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The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation

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Abstract

Scanning electron microscopy was used to study the effects of the addition of ground granulated blast furnace slag (GGBFS) on the microstructure and mechanical properties of metakaolin (MK) based geopolymers. It was found that it is possible to have geopolymeric gel and calcium silicate hydrate (CSH) gel forming simultaneously within a single binder. The coexistence of these two phases is dependent on the alkalinity of the alkali activator and the MK/GGBFS mass ratio. It has been found that the formation of CSH gel together with the geopolymeric gel occurs only in a system at low alkalinity. In the presence of high concentrations of NaOH (> 7.5 M), the geopolymeric gel is the predominant phase formed with small calcium precipitates scattered within the binder. The coexistence of the two phases is not observed unless a substantial amount of a reactive calcium source is present initially. It is thought that voids and pores within the geopolymeric binder become filled with the CSH gel. This helps to bridge the gaps between the different hydrated phases and unreacted particles; thereby resulting in the observed increase in mechanical strength for these binders.

Keywords: Amorphous materials; Microstructure; Calcium–silicate–hydrate; Granulated blast-furnace slag; Metakaolin

1. Introduction

The search for a new environmentally friendly construction material that will match the durability of ancient concrete has provoked interest into the study of alkali activated cementitious systems over the past decades. Alkali activated cements refer to any system that uses an alkali activator to initiate a reaction or a series of reactions that will produce a material that possesses cementitious property. Alkali activated cement, alkali activated slag and fly ash, and geopolymers are all considered to be alkali activated cementitious systems, however, it is expected that the structures of these materials are vastly different and result from different chemical mechanistic paths.

It is commonly acknowledged that calcium silicate hydrate (CSH) is the major binding phase in Portland cement [1,2] and alkali activated slags [3]. However, the binding property of geopolymers is generally assumed to be the result of the formation of a three-dimensional amorphous aluminosilicate network. [4–10]

Davidovits and Davidovics [6,8] proposed that geopolymers are formed by the polymerisation of individual aluminate and silicate species, which are dissolved from their original sources at high pH in the presence of alkali metals. The resultant products are reported to have the general formula $M_n\text{–}[[\text{–Si–}O_2]_z\text{–Al–O}]_n \cdot wH_2O$ where M is the alkali element, –indicates the presence of a bond, z is 1, 2 or 3 and n is the degree of polymerisation. Theoretically, any alkali and alkali earth cation can be used as the alkali element (M) in the reaction, however the majority of research has focused on the effect of sodium (Na^+) and potassium (K^+) ions [7,9–11]. It has not been clearly proven whether other alkali and alkali earth cations, including calcium will participate in the reactions in a similar way.

In terms of chemical composition, the major difference between geopolymers and Portland cement is calcium. It is

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important to note that calcium is not essential in any part of a basic geopolymeric structure. Given that CSH will be formed when soluble calcium and silicate species are present in a neutral to mild pH environment, it is thought that provided sufficient calcium is added to a geopolymeric system, a CSH based cementitious material may form instead.

In recent years, some studies have been conducted on various metakaolin (MK)/lime (calcium hydroxide) and MK-blended cement systems [12–17]. Cabrera and co-workers [14,15,17] found that the activation of metakaolin in the presence of calcium hydroxide caused rapid formation of CSH, C_2ASH_8 (stratlingite) and C_4AH_{13} (tetracalcium aluminate hydrate).

Alonso and Palomo [12,13] 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 [12–15,17] 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. Fig. 1 shows the likely reaction products formed when calcium is added to a geopolymeric system.

To date, there is no published literature dealing with the relationship between the chemistries of geopolymers and CSH based on a metakaolin/ground granulated blast furnace slag (GGBFS) system. The chemical reactions that take place in the MK/GGBFS system are expected to be more complex than in the MK/lime system, as GGBFS consists of a mixture of glassy phases reacting at different rates.

