Physico-chemical, mechanical, microstructure and durability characteristics of alkali activated Egyptian slag

Mohamed Heikal a,b,⇑, M.Y. Nassar a, G. El-Sayed a, S.M. Ibrahim a

a Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
b Chemistry Department, College of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), P.O. Box 90950, Riyadh 11623, Saudi Arabia

HIGHLIGHTS

- Alkali activator contents affected the location and intensities of the conductivity maximum.
- Mix S5 shows the higher values of compressive strength at all curing ages up to 90 days.
- Mix S1 shows higher values of strength in 5% MgSO4 or MgCl2 solution upto 180 days.
- Alkali activated GBFS improves the durability and the resistance to chemical attack.
- The total chloride and total sulphate contents decrease with alkali activated GBFS.

ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form 28 May 2014
Accepted 8 July 2014

Keywords:
Alkaline activation
Electrical conductivity
Thermal analysis
Phase composition
Microstructure and durability

ABSTRACT

The aim of the present work is to study the characteristics of alkali activated Egyptian slag (GBFS) mixed with different contents of Na2O and SiO2. The rate of the kinetic of activation of GBFS has been studied by electrical conductivity, FTIR, DTA/TGA, XRD and SEM techniques. Electrical conductivity of alkali activated slag systems depends mainly on the binder composition, the activator type and its concentration. The increase in alkali activator contents affected the location and intensities of the conductivity maximum. As the hydration time increases the amount of hydration products increase, hence the chemically combined water and combined slag contents increase. SEM images showed the presence of (N,C)ASH gel with low porosity. With the increase of the content of Na2O leads to form a denser closed microstructure, leading to higher compressive strength values. The activated GBFS showed good durability in 5% MgSO4 or 5% MgCl2 solution, i.e., the compressive strength increased gradually with immersing time up to 180 days. The total chloride and total sulphate contents decrease with alkali activated GBFS due to the forming hydrated products that fill some available open pores, thereby inhibiting Cl− or SO4 2− ions penetration; this effect leads to a decreased accessibility of Cl− or SO4 2− ions towards the more dense with low capillary pore structure. It can be concluded that alkali activated GBFS are more durable in 5% MgSO4 or 5% MgCl2 than OPC pastes.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The role of alkali activated cements protect the environment through the utilization of by-product materials in their manufacture and end applications in waste management. The production of alkali-activated concretes is associated with low energy consumption and low CO2 emission, along with the potential to reach high mechanical strength at early ages of curing, resistance to chemical attack and resistance to high thermally treated temperatures. These properties have made concretes based on alkali-activated binders a very interesting [1–3]. Portland cement (OPC) production increases global greenhouse gas emissions such as dioxin, NOx, SO2, and particulates, through the calcination of clinker in hydrocarbon heated furnaces. The high CO2 emissions arising (7% of all CO2 generated) from OPC manufacture have been attributed to calcination of limestone, which leads to formation and release of CO2 and high energy consumption during manufacturing at temperatures up to 1550 °C [4]. Reduction in cement consumption has been attained by the use of industrial by products such as blast-furnace slag (GBFS), fly ash (FA), silica fume (SF) and cement kiln dust (CKD), as partial cement replacement materials [5,6].

⇑ Corresponding author at: Chemistry Department, College of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), P.O. Box 90950, Riyadh 11623, Saudi Arabia. Tel.: +966 534484605; fax: +966 112591678.
E-mail address: ayahheikal@hotmail.com (M. Heikal).
Alkali activation is a process based on the action of solutions of alkali compounds like sodium or calcium hydroxide, sodium carbonate and silicate on the aluminosilicate constituent of the binder. The result is the destruction of the chemical bonds of the type Si—O—Si in the aluminosilicate. Alkali-activated binders (also referred to as ‘geopolymers’) are produced from an aluminosilicate source mixed with an alkaline solution [7]. These binders exhibit technological and ecological advantages in comparison with ordinary Portland cement (OPC), and the industrial use of geopolymers in concrete production in the production of high performance building materials is expanding [8]. A strong dependence on the nature of the alkaline activator in the structural and mechanical development of these binders has been identified throughout the literature. Alkali activated cements (AAC) are the type of the binders synthesized from natural aluminosilicate materials and aluminosilicate waste products such as fly ash, rice husk ash, and slag which are rich in silicium and aluminium [9]. Therefore, the use of alkali activation technology enables the possibility of substantial utilization of waste materials.

Development of geopolymers is the new, knowledge-based, multi-functional materials with higher performance, reduced environmental impact and adjustable to customer needs. Numerous studies have been conducted over the last few decades to determine the composition and microstructure property relationships in such systems [10–14]. Effect of workability, ultra fine materials, pore size distribution, early age strength, mechanical, cracking and shrinkage as well as the residual compressive strength behaviour of alkali activated slag paste (AASP) up to 1200 °C were investigated [15–22]. The workability, durability and strength are affected by the type and concentration of the alkaline activator, solution ratio (Ms = SiO2/Na2O), slag type, fineness, curing conditions, water/cement ratio, activating solution/slag ratio and the use of admixture as well as fibres [23–26]. Purdon [27] investigated the effect of NaOH concentration on strength of AAC. Glukhovsky et al. [28] classified alkaline activators into six groups according to their chemical compositions as a caustic alkalis, non-silicate weak acid salts, silicates, aluminates, aluminosilicates and non-silicate strong acid salts. NaOH, Na2CO3, Na2O-nSiO2 and Na2SO4 are the most widely available and economical activators. The factors affecting on the strength of alkali activated GBFS were the type, and the dosage of alkali as well as the type and fineness of slag. SiO2/Na2O ratio, curing temperature, water/slag ratio and additive as well as [29,30].

The effectiveness of the alkali activator is a very significant factor influencing the intensity and rate of process of alkali activation. It is reported that the best activator is waterglass [31,32]. The best dosage is within the range of 3.0–5.5% Na2O by of slag. The optimum dosage ranges of waterglass solution are 0.75–1.25% for acid GBFS, 0.90–1.30% for neutral GBFS and 1.0–1.5% for basic GBFS. The optimum range of fineness is 4000–5500 cm2/g. It is evident that the effectiveness of activator is a very significant factor which determines the engineering properties of the material. Sodium silicate (SSL) has been extensively used in the activation of aluminosilicate precursors such as GBFS, metakaolin (MK), FA and others [23,33].

