

Alkali Activated Eco-friendly Metakaolin/Slag Geopolymer Building Bricks

H. M. Khater M.Ezzat Abdeen M. El Nagar

Housing and Building National Research Centre (HBRC), 87 El-Tahrir St., Dokki, Giza, P.O. Box 1770 Cairo, Egypt

Abstract

Alkali activation of alumino-silicate materials is a complex chemical process evolving dissolution of raw materials, transportation or orientation and polycondensation of the reaction products. This study explores the physico-mechanical characteristics of geopolymer bricks using eco-friendly slag/metakaolin binder. Alkaline activation of slag – metakaolin binder of geopolymer brick results in formation of C-A-S-H as well as N-A-S-H gel, which adopts different structures depending on the nature of the alkaline activator. Activators used are 10% NaOH solution in addition to 5% liquid sodium silicate both used from the total binder weight), Geopolymer bricks prepared by partial binder substitution of metakaolin (fired kaolin) by water cooled slag in the ratio from 0 up to 100 %, while the used fine sand (passing 1 mm) in the ratio of 15% from the total weight. The properties of the produced geopolymer bricks have been studied through measurement of compressive strength, water absorption, FTIR, XRD and SEM imaging. Results demonstrate the possibility of substitution of metakaolin by water cooled amorphous slag materials in producing geopolymer bricks with superior properties where an increase in mechanical strength with water cooled slag increase up to 40 % was noticed giving compressive strength values exceed 70 MPa which can be used for production of heavy duty bricks which can be applied in a severe weathering condition as well as special purposes building applications, however further increase results in lowering strength values as a but still exceed 30 MPa after 28 days of hydration.

Keywords: slag, metakaolin, bricks, eco-friendly, sustainability.

1. Introduction

Traditional building bricks are mostly manufactured by using soil, lime and clay as raw materials. So, use of wastes as raw materials for the production of building products conserves energy as well as helps in pollution control and adds a solution to the waste disposal problem [1, 2]. Earlier research has shown that it is possible to use 100% fly ash as the binder in mortar by activating them with an alkali activator, such as; caustic alkalis, silicate salts, and non-silicate salts of weak acids, [3,4] also, other studies uses demolition wastes as a source for aluminosilicate materials [5, 6]. Last years, considerable research efforts have been directed towards the development of inorganic geopolymers, due to the wide range of potential applications for these materials.

This inorganic polymer can provide a new environmentally friendly construction material that offers the ecofriendly properties, which will match the durability of ancient concrete. Alkali activated or non- Portland cements refer to any system that uses an alkali activator to initiate a reaction or a series of reactions in order to produce materials that possess cementitious property. Alkali activated cement, alkali activated slag and fly ash, and geopolymers are all considered as alkali activated cementitious systems, however, it is expected that the structures of these materials are vastly different depending on the chemical composition of the geopolymer precursors. It is known that that calcium silicate hydrate (CSH) is the major common binding phase in Portland cement [7, 8] and alkali activated slags which contain high calcium source for CSH formation [9]. However, the binding property of geopolymers assumed to be the result of the formation of a three-dimensional amorphous aluminosilicate network [10].

In comparing geopolymer and Portland cement from the point of chemical composition view, it can be noticed that the major difference between geopolymers and Portland cement is calcium. However, calcium is not essential in any part of a basic geopolymeric structure except in forming CSH by interacting of soluble calcium and silicate species are present in a neutral to mild pH environment in forming nucleation sites for geopolymer formation and precipitation. In recent years, some studies have been conducted on various metakaolin (MK) Cabrera and coworkers [11, 12] found that metakaolin activation in presence of calcium hydroxide caused rapid formation of CSH, C_2ASH_8 (stratlingite) and C_4AH_{13} (tetra-calcium aluminate hydrate). Alonso and Palomo [13, 14] found that in a highly alkaline environment, the alkaline activation of metakaolin in the presence of calcium hydroxide led to the formation of an amorphous sodium aluminosilicate, which has the same characteristics as a geopolymeric gel. This geopolymeric gel formed was found to be similar to that obtained when metakaolin was activated in the absence of calcium hydroxide. CSH gel was also formed as a secondary product when metakaolin was activated in the presence of calcium hydroxide. The nature of the end product as a result of the alkaline activation of an aluminosilicate source in the presence of a calcium source is dependent on various factors [13, 14] such as: the elemental composition, the mineralogy, the physical properties (e.g. surface properties, particle size distribution) of both aluminosilicate and calcium sources, the alkalinity, the nature of the

soluble alkaline metal present, as well as the curing conditions and the use of any pre-treatment.

The chemical reaction between an aluminosilicate source and an alkaline solution, when formulated in adequate proportions, produces a mechanically strong material referred to as an alkali-activated binder, or 'geopolymer' [14]. Metakaolin (MK)-based geopolymers have been widely studied over the past decades [16–18], but one of the main drawbacks of these binders is a tendency towards a large degree of drying shrinkage and cracking [19]. This is associated with the high water demand of the reacting mixes, as a consequence of the high surface area and particle shape of MK due to calcination [20]. This affects the mechanical strength development and stability of these materials, which does not always compare well with the performance of other alkali-activated binders based on industrial by-products, such as granulated blast furnace slag (GBFS) or with lower cost and higher potential for large-scale industrial applications than MK. Other than the lower aspect ratio of the particles, the main difference between these precursors is the presence of calcium in the GBFS which leads to the development of a microstructure enriched in stable and high density phases such as C-S-H gels, which promotes high compressive strengths [21, 22]. The effect of calcium inclusion in geopolymers based on MK has been studied using different sources such as calcium hydroxide [23, 24], GBFS, natural calcium silicate materials [25], and carbonates [26, 27].

Generally, mechanical strength improvement with the inclusion of calcium has been reported, the main binding phases in the microstructure are alkali aluminosilicate ('geopolymer') gel and Al-substituted calcium silicate hydrate (C-S-H) gel. For MK/GBFS blends, it has been identified that the mechanism of activation is highly dependent on both the alkalinity of the alkali activator and the ratio between MK and GBFS, which act together to control the rate of Ca^{2+} dissolution and availability during the reaction [26]. Under lower alkalinity conditions, the dissolution of Ca^{2+} from GBFS is promoted and consequently the formation of C-S-H type gels is favoured, leading to stable gel coexistence, but higher alkalinity tends to lead to $\text{Ca}(\text{OH})_2$ precipitation rather than gel growth.

The main purpose of this article is to produce eco-friendly building bricks from water cooled slag and metakaolin and optimize ratio from both that possess high mechanical and microstructural characteristics. The hardened geopolymer bricks tested using by X-ray diffraction (XRD), FTIR, SEM, compressive strength testing and water absorption are conducted on pastes of Geopolymer based sample, in order to elucidate the optimum ratio from both precursors that results in better in enhancement in mechanical and morphological characteristics

2. Experimental procedures

2.1. Materials

Materials used in this investigation are Water cooled slag as a type from ground granulate blast furnace slag (GGBFS) supplied by the Iron and Steel Factory- Helwan, Egypt and kaolin which is collected from El-Dehesa, South Sinai, Egypt. Sodium hydroxide (NaOH) with purity 99 % in the form of pellets used as alkali activators, obtained from SHIDO Co., Egypt, while liquid sodium silicate (LSS, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) from Fisher company consists of 32 % SiO_2 and 17% Na_2O with Silica modulus $\text{SiO}_2/\text{Na}_2\text{O}$ equal 1.88 and density 1.46 g/cm^3 . The used sand dunes for mortar preparation are sourced from fine sand (<1 mm) from Oases (Wahat)-Road, Egypt.