The MK/GGBFS mass ratio and Na_2O/SiO_2 molar ratio in the alkaline solution used as the alkaline activator were the main parameters investigated in the current study. The findings from this work are fundamental to further work on the relationship between geopolymers and Portland cement in terms of their respective chemical mechanisms. Subsequently, an understanding of the mechanistic relationships between the phases will help researchers to form a new environmentally friendly construction material that possesses the durability of ancient concrete.

2. Experimental work

2.1. Materials

Metakaolin (MK) is a highly reactive metastable clay that is an anhydrous aluminosilicate obtained from calcining kaolin to around 650–700 °C [18]. Metakaolin was used as the primary aluminosilicate source, because it is widely used as aluminosilicate source in geopolymeric systems as well as a mineral admixture in Portland cement.

Metakaolin used in the synthesis was obtained from ECC International (United Kingdom) under the brand name of MetaStar 402 with a particle size distribution of 100%<10 μm. This commercial metakaolin was purified before calcination, and it had less than 0.1 wt.% of CaO (Table 1). It was assumed in this study that all calcium came from ground granulated blast furnace slag (GGBFS). GGBFS was obtained from Independent Cement (Australia) with a size distribution of 100%<50μm. The XRD diffractograms presented in Fig. 2 demonstrate that both MK and GGBFS contain semi-crystalline and amorphous phases (as indicated by the broad hump centred at approximately 27° and 30° 2-theta), with low-intensity peaks corresponding to muscovite and gypsum in MK and GGBFS respectively. It should be

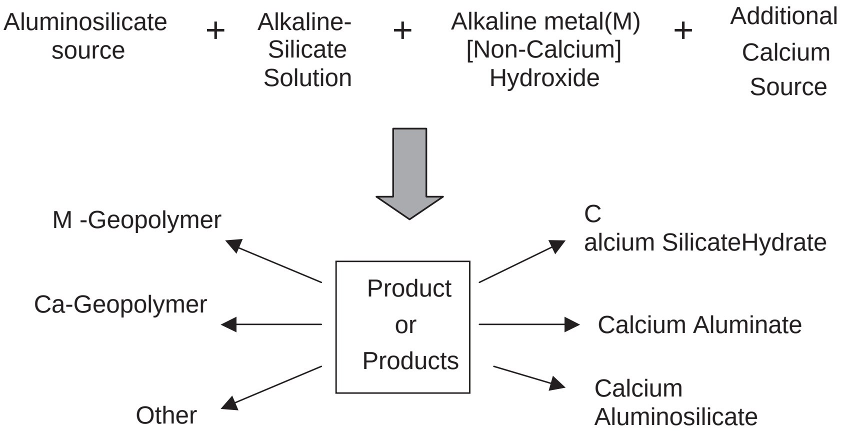

Fig. 1. Concept mapping of the likely products resulting from the alkaline activation of aluminosilicate in the presence of a calcium source.

Table 1
Chemical composition of metakaolin (MK) and ground granulated blast furnace slag (GGBFS)

Constituent	MK	GGBFS
CaO	0.10	43.0
SiO_2	54.78	34.4
Al_2O_3	40.42	14.1
Fe_2O_3	0.76	0.11
SO_3	0	0.58
MgO	0.41	6.3
K_2O	2.72	0.33
Na_2O	0.07	0.30
P_2O_5	0.11	0.005
TiO_2	0.02	0.69
Mn_2O_3	0.01	0.23

noted that it is common practice in Australia to blend gypsum with granulated blast furnace slag during the grinding process.

The sodium silicate solution used in the experiments was supplied by PQ Australia under the brand name of Vitrosol N48 (with 28.7 wt.% SiO_2, 8.9 wt.% Na_2O and 62.4 wt.% H_2O; density 1.37 g/mL). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia. Distilled water was used throughout the experiments. Fine washed sand (100%<2 mm) was used as the aggregate in the samples that were subjected to compressive strength testing. Samples subjected to other analysis were prepared without the addition of washed sand.