The sulphate and chloride ions can enter into deleterious reactions leading to the dissolution of CH, precipitation of gypsum and sulfoaluminates as well as Friedel’s salt, which cause expansion and softening of concrete, respectively [34,35]. The presence of Mg2+ as MgSO4 and/or MgCl2 leads to the distortion of C—S—H through a dissolution of Ca2+ and/or an exchange with Mg2+ to give also Mg—S—H and CH. All the above mentioned reactions are accompanied by decrease in strength [36–40]. El-Didamony et al. [41] represented the experimental trials to activate GBFS to produce cementless binding materials. The results revealed that the increase of NaOH content increase the chemically combined water contents up to 90 days. On the other hand, the bulk density and compressive strength were increased by increasing Na2SiO3 content in presence of NaOH. The increase of compressive strength is due the increase of [SiO4]4− which enhances the C—S—H formation. The durability of alkali activated GBFS mortars and concretes have been studied. Alkali activated GBFS are durable binder in sulphate, sea water and acid resistant [42–48]. Darko and Branislav [49] examined the early hydration of alkali–GBFS metasilicate (Na2SiO3·5H2O) solution at 25 °C. The compressive strength of AAC is higher than OPC mortar. The feasibility of using an alkaline activated GBFS to produce a mortar without using OPC was investigated [50].

The reaction mechanism of aluminosilicates containing a calcium bearing compound differs from the geopolymeric reaction as explained. It has also been reported that the type of calcium bearing compound in the starting material play an important role in the alkali activation of these materials. Alkalis first attack the GBFS particles breaking the outer layer and then a polycondensation of reaction products takes place. Wang et al. [51] suggested that the initial reaction products formed by the dissolution and precipitation, whereas, at later ages, a solid state mechanism is followed where the reaction takes place on the surface of the formed particles, dominated by slow diffusion of the ionic species into the unreacted core. Alkali cation (R+) acts as a mere catalyst for the reaction in the initial stages of hydration, via cation exchange with the Ca2+ ions [52,53]. The alkaline cations act as structure creators. The nature of the anion in the solution also plays a determining role in the hydration, particularly in early ages and especially with regard to paste setting [47,54]. The final products of the GBFS reaction are similar to the products of cement hydration (C—S—H); the major difference being the rate and intensity of the reaction. It has also been observed that the alkalis are bound to the reaction products and are not freely available in the pore solution (this depends on the alkali concentration used, though), thereby a small percentage of the alkalis (around 0.02%) are bound to the reaction products but most of the alkalis remains in the pore solution [55].

This paper studied the influence of different alkaline concentrations on the hydration characteristics and morphology of GBFS system. These characteristics were investigated by changing the initial alkalinity of the hydration condition in order to reveal the affecting mechanism of alkaline condition on its hydration.

2. Experimental techniques

2.1. Materials

Egyptian blast-furnace slag (GBFS) was provided from Iron and Steel Company, Helwan Governorate, Egypt. Its chemical oxide composition is given in Table 1. XRD patterns, FTIR spectra and SEM are shown in Figs. 1–3. Blaine surface area of slag was 4500 ± 50 cm2/g. The diffraction patterns of GBFS was shown in Fig. 1. The diffractogram of the unreacted slag shows a predominantly amorphous material. There is also a broad feature ‘amorphous hump’ between 2θ and 38° 2θ attributed to the amorphous glassy component.

<table>
<thead>
<tr>
<th>Table 1 Chemical composition of starting materials, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide composition (%)</td>
</tr>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>Fe2O3</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>SO3</td>
</tr>
<tr>
<td>Na2O</td>
</tr>
<tr>
<td>K2O</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
<tr>
<td>P2O5</td>
</tr>
<tr>
<td>LOI</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>
NaOH was produced by SHIDO Company with purity 99%, commercial sodium silicate liquid (SSL) was provided from Islamic Silicate Industry, Badr City, Helwan. Sodium silicate liquid consists of 30.7% SiO₂, 10.3% Na₂O and 59% H₂O with silica modulus SiO₂/Na₂O equal 2.98 and density 1.44 g/cm³ was used. Sodium silicate solutions were used as activators and caustic soda content was increased by the addition of sodium hydroxide (NaOH) pellets.

GBFS was firstly crushed in a jaw crushe r to pass through a 2 mm diameter sieve, then passed through a magnetic separator to remove any contamination of iron melt then ground in steel ball mill to reach 4500 ± 50 cm²/g Blaine surface area. Different mixes were prepared from GBFS using mixed activators as shown in Table 2. The pastes were prepared using NaOH (SH) and sodium silicate liquid Na₂O. SiO₂ (SSL) as activators as shown in Table 2. The resulting solution was then allowed to cool down to the room temperature for about 2 h. GBFS was mixed with tap water. The water to binder ratio (w/b) is 0.30 [56].

The mix compositions were prepared as shown in Table 2. The ingredients of each mix were blended in a porcelain ball mill for 1 h using a mechanical roller mill to ensure complete homogeneity. GBFS was placed on smooth, non-absorbent surface, a crater was formed in the centre and the mixing water with the activator was poured into the crater as shown in Table 2. The mixing process was performed according to ASTM specification [56]. The mixture was slightly troweled to absorb the water for about 1 min, and then completed by vigorous mixing for 3 min. The pastes were moulded in one inch cubic moulds, then strong manually pressed into the moulds. The surface of the paste was then smoothed by thin edged trowel. Immediately after moulding, the specimens were cured in 100% RH at 35 °C for 24 h, then demoulded and cured in the humidifier up to 3 days, then cured under tap water after 3 days up to 90 days. For the specimens which were tested for the resistivity against 5% magnesium sulphate and magnesium chloride attack, the specimens were cured up to 7 days (zero time) in tap water then immersed in the aggressive solution 5% MgSO₄ or MgCl₂, up to 180 days. The aggressive solution was renewed monthly to maintain constant concentration.

