Valorization of siliceous wastes of alum industry as an additive for geopolymer cement

Nabil Abdullah

Tarek El-Sokkary

m Gharieb (✉ medo_20109129@yahoo.com)

<https://orcid.org/0000-0001-9913-6220>

Research Article

Keywords: de-aluminated metakaolin (DK), geopolymer, metakaolin, compressive strength, microstructure.

Posted Date: March 7th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1389979/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

In this study an experimental work has been done to test the feasibility of using siliceous wastes of de-aluminated metakaolin (DK) with metakaolin (MK) in the production of geopolymer concrete. The chemical composition and physical properties of de-aluminated metakaolin was tested. For this purpose, metakaolin (MK) was partially substituted with de-aluminated metakaolin (DK) at ratios of 0–60% by weight. The compressive strength was measured by testing standard cubes at 7 and 28 days. The effect of DK on specific gravity, porosity and mechanical characteristics were tested. The internal microstructure, and hydration were investigated by using modern instruments such as, thermogravimetric/thermogravimetric derivative (TGA/TGA), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The findings assure the potentiality for the application of DK as a pozzolanic material. The results showed that the de-aluminated meta-kaolin mixture is a good pozzolanic material.

1. Introduction

Geopolymer is an excellent material for veneer stone fabrication, since it can be casted in situ at the ambient temperature like ordinary concrete but of higher surface quality. Colored geopolymer paste can be fabricated by using meta-kaolin and various pigments. Geopolymer product has better resistance against acid and heat compared to Ordinary Portland Cement (OPC) concrete or mortar [1–4].

Natural stones and OPC can be replaced by geopolymer cement with better physical and chemical properties such as acid and saline water resistance, early development of mechanical strength [5–7].

Geopolymer concrete was patented by clay minerals such as kaolin can be used as alumina and silica for preparation of geopolymer through the activation with alkaline silicate solution [8–10]. It's commonly carried out by the interaction of a fine ground aluminum silicate materials with an alkali metal silicate solution at room temperature forming polymer chain ($-\text{Si}-\text{O}-\text{Al}-\text{O}-$) [11, 12]. Geopolymer concrete is an effective replacement. Geopolymer is a type of amorphous aluminous-siliceous cementitious material which can be produced by polymerization reaction of aluminum silicates materials with alkaline solutions. Geopolymeric concrete can be produced by using of pozzolana, which is waste materials obtained from various activities. The numerous characteristics of inorganic polymer can be determined from civil works in term of the mechanical characteristics such as compressive strength for geopolymeric binder and concrete, resistance to chemicals attack [13–16] excellent repairing substances for ancient constructions, to the modern applications in aircraft which utilizes the nature for anti-fire characteristics of the geopolymer blends ([17, 18]. Various geopolymer blends doesn't ignite, or evolve gases even after extended exposure of heat. Therefore, they are excellent inert materials for aircraft lining cabins, floor panels, sidewalls, and insulators for wires [19, 20].

The inorganic and physical chemistry, with other geological science such as mineralogy, geochemistry and engineering, utilized the unique characteristics of geopolymer. The potential applications of geopolymer includes: refractory, low energy ceramic tiles, tech composites for aircraft interior and automobile decoration artifacts, thermal insulation, thermal shock refractories, concretes, certain blends for construction repairing and supporting, radioactive and toxic waste containment immobilization, archaeological restoration [21–24].

Metakaolinite is a greatly utilized as a one of the precursors starting for manufacturing of geopolymeric binder, and is produced by calcination of kaolinite clay. The thermal treatment of clay minerals in the range from 600 up to 800°C causes dehydroxylation of from the internal structure of the clay mineral. The coordinated hydroxyl groups of the octahedral aluminate sheet are lost and the structure becomes disordered meta-phase in which the internal crystalline structure of clay minerals is collapsed. The stable phase of the distorted kaolinite is reactive and is called pozzolanic material [25, 26]. Calcination of kaolinite at higher temperatures causes reorganization of the internal structure and crystallization forming spinel and mullite minerals [27, 28]. Several studies have reported the using of byproduct or waste materials in the manufacturing of geopolymer concretes, such as fly ash and granulated slag as a aluminum silicate materials [29, 30]. This reaction yields water, while in OPC hardening, water is required for startup of hydration reactions. Upon heating of OPC concrete at 300 °C, dehydration takes place yielding dehydrated products causing shrinkage and formation of calcium oxide and carbonation of calcium at 500 °C, further

heating up to 800 °C calcium carbonate decomposes forming caustic lime, while, geopolymer become stable up to 1000 °C. Ordinary Portland Cement (OPC) is the primary ingredient in concrete of structure of the buildings, and the roads and bridges. Production of cement releases the major greenhouse gas CO₂. Heating of limestone release CO₂, while the burning of fossil fuels for kilns results in CO₂. Hence to reduce CO₂ emissions it is very much required to find an alternative for cement [31, 32].

De-aluminated metakaolin (DK) is a by-product of aluminum sulphate industry and it derives from acid leaching of metakaolin (MK) (e.g. calcined kaolin, Al₂O₃·2SiO₂). As result of the de-alumination process, the SiO₂/Al₂O₃ ratio and B.E.T. values are increased. The increasing of specific surface observed as consequence of acid attack was found due to the increasing of the pore volume without an appreciable increasing of the mean pore size distribution [33].

