ISSN 3023-5669 Journal of Material Characterization and Applications, Vol. **2**, No. 2, pp 30-41 (2024)
www.matcharappjournal.com
https://doi.org/10.5281/zenodo.13709576

SYNTHESIS AND CHARACTERIZATION OF INORGANIC POLYMERS (GEOPOLYMERS) PRODUCED FROM METAKAOLIN USING SODIUM SILICATE AND MILLET HUSK ASH AS ACTIVATORS

Ahmad Zainab Muhammad[a*]
Saleh Muhammad Salga[b]
Salisu Ahmed[c]
Ilu Magaji Barde[d]

[a*]*Umaru Musa Yar'dua University, Faculty of Natural and Applied Sciences, Department of Pure and Industrial Chemistry, Katsina state, Nigeria*
Email: zainab.ahmad@umyu.edu.ng

[b]*Umaru Musa Yar'dua University, Faculty of Natural and Applied Sciences, Department of Pure and Industrial Chemistry, Katsina state, Nigeria*
Email: muhammad.saleh@umyu.edu.ng

[c]*Umaru Musa Yar'dua University, Faculty of Natural and Applied Sciences, Department of Pure and Industrial Chemistry, Katsina state, Nigeria*
Email: ahmed.salisu@umyu.edu.ng

[d]*Umaru Musa Yar'dua University, Faculty of Natural and Applied Sciences, Department of Pure and Industrial Chemistry, Katsina state, Nigeria*
Email: magaji.ilubarde@umyu.edu.ng

Received 12 July 2024; revised 8 August 2024; accepted 16 August 2024

Abstract

The use of inorganic polymers (geopolymers) as cement has been encouraged because of its several advantages over Portland cement. This is due to the huge carbon dioxide (CO_2) emission that is involved which has great effects on climatic conditions. This work synthesized one-part inorganic polymers (geopolymers) using metakaolin, sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), and millet husk ash (MHA). The geopolymers were synthesized by adding water to the calcined kaolin, (NaOH) and (Na_2SiO_3). The resulting paste was cast for the compressive and flexural strength test. The casted samples were cured immediately at 60 ^{0}C for 20 hours and de-molded. They were tested for mechanical properties after 1 and 7 weeks at room temperature. The above procedure was repeated by complete replacement of Na_2SiO_3 with MHA. The 7-weeks cured geopolymers were characterized by FTIR, XRD, SEM, and TGA to confirm the formation of synthesized geopolymers. The samples were also analyzed to study physicochemical properties. It was observed that the highest compressive and flexural strength was obtained at (17.06 N/mm^2 and 2.31 N/mm^2) and (13.50 N/mm^2 and 1.14 N/mm^2) for both Na^2SiO^3 and MHA geopolymers respectively. Therefore, the current study signified that the synthesized geopolymers can serve as a substitute for the cement with less effect on the climatic conditions.

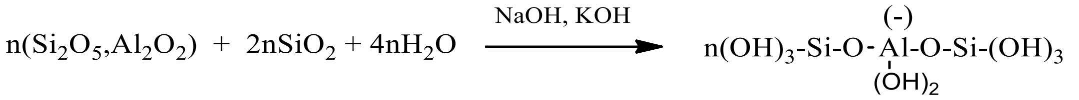
Keywords: Metakaolin, geopolymers, physicochemical properties, characterizations, mechanical properties

1. Introduction

Geopolymers are inorganic polymers that are obtained by the combination of aluminosilicate substances with an alkali activator and the addition of fine and coarse materials, for example, sand [8]. Generally, geopolymers can be either one part or two parts. Two-part geopolymers are produced by the reaction between a concentrated aqueous solution of alkali, silicate, and aluminosilicate precursor i.e. two-part in addition to water. [37] However, due to the handling of hazardous alkali activator solution one-part geopolymers have been developed "Just add water" and it is formed as a result of adding water to the dry solid mixture of an activator and aluminosilicate material.

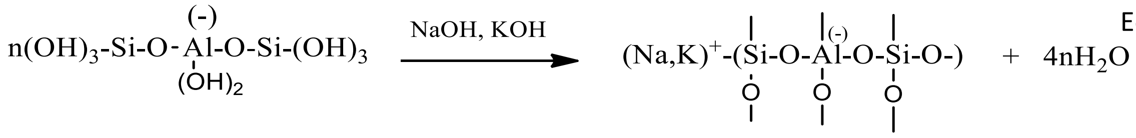
The geopolymerization reaction for both one-part and two-part can be formed using equation 1 and 2;

Eqn. 1



$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O \xrightarrow{NaOH,\ KOH} n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\overset{(-)}{Al}}\text{-O-Si-}(OH)_3$$

Eqn. 2



$$n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\overset{(-)}{Al}}\text{-O-Si-}(OH)_3 \xrightarrow{NaOH,\ KOH} (Na,K)^{+}\text{-(}\underset{\underset{|}{O}}{\overset{|}{Si}}\text{-O-}\underset{\underset{|}{O}}{\overset{|(-)}{Al}}\text{-O-}\underset{\underset{|}{O}}{\overset{|}{Si}}\text{-O-)} + 4nH_2O$$