The chemical compositions of the starting raw materials are given in Table (1). Mineralogical characterization of the raw materials was done using X-ray diffraction analysis in powder form as represented in (Fig. 1). Water cooled slag is a rich aluminosilicate material and composed from the dominant content of SiO_2 , CaO , Al_2O_3 , Fe_2O_3 , and MnO as illustrated from table (1), while its mineralogical composed of amorphous materials.

On the other hand, chemical composition of kaolin showed that it contains high percentage of alumina of about 56% with about 27% of silica, in addition to small content of calcium and magnesium as presented in table (1), however the mineralogical composition shows that it composed of 70 % kaolinite mineral with minor amount of quartz minerals (30%) as shown figure (1). This kaolinite material was thermally treated at 800°C for 2 hrs with a heating rate of 5°C/min., to produce metakaolin (Mk). This temperature was chosen on the basis of an earlier research works, where calcinations below 700°C results in a less reactive metakaolinite with more residual kaolinite, above 850°C crystallization occurs and reactivity declines [28-31].

Table (1): Chemical composition of starting raw materials. (Mass, %)

| Material | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | TiO ₂ | MnO ₂ | P ₂ O ₅ | Cl ⁻ | L.O.I. | SrO | BaO | Total |
|--|------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|-------------------|------------------|------------------|-------------------------------|-----------------|--------|------|------|-------|
| Kaolin | 56.33 | 27.61 | 1.32 | 0.18 | 0.06 | 0.06 | 0.04 | 0.08 | 3.73 | - | 0.13 | 0.05 | 10.17 | - | - | 99.97 |
| Metakaolin (800 ° C for 2hrs) | 57.50 | 35.10 | 1.59 | 0.64 | 0.17 | 0.25 | 0.15 | 0.12 | 2.85 | 0.00 | 0.13 | 0.06 | 1.14 | - | - | 99.70 |
| Water – Cooled Slag (GGBFS) | 36.67 | 10.31 | 0.50 | 38.82 | 1.70 | 2.17 | 1.03 | 0.48 | 0.57 | 4.04 | 0.04 | 0.050 | 0.12 | 0.18 | 3.28 | 99.96 |
| Fine Sand (Sand dunes) | 89.91 | 2.00 | 1.45 | 1.56 | 1.91 | 0.87 | 0.37 | 0.06 | 0.03 | 0.04 | 0.03 | 0.12 | 1.65 | - | - | 99.98 |

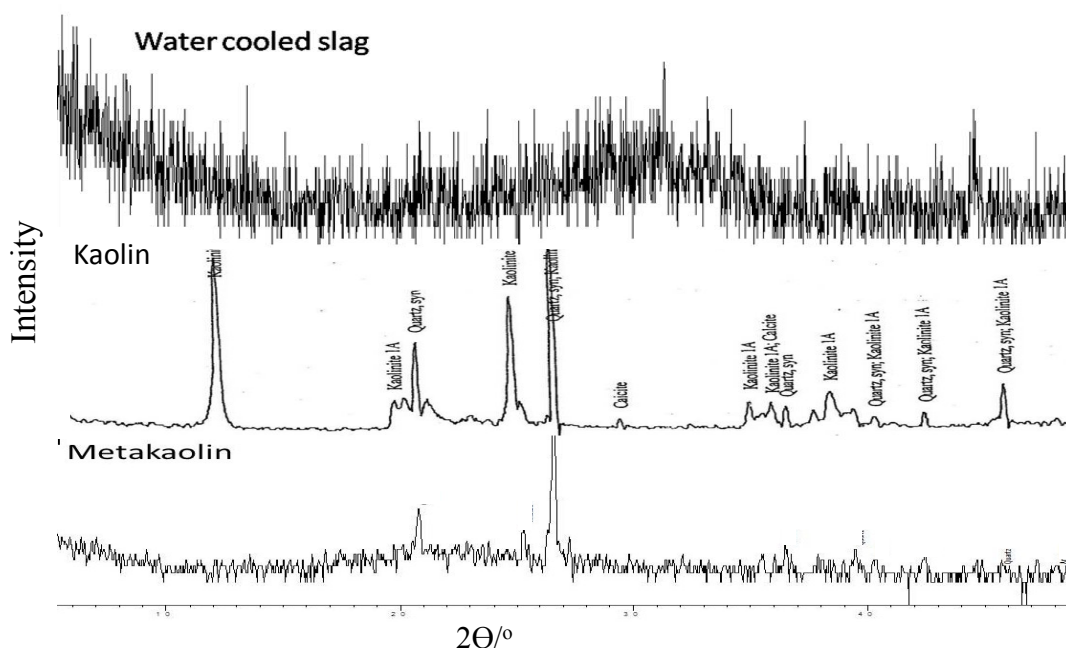


Figure (1): XRD analysis of the starting raw material.

2.2. Geopolymerization and Curing

Geopolymer mixes were made by hand-mixing raw materials of each mixture passing a sieve of 90 μm with the alkaline activator (15% NaOH and 5% of liquid sodium silicate both calculated from the total weight) for 10 min and a further 5 min with an electronic mixer as represented in Table (2). The water-binder ratio (w/b) was 0.289:0.418 by mass. The used fine and that pass 1 mm used in the ratio of 15% from the total weight. The paste mixture was cast into 25×25×25 mm cubic-shaped moulds, vibrated for compaction and sealed with plastic sheet to minimize any loss of evaporable water.

The mix design of the materials used in was tabulated in details in Table (2); where the water content decreases with the water cooled slag increase as the high surface area and particle shape of MK results in high water demand of the reacting mixes [20], while slag has high calcium content which participate in the formation of CSH which has potential for setting decrease; however the addition of water cooled slag enhances the lowering in the added water which positively results in the formation of uniform structure with lower porosity.

The table also illustrate the oxide ratios of the reacting raw materials, where the silica/alumina increases with metakaolin content up to 3.71, where the optimum range of oxide molar ratios [32, 33]: $0.2 < M_2O/SiO_2 < 0.48$, $3.3 < SiO_2/Al_2O_3 < 4.5$, H_2O/M_2O , 10–25 resulting in three dimensional networks with a more branched structure and so homogeneous and compact structure formed and M_2O/Al_2O_3 , 0.8 to 1.6 [34].