It was found that mixing of DK and lime and using isothermal calorimetric tests, DK shows an appreciable pozzolanic activity [34, 35]. The pozzolanic activity of DK in blended cements was also demonstrated by the same method. They also reported that DK exhibits higher B.E.T values than silica fume. Other researchers have also shown that the porous structure of calcined kaolin particles doesn't collapse owing to the acid attack [36].

Zhang et al. [37] investigated the effect of the three key ratios "SiO₂/Al₂O₃, M₂O/Al₂O₃, H₂O/M₂O" on the production of metakaolinite-based geopolymers, where M is alkali metal ions (Na⁺ or K⁺). Several blends of different mole ratios SiO₂/Al₂O₃, Na₂O/Al₂O₃, H₂O/Na₂O were adopted to examine their impacts on the mechanical strength. The results of all tests that were obtained exhibit that the ratios Na₂O/Al₂O₃ and H₂O/Na₂O had direct impact on the compressive strength. It was found that highest compressive strength (34.9 MPa) was recorded at a ratio SiO₂/Al₂O₃ = 5.5, Na₂O/Al₂O₃ = 1.0 and H₂O/Na₂O = 7.0. These ratios achieved complete geopolymerization reaction. Our study showed that the compressive strength increases with increase in quantity of DK to reach maximum at SiO₂/Al₂O₃ = 2.8, Na₂O/Al₂O₃ = 0.9 and H₂O/Na₂O = 13.7. These ratios may differ from the above, this attributed to the raw materials and the preparation of alkaline silicates from DK, and so, the compressive strength of the concrete relies upon the quantity of activated aluminum silicates materials in the precursors, the activating solution type and the curing temperature as reported by [38, 39] confirmed the usability of metakaolin as the starting material for Geopolymers, their works reviewed that curing metakaolin based geopolymer at low temperatures retards the development of compressive strength. From the above results obtained, it was noted that there is no need for higher temperature curing, whereas activation was preceded properly. Geopolymer concrete produced show higher compressive strength without need to add sodium silicate, as sodium silicate was formed during activation process as a result of the chemical reaction between activated silicate in DK and the stoichiometry amount of sodium hydroxide. Workability of geopolymer concrete is very low at the nominal blends. So, superplasticizer of any type or little excess water has to be added to facilitate workability.

In this study an experimental work has been done to test the feasibility of using industrial wastes of de-aluminated metakaolin (DK) as a cementitious-material with metakaolin (MK) in the production of geopolymer concrete. For this purpose, metakaolin (MK) was partially substituted with de-aluminated metakaolin (DK) at ratios of 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60% by weight. The compressive strength was determined by testing standard cubes at 7th and 28th day. The effect of DK on the specific gravity, porosity and mechanical characteristics were studied. The presence of crystalline components, hydration and the internal structure were tested by application of modern instruments such as, thermogravimetric/thermogravimetric derivative (TGA/TGA), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

2. Experimental Procedure

2.1. Materials

Materials used in this investigation are metakaolin (MK) was prepared in ASCE laboratory, It was produced of kaolin was supplied from Sinai for Manganese Company by thermal hydroxylation at 750°C for 2 hr. Figures 1(a, b) and the de-aluminated meta-kaolinite waste (DK) were collected from ASCE, Egypt. Aluminum oxide in DK is significantly lower than corresponding value of MK. This lead to an appreciable increase of SiO₂/Al₂O₃ ratio (from 2.00 for average value of MK to 16.7 for average of DK). In concrete mixes, sand stone was used with specific gravity 2.5. Different conditioning procedures were also adopted for DK before using it as concrete addition: DK was adopted as raw source after drying in oven at 100°C for 12 h. The dry source was

also used after further grinding; the ground source was also used after further dispersion as water slurry (ground-slurry). B.E.T. analysis revealed a high fineness for DK ($43 \text{ m}^2/\text{g}$ for DK) and the specific gravity of 1.36. Nevertheless B.E.T. results seem to be not congruent with laser granulometry test results which indicate DK being coarse whereas particle size-distribution and general view of MK and DK are plotted in Fig. 2 (a, a and b, b) which shows that the diameter of MK in cumulative % is 0 % of $\sim 8.560 \mu\text{m}$ and 0 % of $\sim 1.262 \mu\text{m}$ with an average diameter of $\sim 4.507 \mu\text{m}$. and diameter of DK in cumulative % is 0 % of $\sim 70.33 \mu\text{m}$ and 0 % of $\sim 4.329 \mu\text{m}$ with an average diameter of $\sim 9.445 \mu\text{m}$. This might be attributed to the surface texture of particles characterized by high roughness already observed by [32]. The chemical composition of (MK) and (DK) are shown in Table 1. The composition of DK of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ is about 89.33%. Hence according to IS 3812:2003 this sample can be used as a pozzolanic material (IS 3812:1981). The mineralogical characteristics of MK and DK are shown in Fig. 3 (a, b). XRD show that there is no mineral in the MK samples prepared, just only quartz impurities in the raw kaolin. XRD pattern of DK shows quartz peaks and amorphous background.