In electrical conductivity measurements the test cell was of the co-axial type and included concentric inner and outer electrodes mounted on an insulated base plate as shown in Fig. 4. The electrodes were polished before the experiment [57,58]. The mixing was done with the required amount of water that gives normal consistency in the presence of suitable amount of alkaline activator (SiO₂ + Na₂O). The measurements of the electrical conductivity were begun exactly 3 min after mixing with water (0 time). The pastes were placed in the space between the electrodes. The cell was kept in a cabinet chamber at 100% relative humidity during the test period from 3 min up to 28 days. The electrical conductivity was measured at 35 °C. The electrodes were connected with RLC meter, model SR-720. All data of the electrical conductivity were measured during the setting and hardening at relativity low AC frequency 1V and 1000 Hz for resistance measurements.

### Table 2

Composition of the investigated mixes containing alkaline activator (SiO₂ + Na₂O), mixing with 1 kg of GBFS.

<table>
<thead>
<tr>
<th>Mix no.</th>
<th>SiO₂ (mol/kg of GBFS)</th>
<th>Na₂O (mol/kg of GBFS)</th>
<th>H₂O (mL/kg of GBFS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.50</td>
<td>0.25</td>
<td>300</td>
</tr>
<tr>
<td>S2</td>
<td>0.50</td>
<td>0.50</td>
<td>300</td>
</tr>
<tr>
<td>S3</td>
<td>0.50</td>
<td>0.75</td>
<td>300</td>
</tr>
<tr>
<td>S4</td>
<td>0.50</td>
<td>1.00</td>
<td>300</td>
</tr>
<tr>
<td>S5</td>
<td>0.50</td>
<td>1.25</td>
<td>300</td>
</tr>
<tr>
<td>S6</td>
<td>0.50</td>
<td>1.50</td>
<td>300</td>
</tr>
<tr>
<td>OPC</td>
<td>–</td>
<td>–</td>
<td>270</td>
</tr>
</tbody>
</table>
The compressive strength was done on a compression machine of SEIDNER, Riedinger, Germany, with maximum capacity of 600 kN force. The compressive strength was carried out on four samples as described by ASTM Specifications (ASTM Designation: C-150, 2007). The bulk density was measured on at least three similar cubes of the same age [38]. After, the determination of bulk density, four cubes of the same age were dried in a furnace at 105°C for 24 h then weighed after cooling in a desiccator. The total porosity of the cement pastes could be calculated [38]. The hydration of cement pastes were stopped by pulverizing 10 g of representative sample in a beaker containing methanol-acetone mixture (1:1), then mechanically stirred for 1 h. The mixture was filtered through a gauze crucible, C4A7, and washed several times with the stopping solution then with ether. The solid was dried at 70°C for 1 h complete evaporation of alcohol then collected in polyethylene bags; sealed and stored in desiccators for analysis [38]. The combined water content (Wc) considered as the percent of ignition loss of the dried samples (on the ignited weight basis). Approximately 2 g of the predried sample were gradually ignited up to 800°C for 1 h soaking time [38].

Anhydrous slag content determined according to the methods reported in earlier publication [59]. 1 g sample is treated with 5 g salicylic acid, 70 ml methanol, and 30 ml methanol. After the mixture has been stirred for 1 h, the resulting solution is stored for 24 h in an airtight container. The solution is then filtered on a G4 glass filter and the filter residue is washed with 200 ml methanol.

Total chloride was determined by weight into a stopper conical flask, approximately 2 g of the predried sample were put into a 250 ml beaker containing concentrated HCl and 100 ml of distilled water were added, then boil for 5 min, filter and wash several times with distilled water. Add to the filtrate 10 ml of 10% BaCl2, digest, filter and ignite at 1000°C for 30 min. The total sulfate content was calculated as:

\[
\text{SO}_4^{2-} = \frac{\text{weight of ppt}}{M} \times 34.1
\]

where \(M\) is the weight of sample in grams [38].

Total chloride was determined by weight 2 g into a stopper conical flask, dispersed with 25 ml water and then added 10 ml of nitric acid (sp. gr. 1.42). Add 50 ml hot water, heat to near boiling and keep warm for 10–15 min. If the supernatant liquid is turbid, filter through filter paper and wash with hot water, then cool to room temperature. An excess of standard 0.1 N AgNO3 was added and 2–3 ml of nitrobenzene to coagulate the precipitate, stopple the flask and shake vigorously, then add 1 ml of ammonium ferric alum as indicator and titrate against standard 0.1 N ammonium thiocyanate [38].

3. Results and discussion

3.1. Electrical conductivity

The variations of electrical conductivity were studied with the increase of the hydration time [58,61,62]. Electrical conductivity of alkali activated GBFS with different content of Na2O from 0.25 to 1.50 mol/kg of GBFS was given in Fig. 5. The increasing of the alkalinity condition can promote the hydration of alkali activated GBFS, which increases the degree of hydrolytic destruction of the GBFS. The addition of alkali cations into the activating solution have two effects; first, it increases the pH in the solution; (higher amounts of OH− ions) that helps to sever the Si−O−Si and Si−O−Al bonds of the alkali activated GBFS into silicate and aluminous species [7]; second, the alkali cation balances the electric charge in the tetrahedral Si and Al structure [63].