2.2. Synthesis

Sodium hydroxide pearl was mixed with sodium silicate solution to form an alkaline solution with two different molar ratios ($Ms = SiO_2/Na_2O = 2.0$ and 1.2). The hot liquid was then left overnight to cool to ambient temperature.

Samples with six different ratios between MK and GGBFS were synthesised in this study: MK/(MK+GGBFS) being 0, 0.2, 0.4, 0.6, 0.8 and 1. The mass ratios between the activator solution (sodium hydroxide and sodium silicate solution) and dry mix (MK and GGBFS) were 1.45 and 1.63 for Ms = 2.0 and 1.2 respectively. These particular ratios were chosen so as to provide for equal moles of water present in the structures of all the matrices synthesised.

MK and GGBFS were mixed thoroughly until a uniform blend was produced. The alkaline activator was then stirred with the dry mix to form a paste. The paste was typically mixed for 3 min to ensure the mixture was homogeneous. For samples subjected to compressive strength testing, washed sand (with mass ratio = sand/(MK+GGBFS) = 3) was added to the homogeneous paste gradually until a uniform mixture was formed. The paste or mortar was then poured into cylindrical moulds (50 mm diameter and 100 mm length) and allowed to cure in a laboratory convection oven at 40 °C for 24 h before being extracted from the moulds and hardened at room temperature (25 °C) until testing. All samples were cured at atmospheric pressure. It should be noted that compressive strength tests were conducted on matrices up to 240 days (after curing); however the microstructural analysis has been conducted only on samples at 7 and 28 days (after curing).

2.3. Analysis

Compressive strength testing was performed as per Australian Standard (AS1012.9-1999) using three 50 mm diameter cylinders having a 1:2 diameter to length ratio. All compressive strength measurements presented are the average of three samples. Samples were tested after 7, 28, 90 and 240 days. An ELE International Auto Test Compression Machine was used. Compressive strength testing was only conducted on samples with the addition of washed sand. Before testing, the top face of the specimen was cut in parallel with the bottom face by using a diamond saw. The top surface of the sample was capped with fast setting Boral Dental Plaster to ensure the diameter and length ratio remained at 1:2. The sample was then left

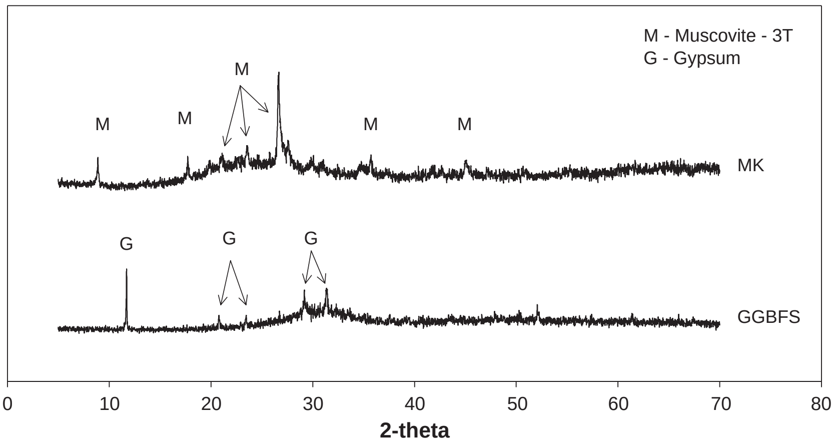

Fig. 2. XRD of raw metakaolin (MK) and ground granulated blast furnace slag (GGBFS).

overnight at room temperature and atmospheric pressure. The compressive test was conducted on the following day.