2.2. Geopolymerization and curing

Geopolymer samples were prepared by added dry materials of DK to MK in percentages of 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60% by weight, and alkali metal activating solutions (sodium silicate and sodium hydroxide) and water in a 70-L pan mixer are given in Table 2. Combination of sodium hydroxide and sodium silicate with two ratios of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (1.94 and 1.32) were applied as alkali metal activating solution in this research. Sodium hydroxide in platelet form was dissolved in distilled water to produce 11.6 M sodium hydroxide solution. While, sodium silicate of specific gravity 1.52 and a modulus silicate ratio (Ms.) of 2 (where Ms. = $\text{SiO}_2/\text{Na}_2\text{O}$, $\text{Na}_2\text{O} = 14.7\%$, $\text{SiO}_2 = 29.4\%$) was applies. For improvement of the workability of geopolymer pastes, the suitable amount of water needed for geopolymer mixing was determined, normal consistency was measured applying Humboldt Vicat's apparatus [40, 41]. The dry components of the precursors were blended firstly and the alkali activating solution were then added into the pan and mixed thoroughly for about 4 min until the mixture became glossy and well blended. The mixture was then poured into 5 cm^3 shaped moulds, vibrated for perfect compaction and insulated with a cover to prevent loss of water as most as possible. All blends were kept undisturbed for curing at the ambient temperature for (24 hrs.), demolded and then subjected to further curing at the room condition $23\text{--}25^\circ\text{C}$, and then tested for compressive strength determination. The resulted fragments were then immersed in acetone for 24 h before being dried at 60°C , and pulverized for analysis [42].

2.3. Methods of investigation

The chemical examination was done applying Axios (PW4400) WD-XRF Sequential Spectrometer, while compressive strength tests were carried out using five tones German Brűf pressing machine with a loading rate of 100 kg/min determined according to [43] XRD investigation was done on a Philips PW 3050/60 Diffractometer using a Cu-K α source with a post sample K α filter. XRD patterns were collected from 0° to 50° 2θ (step size $0.02^\circ 2\theta$ and speed $0.4^\circ/\text{min}$). Silica was used as an internal standard. Data were identified according to the XRD software.

Bulk density was calculated using the formulae ASTM D6023-16:

$$\text{Bulk Density} = D / (W - S) \text{ (g/cm}^3\text{)}.$$

Where: D = Weight of sample, S = Weight of suspended sample in water, and W = Weight of soaked sample suspended in air. The total-porosity was done at the same period of time. It was measured by the same equation applied previously in [44, 45] as follows:

$$\text{The total porosity} = \frac{W_1 - W_3}{W_1 - W_2} \times 100,$$

Whilst the percentage of absorbed water was recorded by:

$$\text{Water-absorption (\%)} = [(W_1 - W_3) / W_3] \times 100.$$

Where: W₁: saturated-weight, W₂: suspended-weight and W₃: dried-weight at $105 \pm 2^\circ\text{C}$.. FTIR used for illustration of the crystalline and the amorphous constituents of geopolymer structure using Jasco-6100 with the aid of KBr binder in the range

from 400 to 4000 cm^{-1} [46, 47].

The morphology and microstructure of hardened geopolymer composites was examined by SEM [Inspect S-FEI Company, Netherland] equipped with EDX. Thermogravimetry conducted using DT-50 Thermal Analyzer (Schimadzu Co-Kyoto, Japan), where the samples were crushed, transferred immediately to an alumina crucible, held under isothermal conditions for 60 min at 40 °C to equilibrate in a nitrogen environment (N_2 flowing at 200 ml/min), and then heated to 1000 °C at 10 °C/ min in the same gas environment.

3. Results And Discussion

3.1. Bulk-density

The density of the studied pastes increases when adding DK to MK. This clear contradiction in the density increases with increasing DK content is illustrated in Fig. 4. The presence of 25% DK (M6) increases the 28-d density by 3.53%. The increasing in the density with the presence of DK is not expected due to its relatively low specific gravity (1.36) compared to that of MK (2.5). Evidently, the density of all samples increases with addition of DK. This refers to the addition of DK which is an active pozzolanic material in the hydration reaction this could be pertaining to the building up of hydration-components that fill the pores of the solidified pastes causing rise of the bulk-density. It is worth mentioning that the fine MK powder (size 4.5 μm) lower fresh bulk-density than those containing larger particles sizes of DK (9.4 μm). This clarifies that the particle-size has a significant impact on the bulk-density.

3.2. Total-porosity and water-absorption

Figure 5 illustrates the total-porosity of the investigated specimens at 28 days. Generally, the total-porosity decreases with older hydration age. This is related to the continuous hydration and accumulation of hydration-products that occupies the available micro-pores within the binder matrix causing a pore size decreasing and reducing the total-porosity as well. As can be noticed from Fig. 7, the presence of 25% DK (M6) marginally decreases the total-porosity at 28 days as compared to the reference. This reduction refers to the filling and pozzolanic impact of the fine DK particles. These fine-particulates and hydration products can precipitate in the pores of the solidified geopolymer blend and corresponding increase in the density. Oppositely, the presence more than 25% DK increases the total-porosity. As the amount of DK increases, the total-porosity increases. This result are expected because if the amount of the finest particles is higher than the optimum packing arrangement, the packing density reduces due to the clustering, leaving fin holes in between the clusters.