Electrical conductivity of alkali activated GBFS systems depends mainly on the binder composition, the activator type and its concentration. Fig. 5 showed that the initial electrical conductivity increases with the Na2O content increases, free OH− and Na+ ions were released from the pores of the fresh paste (the initial stage – predormant period). After 20–30 min the results showed a decrease in the electrical conductivity values, indicating the geopolymerization reaction progress by the consumption of OH− and Na+ ions. Mix S1 (0.25:0.50: Na2O:SiO2 mol/kg of GBFS) shows the lowest value of initial electrical conductivity. The increase of the alkali activator contents, the initial electrical conductivity increases as shown for mixes S2, S3, S4, S5, and S6 (0.50–1.50:0.50; Na2O: SiO2 mol/kg of GBFS). As the concentration of alkali activator increases, very high ionic association starts taking place, then the concentration of ions start decreasing (initial rapid reaction period). Evidently, the conductance–time curves show one conductivity maximum followed by a sharp decrease in the conductivity value. The decrease in the conductivity values is mainly attributed to the formation of electrically insulating layers around the alkali activated GBFS particles and/or the decrease in the number of ions as a result of the formation of hydration products. A very thin layer consisting of Ca/Si ratio C−S−H, C−A−H and C−A−S−H, which has a very low solubility, precipitates very quickly through the solution, this can be observed after 20–30 min [64]. The increase in alkali activator contents affected the location and intensities of the conductivity maximum. Conductance increases with alkali activator contents due to the high content of free OH− and Na+ ions. This effect leads to an increase in the intensity of the conductivity maximum, which is also shifted to a short time. With the increase in the amount of alkali activator contents to reach 1.50 Na2O mol/kg of GBFS, the conductivity maximum increases. The activation of GBFS proceeds via two steps. The first step is the pre-induction period (wetting and the slag particles start to dissolve). As the hydration proceeds, OH− in the solution can break Ca−O−Si−O−Al−O− bonds. These dissolved species exist in water in the form of (H2SiO4)3−, (H3SiO4)−, (H4AlO4)2− and Ca2+ as a result of this the electrical conductivity increases, this period is called the induction period. After this period the layer consisting of low Ca/Si ratio C−S−H, C−A−H and C−A−S−H precipitated very quickly through the solution [64]. Increasing the curing age permits more accumulation of hydration products that confirm the decrease in electrical conductivity. Alkali
activated GBFS pastes activated with Na2O:SiO2 after 28 days of reaction presented the formation of large amounts of amorphous C—S—H, C—A—H and C—A—S—H gel (geopolymer) [65,66].

3.2. Chemically combined water contents

Chemically combined water (Wc) contents of alkali activated GBFS cured up to 90 days are graphically represented in Fig. 6. The Wc content can be adopted as a criterion to evaluate the relative amount of hydration products and the relative hydration degree between different samples with the same kind of hydration products. It is clear that the combined water contents of the alkali activated GBFS pastes gradually increases up to 90 days. This is due to the continuous hydration and accumulation of hydrated products, which deposed in the available open pores. Fig. 6 shows the Wc contents of the 6 samples at the ages of 3, 7, 28 and 90 days. The increase of the hydration age, the Wc content of alkali activated GBFS increases with increases the contents of Na2O from 0.25 to 1.5 mol/kg of GBFS in the presence of 0.50 mol of SiO2/kg of GBFS. The increasing of the alkalinity condition can promote the hydration of alkali activated GBFS, which increases the degree of hydrolytic destruction of the GBFS. The Wc content of mix S1 at the age of 3 days is 2.98%, but those of mix S6 at the same age reaches 6.07%, indicating that the degree of hydrolytic destruction of alkali activated GBFS increases with the content of Na2O.

Fig. 6 indicates that the influence of increasing alkalinity of hydration condition on the hydration of GBFS changes with age. Increasing alkalinity of hydration condition has an obvious promoting effect on the hydration of GBFS within 7–28 days. At the age of 90 days, the Wc contents of mixes S1, S2, S3, S4, S5, and S6 were 9.38%, 10.32%, 10.99%, 11.01%, 12.46% and 12.63% respectively. As the hydration time increases the amount of hydration products increase, hence the chemically combined water content increases, this is mainly due to the higher hydraulic properties of GBFS with the increasing of alkaline concentration.

3.3. Combined slag contents

The results of combined slag contents of alkali activated GBFS pastes are graphically plotted as a function of curing time up to 90 days in Fig. 7. The combined slag content increases with curing time due to the activation of GBFS hydration. C—S—H gel and C—A—S—H hydrated products are responsible for the strength increase in matrices containing GBFS. The formation of C—S—H and C—A—S—H within the binder work as a micro-aggregate, the resultant binder is homogeneous and dense, resulting in increased mechanical strength as shown later [67]. The activation of GBFS with Na2O:SiO2 depends on the concentration of OH– ions, the compositions of the layers (the concentration of −Si—OH and =Al—OH groups) and the solution. At higher concentration of OH– ions the silicate and aluminate species get into the solution as hydroxocomplexes-silicate and alumin ate anions, mostly condensed. The slag disintegration mechanism proceeded with regard to the types of oxygen O2– present in GBFS. Three types of oxygen anion: double-fixed (siloxane bond =Si—O—Si=), single-fixed (=Si—O—Me— bond) and free in (Me—Me—Me— bond), where Me is a divalent cation. The reaction in aqueous medium may proceed according to the following equations:

\[\equiv \text{Si}—\text{O}—\text{Si}= + \text{H}_2\text{O} \rightarrow 2\equiv\text{Si}—\text{OH}\]

\[\equiv\text{Si}—\text{O}—\text{Me}—\text{O}—\text{Si}= + \text{H}_2\text{O} \rightarrow 2\equiv\text{Si}—\text{OH} + \text{Me}^{2+} + \text{OH}^-\]

\[\equiv\text{Si}—\text{O}—\text{Me}—\text{O}—\text{Me}—\text{O}—\text{Si}= + 3\text{H}_2\text{O} \rightarrow 2\equiv\text{Si}—\text{OH} + 2\text{Me}^{2+} + 4\text{OH}^-\]

The surface silanol groups are neutralized in alkaline media, they act as a cation exchanger.

\[\equiv\text{Si}—\text{O}—\text{Na}—\equiv + \text{H}_2\text{O} \rightarrow \equiv\text{Si}—\text{O}—\text{Na} + \text{H}_2\text{O} \]

Alumina is present in a similar formation, giving rise to soluble aluminate anion Al(OH)3– hydroxocomes and surface groups, =Al—OH. As seen in the above equations, the equilibrium between the solid phase and aqueous solution depends on the concentration of OH– ions. The siliceous species could exist in the form of [(HO)2SiO4]3– and [HOSiO3]2– under highly alkaline conditions [66]. C—S—H is generated by the reaction of Ca2+, HOSiO32– and OH– ions:

\[\text{Ca}^{2+} + \text{HOSiO}_3^{2-} + \text{OH}^- \rightarrow \text{CaSiO}_4\text{H}_2\text{O}\]