X-ray diffractograms were recorded on a PHILIPS PW1800 machine using a CuKα anticathode and a scanning rate of 2°/min from 5° to 70° 2-theta to give the structural information on each sample. Identification of various crystalline phases was done by comparing the diffraction patterns to JCPDS (Joint Committee on Powder Diffraction Standards) data. The specimens were prepared for XRD by mechanical grinding.

A Philips XL30 scanning electron microscope, operated at 20 keV was used to analyse the surface morphology of each sample. EDS (Energy Dispersive Spectroscopy) was used to analyse the elemental composition at the surface of each sample. A DYNAVAC sputter coater was used to coat each sample with carbon.

3. Results and discussion

3.1. Compressive strength

The effects of the different MK/(MK+GGBFS) ratios and alkalinity on the mechanical strengths of the resultant products are summarised in Tables 2 and 3. The most significant factor observed to control the compressive strength is the mass ratio between MK and GGBFS used. The results from Tables 2 and 3 clearly demonstrate that an optimum MK/GGBFS ratio exists to give the highest compressive strength of the resultant geopolymer matrix. Regardless of the Na_2O/SiO_2 ratios used in the synthesis, the resultant compressive strength of the matrices increased when a moderate amount (20 wt.% of the total mass between MK and GGBFS) of GGBFS was added to the system. However, the addition of GGBFS was destructive if it was added in a significant amount (more than 40 wt.% of total mass).

It is also shown in Tables 2 and 3 that the compressive strengths of the matrices containing less than 40 wt.% of GGBFS, increased with time in all cases. However the compressive strengths of the matrices containing more GGBFS (Matrices 5, 6, 11 and 12) reached their highest strength at approximately 7 days. The rapid loss in mechanical strength of these matrices (after 7 days) was due to the development of cracks, which resulted in crumbling of each matrix when an external force was applied.

Table 2
Compressive strengths of matrices synthesised using Ms = 1.2 and $(NaOH+NaSiO_3)/(MK+GGBFS) = 1.63$ at 1, 7, 28, 90 and 240 days

Matrix	MK/ (MK+GGBFS)	Compressive strength (MPa)				
		1	7	28	90	240
1	1	35.4	36.2	38.4	37.6	37.7
2	0.8	32.8	38.6	40.5	45.1	46.2
3	0.6	26.7	25.4	15.2	13.7	13.5
4	0.4	20.3	23.1	9.2	9.9	9.1
5	0.2	13.5	23.7	8.7	<5.0	<5.0
6	0	14.1	17.8	6.0	<5.0	<5.0

Table 3
Compressive strengths of matrices synthesised using Ms = 2.0 and $(NaOH+NaSiO_3)/(MK+GGBFS) = 1.45$ at 1, 7, 28, 90 and 240 days

Matrix	MK/ (MK+GGBFS)	Compressive strength (MPa)				
		1	7	28	90	240
7	1	32.1	34.6	35.2	35.7	35.6
8	0.8	39.3	47.1	54.2	58.2	59.1
9	0.6	38.0	41.5	52.7	54.3	53.8
10	0.4	31.4	29.1	34.6	32.7	28.7
11	0.2	20.2	23.0	8.9	<5.0	<5.0
12	0	8.9	17.8	5.3	<5.0	<5.0

Previous studies [19–21] have found that calcium has a positive impact on the compressive strength of geopolymeric binders. The current findings are in agreement with these studies. It is confirmed that the addition of calcium will benefit the mechanical properties of the matrices. However, it is still not clear why and how the presence of calcium will play such a significant role in determining the properties of a geopolymer.

Given that the particle size of MK is much smaller than GGBFS, the surface area of MK is significantly higher than that of GGBFS. For this reason, it is thought that when dissolution takes place the MK will be more reactive than GGBFS. Subsequently, the viscosity of the initial suspension with more MK will be higher than that which contains more GGBFS.