Table (2): Composition of the geopolymer mixes.(Mass, %)

| Mix no. | Meta-kaolin (MK) | Water cooled slag | Sand (<1mm) | Na ₂ SiO ₃ | NaOH | Water/binder | T.M ₂ O /Al ₂ O ₃ | SiO ₂ / Al ₂ O ₃ | T.W. /M ₂ O | T.M ₂ O /SiO ₂ |
|-----------|------------------|-------------------|-------------|----------------------------------|-----------|--------------|--|---|------------------------|--------------------------------------|
| M1 | 100 | - | 15 | 5 | 10 | 0.416 | 0.511 | 1.68 | 13.15 | 0.178 |
| M2 | 80 | 20 | 15 | 5 | 10 | 0.369 | 0.605 | 1.82 | 11.47 | 0.195 |
| M3 | 60 | 40 | 15 | 5 | 10 | 0.348 | 0.737 | 2.02 | 10.63 | 0.215 |
| M4 | 40 | 60 | 15 | 5 | 10 | 0.324 | 0.933 | 2.31 | 9.73 | 0.238 |
| M5 | 20 | 80 | 15 | 5 | 10 | 0.308 | 1.256 | 2.78 | 9.10 | 0.266 |
| M6 | - | 100 | 15 | 5 | 10 | 0.289 | 1.891 | 3.71 | 8.40 | 0.299 |

All mixes were left to cure undisturbed at ambient temperature for 24 hours, and then cured at a temperature of 40 °C and 100 % relative humidity. At the end of the curing regime, the specimens were subjected to the compressive strength measurements and then the resulted specimens were subjected for stopping of the hydration process by drying the crushed specimens for 24 hrs at 105°C [35, 36] and then preserved in a well tight container until the time of testing.

2.3. Methods of Investigation

Chemical analysis was carried out using Axios, Wave Length Dispersion X-ray Fluorescence (WD-XRF) Sequential Spectrometer (Panalytical, Netherland, 2009). The X- ray diffraction -XRD analysis was carried out using a Philips PW3050/60 Diffractometer. The data were identified according to the XRD software. Perkin Elmer FTIR Spectrum RX1 Spectrometer (Fourier Transformation Infra-Red) was used to evaluate the functional groups in the sample. Small amount of potassium bromide (KBr) and geopolymer powder were mixed and placed in the sample holder then the mix was pressed at 295 MPa for 2 minutes to produce specimen for examination, The wave number was ranging from 400 to 4000 cm⁻¹ [37, 38].

Water absorption measurements of the bricks were carried out according to ASTM C140 [39]. The percentage absorption was calculated using the equation:

$$\text{Absorption (\%)} = [(W2 - W1) / W1] \times 100$$

where W1 = weight of specimen after complete drying at 105°C, W2 = final weight of surface dry sample after immersion in water for at least 24 hours.

Compressive strength tests were carried out using five tones German Bruf pressing machine with a loading rate of 100 Mpa/s determined according to ASTM-C109 [40]. The microstructure of the hardened specimens was studied using Scanning Electron Microscopy - SEM Inspect S (FEI Company, Netherland) equipped with an energy dispersive X-ray analyzer (EDX). Removing of the free water was accomplished by using drying of the crushed specimens for 24 hours at 105°C [35, 36].

3. Results and Discussion

3.1. Mineralogical investigation

XRD pattern of 28 days alkali-activated MK - geopolymer brick specimens incorporating various ratio of water cooled slag, activated with sodium hydroxide and sodium silicate in the ratios illustrated previously in table (2), and illustrated in Figure (2). The pattern illustrate a broad band in the region of 6° to 10° 2θ for aluminosilicate gel and broad bands in the region of 17° to 35° 2θ characterizing glassy phase of geopolymer constituents. It can be seen transformation of crystalline constituents that appear in 100% Mk and increase in their transformation into amorphous one up to 40% slag addition as reflected on the increased broadness of the amorphous regions between 17 to 35°, this in conjunction with increased the band for aluminosilicate gel at 6:10° reflecting the increased dissolution of the aluminosilicate materials and increased content of the three dimensional network. However, further increase in the slag ratio results in an increased dissolved calcium as reflected on peak at 29.4° that results from the interaction of freely dissolved silica with Ca species in the matrix forming CSH that will form CSH binding material, in spite this binder can positively affect the structure by acting as nucleation sites for geopolymer formation and crystallization [41], it results in removing a proportion of the excess silicate from solution [42], thereby reducing the super-saturation levels which are the primary driving force for nucleation and crystal growth. This will therefore compete with the accelerating effects of added nucleation to further complicate description of kinetic effects, and so negatively affect the formed geopolymer structure.

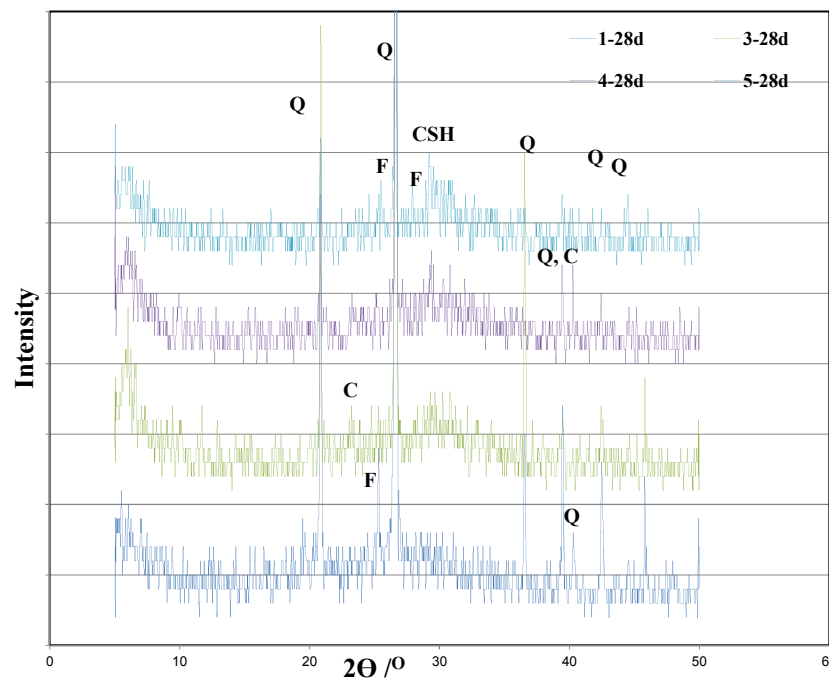


Fig. (2): XRD pattern of 28 days alkali activated Geopolymer brick specimens having various slag ratios as a partial replacement of metakaoline. [Q:Quartz, F: Feldspars, C:Calcite, CSH: Calcium silicate hydrate]

On investigating the effect of curing time up to 90 days on the optimum geopolymer specimen which incorporate 40: 60 wt., % slag to metakaolin, XRD pattern Figure (3), illustrate the increase in CSH phases as a result of increased dissolution in the binding slag's calcium and interacting with available free silica, also an increased transformation in the amorphous geopolymer structure into crystalline zeolite (Faujasite) with time is predominant which confirmed by the increased intensity of peak at 6.22, 11.96, 15.25° (2θ) , also CSH main peak at 29.4° (2θ) emphasize the increased dissolution of calcium as well as silica forming additional CASH binder phases in addition to CSH. There is small peak for calcite at 23.05° which may be resulted from the carbonation of CSH as well as any free alkalis within the matrix.