C—S—H is primarily responsible for the strength [68]. Jiaying and Peinan [69] showed that the GBFS has hardly any activity in water, while in alkali hydration and hardening are pronounced. The Si—O layer of the GBFS structure is destroyed by an alkali activator and hydration products, such as C—S—H gel and hydrocaluminate are formed by rearrangement of SiO42– and AlO2– and produced gehlenite like hydrate (C3ASH8). GBFS—cement reacts with water, producing calcium aluminosilicate (C3ASH8), calcium aluminate, C3AH6 hydrates and Ca(OH)2, those products have the same properties as in the hydration of
pure Portland cement. In the alkali Ca(OH)₂ solution, Ca²⁺, AlO₄⁻⁵/Cₐ₀, and SiO₄⁻⁴/Cₐ₀ ions enter into the solution and form new hydrate (such as the hydrated silicate and the hydrated aluminate). Combined slag content increases as the concentration of alkali activated mixture. The increase of Na₂O contents from 0.25 mol to 1.50 mol in the presence of 0.50 mol of SiO₂ tends to increase the hydration of alkali activated GBFS at later ages of hydration (90 days). This can be seen from the gradual increase of combined slag contents after 90 days of hydration age.

3.4. Compressive strength

The compressive strength of hardened alkali activated GBFS cured up to 90 days. These values are graphically represented in Fig. 8. The compressive strength of all mixes increases with curing time. Mix S5 shows the higher values of compressive strength at all curing ages of hydration. As the amount of alkali activator increases, the compressive strength enhances. From the data represented in Fig. 8 it is clear that the values of the compressive strength increase is due to the higher rate of hydration as well as formation of more hydrated products. Compressive strength of mixes S3, S4, S5 and S6 sharply increases from 7 up to 90 days due to its reactivity at later ages. The compressive strength of hardened activated GBFS increases by the alkali contents, which accelerate the activation process. Further increase in Na₂O content (till 1.25–1.5 mol/kg) was reported to result in a decrease of compressive strength [34]. One plausible reason is that increasing of Na₂O content contents in activating solution may resulted in reduced level of long-range structural ordering products [10]. The compressive strength is in a good agreement with TGA/DTA analysis. The improvement on compressive strength is related to the reorganization in the microstructure of alkali activated GBFS system.

3.5. Bulk density

The bulk density of hardened activated GBFS cured up to 90 days is graphically plotted in Fig. 9. It is clear that the bulk density increases with curing time up to 90 days. The bulk density of alkali activated GBFS increases with curing time due to the continuous activation and formation of hydrated products. These hydrated products are deposited in the open pores that increase the bulk density of the activated slag. The increase of alkali activator enhances the bulk density of the investigated pastes. The alkali activator enhances the production of higher concentration of [SiO₄]⁻⁴ which increases the rate of hydration and formation of more C–S–H and C–A–S–H. As the amount alkali activator content increases (X Na₂O mol/kg), the bulk density accordingly increases; this is mainly due to the high formation of hydrated products have high specific gravity.

3.6. Total porosity

The total porosity for alkaline activated GBFS is graphically plotted as a function of curing time Fig. 10. As the alkali activation of GBFS increases, more hydration products are formed, which precipitated in some available open pores leading to decrease the total porosity. The addition of 1.25 mol of Na₂O (mix S5) gives the lower values of total porosity. The sharp decrease in the total porosity values of mixes S3 and S4 was shown up to 90 days of hydration. On the other side, the decrease in the total porosity values occurred after 28 days for mix S5 and S6. This is mainly due to the increase of the content of alkali activator, which accelerates the activation of GBFS forming more hydration products. These hydration products fill a part of the available pore volume of the paste; therefore the total porosity decreases.

3.7. Thermo-gravimetric analysis

Figs. 11–13 present TGA/DTA thermograms of alkaline activated mixes S1, S3 and S6 cured for 3, 7 and 90 days. The weight loss of mix S1 at 1000 °C was found to be 3.88%, 8.93% and 10.48%, where for mix S3 was 5.24%, 9.77% and 10.94%, as well as for mix S6 was 6.57%, 10.36% and 11.76% at 3, 28 and 90 days, respectively. The increase in weight loss is related to the progress of geopolymerization process. The weight loss observed in TGA for geopolymerized paste is attributed to the decomposition (water loss) of these
The endothermic peaks located below 200 °C related to C—A—S—H and C—A—H as well as and the peak located at 260–360 °C due to the decomposition of CaH13 and C—A—H and C—A—S—H [70]. The endothermic peak located at 650–720 °C related to the decomposition of carbonate.

The weight loss due to the dehydration of interlayer water of C—S—H of mix S1 was 2.224%, 4.017% and 6.004%, where for mix S3 was 2.824%, 4.817% and 6.684%, as well as for mix S6 was 4.409%, 5.437% and 7.114% for the pastes cured after 3, 28 and 90 days, respectively. A general increase in weight loss with curing time is observed, which may be associated with a greater degree of alkaline activation [71]. The weight loss generally increases with Na⁺ concentration, can be related to a higher degree of chemically bounded water and OH⁻ groups, provided alkaline activation, in the binding phase. The exothermic peak located at 850–870 °C is attributed to the crystallization of the pseudo-wollastonite phase (monocalcium silicate, CS). This exothermic peak is characteristic for the decomposition of C—S—H [72].

The main features of thermograms are characterized by an increase in the areas and intensities of the peaks located at 60 and 101.75 °C, which is due to the dehydration of free water and interlayer water of C—S—H, the peak area and its crystallinity increase with of curing time. As shown from TGA/DTA thermograms an increase in the areas and intensities of the peaks characteristic for C—S—H with the pH value of initial hydration condition (increases the contents of Na₂O) and age of the hydration up to 90 days. As the curing time increases the exothermic peak located at 850–870 °C shows an increase in the areas and intensities of the crystallization of the pseudo-wollastonite phase.