Production of ordinary Portland cement contributes 5% to 7% of the production of total CO_2 evolution [15] Approximately 556 ml of CO_2 is emitted with the production of each 1000 kg of Portland cement [23]. To these effects, researchers embarked on synthesizing geopolymers to substitute ordinary Portland cement for the safety of the environment. Metakaolin is an ordinary material for the laboratory to initiate the synthesis of geopolymer products and is obtained by the calcination of kaolin which can be used to produce pozzolana with high-strength and performance concrete materials [32]. It is a white powder of $Al_2O_32SiO_2$, dehydrating kaolin. ($Al_2O_32SiO_2.2H_2O$), hydrated kaolin heated to a temperature of 700-900 ^0C. The geopolymer production is independent of the activators. The use of activators enhanced the dissolution of metakaolin. [2]. Activators used in one-part geopolymer can be any alkaline solution or agricultural waste with a high amount of silica content. Therefore the use of NaOH and Na_2SiO_3 enhances the solubility of raw material and develops the rate of strength of the synthesized geopolymers [7] [17]. Agricultural wastes encounter problems with the accumulation of waste annually; therefore the burnt ashes had the considerable advantage of being used as cementitious materials. The importance of using agro waste to substitute binder or activator is to reduce the cost of buying cement, effective alternative utilization of the waste apart from using it as manure and minimizing environmental pollution.

Pozzolana as cementitious materials, Pozzolana can be defined as a mixture of aluminium and silicon called aluminosilicate substance which when itself possesses little or no cementitious value but when in firmly divided form and in the presence of water molecule, chemically combined with the soluble base at ambient temperature to form compounds with cementing properties [5] [19]. Pozzolana can either be natural or artificial such as diatomaceous earths and volcanic ashes respectively. Example of pozzolanic materials includes kaolin, fly ash, blast furnace slag, and agricultural husk ashes. The pozzolana must contain at least 70 % of SiO_2, Al_2O_3 and Fe_2O_3 [5]. [3], Used guinea corn husk ash (GCHA) to replace ordinary Portland cement, three concrete blocks were cast and cured for 1, 2, and 4 weeks. The replacement of cement by (GCHA) was from (0-20 %). and it was found that 5 % and 10 % exhibited good strength. [18], uses millet husk ash (MHA) as a partial replacement material with different percentages i.e. 0 %, 5 %, 10 %, 15 %, and 20 % by the weight of cement. Three cubes were cast and cured for 1 and 4 weeks, the experimental results showed that there was a considerable increment in compressive strength at 5 % of MHA when replaced with cement. Therefore, MHA used in concrete improves the production of concrete. [33] studied the substitution of commercial Na_2SiO_3 with rice husk ash (RHA). Fly ash, (FA), ground granulated blast furnace slag, (GBFS), and binary 50FA:50GBFS were activated with a mixture of NaOH and either Na_2SiO_3 or RHA. The pastes were characterized for mechanical strength, XRD, FTIR and SEM. The findings showed that RHA can be used to yield alkali-activated material.

2. Materials and method

Kaolin, Sodium metasilicate nonahydrate, ($Na_2SiO_3.9H_2O$) with 95.0 % and has percentage composition of (Na_2O = 21.8 %, SiO_2 = 21.13 % and H_2O = 57.0 %) from a central drug house. Pellet of sodium hydroxide, (NaOH) Analytical reagents From H.K. Chemical Reagent Co.LTD with 99.0%. Sulphuric acid, ($H2SO_4$) AR from (JHD Company) 97-99 %. Mechanical strength tests were conducted by a triaxial frame compression machine. X-ray fluorescence analysis was conducted using ARL QUANT'X EDXRF Analyzer. X-ray diffraction analysis was conducted using an Empyrean XRD machine. Fourier transform infrared spectroscopy was analyzed using Agilent technology FTIR machine (630). Scanning Electron Microscope (SEM) was conducted using SEM 800-07334. Thermogravimetric (TGA) analysis was done by a Perkin Elmer thermal analyzer with a heating rate from 30 ^{0}C to 950 ^{0}C at 10 ^{0}C/min under a nitrogen atmosphere. Sample Collection and Pretreatments: The sample (Kaolin) was obtained from Tsaunin Danmarke, Katsina State. It was sieved using 150 μm mesh and calcined at 700 ^{0}C for two hours to convert to metakaolin [26]. Millet husk was obtained from Batsari road, Katsina State, purified, and heated to ash at 700 ^{0}C using Muffle Furnace. Both the metakaolin and the ash were analyzed by X-ray Fluorescence. Determination of specific gravity (Sp): Specific gravity (Sp) was determined according to the procedure reported by [31] it was calculated using equation 3;

$$\mathrm{Sp\ (g/cm3)} = \frac{\mathrm{WPS - WP}}{\mathrm{WPS - WP + (WA - WB)}} \qquad \text{Eqn. 3}$$

WP = mass of empty, clean and dry pycometer
WPS = mass of pycometer bottle containing the dry sample.
WB = mass of pycometer containing the dry sample and distilled water
WA = mass of pycometer bottle filled with distilled water only

Determination of Loss on ignition: The procedure reported by [34] was adopted and the loss on ignition was calculated using equation 4;

$$\% \text{ loss on ignition} = \frac{\text{loss in weight}}{\text{weight of original sample}} \times 100 \qquad \text{Eqn. 4}$$

Formulation of Inorganic Polymer (Geopolymer): The method reported by [25] [33] [35] was adopted with slight modifications. 10 % of the activator is used in this study to activate (90 g) of metakaolin. The geopolymer pastes were formulated according to standard practice [9]. Acid resistance test for the synthesized geopolymers: The method reported by [21] [30] [40] was adopted. This type of test was conducted by the immersion of 4-weeks cured geopolymers in 5 % (H_2SO_4) for 4 days. The weight and compressive properties were measured after the immersion. The chemical stability of the synthesized geopolymers was analyzed and characterized by FTIR, SEM, XRD, and TGA. Evaluation of water absorption (WA): The cured samples were dipped in water at 26 ^{0}C for 1 day. The samples were removed and saturated weight (WS), of the specimen was measured, all the samples were dried at 105 ^{0}C for 1 day, and dry weight was also measured (Wd) [24] [35]. The WA can be calculated using equation 5;

$$\text{WA} (\%) = \frac{\text{WS} - \text{Wd}}{\text{Wd}} \times 100 \qquad \text{Eqn. 5}$$

Physicochemical analysis: Slump tests were conducted according to British adoption for European standards. The setting time test is by [13] a metallic mold called a slump cone is used to determine the free flow or slump of the material and a vicat apparatus is used to identify both the final and initial setting time.