Figure 6 illustrates the percentage of water-absorption by the tested specimens at 28 day. As expected, the trend of the water absorption is directly proportion with those of total-porosity. The presence of 25% DK (M6) reduces the percentage of water-absorption at 28th day, whilst the presence more than 25% increases it. As the quantity of DK increases, the water-absorption increases.

3.3. Compressive strength

Variation of compressive strength with different combinations of SiO_2 and Al_2O_3 and different ratios of Na_2O are given in Tables (3, 4) and the results are also graphically illustrated as a function of curing period in Figs. (7, 8). The results reveal that the compressive strength increases with increasing hydration time for all curing conditions due to continuous geopolymerization and hydration reactions, also the compressive strength maximize at 25% (M6) and then decreased with further addition up to 60% (M13). It was found that the addition of DK increase the compressive strength, it reach to a maximum value of 64 MPa at a percentage of 25% DK (mix 6). It was found also that addition of DK up to 55% provide satisfactory compressive strengths with 7th and 28th day. The variation of strength is indicated in Tables (3, 4) and Figs. (7, 8). DK obtained as solid waste derived after de-alumination process for production of aluminum sulfate (coagulant used in water treatment in Egypt). It was used as a source of active silica along with meta-kaolin for manufacturing of veneer tiles of geopolymer concrete. The effect of the three key ratios " $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{M}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{M}_2\text{O}$ " on the production of metakaolinite-based geopolymers, where M express the alkali metal ions (Na or K ion). A total of 13 geopolymer pastes with different mole ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ were prepared to examine the effects on mechanical strength. The gradation analysis of experimental results that were obtained revealed that

$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ had significant impact on the compressive strength. The compressive strength increases (64 MPa) with increase in quantity of DK to reach maximum at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.8$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.9$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 13.7$ these ratios were considered as fully reacted geopolymer concrete.

3.4. Thermal analysis

Figures (9, 10) show the differential thermogravimetric curves for geopolymer composites with various ratio of DK. The pattern shows the main endothermic peaks at about 80, 170, 450, and 700 °C whereas the first peak of the characteristic endotherm represents the mobilized water resulted from the polymeric reactions, localized in macro pores of the geopolymer product [48, 49], the second peak represents the dehydroxylation step of the strongly bound water in zeolite, as well as the dehydroxylation of strongly bound water in a C-S-H gel [50]. There are another endothermic peak at about 700 °C for calcium carbonates [51] resulting from the natural processes on the slag before sample preparation. The Figure illustrates the growth in the strength of endothermic peak at about 80 °C with curing time in mix M6 at 28 days as a results of continuous hydration and development of geopolymer reactions with aging, while there is a significant shifting in this endotherm to higher temperature informing the presence of aluminum silicate gel with strongly bound water within the geopolymeric chains. Through the examination of the effect of the added DK, the endotherm for free water, increased with DK addition to about 25% then exposed to be shifted to low temperature indicating the growth of amorphous geopolymer content with weakly bound free water. It can be witnessed that here is a clear endothermic peak for water escaped of C-S-H gel and aluminum silicate gel at 170 °C which increased in strength with DK addition up to 25% as a results of the building up in geopolymerization reactions which used the free silica in geopolymer production than in CSH aluminosilicate gel. A weak peak appeared at 700 °C, which refers to the destruction of carbonate into carbon dioxide [52]. There is wide peak in the carbonate endotherm at 700 °C whereas the excess free alkali metal hydroxide that is not consumed in geopolymer formation as a result of Faujasite zeolite which partially hinders geopolymerization and this may cause efflorescence. The weight loss of DK based geopolymer mixes M1, M5, M6 and M7 at 28 days were 3.429, 4.533, 5.082 and 3.536%, respectively. It can be seen the total weight loss increases with DK increase up to 25% (M6) as an indication for geopolymer synthesis.

3.5 Fourier transforms infrared spectroscopy (FTIR)

FTIR spectra of the solidified geopolymer pastes which having different ratio of DK are shown in Fig. (11). As can be seen, there are main wide bands of O-H stretching and bending located in the range of 3430–3460 cm^{-1} and 1650 cm^{-1} that characterize water of crystallization of the hydrated compounds such as C–S–H and C–A–H [53]. The band intensities of the sample M6 is relatively bigger than the other blends. These confirm the higher strength of the M6 sample. The bands located between 1420–1460 cm^{-1} representative to stretching vibrations of O–C–O bond of carbonate compounds, which resulted from the reaction of carbon dioxide with the leached out alkali hydroxide [54]. The strongest band located at 950–1100 cm^{-1} is essentially resulted from the asymmetric stretching vibration of (T–O–Si), where T is tetrahedral silicon or aluminum. As seen, the bands featured for asymmetric stretching vibration of Si–O–T located at approximately 980 cm^{-1} are displaced to a lower frequency for M6 sample. This displacement is an evidence for the formation of amorphous aluminum silicate phases, indicating to new highly cross-linked geopolymer network [55]. The intensity of the band of M6 sample is higher than the other samples. The higher intensity of the band is an indication of increasing the mean chain length of aluminum silicate polymers [56]. Furthermore, the symmetric stretching vibration (Si–O–Si) in the region of 770 cm^{-1} and 690 cm^{-1} and bending vibration (Si–O–Si) and (O–Si–O) in the region of 500 cm^{-1} band intensities of M6 sample are relatively higher than other samples.