Thermogravimetric data for alkali-activated GBFS paste using different contents of Na₂O and sodium silicate are shown in Figs. 11–13. These tend to have a broader first peak located at (60–100.75 °C) when the amount of Na₂O is increased. The second peak (280–360 °C) can be clearly distinguished for 1.50 mol/kg of Na₂O (Fig. 13), and it progressively overlaps with the first peak when the concentration of the solution is increased, this is because zeolitic-like phases are less likely to form in highly concentrated solutions due to increased difficulties in phase transport and reorganization.

### 3.8. X-ray diffraction

Figs. 14–16, presented the XRD patterns of alkali-activated GBFS samples. It can be observed that the hump peak in the range of 20–38° 2θ changes in the period of curing time at 1 day to 90 days, suggesting that poor crystalline C—S—H and C—A—S—H gel produced in the pastes [73]. Indeed, once GBFS powder is mixed with the alkaline solution, geopolymer gel and C—S—H gel could be formed after setting and hardening. The geopolymer exhibits increase in the mechanical properties as shown in Fig. 8. For all XRD diagrams, broad and diffuse peaks are shown around $d = 2.96–3.03$ Å, implying amorphous or short-ordering structure phases generally present in alkali-activated GBFS. In alkali-activated GBFS, regardless of the presence of the strong peak at $d = 3.07$ Å is attributed to C—S—H(I) phases, which are composed of synthetic calcium silicate hydrate type (I). The formation of CSH or C—S—H(I) in alkali-activated slag has been reported in the literatures [47,73].

The hydrotalcite phase was also synthesized in both of the alkali-activated GBFS samples ($d = 7.77–7.79, 3.85–3.87, 3.85, 2.58, 2.28–2.29, 1.98$ Å). Several previous studies have reported that a hydrotalcite phase forms in alkali-activated GBFS pastes and pointed out that this phase is also a major phase of alkali-activated slag together with CSH(I) [73]. It is note that new phases, tobermorite and calcium silicate hydrate (CSH) gel, are generated during curing time of 28–90 days.
3.9. Fourier transformation infrared spectroscopy

Figs. 17–19 show the FTIR spectra of alkaline activated GBFS pastes. The bands at 460–465 cm\(^{-1}\) are attributed to in plane Si–O bending and Al–O linkages [74]. The band at around 1002 cm\(^{-1}\) is due to T–O–Si (T: Si or Al) asymmetric stretching vibration (950–1200 cm\(^{-1}\)) as a result of TO\(_4\) reorganization that takes place during synthesis [75]. The band located at 1002 cm\(^{-1}\) are a major fingerprint of the inorganic polymeric matrix and define the extent of polysialation or aluminium incorporation [75,76]. The very strong peaks seen at ~1002 cm\(^{-1}\) (as well as at ~458 cm\(^{-1}\)) are assigned to long chain bonds and/or the excess of Al–Si gel formed [76].

The FTIR band at 1040 cm\(^{-1}\) in the initial sample progressively shifted as a function of the reaction time to 1030 cm\(^{-1}\) after 90 days (Figs. 17–19). This band was attributed to asymmetrical stretching Si–O(Si) and Si–O(Al) vibrations in external tetrahedral sites, and the shift indicates that aluminium species are inserted into the framework. Bands at 1040 cm\(^{-1}\) are assigned to stretching of Si–O–Si bonds at the surface of the unreacted silica particles [77], and bands at 1100, 800 and 475 cm\(^{-1}\) relate to stretching, bending and rocking of the Si–O–Si bonds within the network of the unreacted GBFS particles. Bands at 545, 625 and 700 cm\(^{-1}\) are also, related to vibrations in the unreacted particles of GBFS.
The main binder gel appears at 1010 cm⁻¹, assigned to the asymmetric stretching mode of the Si−O−T (T: tetrahedral Si or Al) bonds within the reaction products. The position of this band is consistent with both the C–(A)–S–H structure formed by the activation of GBFS \([66,78,79]\). The band at 999–1010 cm⁻¹, it is typically associated with the binding gels (C–(A)–S–H and N–A–S–H), relatively low wavenumber can be attributed to a reduced content of calcium in the C–(A)–S–H formed from the activation of the GBFS, and increased incorporation of Al into this gel, as the availability of this element increases in the systems by the dissolution.

Atmospheric carbonation is evident at the region of 1455 and 875 cm⁻¹; part of the excess Na present in the matrix is carried to the surface where it reacts with carbon dioxide. The band at 875 cm⁻¹ was not observed in the initial sample, but it was present in all the FTIR spectra of samples after the pozzolanic reaction attributed to the carbonation of samples during manipulation once in all the FTIR spectra of samples after the pozzolanic reaction finished. The bands are associated with pure CaCO₃, attributed to out-of-plane deformation and asymmetric stretching vibrations, respectively. Both bands shift to higher wave numbers after the activation process which, relates to CO₂ impurity species. This, together with the higher intensity of the peaks appearing in the spectrum of the sample activated at 28 days was observed (Figs. 17–19).

The presence of unreacted particles gives rise to a series of bands located at, 1084, 796–778, 697, 668, 522 and 460 cm⁻¹ in the IR spectrum [80]. Although, these bands persist after activation, a reduction in intensity is observed, which indicates that presence of unreacted particles has partially reacted. The higher reduction observed for the sample containing 1.50:0.50; Na₂O:SiO₂ mol/kg implies greater reactivity (Fig. 19), which leads to further development of the alkali-activation reaction products. These results are consistent with the lower porosity and improved compressive strength presented by the samples alkali-activated with 1.50:0.50; Na₂O:SiO₂.