Given that the same amount of water was used in all samples in this investigation, it follows then that the gel resulting from the activation of GGBFS is less viscous than that formed from the activation of MK. It is thought that if excess water in the less viscous gel is not consumed during the hydration process, free water will diffuse out of the matrices with time. This diffusion of excess water from the matrices may leave behind more inner pores within the structure, which may consequently induce cracking throughout the matrices.

Strength development of Portland cement involves the formation of CSH and calcium hydroxide, and it is generally believed that the CSH gel is the component that gives the strength to the resultant binder [1]. The main role of GGBFS is assumed to contribute dissolved calcium species, which will react with the silicate and aluminate to form various forms of calcium silicate hydrates and calcium aluminium hydrates. However, the pH values in both systems investigated in this study are approximately 14. Phair et al. [22] have shown that the solubility of calcium decreases with increasing pH, which was attributed to the formation of calcium hydroxide. Precipitation of calcium hydroxide will occur when the MK and GGBFS are mixed in such a highly alkaline medium. Calcium hydroxide is highly unstable, which will further react with carbon dioxide in the air to form calcium carbonate (carbonation) [23]. It is generally agreed that the presence of excess calcium hydroxide in the resultant structure and the subsequent carbonation process are one of the main causes of the deterioration of concrete [23].

In addition, the precipitation of calcium hydroxide will also have prevented calcium species to participate in the formation of CSH or C_4AH_{13}, which are commonly found as a major product in the alkali-activation of MK in the presence of calcium hydroxide [17]. It is therefore expected in systems where there is excess GGBFS present that a substantial amount of calcium hydroxide will be formed, which leads to a rapid reduction in strength with time.

For the geopolymeric binder with 100% metakaolin (Matrices 1 and 7), it was found that the compressive strength of these matrices increased with increasing sodium hydroxide concentration. This observation is in agreement with previous findings [22,24] that geopolymerisation is accelerated in a highly concentrated alkaline environment. It is generally believed that the initial dissolution process is caused by the presence of hydroxyl ions. The presence of higher amounts of hydroxyl ions will favour the dissociation of different silicate and aluminate species, subsequently promoting further polymerisation between them.

When a lower alkalinity (Ms = 2.0) was used, the presence of 20–40 wt.% of GGBFS gave an optimum compressive strength. On the other hand, when a higher alkalinity (Ms = 1.2) was used, a lesser amount of GGBFS (0–20 wt.% of GGBFS) was required to give an optimum strength. The shift in the optimum MK to GGBFS ratio indicates that the nature and characteristics of the resultant binders has changed after GGBFS was added to the system.

The difference in compressive strength between the pure MK-binders synthesised at different alkalinity is small in comparison to the change between matrices synthesised at different alkalinity with the addition of GGBFS. This has indicated that GGBFS plays different roles in the MK/GGBFS system and it is dependent on the alkali concentration of the silicate activator solution. Moreover, the early compressive strengths (up to 28 days) of MK binder and binder with 20 wt.% GGBFS added synthesised at higher alkalinity (Ms = 1.2) are similar. This suggests that the geopolymeric gel is the component that contributes to the strength of the binder at high alkalinity. At a lower alkalinity (Ms = 2.0), the presence of the alkali activated product of GGBFS contributes significantly to the binder compressive strength.

The compressive strength results have confirmed that the addition of a moderate amount of calcium source into a MK system will improve the mechanical properties of the resultant matrix. Many attempts have been made to explain the increase in compressive strength in geopolymeric binders synthesised in the presence of a calcium source, however, the investigation is still incomplete. Before any progress can be made towards understanding the chemical mechanism involved in the alkali activation of MK in the presence of GGBFS, it is essential to examine and analyse the products at different hydration stages. The present study has focused on the characteristics of hydration products at 7 and 28 days of curing. Further discussion on the effect of the microscopic change in hydration products due to the presence of GGBFS on the mechanical properties of the resultant binder will be presented later in this paper.