3. Results and discussion

Table 1. Chemical constituents of metakaolin and millet husk ash.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	CaO	P_2O_3	SO_3	TiO_2
Metakaolin	51.31	38.76	1.62	2.08	4	0.04	0.11	0.51	0.04
MHA	57.01	3.71	0.92	16.24	4.51	2.01	4.5	3.39	0.07

The kaolin was converted to calcined kaolin (metakaolin) at 700 ^{0}C for two hours [26] and the millet husk was heated to ash at 700 ^{0}C [3]. The percentage composition of each oxide was determined as shown in Table 1. It was observed that the total of SiO_2, Al_2O_3, and Fe_2O_3 in metakaolin was found to be 91.69 % and 69.64 % for Millet husk ash (MHA), these percentages have met the requirement to act as pozzolana similar to the literature described by[12] which stated that a reactive SiO_2 is not be less than 25 % by mass [3] Based on this requirement both the metakaolin and millet husk ash qualifies the grading for pozzolana.

Table 2. Physical properties of metakaolin and millet husk ash.

Properties	Metakaolin	MHA
Colour	Pink	Grey
specific gravity (g/cm3)	2.33	2.10
loss on ignition (%)	1.06	5.70

Table 2 explains the physical properties of the starting materials. It was observed that millet husk ash had a higher value of a loss on ignition compared to the metakaolin this is attributed to the fact that during the calcination of kaolin, most of the moisture and organic matter were decomposed. The specific gravity of metakaolin was found to be 2.33 g/cm^3 and that of millet husk ash was 2.10 g/cm^3, this was close to the result obtained by [3] [26] reported 2.23 g/cm^3 as the specific gravity of guinea corn husk ash and 2.64 g/cm^3 for metakaolin respectively).

Table 3. Properties of synthesized sodium silicate geopolymers (SSG) and millet husk geopolymers (MHG).

Properties of geopolymers	SSG	MHG	ASTM Standard
Initial Setting Time (Minutes)	210.00	300.00	≥60
Final Setting Time (Minutes)	250.00	360.00	≤ 600
Slump test (mm)	30.00	40.00	-
pH after immersing in water	8.83	9.17	-
pH before and after immersing H_2SO_4	2.94/3.29	2.94/3.01	-
Water absorption (%)	15.00	17.10	-

Table 3 presents the properties of sodium silicate geopolymers (SSG) and millet husk ash geopolymers (MHG). The results obtained for slump and setting time tests indicated that SSG has lower values for both slumps, and setting time as observed in Table 3. This is because during the formulation of SSG, more heat was released (exothermic reaction) due to the excess of Na_2O presence in Na_2SiO_3 and NaOH but in MHG only NaOH was used. This is attributed to the fact that the reactive oxide presence in the Na_2SiO_3 led to the development of sodium aluminosilicate hydrate gel (NASH) therefore the paste tends to set rapidly in SSG.

The flowability and setting time decrease due to an excess amount of Na_2O [35]. It was determined by this experiment, that the pH of all the geopolymers was basic as observed in Table 3. The pH of both the geopolymers after immersion in both acid and water was found to increase and this indicated that the NaOH presence dissolved in water and formed a basic solution while for the acid resistance test, it was indicated that Na_2O raised the pH of the acid which confirmed the basic nature of the materials. The water absorption was conducted to measure the durability of the produced geopolymers. As observed from Table 3, SSG possesses a low amount of water absorption when compared to MHG. This signifies that the NASH gel presence in SSG makes the structure dense and contains small pores that allow the penetration of water compared to MHG. This work is similar to the studies of [24] [39] where they determined that higher alkali contents significantly develop mechanical strength with the reduction of absorbed water. [24] also described that ambient curing signifies lower water absorption than heat curing this is the reason that all the geopolymers have slightly higher values for water absorption due to oven curing at 60 ^{0}C was adopted.

Table 4. Mechanical strength of produced geopolymers after 1 and 4 weeks of curing.

