day compressive strengths were obtained at a $NaOH/Na_2SiO_3$ ratio of 1:1.5, with values of 33.7, 29.8, 28.3 and 26.1 MPa for OG, LA, OS and EK based binders, respectively. However, further increase to 1:2.5 adversely affected the strength, suggesting that excess availability of soluble silica species in Na_2SiO_3 could be causing changes in dissolution kinetics, mixture viscosity and gel formation.

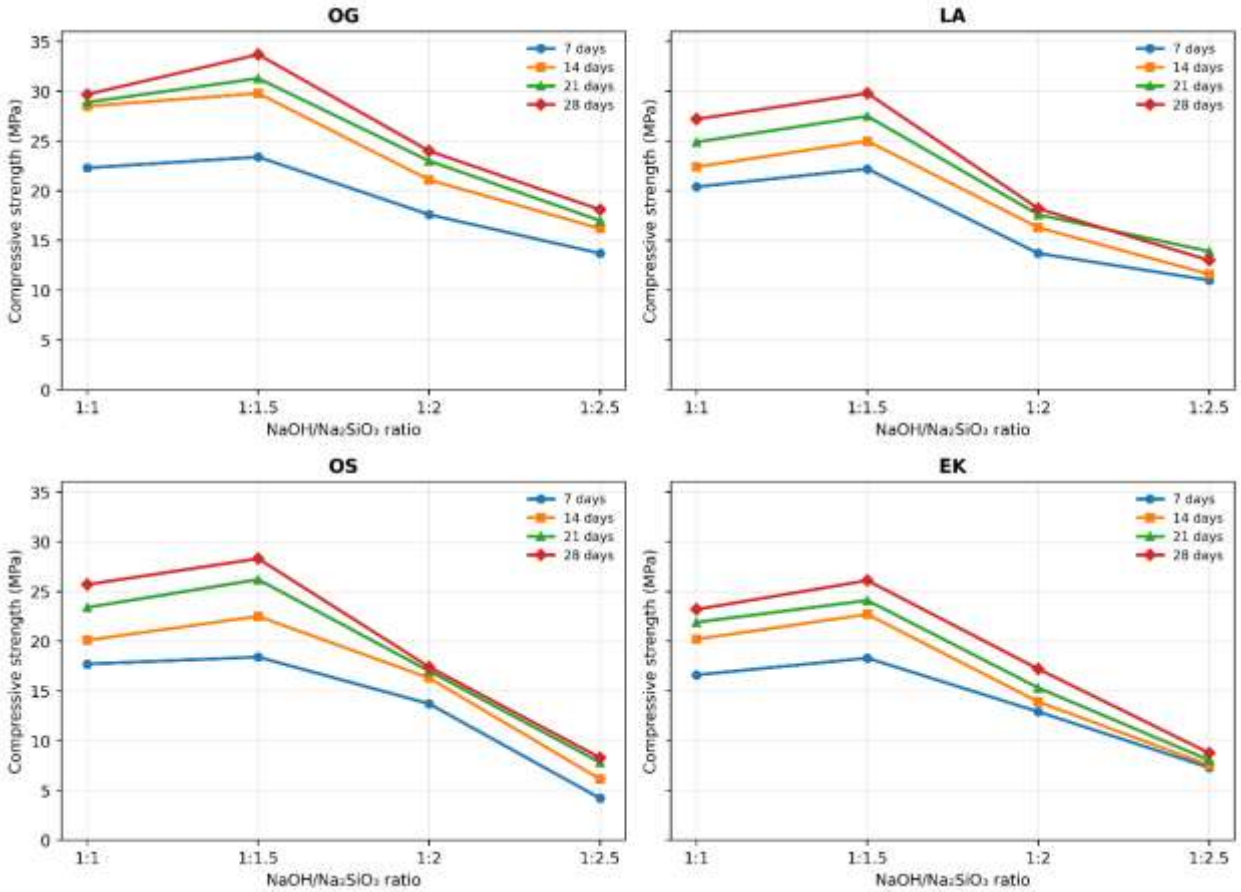

Fig. 6: Compressive Strength (MPa) of the Geopolymers with Varying NaOH/ Na_2SiO_3 ratio

4. CONCLUSION

This study demonstrated the suitability of Nigerian mining waste clays (MWCs) as sustainable aluminosilicate precursors for geopolymer binder production and established the optimal values for the major process conditions. Thermal analysis confirmed significant dehydroxylation and transformation of the clay minerals to reactive phases within approximately 430–740 °C, with the optimum calcination temperature varying among the clay sources. Based on compressive strength development, the optimum temperatures were 700 °C for OG, 740 °C for LA, 600 °C for OS and 700 °C for EK, while 6 h was identified as the optimum calcination time. An 8 M NaOH concentration and 1:1.5 NaOH/Na_2SiO_3 activator ratio produced the most favourable strength development across the investigated clays. At the optimum activator ratio, the 28-day compressive strengths reached 33.7, 29.8, 28.3 and 26.1 MPa for OG, LA, OS and EK, respectively. Excessive calcination and higher sodium silicate proportions resulted in reduced strength, indicating the importance of controlling thermal treatment and activator composition. Overall, the findings establish that locally sourced Nigerian mining waste clays can be effectively converted into reactive geopolymer precursors through appropriate process optimisation, providing a sustainable route for waste valorisation and the development of lower-carbon alternative binders to conventional Portland cement.

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