3.6 Microstructure analyses

The micrographs of electron microscopic scanning for geopolymer pastes at the 28th day which have having different ratio of DK are shown in Fig. (5). The micrograph for control blend M1 show micro-porous matrix formation with the distribution of both CSH and geopolymer within the matrix [Fig. (5a)], while applying more DK up to 25% (M6) results in the generation of intensified homogenized geopolymer structure with growth of the amorphous (N-A-S-H) gel and the binding gels (C–A–S–H) that has advanced impact on the micro-structural characteristics forming compacted three-dimensional network from geopolymer strains [Fig. (5b)]. Adding more DK results in an increased dissimilarity with large spaces between its components causing reduction of the effectiveness of the reactions [Fig. 5c] as interpreted from the FTIR and DTG.

4. Conclusions

The following items were concluded from the study on decorative tiles fabrication made of geopolymers.

- The geopolymer concretes produced with different combination of MK and DK are able to produce decorative plates of high grades (much more than 64 MPa) by self-curing mechanisms.
- The influences of DK on strength of geopolymer paste mixes were studied. It has been observed that the increasing the quantity of DK increases the compressive strength of geopolymer to a certain limit of $\text{SiO}_2/\text{Al}_2\text{O}_3$.
- The measured compressive strength of geopolymer mix is in the range from 18 MPa to 64 MPa and maximum of 64 MPa for $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.8 and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 0.9 and $\text{H}_2\text{O}/\text{Na}_2\text{O}_3$ ratio of 13.7.
- Sodium silicate has been prepared during geopolymers synthesis by the reaction between DK and NaOH that increased the building up strength of the fabricated geopolymeric plates by inducing the activation and speciation of the siliceous and aluminum ions of the raw materials, and the self-preparation of silicates compensates shortage of silicate in the raw materials at the same time.
- Apart from less energy intensiveness, the geopolymer concrete utilizes the industrial wastes for producing the binding system in concrete. There are both environmental and economic benefits of using MK and DK.

References

1. **Astutiningsih, S. and Liu, Y. 2005.** "Geopolymerization of Australian Slag with effective dissolution by the Alkali", Proc. of the World Congress Geopolymer 2005, Geopolymer Institute, Saint Quentin, France June 29th, 69-73.
2. **Rashad, A. M., Khafaga, S. A. and Gharieb, M.,** "Valorization of fly ash as an additive for electric arc furnace slag geopolymer cement", Constr. Build. Mater. 294 (2021). <https://doi.org/10.1016/J.CONBUILDMAT.2021.123570>.
3. **Rashad, A. M. and Gharieb, M.,** "Solving the perpetual problem of imperative use heat curing for fly ash geopolymer cement by using sugar beet waste", Constr. Build. Mater. 307 (2021). <https://doi.org/10.1016/J.CONBUILDMAT.2021.124902>.
4. **Gharieb, M., Mosleh, Y. A. and Rashad, A. M.,** "Properties and corrosion behaviour of applicable binary and ternary geopolymer blends", Int. J. Sustain. Eng. 14 (2021) 1068–1080. <https://doi.org/10.1080/19397038.2021.1913532>.
5. **Palomo, A., Blanco-Varela, M.Y., Ranizo, M. L., Puertas, F., Vazques, T. and Grutzeck, M. W. 1999.** "Chemical stability of cementitious materials based on metakaolin", Cement and Concrete Research, 29, 997-1004.
6. **Davidovits, J. 2002.** "Technical talk: Geopolymer Applications", Curtin University, Western Australia, October 25th.
7. **Davidovits, J. 1982.** US Patent no. 4, 399,386.
8. **Rahier, H., Van Mele, B. and Wastiels, J. 1996.** "Low-temperature synthesized aluminosilicate glasses. Part II Rheological transformation during low-temperature cure and high-temperature properties of a model compound", Journal of Materials Science, 31, 80-85.
9. **Rahier, H., Van Mele, B., Wastiels, J. and Wu, X. 1996.** "Low-temperature synthesized aluminosilicate glasses. Part I Low-temperature reaction stoichiometry and structure of a model compound", Journal of Materials Science, 22, 71-79.
10. **Rahier, H., Simons, W., and Van Mele, B. 1997.** "Low-temperature synthesized aluminosilicate glasses. Part III Influence of the composition of the silicate solution on production, structure and properties, Journal of Materials Science, 32, 2237-2247.
11. **Chindraprasirt, P., Chareerat, T., and Sirivivatnanon, V. 2007.** "Workability and strength of coarse high calcium fly ash geopolymer", Cement and Concrete Composites, 29, 224-229.
12. **Yip, C. K., Lukey, G. C., Provis, J. L., van deventer, J. S. J. 2008.** "Effect of calcium silicate sources on geopolymerization", Cement and Concrete Research, 38, 554-564.
13. **Sathia, R., Babu, K. G. and Santhanam, M. 2008.** "Durability study of low calcium fly ash geopolymer concrete", the 3rd. ACF International Conference – ACF/VCA.
14. **Thokchom, S., Ghosh, P. and Ghosh, S. 2010.** "Performance of Fly ash Based Geopolymer Mortars in Sulphate Solution", J. Eng. Tech. Rev., 3, 1, 36-40.