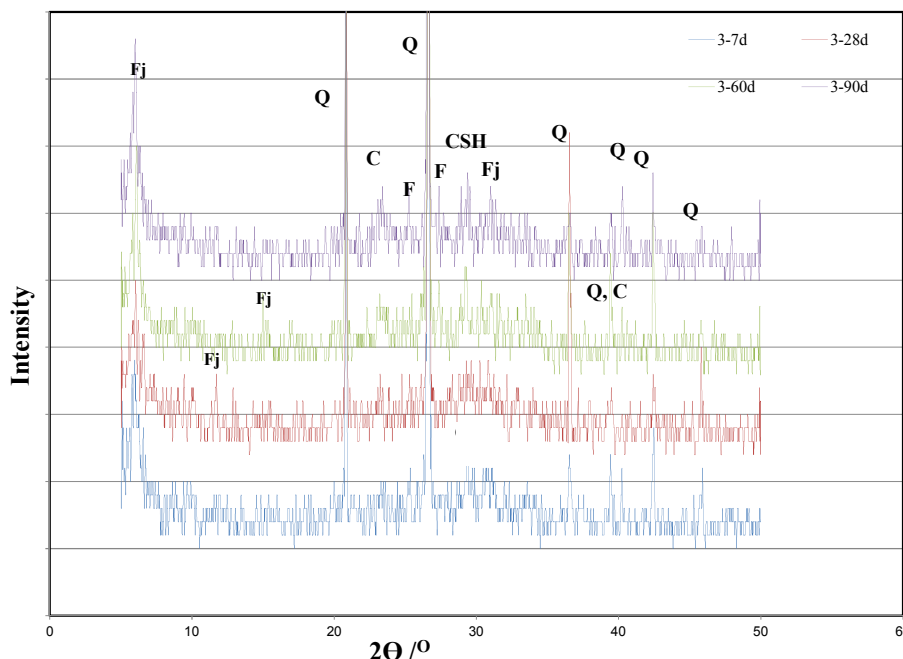


Fig. (3): XRD pattern of alkali activated Geopolymer brick specimens having various slag ratios as a partial replacement of metakaoline cured up to 90 days. [Q:Quartz, F: Feldspars, C:Calcite,Fj: Faujasite, CSH: Calcium silicate hydrate]

3.2. Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectra of 28 days cured geopolymer specimens having slag content as a partial replacement of metakaolin are shown in Fig. (4). The characteristics bands for the present geopolymer structure are: hydration groups and combined water allocated for stretching vibration of O-H bond at about 3480 cm^{-1} and bending vibration for H-O-H at about 1630 cm^{-1} , stretching vibration of CO_2 located at about $1430\text{--}1450\text{ cm}^{-1}$, asymmetric stretching vibration (Si-O-Si) at about 1060 cm^{-1} for non-solubilized silica, asymmetric stretching vibration (Ti-O-Si) at about $960\text{--}1000\text{ cm}^{-1}$ where T=Si or Al, out of plane bending vibration of CO_2 at about 870 cm^{-1} , symmetric stretching vibration (Al-O-Si) between $742\text{--}773\text{ cm}^{-1}$, symmetric stretching vibration (Si-O-Si) in the region $660\text{--}672\text{ cm}^{-1}$ and bending vibration (Si-O-Si and O-Si-O) in the region $440\text{--}450\text{ cm}^{-1}$.

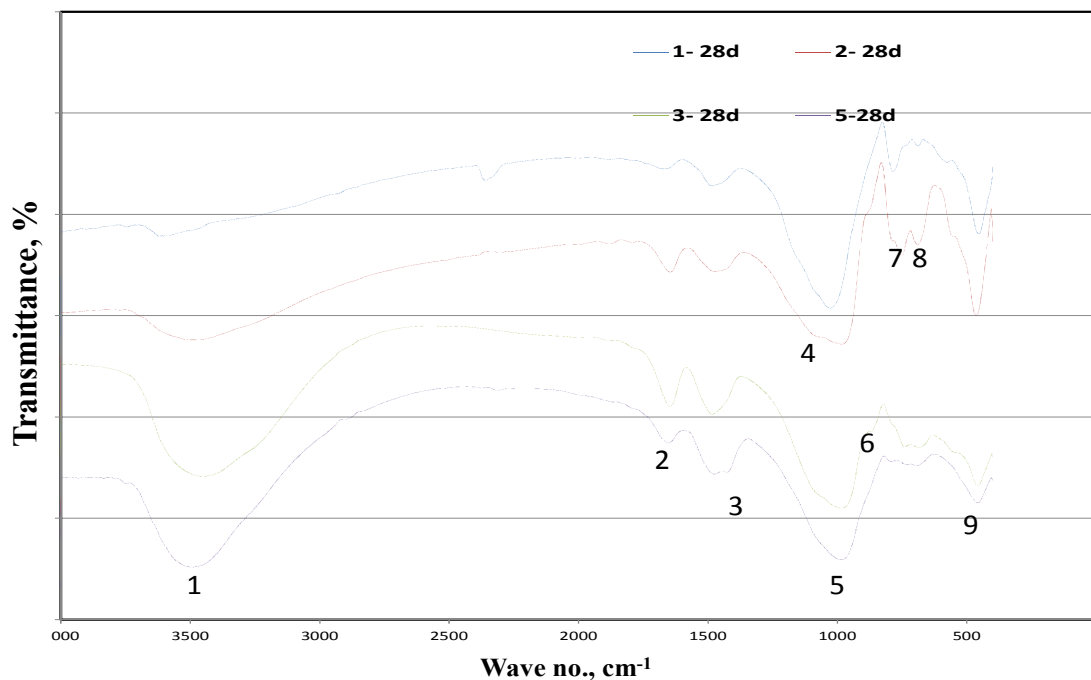


Figure (4): FTIR spectra of 90 days cured ($40\text{ }^{\circ}\text{C}$ and $100\%\text{R.H.}$) Mk- geopolymer specimens

having various water cooled slag content. [1: Stretching vibration of O-H bond, 2: Bending vibrations of (HOH), 3: Stretching vibration of CO_2 , 4: Asymmetric stretching vibration (Si-O-Si), 5: Asymmetric stretching vibration (T-O-Si), 6: Symmetric stretching vibration of CO_2 , 7: Symmetric stretching vibration (Al-O-Si), 8: Symmetric stretching vibration (Si-O-Si), 9: Bending vibration (Si-O-Si and O-Si-O)]

The pattern indicates an increased growth in the hydration bands and combined water at about 3450 and 1630 cm^{-1} with increasing the slag content, where the increased calcium content in the slag form more hydration materials (CSH, CASH) that acquire more water content in addition to the chemically combined water within the matrix structure.