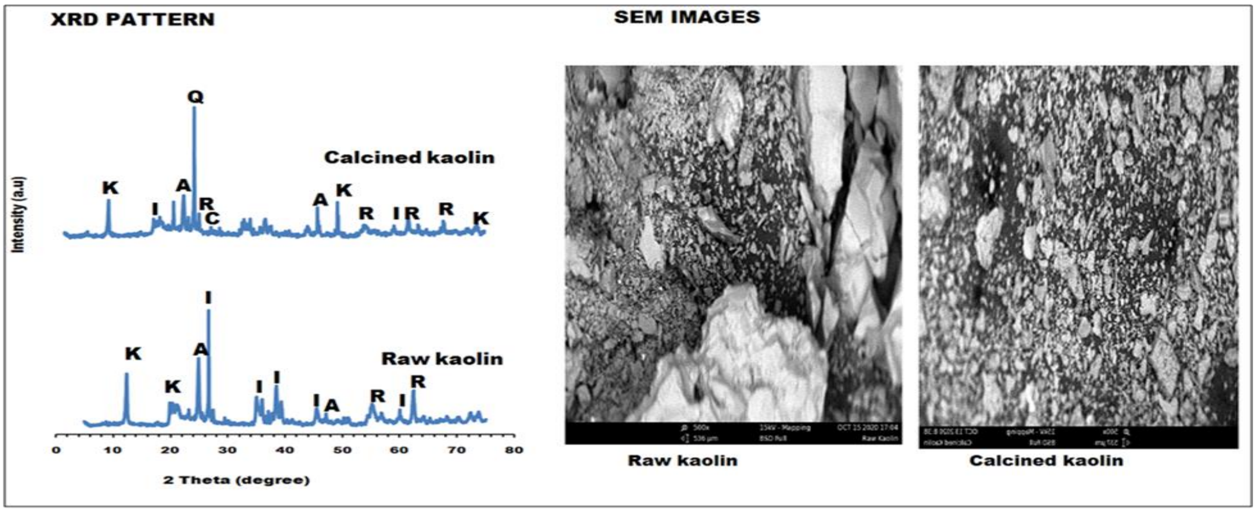
Mechanical Strength Test	SSG	MHG
Compressive Strength after 1week	3.73	2.28
Compressive Strength after 4 weeks	17.06	13.5
Flexural strength after 1week	0.47	0.3
Flexural strength after 4 weeks	2.31	1.14

The Mechanical strengths were determined at 1 and 4 weeks of ambient curing as shown in Table 4. The good mechanical strength possessed by geopolymers was due to the heat curing at 60 ^{0}C akin to the report made by [10] [41] which described that heat curing gives better compressive strength than ambient curing. The heat may help the binder to dissolve in the activator as a result of the addition of water to form a hydroxylated form of aluminosilicate precursor which later undergoes a Polycondensation reaction to form a geopolymer backbone. The results revealed that SSG had higher mechanical strength with maximum compressive and flexural strength at 4- weeks of curing compared to MHG as observed in Table 4. The highest mechanical strength was similarly reported by [10] [27]. The higher amount of Na_2O in SSG increases the reactivity of metakaolin due to faster dissolution and improved polymerization and hardening of the gel phase thereby producing good mechanical properties geopolymers [39].

Table 5. Absorption bands of FTIR spectra of metakaolin and produced geopolymers.

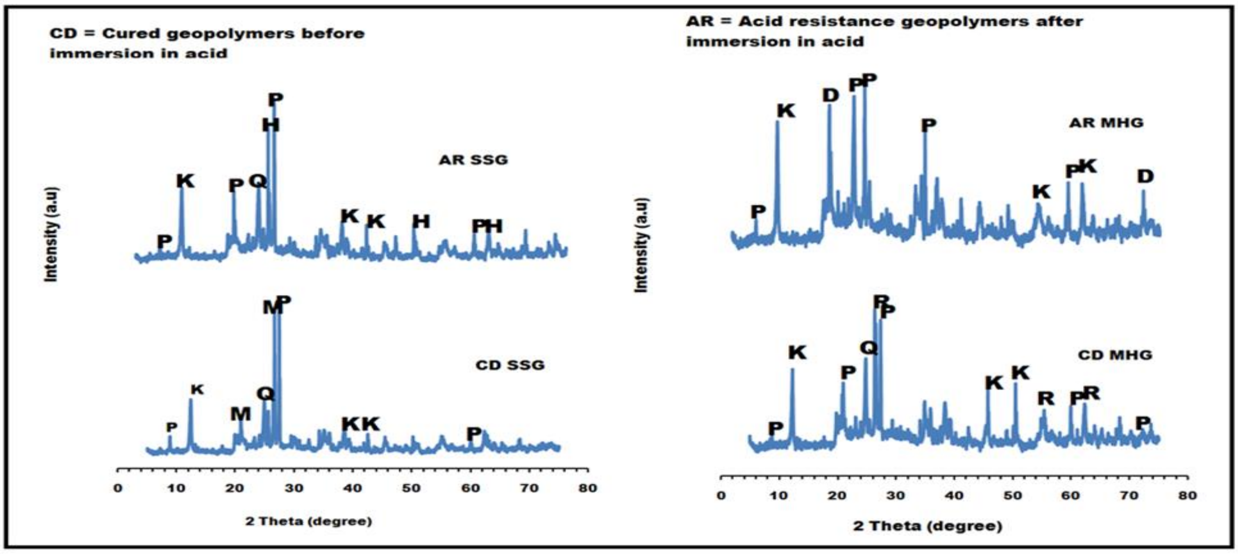
Type of bond	Raw/Metakaolin	SSG before/after immersion in H_2SO_4	MHG before/after immersion in H_2SO_4
δ -O-H	3685/3622	3361/3335	3361/3346
ν H-O-H	-/-	1640/1640	1640/1640
δ Si-O and Al-O	-/-	1398/disappeared	1391/disappeared
δSi-O-T(T=Si or Al)	1026/1011	981/1004	940/1004
νSi-O-T(T=Si or Al)	754/754	747/750	747/750