3.2. Crystallinity of hydration products

XRD was used to study the changes in crystallinity before and after alkaline activation. It should be noted that the reactants used and most of the binders produced in this study contain a very high percentage of amorphous to semi-crystalline phases. It is difficult therefore to identify all the crystalline phases according to JCPDS. X-ray diffraction analysis was conducted over the scanning range from 5° to 70° 2-theta, but the XRD results shown are reported between 20° and 50° 2-theta, where the important regions are situated.

The X-ray diffractograms (Figs. 3 and 4) show the effect of different MK/(MK+GGBFS) ratios and Na_2O/SiO_2 ratios on the crystallinity of the material before and after alkali activation. These X-ray diffractograms were plotted as the difference between the XRD pattern of the resultant binder at 28 days after the activation and before activation, which was calculated by subtracting "XRD pattern before activation" from "XRD pattern after activation." The reason why a "difference" was plotted instead of using the XRD pattern obtained for the resultant binder, is the high amorphous contents of resultant binders and raw materials used, which show a large number of unidentifiable peaks. The use of "difference" XRD patterns will highlight the crystalline phases created and destroyed during the alkali activation.

Both MK and GGBFS consist mainly of semi-crystalline and amorphous phases (as indicated by the broad "hump" in XRD, Fig. 2.), with some low-intensity peaks corresponding to muscovite and gypsum respectively. These minor crystalline phases were partially dissolved when the materials were alkaline activated. The binders formed after the activation were mainly amorphous to semi-crystalline, but some very weak minor crystalline phases that could not be clearly identified by JCPDS, could still be observed.

There is no new crystalline phase formed as a result of the alkali activation of MK in the absence of GGBFS. From the XRD patterns of the resultant MK binder synthesised at different Na_2O/SiO_2 ratios, there is a hump starting at about 20° through to 40° 2-theta. Previous XRD studies [22] on geopolymeric binders have reported similar characteristics. It was suggested [11,20,22] that such a hump is due to the presence of amorphous silica in the binder. When comparing the binders before and after the

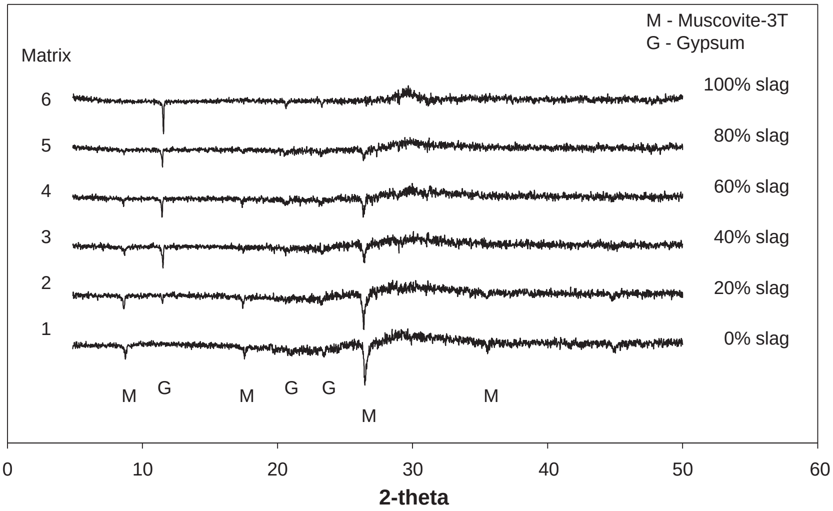

Fig. 3. Differences between the XRD diffractograms of matrices (1–6) before and after (28 days) alkaline activation (Ms = 1.2).

alkaline activation for the MK-binder (Fig. 3 Matrix 1 and Fig. 4 Matrix 7), it was found that there are small changes to the intensity of the hump at around 28–31° 2-theta for both 100% MK binders activated regardless of the Na_2O/SiO_2 ratios used. Since the XRD humps found at around 28–32° 2-theta shown for both diffractograms have similar characteristics, it can be concluded that the crystallinity of the resultant product from the alkaline activation of MK is independent of Na_2O/SiO_2 ratio used within the range studied in this investigation.