The main asymmetric band for T-O-Si related to the amorphous geopolymer structure shifted from high wave number (1000 cm^{-1}) when using solely metakaolin binding material into lower wave number with increasing slag content up to complete replacement, where the zeolite structure formed in MK- based geopolymer decreases, whilst the vitreous geopolymer structure increases, however it can be noticed a decrease in intensity of the asymmetric band beyond 40% slag up to 100% slag as the Si/Al ratio increased from 2.02 when using 40% slag up to 3.71 for 100% slag.

At 40% slag the formed geopolymer structure is poly sialate-siloxo which has high tendency for branching and forming three dimensional networks, also there is a decrease in the asymmetric band for non-solubilized silica with slag increase due to the decrease in the unreacted MK' silica as well as the increased activation resulted from the increased pH at the previous Si/Al ratio [43]. The increased Si/Al ratio with slag addition results in the decrease in the medium pH and so affect the structure of the formed geopolymer structure and so results in the shifting in the asymmetric band into high wave number reflecting the increased zeolite content. This is in alignment with the XRD data where the intense feldspar structure as well as quartz content decreases with slag, where the binding CSH phases increases which has an important role in binding the reacting materials however it may interfere with the required silica needed for geopolymer formation and accumulation [42].

Bands at about 777 , 694 and 440 cm^{-1} for symmetric vibration band of (Al-O-Si), symmetric band of (Si-O-Si) and bending vibration (Si-O-Si and O-Si-O) are directly proportional to the asymmetric vibration for the non-solubilized silica and reflects the increased dissolution and polymerization of aluminosilicate gel with

slag up to 40% [44]. The intensity of the carbonate 867cm^{-1} (δ C–O) decreases with slag increase, while the carbonate band at about $1430\text{--}1450\text{ cm}^{-1}$ (ν C–O) subjected to a decreased intensity, however up on full slag replacement it can be seen splitting of this peak into two peaks indicates the distorted nature of CO_3 mineral [45, 46], This could be attributed to partial carbonation of C-S-H gel in air atmosphere

On studying the effect of curing time on the optimum mix that incorporate 40% slag [fig. (5)], the main asymmetric band at about 950 cm^{-1} increases with time as a results of increasing the rate of geopolymer formation and accumulation in the open pores resulting in the formation of well compacted structure, this is in consistent with the increased hydration band at about 3470 cm^{-1} , reflecting the increased combined water content in the geopolymer network as well as the formed CSH and CASH phases. This increased intensity of the amorphous geopolymer peak is in alignment with the decreased bands intensity at about 777 , 694 and 440 cm^{-1} for symmetric vibration band of (Al–O–Si), symmetric band of (Si–O–Si) and bending vibration (Si–O–Si and O–Si–O) [44] which emphasize the increased dissolution of the unreacted silica and forming additional geopolymer chains.

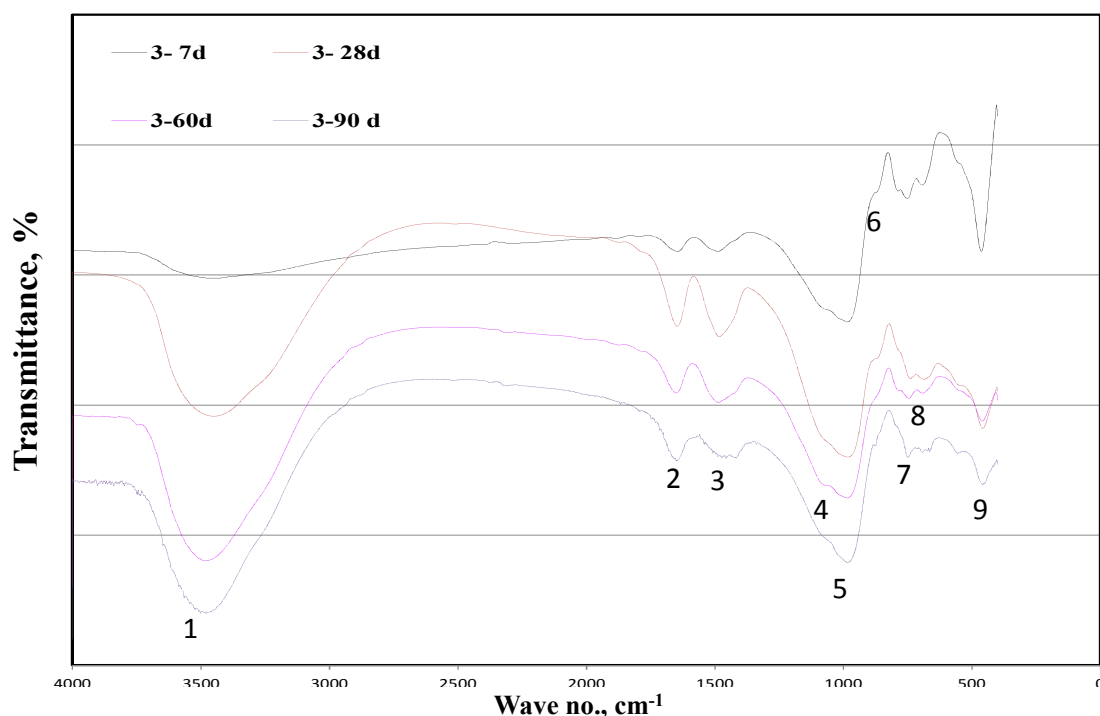


Figure (5): FTIR spectra of Mk- geopolymer specimens having various slag content cured up to 90 days. [1: Stretching vibration of O-H bond, 2: Bending vibrations of (HOH), 3: Stretching vibration of CO_2 , 4: Asymmetric stretching vibration (Si–O–Si), 5: Asymmetric stretching vibration (T–O–Si), 6: Symmetric stretching vibration of CO_2 , 7: Symmetric stretching vibration (Al–O–Si), 8: Symmetric stretching vibration (Si–O–Si), 9: Bending vibration (Si–O–Si and O–Si–O)]

3.3. Compressive strength

Results of compressive strength of the hardened MK - geopolymer as a function of various slag content cured up to 90 days are shown in (Fig. 6). Results show the increase of strength in all mixes as the hydration age progressed. This is attributed to the continuous pozzolanic reaction of slag and MK specimens. The compressive strength values increased with water cooled slag up to 40%, where a wide gap in compressive strength compared to the MK-based samples observed, which can be attributed to the reaction of the Ca supplied by the GBFS with some of the excess dissolved silicate present, forming additional strength-giving CSH gel that acts also as a nucleating agent for geopolymer formation and accumulation [47, 48], generally, increased incorporation of GBFS in the mixes leads to higher compressive strength than the control MK – geopolymer samples.