The presence of a signal at the band region of 3685 cm^{-1} can be described as the stretching vibration due to the hydroxyl group present in the raw kaolin. This frequency had moved to the lower band of 3622 cm^{-1} in the metakaolin, this indicated that the calcinations have reduced the traces of water and the band at 1026 cm^{-1} had moved to 1011 cm^{-1} as indicated in Table 5. Furthermore, [38], explained that the band appearance from 1000 cm^{-1} – 1023 cm^{-1} indicates an amorphous nature of Si-O of the starting materials which corresponds to the 1011 cm^{-1} broadband observed in the metakaolin of the samples. In the formation of SSG and MHG, the presence of broadband of the -OH band at approximately 3361 cm^{-1} and 1640 cm^{-1} in both SSG and MHG were due to the stretching and bending vibration of the hydroxyl group respectively. These bands indicated the generation of geopolymerization products (NASH) [16], [29]. The band that appeared at Si-O-T at 1011 cm^{-1} reduces to a smaller wave number as observed from the table and these bands tend to accelerate and improve geopolymerization reaction [4]. Therefore shifting of peaks toward decreasing wave number is an indication of a geopolymerization reaction in which there may be an interaction between the binder and the activator during the reaction [11], [40]. The formation of new peaks in both SSG and MHG confirmed the formation of geopolymers [22].



K-kaolinite, Q-quartz, C-calcite, A-anatase, I-illite, R-rutile.

Fig 1. XRD and SEM images of the raw and calcined kaolin.

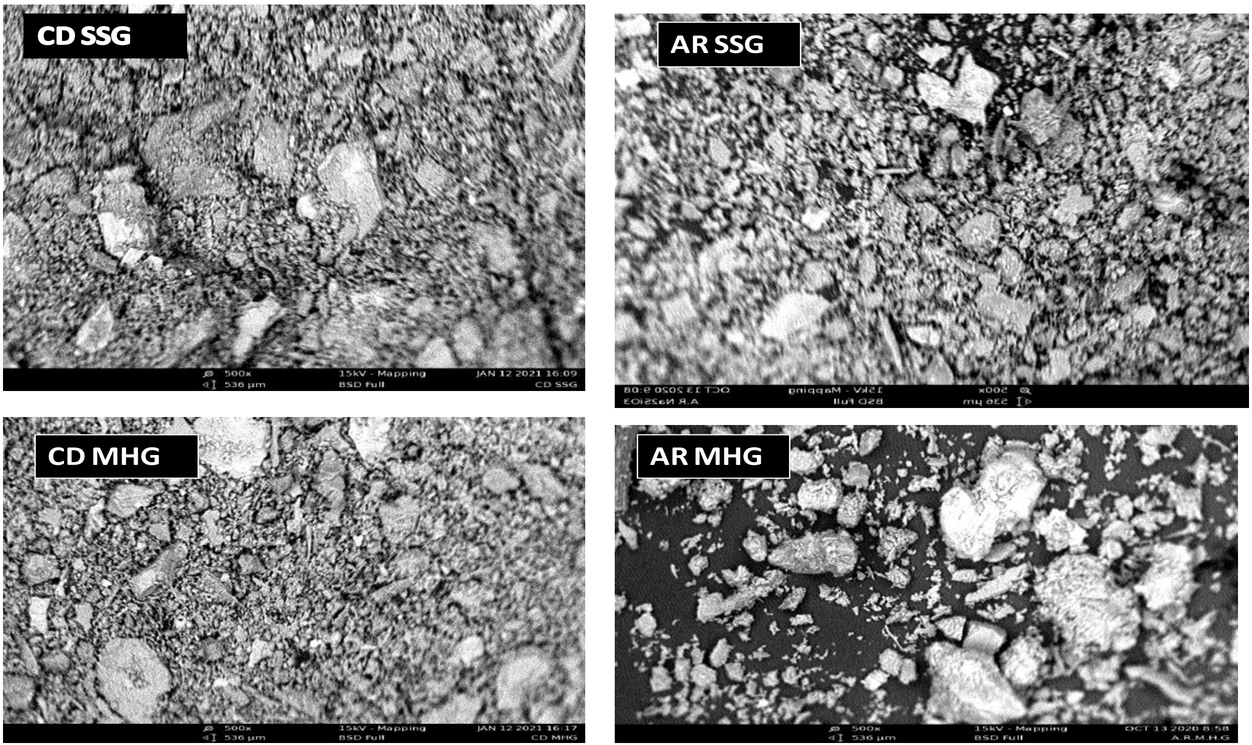


K-kaolinite, Q-quartz, R-rutile, H-Hedenbergite, D-dravite, P-phlogophite, and M-microcline

Figure 2. XRD pattern of calcined kaolin, SSG and MHG before and after immersion in acid.

X-ray diffraction (XRD) was presented in both Figures 1 and 2. The analysis was performed to identify the crystallinity of the samples. As observed from the results kaolin has four different crystals named kaolinite, ($Al_2Si_2O_5(OH)_4$ at 120), illite, ($K_{4.00}Al_{16.00}Si_{8.00}O_{48.00}$ at 190), anatase ($Ti_{4.00}O_{8.00}$ at 250) and rutile, ($Ti_{2.00}O_{4.00}$ at 270), and two different crystals were formed after calcination that is quartz (SiO_2 at 260), and calcite, ($CaCO_3$ at 290), which may be attributed due to the exposure to a higher temperature during calcination and the formation of calcite was attributed due to the surface carbonation and metakaolin was found to have a small quantity of calcium oxide as shown by XRF analysis and this leads to the formation of calcite crystal. The presence of these crystals indicated incomplete calcinations as observed by FTIR analysis. The small rise observed in the XRD pattern at 2 theta between 180-340 indicated that the metakaolin contained an amorphous structure that can take part during chemical reactions [6], [16].