The interpretation of the wide and intense band appears from 990 cm⁻¹ to 1200 cm⁻¹ may be difficult, as bond vibrations of different compounds tend to overlap, producing a highly complex spectrum. While in the unreacted GBFS particles this band appears at 1015 cm⁻¹, in the activated samples it shifts to lower wavenumbers (1001 cm⁻¹). This shift occurs due to the formation of aluminosilicate gel, as the asymmetric stretching vibrations of the newly formed Si−O−T (T = Al, Si) bonds originate a new band growing at 990 cm⁻¹ as shown in Figs. 18 and 19. Although a gel with a higher Si/Al ratio is expected for the 1.50:0.50; Na₂O:SiO₂ paste, the nature of the gel formed could not be clearly distinguished from FTIR results, due to the Al-enriched gel phase band (1015 cm⁻¹, from [81], and the primary band of the Si−O−T bonds in the gel overlap. Furthermore, the bands associated with the vitreous phases of the raw material were also expected to appear in this region (950–1100 cm⁻¹) [80]. Although they could not be distinguished, the intensity was expected to decrease as the aluminosilicate gel formation proceeded.

After 90 days, there is a reduction in the intensity of the main Si−O−Si band, indicating that the solid silica is dissolving. At the same time, a new band starts forming at about 950 cm⁻¹ and the intensity of this band increases over time. This particular band is associated with the Si−O−T stretch within the newly formed geopolymer network [76], and it appears to grow at a similar rate in both samples depicted in Figs. 17–19.

Band descriptions are as follows: bending vibration of HOH in the region of 1595–1628 cm⁻¹, stretching vibration of CO₂ located at about 1430 cm⁻¹, asymmetric stretching vibration of T−O−Si at about 990–1100 cm⁻¹, where T = Si or Al, Si−O stretching in the region of 880 cm⁻¹, symmetric stretching vibration of Si−O−Si between 770 and 780 cm⁻¹, symmetric stretching vibration of Si−O−Si and Al−O−Si in the region 675–685 cm⁻¹ and bending vibration of Si−O−Si and O−Si−O in the region 450–460 cm⁻¹. The bending vibration of Si−O−Si appeared to increase in sharpness with increasing the Na₂O content from 0.25 to 1.5. The broadness of HOH band implies the overlap of more bands with higher intensity which is mainly related to the combined water in CSH, and so, the increase of this peak reflects the increase of binding materials of this specimen. This band decreases sharply with the Na₂O content from 0.25 to 1.5 at 90 days, due to the formation of two-dimensional polysialatedisiloxo crosslink than forming CSH which in turn acts as a seedling agent for geopolymer accumulation.

In conclusion, various infrared absorption bands may be used for the identification of bonds such as Si−O, Al−O and S−OH in the inorganic polymer structure. These bands are formed when GBFS particles react with the activating solution and solubilization of elements takes place. Stretching vibrations of the bond T−O−Si seen between 950 and 1200 cm⁻¹ indicate the formation of gel during polycondensation.

3.10. Scanning electron microscopy

Figs. 20–22 show the SEM micrographs of samples S1, S3 and S6 hydrated for 3, and 90 days respectively. Fig. 20 shows SEM micrograph of S1 sample hydration at 3 days under alkaline condition (0.25:0.50; Na₂O:SiO₂ mol/kg), micrograph represented the formation of thin film of hydration products on the surface of alkaline activated GBFS paste. This initial hydration products are amorphous with a honeycomb like structure C−S−H gel with the metastable state. H₂O and OH⁻ permeate through the initial hydration products and reacted with GBFS particles with the increase of hydration age, to produce more hydration products.

With the increase of the hydration age (90 days), the surface of active components of alkaline activated GBFS paste are corroded more obviously and hydration products can be clearly observed on the surface of alkaline activated GBFS particles. SEM micrograph deposited the hydration products on the surface of alkaline activated GBFS particles are more obvious. Most of the gel produced by alkaline activated GBFS paste hydration is the hydration products similar to the C−S−H gel as well as flake crystal of calcium aluminate hydrates.

Figs. 21 and 22 represented the SEM micrographs of S3 and S6 hydrated for 3, and 90 days respectively. The increasing of the alkalinity condition increase the promoting effect on the early hydration of alkaline activated GBFS. The gel was formed on the surface of alkaline activated GBFS particles appeared in the structure (Figs. 21 and 22). Globules of C−S−H or C−A−S−H are concentrated in the matrix. The micrograph shows the flocculent and porous structures as well as wider pores are available for crystallization of the formed hydrates. Pastes cured for 90 days have a compact-dense microstructure displayed a more dense arrangement of microcrystalline C−S−H and C−A−H as the main hydration products (Figs. 21 and 22). The amount of amorphous gel is very high, occupying an important part of the volume in the sample. Furthermore, SEM images showed an important amount of (N,C)A−S−H gel and low porosity of the developed matrix [65]. With the increase of the content of Na₂O, Na₂O leads to form a denser closed microstructure, leading to higher compressive strength values. Furthermore, all the pastes presented unreacted particles surrounded by hydration products.

3.11. Resistance to aggressive attack
3.11.1. Magnesium sulphate solution

The problem of aggressive attack of sulphate and chloride ions has been of considerable scientific and technological interest
because this attack is one of the factors responsible for concrete damage. Sulphate ions can enter into chemical reactions with certain constituents of concrete producing sulphaaluminate hydrates and gypsum, which cause the expansion of concrete [35,38]. Magnesium sulphate causes distress into concrete decreasing OH⁻ concentration; C₆ASH phase may be decomposed and caused losses in strength [82].