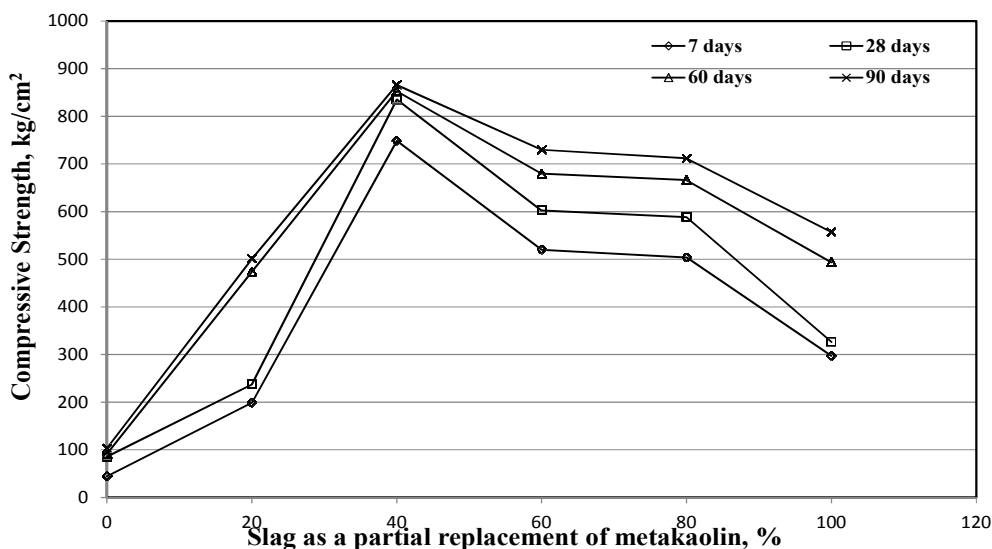
The decreased compressive strength up on increasing slag ratio more than 40% leads to the increased calcium content that will interfere with the available soluble silica required for geopolymer reaction [42], also presence of a higher concentration of soluble silica reduces the pH of the activating solution, and therefore also the free hydroxide concentration. This effect is due specifically to the presence of Ca, and is quite distinct from the detrimental effect of excess Si in the MK-based geopolymers which contain no Ca. The highest strength (but also the highest variability in strength) in these sample sets is observed with 40% GBFS at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.02$; while the GBFS content at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.71$ is higher, consistent with the increased tendency towards C–(A)–

S–H formation in the presence of higher concentrations of dissolved silica.

The compressive strength of the MK-based geopolymer with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.68$, can be considered as negligible as compared with those of the corresponding sample with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.0$ (40% slag). This is can be related to the previously summarized the ratios (i.e., $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$), where $\text{H}_2\text{O}/\text{Na}_2\text{O}$ decreases with slag increase as the fine structure of the Mk acquire much water that affect negatively on the porosity and consequently compressive strength. Barbosa et al. [49] who have conducted a test on calcined kaolin geopolymers found that $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.25, and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio of 10.0 were the optimum chemical composition, which can be observed from table (2) where 40 % slag almost satisfy the previous limits.

The data of compressive strength confirmed and emphasized by XRD and FTIR as and increased amorphous geopolymer structure with increased slag content in addition to shifting of the main asymmetric band of Al-O-Si to a lower wave number reflecting the increased vitreous content for 40% replacement by MK, also the increased CSH emphasized at about 3500 cm^{-1} in FTIR and at about $29.4^\circ (2\theta)$ in XRD which is coherent with the increased homogeneity and compaction for the aforementioned mix.

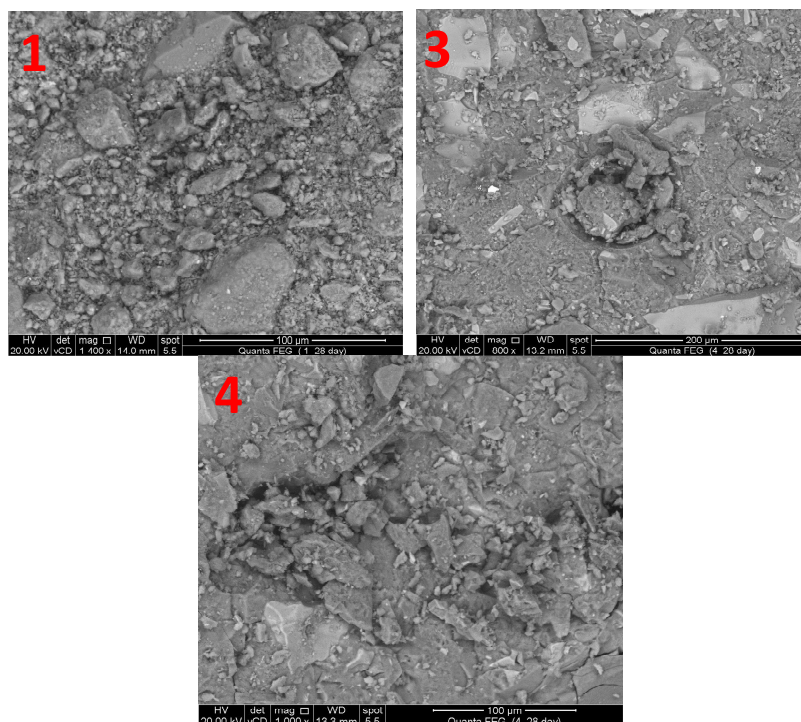
The compressive strength results give a values of 748, 835 and 866 Kg/cm^2 after 7, 28 and 90 days, respectively, then slightly decreases with slag up to 80 % slag replacement, then subjected to sudden decrease in strength up on full replacement giving a compressive strength values of about 297,326 and 557 Kg/cm^2 after 7, 28, and 90days of curing, respectively, so it is clear that most of the samples in this section can be classified according to IS:1077 [50] as a heavy duty bricks that can be used for heavy duty structures as bridges, foundation, or industrial buildings, except MK- based geopolymer. However, 20% slag replacement gives a compressive strength values that can be classified according to the previous standards as class 30 which can withstand against severe weathering according also to ASTM- C 62 [51] after 28 days.



Figure(6): Compressive strength of alkali activated Geopolymer brick specimens having various slag ratios as a partial replacement of metakaoline cured up to 90 days.

3.4. Scanning electron microscopy (SEM)

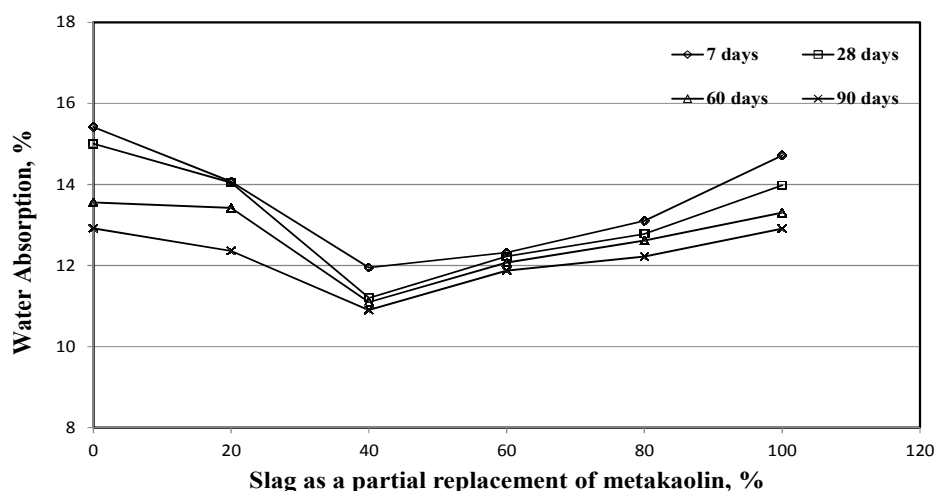
Microstructure of the 28 days Mk geopolymer specimens incorporated various slag content are shown in Fig. (7). It can be noticed that for MK- specimens {Figure (7.1)}the matrix heterogeneity with the spreading of few geopolymer plates within the matrix, also unreacted non-solubilized quartz particles spread all over the surface and inhibit the interaction with the geopolymer chains; this is in coincide with the XRD and FTIR illustrations. Replacing MK by amorphous slag (40%) results in the formation of more homogeneous matrix without any apparent interfacial transition zone (ITZ) near the aggregates; also there is coexistence of geopolymer chains along with CSH binding gel that acts as seeding agent for geopolymer accumulation and so results in a more compact and dense structure {Figure (7.2)}. Further increase in water cooled slag (60 %) results in increased dilution in the matrix by forming more CSH and decrease in the formation of geopolymer gel as reflected on the structure heterogeneity {figure (7.3)}, this related mainly to the alteration in the silica to alumina ratio by consuming dissolved silica as stated before.