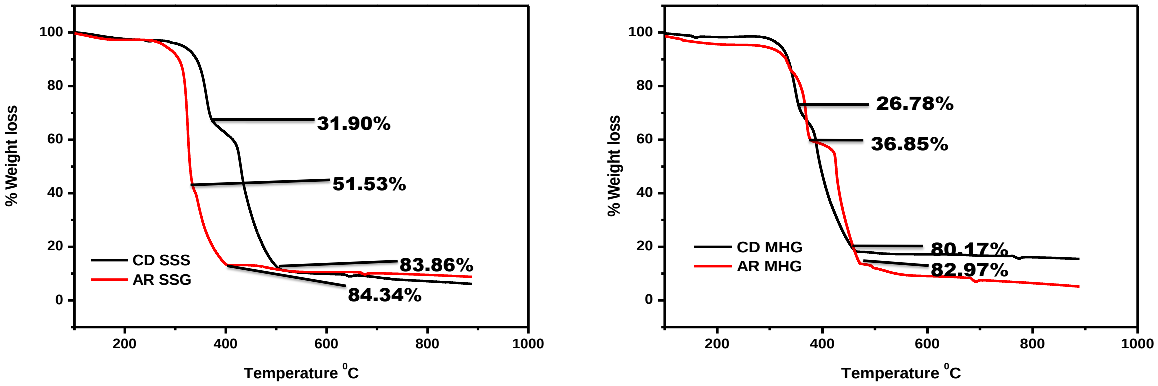
Figure 2 described that some of the crystals present in metakaolin disappeared and the formation of new crystals was also observed which indicated that a chemical reaction had occurred between the binder and the activator. Kaolinite, quartz and rutile do not participate in the geopolymerization and remain as impurities in geopolymeric matrix It was observed that the peaks found in MHG are more intense with the formation of phlogopite, ($KMg_3(AlSi_3O_{10})(OH)_2$ at 80) unlike SSG the peaks are less intense with the formation of phlogopite and microcline, ($KAlSi_3O_8$ at 270), this showed that silica and alumina in the raw materials and activator undergoes a chemical reaction better in SSG than MHG which make the SSG have good mechanical properties. The XRD also supported FTIR results whereby the shift of peaks corresponds to the new crystal formation in the geopolymers matrix.



CD = Cured geopolymers before immersion in acid and AR = Acid resistance after immersion in acid

Figure 3. SEM Images metakaolin, SSG and MHG before immersion (CD) and after immersion (AR) in acid.

The morphology of the raw kaolin as observed in Figure 3 was different from that of metakaolin due to variation in particle size after calcination which reduces the particle size. The metakaolin was observed to have a heterogeneous mixture with smaller particles scattered all over the structure this showed a crystalline surface and amorphous structure with small pores embedded in the structure. It was observed that the produced geopolymers have a dense-gel-like matrix which indicated the dissolution of the metakaolin aluminosilicate matrix in the activator [20]. The images showed that not all the materials were reacted. The unreacted materials indicated that a partial reaction had taken place in the system. These results also agreed with the water absorption which described that lower water absorption for SSG was attributed to the dense structure with small pores inside the matrix, unlike MHG.



CD = Cured geopolymers before immersion in acid and AR = Acid resistance after immersion in acid

Figure 4. TGA thermogram of SSG and MHG before immersion (CD) and after immersion (AR) in acid.

Thermogravimetric analysis was presented in Figure 4, from the thermograms, it was found that both the geopolymers produced have two main degradation patterns the first decline in both the geopolymers was associated with the dewatering process this is where free water and adsorped water presence in the geopolymer were removed [14]. The second degradation might be due to the dehydration of closely bound hydrated water found in NASH matrix [36]. The high contents of hydrous phases (NASH) are the result of high contents of alkali additives which allow the dissolution of metakaolin network forming Si^{4+} and Al^{3+} ions thereby increasing compressive strength and cementing activities of one-part geopolymers[1]. Therefore, the total percentage in weight decomposed by SSG was found to be 83.86 % and this makes it have higher NASH with better compressive strength with slightly less thermal stability compared to MHG with 80.17 %.

Table 6. Percentage weight loss of produced geopolymers after immersion in acid.

Acid resistance Test	SSG	MHG
Weight before immersion	243.18	246.02
Weight after immersion	221.6	220.8
% Loss in Weight	8.87	10.25
Comp. Strength before immersion	17.06	13.5
Comp. Strength after immersion	12.83	9.67
% Loss in Compressive Strength	24.79	28.37

Table 6 describes the loss in weight and compressive properties of the samples after the acid resistance test. It was shown that the loss of weight and compressive properties of SSG was lower compared to that of MHG. This loss in weight was explained by FTIR, SEM, XRD and TGA. The new peaks found in SSG and MHG disappeared and a shift of the peak of Si-O-Si or Si-O-Al to a higher band is shown in Table 5. This shift of peaks indicated partial depolymerization of the amorphous gel matrix and this resulted in loss of compressive properties of the geopolymers [28]. It was observed from XRD analysis, that the microcline crystal presence in SSG was dissolved and formed a new crystal called hedenbergite, ($CaFeSi_2O_6$ at 290) while in MHG quartz and rutile were dissolved and another crystal was formed called dravite, ($Na(Mg_3)Al_6(Si_6O_{18})(BO_3)3(OH)_3Fe(OH)_2$ at 340) and all new crystals were formed by the XRF results of the starting materials. The peaks that appeared in geopolymers after immersion were observed to be very intense compared to the geopolymers before immersion and this also led to the reduction of mechanical properties. The SEM images showed some deterioration of some parts as observed in Figure 3 which may be due to the destruction of Al-O and Si-O bands as determined by FTIR analysis. And this makes the strength of the geopolymers to be reduced. The TGA results described that the total percentage of weight decomposed by AR SSG was found to be 84.34% and 82.97 % for that of MHG, the presence of alkali in the binder or in the activator is responsible for neutralizing the acid thereby stopping the sample from further destruction [40].