15. **Rashad, A. M. and Gharieb, M. 2021.** "An investigation on the effect of sea sand on the properties of fly ash geopolymer mortars", *Innovative Infrastructure Solutions*. 6:53. <https://doi.org/10.1007/s41062-020-00421-9>.
16. **Ouda, A. S. and Gharieb, M. 2020.** "Development the properties of brick geopolymer pastes using concrete waste incorporating dolomite aggregate", *Journal of Building Engineering*, 27, 100919.
17. **Barsoum, M. W. and Ganguly, A. 2006.** "Microstructural Evidence of Reconstituted Limestone Blocks in the Great Pyramids of Egypt." *Journal of the American Ceramic Society*, 89.
18. **Khater, H. M. and Gharieb, M. 2020.** "Optimization of geopolymer mortar incorporating heavy metals in producing dense hybrid composites", *Journal of Building Engineering* 32, 101684. <https://doi.org/10.1016/j.jobbe.2020.101684>.
19. **Kong, D. L. Y. and Sanjayan, J. G. 2010.** "Effect of elevated temperatures geopolymer paste, mortar and concrete", *Cement Concrete Res.*, 40, 334-339.
20. **Silva, P. D., Sagoe-Crenstil, K. and Sirivivatnanon, V. 2007.** "Kinetics of geopolymerization: Role of Al_2O_3 and SiO_2 " *Cement Concrete Res* 37, 512-518.
21. **Davidovits, J. 1976.** "Solid phase synthesis of a mineral block polymer by low temperature polycondensation of aluminosilicate polymers", *IUPAC International Symposium on Macromolecules Stockholm; Sept. Topic III, New Polymers of high stability*.
22. **Khater, H. M., & Ghareib, M. (2020).** Utilization of alkaline Aluminosilicate activation in heavy metals immobilization and producing dense hybrid composites. *Arabian Journal for Science and Engineering*, 1-16.
23. **Gharieb, M., Mosleh, Y. A., & Rashad, A. M. (2021).** Properties and corrosion behaviour of applicable binary and ternary geopolymer blends. *International Journal of Sustainable Engineering*, 1-13.
24. **Davidovits, J. 2008.** "Geopolymer Chemistry and Applications. Institute Geopolymer, Saint-Quentin: France, 2nd Ed, 32.
25. **Dieter, G.E. 1987.** "Mechanical metallurgy", Mc-Graw Hill, 326-327.
26. **Astutiningsih, S. 2005.** "Alkali activation and curing of aluminosilicate based- geopolymers", PhD Theses, The University of Western Australia, 98.
27. **Mendelovici, E. 1997.** "Comparative study of the effects of thermal and mechanical treatments on the structures of clay minerals", *Journal of Thermal Analysis* 49,3, 1385–1397.
28. **McManus, J., Ashbrock, S. E. and MacKenzie, K. J. D. 2001.** "Wimperis S. ^{27}Al multiple- Quantum MAS and ^{27}Al (1H) CPMAS NMR study of amorphous aluminosilicates". *Journal of Non-Crystalline*, 282, 278–290.
29. **Buchwald, A. 2006.** "What are geopolymers? Current state of research and technology, the opportunities they offer, and their significance for the precast industry", *Concrete Precasting Plant and Technology*, 72, 7, 42–49.
30. **Duxson, P, Fernandez-Jiménez, A., Provis, J., Lukey, G., Palomo, A. and van Deventer, J. 2007.** "Geopolymer technology: the current state of the art", *Journal of Materials Science*, 42, 9, 2917–2933.
31. **Praveen Kumar T.R., Sudheesh, C, and Sasi Kumar, S. 2015.** "Strength Characteristics of Saw Dust Ash Based Geopolymer Concrete", *International Journal for Chem. Tech. Research*, Vol. 8(2), 738-785.
32. **Gharieb, M., and Rashad, A.M. 2020.** "An initial study of using sugar-beet waste as a cementitious material", *Construction and Building Materials* 250, 118843.
33. **Vollet, D. R., Macedo, J. C. D. and Mascarenhas Y. P. 1994.** "Pore structure characterization of kaolin, metakaolin and their acid-treated products using small angle X-ray scattering", *Appl. Clay Sci.* 8 (6), 397-404.
34. **Mostafa, N. Y., El-Hemaly, S. A. S., Al-Wakeel, E. I., El-Korashy, S. A. and Brown, P.W. 2001.** "Characterization and evaluation of the pozzolanic activity of Egyptian industrial by-products I: Silica fume and de-aluminated kaolin" *Cem. Conc. Res.* 31, 467-474.
35. **Mostafa, N. Y. and Brown, S. A. 2005.** "Heat of Hydration of high reactive pozzolana in blended cements: Isothermal conduction calorimetry" *Termochimica Acta*, 435, 162-167.
36. **Macedo, J. C. D., Mota, C. J. A., Menezes, S. M. C. and Camorin, V. 1994.** "NMR and acidity studies of de-aluminated metakaolin and their correlation with cumin cracking", *Appl. Clay Sci.*, 8 (5), 321-330.