3.11.1.1. Compressive strength. The compressive strength of alkali activated GBFS as well as OPC immersed in 5% MgSO₄ solution up to 180 days is graphically plotted in Fig. 23. The data show that the compressive strength of alkaline activated slag increases with curing time as the hydration progresses up to 180 days. The compressive strength of mix S1 shows higher values, due to a good pozzolanic activity in alkaline activation that exhibits higher resistance to sulphate medium up to 180 days. The immersion of alkali activated GBFS pastes in 5% MgSO₄ solution enhances the activation of GBFS pastes. The high compressive strength of OPC pastes at zero time is due to its higher rate of hydration compared to alkali activated GBFS. It is clear that the compressive strength of alkali activated GBFS increases up to 180 days. Alkali activated GBFS improves the durability and the resistance to chemical attack, this is due to the continuous activation of GBFS forming C₆ASH as well as C₆ASH. The compressive strength of OPC pastes immersed in 5% MgSO₄ increases up to 180 days then decreases [10,35,38,42]. The decrease of strength of OPC pastes after 180 days is mainly due to the presence of high values of alite and belite, which liberate Ca(OH)₂ [35,38,42]. The liberated Ca(OH)₂ available in the hydrated cement matrix reacted with MgSO₄ to form gypsum. The formed gypsum reacted with calcium aluminate phases of both hydrated and the unhydrated portions of cement in the matrix to form expanding ettringite [82–85]. On the other side, the presence of magnesium ions as MgSO₄ or/and
MgCl₂ leads to the distortion of C–S–H through a dissolution of Ca²⁺ or/and an exchange with Mg²⁺ to Mg–S–H and Mg(OH)₂, which have no binding properties [35,38]. By comparing the alkali activated slag with OPC, it is found that the strength of alkali activated slag increases up to 180 days, due to the formation of additionally C–S–H [70], without the formation of expanding and softening chloroaluminate and ettringite hydrated products.

3.11.1.2. Total sulphate content. The total sulphate content of alkali activated GBFS as well as OPC immersed in 5% MgSO₄ solution up to 180 days is graphically represented in Fig. 24. The data show that the total sulphate contents of alkali activated GBFS has the lower values of sulphate content up to 180 days of immersion in 5% MgSO₄ solution. The resistance towards sulphate attack solution increases with the increase of alkali activated contents. This is mainly due to the decrease of the total porosity which hinders the penetration of sulphate ions in the matrix. The values of total sulphate contents increase with the immersing time due to immersing of pastes in aggressive medium containing sulphate ions (5% MgSO₄). OPC pastes give higher values of total sulphate content than those alkali activated GBFS. S5 has a lower values of total sulphate content up to 180 days, this can be attributed to the fact that the alkali activated GBFS do not have free lime content in its matrix and geopolymers themselves are not easily attacked by aggressive medium containing sulphate ions as shown in Fig. 24 [46].

3.11.2. Magnesium chloride solution

The corrosive action of chlorides is due to the formation of chloroaluminate hydrates, which causes softening of concrete. Attack of chlorides proceeds by ionic penetration of Cl⁻ in concrete. This penetration is independent of the chloride concentration and the concrete penetrability to the salt solution as a whole. Diffusion seems to be depend not only on the porosity of the matrix but also on the nature of the paste. Moreover, Cl⁻ ionic diffusion depends not only on the permeability and binding capacity of Cl⁻ ions, but also on the ion-exchange capacity of the system.

3.11.2.1. Compressive strength. The compressive strength values of hydrated alkali activated GBFS pastes immersed in 5% MgCl₂ solution up to 180 days are graphically represented in Fig. 25. The compressive strength increases with curing time, due to the continuous hydration. The compressive strength of mix S1 shows a sharp increase up to 28 days, and then it increases slowly up to 180 days. The compressive strength of mix S5 increases gradually up to 180 days due to good resistance to chloride medium whereas, the values of compressive strength of OPC shows a lower values from 28 days up to 180 days. OPC contains free lime content in its matrix due to hydration reactions of Portland cement portion, this free lime and also the hydrated Portland cement matrix C–S–H gel of the matrix are easily attacked by acids in general [42,82].

3.11.2.2. Total chloride content. The total chloride contents of alkali activated GBFS pastes immersed in 5% MgCl₂ solution up to 180 days is graphically plotted in Fig. 26. The total chloride content increases with curing time for all mixes up to 180 days. The total chloride sharply increases after 1 week, then slowly increases up to 180 days for all pastes. The total chloride content decreases with alkali dosages due to the pozzolanic reaction to form C–S–H that fill some available open pores, thereby inhibiting the chloride ion penetration; improve the microstructure of pore systems. The increase in total chloride contents of OPC paste is mainly due to the reaction of MgCl₂ with CH forming CaCl₂ and Mg(OH)₂2. CaCl₂ reacts with C₃A and/or C₃AF to form chloroaluminate hydrate (C₃A·CaCl₂·10H₂O). Also, MgCl₂ reacts with calcium silicate hydrates form calcium chloride, magnesium hydroxide and silica gel. The alkali activated GBFS do not have free lime content in its matrix and geopolymers themselves are not easily attacked by aggressive medium containing [46]. These is mainly due to the accumulation of excessive amounts of hydrates within the pore systems at larger hydration times; this effect leads to a decreased accessibility of chloride ions towards the more dense with low capillary pore structure of the hardened pastes on the prolonged hydration.
Fig. 26. Total chloride of hardened cement pastes subjected to 5% MgCl₂ solution up to 180 days.

4. Conclusions

The main conclusions could be derived from this investigation are summarized as follows:

1. Electrical conductivity of alkali activated GBFS depends mainly on the binder composition, the activator type and its concentration. Alkali activator contents affected the location and intensities of the conductivity maximum.
2. Mix S5 shows the higher values of compressive strength at all curing ages up to 90 days.
3. The improvement on compressive strength is related to the reorganization in the microstructure of alkali activated GBFS system.
4. The compressive strength of mix S1 shows higher values in 5% MgSO₄ or MgCl₂ up to 180 days, due to a good pozzolanic activity in alkaline activation that exhibits higher resistance to sulfate medium up to 180 days.
5. Alkali activated GBFS lead to good durability and high resistance to chemical attack.
6. By comparing the alkali activated slag with OPC, it is found that the strength of alkali activated slag increases up to 180 days, due to the formation of C–S–H and geopolymer with the absence of chloroaluminate and ettringite.
7. Total sulphate of mix S5 have a lower value up to 180 days.
8. The total chloride and total sulphate contents decrease with alkali activated GBFS due to the forming hydrated products that fill some available open pores, thereby inhibiting Cl⁻ and SO₄²⁻ ions penetration; this effect leads to a decreased accessibility of Cl⁻ or SO₄²⁻ ions towards the more dense with low capillary pore structure of the hardened pastes on the prolonged hydration.
9. It can be concluded that alkali activated GBFS are more durable in 5% MgSO₄ or 5% MgCl₂ than OPC pastes.

References