4. Conclusions

Finally, based on this study the replacement of sodium silicate with millet husk ash was effective as confirmed by characterizations and It was determined that the highest compressive properties of 17.06 N/mm^2 were obtained for SSG and 13.50 N/mm^2 for MHG after 4-weeks of curing and these were met with the international standard for making cementing materials.

5. Acknowledgement

Special thanks goes to my beloved institution Umaru Musa Yar'adua University for the support and sponsorship of my research work, I would like to extend my gratitude to the Department of Civil Engineering Hassan Usman Katsina Polytechnic Katsina and Bayero University Kano for their assistance during mechanical strength tests and also special thanks and appreciation to my family and friends for their support and encouragement for the successful completion of the research work, finally my sincere appreciation to the Journal of Material Characterization and Applications for their sacrifice to make the research work to be published as recognized paper.

References

[1] H. A. Abdel-Gawwad and S. A. Abo-El-Enein, A novel method to produce dry geopolymer cement powder, HBRC Journal, **12**(1), 13-24, (2016).

[2] M. Abdelmawla, A. Abdelaal, M. Beheary, N. Abdullah, and T.A Razek, Solidification of alum industry waste for producing geopolymer mortar, Egyptian Journal of Chemistry **63**(11), 4285-4294, (2020).

[3] T. Alkamu, E. P. Datok, and D. D. Jambol, Guinea corn husk ash as partial replacement of cement in hollow concrete block production, Journal of Emerging -trends in Engineering and Applied Sciences **8**(6), 263-268 (2017).

[4] M. H. Al-Majidi, A. Lampropoulos, A. Cundy, and S. Meikle, Development of geopolymer mortar

under ambient temperature for in situ applications, Construction and Building Materials **120**, 198-211, (2014).

[5] American Society for Testing and Materials Standard Specification for Testing Pozzolanas. J. ASTM Int. ASTM C618 The USA (2001).

[6] S. Andrejkovičová, A. Sudagar J. Rocha C. Patinha W. Hajjaji, E. Ferreira da Silva, A. Velosa and F. Rocha, The effect of natural zeolite on microstructure, mechanical and heavy metals adsorption properties of metakaolin based geopolymers, Applied Clay Science **126**, 141–152 (2016).

[7] E. Arioz, O. Arioz, and O. Mete Kockar, An Experimental Study on the Mechanical and Microstructural Properties of Geopolymers, Procedia Engineering **42**, 100-105, (2012).

[8] L. Assi, Understanding geopolymerization process for enhancement of mechanical properties of fly ash based-geopolymer concrete. Doctoral Dissertation, https://scholarcommons.sc.edu/etd/4981 (2018).

[9] ASTM C Standard Practice for Mechanical Mixing of Hydraulic Cement 305-14 (2014). Pastes and Mortars of Plastic Consistency, J. ASTM Int., West Conshohocken, PA.

[10] O. Ayeni, Performance of a Nigerian metakaolin-based geopolymer as a sustainable building material. A Thesis presented to the Department of Materials Science andEngineering. African University of Science and Technology, Abuja Nigeria. www.aust.edu.ng (2017).

[11] T. Bai, Z. Song H. Wang Y.C. Wu and W. Wei Huang, Performance evaluation of metakaolin geopolymer modified by different solid wastes, J. Cleaner Prod. **226**, 114-121, (2019).

[12] BS EN British Standard Institution, Cement Composition, specification and conformity criteria for common cement. London 197-1 (2000).

[13] BS EN British Standard Institution, Admixtures for concrete, mortar and grout. Test methods for Determination of setting time 480-482 (2006).

[14] A. Carlos, P. Susana J. M. Arredondo-Rea, J. Gómez-Soberón, L. Alamaral-Sánchez, M. Ramón Corral-Higuera, J. Chinchillas-Chinchillas, and H.A.T. Octavio, Experimental study of XRD, FTIR and TGA techniques in geopolymeric materials, International Journal of Advances in Computer Science & Its Applications – IJCSIA **4**(4), 221–226 (2014).

[15] C. Chen, G. Habert, Y. Bouzidi and A. Jullien, Environmental impact of cement production: detail of the different processes and cement plant variability evaluation. J. Clean. Prod. **18**, 478–485 (2010).

[16] L. Chen, Z. Wang, Y. Wang, and J. Feng, Preparation and properties of alkali-activated metakaolin-based geopolymers, Materials. **9**(9), 767 (2016).

[17] O. M. Damilola, Syntheses, characterization and binding strength of geopolymers: a review, International Journal of Materials Science and Applications **2**(6), 185-193 (2013).

[18] N. Das Bheel, F. A. Memon, S. L. Lal Meghwar, A. Abro, and I. Ali Shar, Millet husk ash as environmentally friendly materials in cement concrete, Energy, EESD 5th International Conference, Jamshoro, Pakisan. doi:10.1016/j.conbuildmat.011.12.079 (2018).