37. **Zhang, Y., Sun, W. and Li, Z. 2010.** "Composition design and microstructural characterization of calcined kaolin-based geopolymer cement", *Applied Clay Science*, 47, 271– 275.
38. **Ferone, C., Colangelo, F., Roviello, G., Asprone, D., Menna, C., Balsamo, A., Prota, A., Cioffiand, R. and Manfredi, G. 2013.** "Application-oriented chemical optimization of a metakaolin based geopolymer", *Materials*, 6, 1920-1939.
39. **Andrea, V. K. and Harald, H. 2004.** "Investigation of geopolymer binders with respect to their application for building materials". *Ceramics– Silicaty*, 48, 3, 117-120.
40. **Ouda, A. S. and Gharieb, M. 2021.** "Behavior of alkali-activated pozzocrete-fly ash paste modified with ceramic tile waste against elevated temperatures and seawater attacks", *Construction and Building Materials*, 285, 122866. <https://doi.org/10.1016/j.conbuildmat.2021.122866>.
41. **Suwan, T. and Fan, M. 2014.** "Influence of OPC replacement and manufacturing procedures on the properties of self-cured geopolymer", *Constr. Build. Mater.*, 73, 551-61. [<http://dx.doi.org/10.1016/j.conbuildmat.2014.09.065>].
42. **Ke, X., Bernal, S. A., Ye, N., Provis, J. L. and Yang, J. 2014.** "One-Part Geopolymers Based on Thermally Treated Red Mud/NaOH Blends", *J. Am. Ceram. Soc.*, 1-7.
43. **ASTM C109M, 2016.** "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars", *Annual Book of ASTM Standards*; ASTM International: West Conshohocken, PA, USA.
44. **Ugheoke, B. I., Onche, E. O., Namessan, O. N. and Asikpo, G. A. 2006.** "Property Optimization of Kaolin - Rice Husk Insulating Fire - Bricks", *Leonardo Electronic Journal of Practices and Technologies*, 9, 167-178.
45. **Abo-El-Enein, S. A., El-kady, G., El-Sokkary, T. M. and Gharieb, M. 2015.** "Physico-mechanical properties of composite cement pastes containing silica fume and fly ash" *HBRC, Journal*, 11, 7–15.
46. **Alexandre Silva de Vargas, Denise. C. C., Dal Molin, Ângela, B., Masuero, Antônio, C. F., Vilela, Joao Castro-Gomes, Ruby, M. and Gutierrez. 2014.** "Strength development of alkali-activated fly ash produced with combined NAOH and CA(OH)₂ activators", *cement and concrete composites*, 53, 341-349.
47. **Panias, D., Giannopoulou, I. P. and Perraki, T. 2007.** "Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers", *Colloids and Surfaces A: Physico-chem. Eng. Aspects*, 301, 246–254.
48. **Weitzel, B., Hansen, M. R., Kowald, T. L., Müller, T., Spiess, H. W. and Trettin, H. F. R. 2011.** "Influence of Multi walled Carbon Nanotubes on the Microstructure of CSH-Phases", In proceeding of 13th congress on the Chemistry of Cement, 3-8 july 2011, Madrid, Spain.
49. **Alarcon-Ruiz, L., Platret, G., Massieu, E. and Ehrlacher, A. 2005.** "The use of thermal analysis in assessing the effect of temperature on a cement paste", *Cem. Concr. Res.*, 35(3), 609–613.
50. **Buchwald, A., Tatarin, R. and Stephan, D. 2009.** "Reaction progress of alkaline-activated metakaolin-ground granulated blast furnace slag blends", *J. Mater. Sci.*, 44, 5609–5617.
51. **Bernal, S. A., Provis, J. L., Rose, V. and Mejía de Gutiérrez, R. 2011.** "Evolution of binder structure in sodium silicate-activated lag metakaolin blends", *Cem. Concr. Compos.*, 33(1), 46–54.
52. **Bernal, S. A., Rodríguez. E. D., de Gutiérrez, R. M., Gordillo, M. and Provis, J. L. 2011.** "Mechanical and thermal characterisation of geopolymers based on silicate-activated metakaolin/slag blends", *J. Mater. Sci.*, 46(16), 5477–86.
53. **Duxson, P., Provis, J. L. and van Deventer, J. S. J. 2009.** "Geopolymers: Structures, Processing, Properties and Industrial Applications", *Wood head Publishing*, Abingdon UK.
54. **Puligilla, S. and Mondal, P. 2013.** "Role of slag in microstructural development and hardening of fly ash-slag geopolymer", *Cement Concr. Res.*, 43, 70-80.
55. **Autef, A., Joussein, E., Poulesquen, A., Gasgnier, G., Pronier, S., Sobrados, I., Sanz, J. and Rossignol, S. 2013.** "Influence of metakaolin purities on potassium geopolymer for- mulation: the existence of several networks", *J. Colloid Interface Sci.*, 408, 43–53.
56. **Rees, C. A., Provis, J. L., Lukey, G. C. and van Deventer, J. S. J. 2007.** "Attenuated total reflectance fourier transform infrared analysis of fly ash geopolymer gel aging", *Langmuir*, 23, 8170–8179.