Figure(7):SEM micrographs of 28 days alkali activated MK- Geopolymer specimens having various water cooled slag ratio.1) 0% slag, 3) 40% slag, and 4) 60 % slag

3.5. Water absorption

The water absorption of the MK- geopolymer specimens { figure (8)} have the opposite pattern to the compressive strength profile, where the absorption decrease up to 40% slag as well as decreases with curing time up to 90 days, where increased geopolymer formation at 40 % slag results in a decrease in the porosity within the matrix and so absorption, while for control MK mix the highly fine structure and surface area need much water and so increased porosity. On further increasing slag content, water absorption increase as results of increasing Si/Al ratio and decrease in the rate of Geopolymerization process, which in turn affect the structure and leads to less dense structure. Water absorption values after 28 and 90 days for control mix are 15, and 12.92%; for 40% slag are 11.2 and 10.9 %; and for 60 % slag are 12.23 and 11.88%, consequently, all lower than required for sever weathering building bricks as specified by ASTM C62 [51].



Figure(8): Water absorption of alkali activated Geopolymer brick specimens having various slag ratios as a partial replacement of metakaoline cured up to 90 days.

4. Conclusion

This research has been performed with the general aim of synthesizing Slag/MK Geopolymer brick and investigating its physical, mechanical and micro structural characteristics. In relation to the objectives of this research, the major findings are summarized as follows:

1. It was found that partial replacement of MK by slag up to 40% in Geopolymer brick specimens results in the formation of well compacted dense structure forming polysialatesiloxo with Si/Al ratio of 2.02, while further increase in slag results in formation of polysialate-multisiloxo with higher Si/Al ratio 2.30 up to 3.71 and lower tendency in formation of three dimensional geopolymer network, which resulted in decline in binding characteristic of Geopolymer and formed less dense structure.
2. SEM micrographs have proved that Si/Al ratio plays important role in geopolymerization process, where a very dense and compact structure formed at Si/Al ratio of 2, while further increase results in the formation of more porous structure with low mechanical properties.
3. XRD and FTIR spectra confirm the intense amorphous geopolymer structure up on using 40% slag, while the increased crystalline phases are predominant with further slag increase.
4. It was concluded that the produced that Geopolymer specimens produced from blended MK / slag in this research can compete the fired clay and refractory brick mechanically and physically, up to 100% slag, while using 40 % slag results in the formation of geopolymer brick with superior characteristics and giving compressive strength values exceed 83 MPa after 28 days, which can be used for production of heavy duty bricks as well as refractory bricks [50], also can be applied in a severe weathering conditions ASTM- C62 [51].
5. The produced geopolymer bricks possess more than 90 % reduction in carbon dioxide as compared with other traditional clay bricks.
6. Water absorption of mostly all the produced geopolymer bricks are in the range 11 to 15.5% which is lower than required for the severe weathering clay bricks according to ASTM-C62 [51].

Acknowledgments

This project was supported financially by the Science and Technology Developments Fund (STDF), Egypt, Grant No.8032.

5. References

1. Scarano, J.; Belz, G.; Dinelli, G., "Quality control and industrial reutilization potential of FGD gypsum", *Ann. Chim*; 88: 211–222(1998).
2. Kumar, S., "A perspective study on fly ash–lime–gypsum bricks and hollow blocks for low cost housing development", *Construct. Build.Mater.* 16: 519–525(2002).
3. Bakharev, T.; Sanjayan, J.G.; Cheng, Y.B., ^a. "Alkali activation of Australian slag cements", *Cement and Concrete Research*; 29(1): 113- 120(1999).
4. Talling, B.; Brandstetr, J., "Present State and Future of Alkali-Activated Slag Concretes", Paper presented at the third international conference on fly ash, silica fume, slag, and natural pozzolans in concrete, Trondheim, Norway(1989).