[19] N. Doğan-Sağlamtimur, A. Bilgil, M. L. Demir, S. Yılmaz, M. Polat, E. Özen, and H. Halil Dördü, A reuse study from Niğde, Turkey: the conversion of industrial ash to geopolymers, Desalination and Water Treatment, **57**(6), 2604-261 5(2015).

[20] M. El-Alouani, S. Alehyen, M. El Achouri, and M. Taibi, Preparation, characterization, and application of metakaolin-based geopolymer for removal of methylene blue from aqueous solution, Journal of Chemistry, **2019**(1), 4212901 (2019).

[21] H. R. Gavali, and R.V. Ralegaonkar , Evaluation of developed alkali-activated bricks for energy-efficient building construction, Proceedings of the Institution of Civil Engineers – Energy, **173**(4), 177-183 (2020).

[22] X. Guo, H. Shi,and W.A. Dick, Compressive strength and microstructural characteristics of class C fly ash geopolymer. Cem Concr Compos. **32**, 142–147 (2010).

[23] A. Hasanbeigi, C. Menke and L. Price, The CO_2 abatement cost curve for the Thailand cement industry, J. Clean. Prod. **18**, 1509–1518 (2010).

[24] G. F. Husein, J. Mirza, M. Ismail, M. W. Hussin, M. A. M. Arrifin, and A. A. Hussein, The effect of sodium hydroxide molarity and other parameters on water absorption of geopolymer of mortars, Indian Journal of Science & Technology, **9**(48), 1-9 (2016).

[25] V. Jittin, and A. Bahurudeen, Production of cleaner binders by reusing agricultural by-products: an approach towards zero cement concrete for sustainable future infrastructure, J.

Cleaner Prod. **451**, 141990 (2024).

[26] W. I. Khalil, Q. J. Frayyeh, and M. F. Ahmed, IOP Conf. Series: Materials Science and Engineering, **518**(2), 0222053 (2019).

[27] M. Kheradmand, Z. Abdollahnejad and F. Pacheco-Torgal, Performance of a fly ash geopolymer based binder with calcium hydroxide, portland cement and metakaolin as additives. The Open Civil Engineering Journal, **12**,167-186 (2018).

[28] Y. M. Liew, H. Kamarudin, A. M. Mustafa, M. Al Bakri Luqman, I. KhairulNizar, C. M. Ruzaidi and C. Y. Heah, Processing and characterization of calcined kaolin cement powder,Construction and Building Materials **30**, 794–802 (2012).

[29] C. Ma, B. Zhao, S. Guo, G. Long, and Y. Xie, Properties and characterization of green one-part geopolymers activated by composite activators. J. Cleaner Prod. **220**, 188-199 (2019).

[30] A. I. Maulana, N. K. Wardani, D. Syamsidar. A. Ariani, B. Nurfadila, and C. Subaer, Development of hybrid composite rice husk (RHA) geopolymer for bricks bearing buildings, MATEC Web Conf. 97, (2017).

[31] M. A. Mustafa Al Bakri, K. Hussin, M. Bnhussain, K, Ismail, Z. Yahya,and R. Abdul Razak, Fly Ash-based geopolymer lightweight concrete using foaming agent, Int. J. Mol. Sci. **13**(6), 7186-7198 (2012).

[32] B. C. McLellan, R. P. Williams, J. Lay, A. Arie van Riessen, and G. D. Corder, Costs and carbon emissions for geopolymer pastes in comparison to ordinary Portland cement, J. Cleaner Prod. **220**, 188-199 (2011).

[33] J. M. Mejia, R. M. Gutierrez and F. Puertas, Rice husk ash as a source of silica in alkali-activated fly ash and granulated blast furnace slag systems, Materials de Construction **63**(311), 361-375 (2013).

[34] K. Mudavath, ASTM loss on ignition. ASTM 114 and AASHTO T 105, (2018).

[35] B S. Muhammad, S. Haruna, M. M. A. Wahab, M. S. Lie W, and A. Haruna, Mechanical and microstructural properties of high calcium one-part geopolymer cement made with granular activator, Heliyon 5(9), e02255 (2019).

[36] M. X. Peng, Z. H. Wang, Q. G. Xiao, F. Song, W. Xie, L. Cai Yu, H. W. Huang and S. J. Yi, Effects of alkali on one-part alkali-activated cement synthesized by calcining bentonite with dolomite and Na_2CO_3. Applied Clay Science **139**, 64–71 (2017).

[37] A. E. Rojas-Martínez, J. R. González-López, M. A. Guerra-Cossío, and G. Hernández-Carrillo, Sulphatebased activation of a binary and ternary hybrid cement with Portland cement and different pozzolans. Construction and Building Materials 421, 135683 (2024).

[38] T. Suwan, Development of self-cured geopolymer cement. A thesis submitted for the degree of Doctor of Philosophy in the Department of Mechanical, Aerospace & Civil Engineering Brunel University London (2016).

[39] S. Thokcom, P. Ghosh, and S. Ghosh, Effect of water absorption, porosity and sorptivity on the durability of geopolymer mortars, arpn Journal of Engineering and Applied Sciences **4**(7), 28-32 (2009).

[40] S. A. A. Tique, A. R. Maleb, R. J. Dunca, D. E. Yu and B. A. M. Promentilla, Chemical stability and leaching behavior of one-part geopolymer from soil and coal fly ash mixtures, Minerals. **8**(9), 411 (2018).

[41] K. Vijai, R. Kumutha, and B. G. Vishnuram, Effect of type of curing on strength of geopolymer concrete, International Journal of the Physical Sciences. **5**(9), 1419-1423 (2010).