Table 1: Chemical analysis of DK and MK from ASCE

Parameter	Value % (mass)		EN 450-1 Limits
	DK	MK	
SiO ₂	82.83	52.2	Not less than 25%
Al ₂ O ₃	6.00	33	-
Fe ₂ O ₃	0.50	1.41	-
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	89.33	86.61	Not less than 70%
TiO ₂	3.20	2.2	-
MgO	0.09	0.19	Less than 4%
CaO	0.15	0.51	-
Na ₂ O	0.03	0.16	Less than 5%
K ₂ O	0.05	0.07	-
SO ₃	0.85	0.39	Less than 3%
P ₂ O ₅	0.01	0.12	Less than 5%
SrO	0.046	-	-
Cl ⁻	0.06	0.11	Less than 0.1%
L.O.I	5.84	5.05	Category A: not greater than 5.0% by mass Category B: Not greater than: 7.0% by mass Category C: Not greater than 9.0% by mass

Table 2: The mix combinations of starting-materials

Mix No.	Ratios of binder in geopolymer	
	Metakaolin (MK), %	De-aluminated metakaolin (DK), %
M1	100	0
M2	95	5
M3	90	10
M4	85	15
M5	80	20
M6	75	25
M7	70	30
M8	65	35
M9	60	40
M10	55	45
M11	50	50
M12	45	55
M13	40	60

Table 3: Compressive strength at the 28 day for a molar ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ between 0.83-0.96

No.	DK		H ₂ O	NaOH	H ₂ O	MK		SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	H ₂ O/Na ₂ O	Compressive strength, (mpa)	
	Molar ratio			Na ₂ O	Total	Molar ratio		Molar ratio	Molar ratio	Molar ratio	7 days	28 days
	SiO ₂	Al ₂ O ₃		Moles	Moles	SiO ₂	Al ₂ O ₃					
M1	0	0	23	2.32	31.8	4.68	2.43	1.90	0.96	13.7	12	18
M2	0.5	0.029					2.0	0.94	24		35	
M3	1.0	0.058					2.28	0.93	36		44	
M4	1.5	0.087					2.2.45	0.92	41		54	
M5	2.0	0.116					2.60	0.91	51		60	
M6	2.5	0.145					2.80	0.90	55		64	
M7	3.0	0.174					2.95	0.89	53		62	
M8	3.5	0.203					3.10	0.88	40		55	
M9	4.0	0.232					3.26	0.87	38		48	
M10	4.5	0.261					3.41	0.86	37		46	
M11	5.0	0.290					3.56	0.85	32		39	
M12	5.5	0.319					3.70	0.84	29		34	
M13	6.0	0.348					3.84	0.835	26		31	

Table 4: Compressive strength at the 28 day for a molar ratio of Na₂O/Al₂O₃ between 0.70-0.8

NO.	DK		H ₂ O	NaOH	H ₂ O	MK		SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	H ₂ O/Na ₂ O	Compressive strength, (mpa)	
	Molar ratio			Na ₂ O	Total			Molar ratio	Molar ratio	Molar ratio		
	SiO ₂	Al ₂ O ₃		Moles	Moles	SiO ₂	Al ₂ O ₃	7 Days	28 days			
M1	0	0	22	1.94	26.7	4.68	2.43	1.90	0.80	13.7	8	12
M2	0.5	0.029					2.0	0.799	17		25	
M3	1.0	0.058					2.28	0.78	32		38	
M4	1.5	0.087					2.2.45	0.77	39		51	
M5	2.0	0.116					2.60	0.76	41		52	
M6	2.5	0.145					2.80	0.75	45		54	
M7	3.0	0.174					2.95	0.74	33		44	
M8	3.5	0.203					3.10	0.73	30		43	
M9	4.0	0.232					3.26	0.73	30		40	
M10	4.5	0.261					3.41	0.72	33		40	
M11	5.0	0.290					3.56	0.71	28		35	
M12	5.5	0.319					3.70	0.705	22		30	
M13	6.0	0.348					3.84	0.70	16		22	

Figures

Figure 1

Thermal gravimetric analysis (TGA / DTGA) of (a) raw kaolin and (b) raw kaolin after heat treatment at 750 °C for 2 hr

Figure 2

Particle size-distribution and general view of (a), (a') MK and (b), (b') DK

Figure 3

XRD traces of (a) MK and (b) DK

Figure 4

Bulk density of the different combinations of SiO_2 and A_2O_3 and at Na_2O ratio of 2.32 at curing times of 28 days

Figure 5

Total porosity of the different combinations of SiO_2 and A_2O_3 and at Na_2O ratio of 2.32 at curing times of 28 days

Figure 6

Water absorption of the different combinations of SiO_2 and A_2O_3 and at Na_2O ratio of 2.32 at curing times of 28 days

Figure 7

Variation of compressive strength with different combinations of SiO_2 and A_2O_3 at Na_2O ratio of 2.32

Figure 8

Variation of compressive strength with different combinations of SiO_2 and Al_2O_3 at Na_2O ratio of 1.94

Figure 9

Thermal-gravimetric analyses (TGA curves) of the different combinations of SiO_2 and Al_2O_3 at Na_2O ratio of 2.32 at curing times of 28 days

Figure 10

Thermal-gravimetric analyses (DTG curves) of the different combinations of SiO_2 and A_2O_3 at Na_2O ratio of 2.32 at curing times of 28 days

Figure 11

FTIR spectra for different combinations of SiO_2 and A_2O_3 at Na_2O ratio of 2.32 at curing times of 28 days

Figure 12

SEM micrographs of the of the different combinations of SiO_2 and A_2O_3 at Na_2O ratio of 2.32 made of M1, (a), M5 (b), M6 (c) and M7 (d) after curing age of 28 days