5. Khater, H.M., "Utilization of Demolished Concrete, Demolished Walls, Grog and Hydrated Lime in Building Materials", *International Journal of Mechanic Systems Engineering*; 3(3): 97-100, (2013).
6. Khater, H.M.; Zedane S.R., "Geopolymerization of Industrial By-Products and Study of their Stability upon Firing Treatment", *International Journal of Engineering and Technology*; 2 (2): 308-316(2012).
7. Taylor, H.F.W., "The Chemistry of Cements", vol. 1, 1st ed., Academic Press, London, 1964.
8. Gani, M.S.J., "Cement and Concrete", 1st ed., Chapman and Hall, London, 1997.
9. Richardson, I.G.; Cabrera, J.G., "The nature of C-S-H in model slag cements", *Cem. Concr. Compos*; 22: 259-266(2000).
10. Lee, W.K.W.; van Deventer, J.S.J., "Structural reorganization of class F fly ash in alkaline silicate solutions", *Coll. Surf. ; A* 211: 49- 66 (2002).
11. Frias, M.; Sanchez de Rojas, M.I.; Cabrera, J., "The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars", *Cem. Concr. Res.*; 30: 209-216 (2000).
12. Cabrera, J.; Rojas, M.F., "Mechanism of hydration of the metakaolin- lime-water system", *Cem. Concr. Res.*; 31:177-182 (2001).
13. Alonso, S.; Palomo, A., "Alkaline activation of metakaolin and calcium hydroxide mixtures: influence of temperature, activator concentration and solids ratio", *Mater. Lett.*; 47 :55- 62(2001).
14. Alonso, S.; Palomo, A., "Calorimetric study of alkaline activation of calcium hydroxide-metakaolin solid mixtures", *Cem. Concr. Res.*; 31: 25- 30 (2001).
15. Shi, C.; Krivenko, P.V.; Roy, D.M., "Alkali-activated cements and concretes", Taylor & Francis, Abingdon, UK(2006)
16. Davidovits, J., "Inorganic polymeric new materials", *J Thermal Analysis*; 37:1633-1665(1991).
17. Palomo, A.; Glasser, F.P., "Chemically-bonded cementitious materials based on metakaolin", *Brit Ceram Trans J.*; 91:107-112(1992).
18. Provis, J.L.; van Deventer, J.S.J., "Geopolymers: Structures, Processing, Properties and Industrial Applications, Woodhead. Cambridge, UK (2009eds).
19. Perera, D.S.; Uchida, O.; Vance, E.R.; Finnie, K.S., "Influence of Curing Schedule on the Integrity of Geopolymers", *J Mater Sci*; 42(9):3099(2007). doi:10.1007/s10853-006-0533-6.
20. Provis, J.L.; Duxson, P.; van Deventer, J.S.J. "The role of particle technology in developing sustainable construction materials", *Adv Powder Technol*; 21(1):2 (2010).
21. Lecomte, I.; Henrist, C.; Liegeois, M.; Maseri, F.; Rulmont, A.; Cloots, R., "Micro-structural comparison between geopolymer and alkali activated slag cement and Portland cement", *J Eur Ceram Soc.*; 26:3789-3797(2006).
22. Lloyd, R.R., "Accelerated ageing of geopolymers", In: Provis JL, van Deventer JSJ (eds) *Geopolymers: Structures, Processing, Properties and Industrial Applications*. Woodhead, Cambridge, UK, p 139(2009)
23. Alonso, S.; Palomo, A., "Calorimetric study of alkaline activation of calcium hydroxide -metakaolin solid mixture", *Cem Concr Res.*; 31:25-30(2001).
24. Alonso, S.; Palomo, A., "Alkaline activation of metakaolin and calcium hydroxide mixtures: influence of temperature, activator concentration and solids ratio", *Mater Lett*; 47(2):55-62(2001).
25. Yip, C.K.; Lukey, G.C.; Provis, J.L.; van Deventer, J.S.J., "Effect of calcium silicate sources on geopolymerisation", *Cem Concr Res.*; 38(4):554(2008).
26. Yip, C.K.; Provis, J.L.; Lukey, G.C.; van Deventer, J.S.J., "Carbonate mineral addition to metakaolin-based geopolymers", *Cem Concr Res* 30:979-985(2008).
27. Sakulich, A.R.; Anderson, E.; Schauer, C.; Barsoum, M.W., "Mechanical and microstructural characterization of an alkali-activated slag/limestone fine aggregate concrete", *Constr Build Mater.*; 23:2951 (2009).
28. Kakali, G.; Perraki, T.; Tsivilis, S.; Badogiannis, E., "Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity", *Applied Clay Science*; 20:73-80 (2001).
29. Wenying, G; Guolin, W; Jianda, W; Ziyun, W; Suhong, Y, "Preparation and Performance of Geopolymers", *Journal of Wuhan University of Technology- Mater Sci Ed.*; 23(3):285-430(2008).
30. Khater, H.M., "Calcium Effect on Geopolymerization of Alumino silicate Wastes", *J. Mater. Civ. Eng.*; 24(1): 92-101 (2012), doi.org/10.1061/ (ASCE) MT.1943-5533.0000352.
31. Khater, H.M., "Effect of Silica Fume on the Characterization of the Geopolymer Materials", *International Journal of Advanced Structural Engineering (springer open journal)*;5(12):1-10 (2013) doi:10.1186/2008-6695-5-12.
32. Davidovits, J. «Mineral Polymers and Methods of Making Them». US Patent 4,349,386, 1882.
33. Davidovits, J., "Chemistry of Geopolymeric Systems Terminology" proceeding of, Second International Conference Geopolymer: 9-40 (1999).
34. Davitovits, J.; Davitovits, M.; Davitovits, N., US Patent, No. 5,342,595, 1994.

35. Khater, H.M., “Effect of cement Kiln dust on geopolymer composition and its resistance to sulfate attack”, *Green materials Journal*;1(1):36-46 (2013).
36. El-Sayed, H.A.; Abo El-Enein, S.A.; Khater, H.M.; Hasanein, S.A., “Resistance of Alkali Activated Water Cooled Slag Geopolymer to Sulfate Attack”, *Ceramics – Silikáty*;55 (2): 153-160 (2011).
37. Panias, D.; Giannopolou, L.P.; Peraki, T., “Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers”, *Colloids and surfaces A: physicochem. Eng. Aspects*; 301:246-254(2007).
38. Bakarev, T., “Thermal behavior of geopolymer prepared using class F fly ash and elected temperature curing”, *Cement and concrete Research*; 36:1134-1147(2006).
39. ASTM C140, “Standard test methods for sampling and testing concrete masonry units and related units”, (2012).
40. ASTM C109, “Standard test method for compressive strength of Hydraulic Cement Mortars” 2012.
41. Temuujin, J.; Van Riessen, A.; Williams, R., “Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes”, *Journal of Hazardous Materials Journal of Hazardous Materials*; 167(1-3): 82-88(2009).
42. Catalfamo, P.; Di Pasquale, S.; Corigliano, F.; Mavilia, L., “ Influence of the calcium content on the coal fly ash features in some innovative applications”, *Resourc. Conserv. Recyc.*; 20: 119–125 (1997).
43. Davidovits, J., “Geopolymer, Chemistry and Applications”, 3rd printing. Institut Geopolymer, Saint-Quentin, France. 585 pp, 2008.
44. Alexandre Silva de Vargas, Denise.C.C. Dal Molin, Ângela.B. Masuero, Antônio.C.F. Vilela, Joao Castro-Gomes, Ruby M. Gutierrez, “Strength development of alkali-activated fly ash produced with combined NaOH and CA(OH)₂ activators”, *cement and concrete composites*, 2014; 53: 341-349.
45. Kalinkin, A. M.; Politov, A. A.; Boldyrev, V. V.; Kalinkina, E. V.; Makarov, V. N.; Kalinnikov V. T., " Study of Mechanical Activation of Diopside in a CO₂ Atmosphere". *J. Mater. Syn. Proc.*; 38, 163–167 (2002).
46. Kalinkin, A. M.; Kalinkina, E. V.; Politov, A. A.; Makarov, V. N.; Boldyrev, V. V., "Mechanochemical interaction of Ca silicate and aluminosilicate minerals with carbon dioxide". *J. Mater. Sci.* 39, 5393–5398 (2004).
47. Van Deventer, J.S.J.; Provis, J.L.; Duxson, P.; Luckey, G.C., “Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products”, *J. Hazard. Mater.*; A139 :506–513(2007).
48. Lee, W.K.W.; Van Deventer, J.S.J., “The effect of ionic contaminants on the early age properties of alkali-activated fly ash based cements”, *Cement Concrete Res.*; 32: 577–584 (2002).
49. Barbosa, V.F.F.; MacKenzie, K.J.D.; Thaumaturgo, C., “Synthesis and characterization of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers”. *Int J Inorg Mater*;2(4):309–17(2000).
50. IS: 1077-1992 “Common burnt clay building bricks-specification”, 5th edition, 2008.
51. ASTM C62, “Standard Specification for Building Brick (Solid Masonry Units Made From Clay or Shale)”, 2012.