There is no new crystalline peak associated with the alkali activation of GGBFS. Therefore it can be concluded that crystalline CSH is not a product or it is not a dominant product formed as a result of the alkaline activation of GGBFS under the conditions used in this investigation. This is in agreement with previous findings by van Jaarsveld and van Deventer [11] that crystalline CSH is not formed in a high pH ($pH > 14$) environment. However, amorphous CSH within a geopolymeric gel could be part of the resultant product, as will be shown later.

It should be noted that the crystalline peaks associated with crystalline calcium hydroxide (portlandite) were not observed in the structure either. However, this does not exclude the possible formation of amorphous calcium hydroxide. As discussed earlier, it is expected that calcium hydroxide will be precipitated from the alkaline solution once soluble calcium species are present in the solution phase during the initial dissolution step.

XRD patterns of binders with various amounts of MK and GGBFS present are shown to have the same features as those patterns generated by MK and GGBFS individually, so that no new crystalline phases formed as a result of the reaction. The amorphous nature of the products and the interference between peaks of different phases, make it impossible to identify the resultant products formed when MK and GGBFS are alkali activated at the same time.

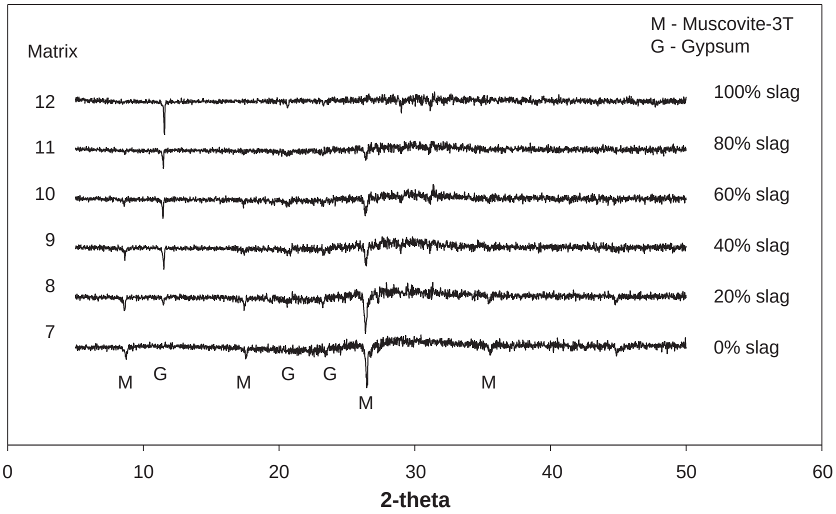

Fig. 4. Differences between the XRD diffractograms of matrices (7–12) before and after (28 days) alkaline activation (Ms = 2.0).

3.3. Microstructure of hydration products

Electron microscopy was employed to examine the microscopic effect of GGBFS on alkali activation of MK between 7 and 28 days after curing. When MK is activated by alkaline silicate solution, a geopolymeric binder will be formed with no new phases identified by XRD, regardless of the Na_2O/SiO_2 ratio. Fig. 5 shows a representative scanning electron micrograph of a geopolymer binder (Matrix 7) with 100% MK alkali activated at Ms = 2.0.

Fig. 6 shows a representative scanning electron micrograph of a geopolymer binder (Matrix 8) containing 80 wt.% of metakaolin and 20 wt.% of GGBFS with Ms = 2.0 at 14 days. This micrograph is representative of the microstructural features found in such systems at this stage of the hydration process. Two separate phases were formed as a result of the alkali activation of metakaolin in the presence of GGBFS. EDS analysis was conducted on the sample and the results are summarised in Table 4. It was found that the elemental composition of area A was dominated by silicon, aluminium and sodium with less than 2 wt.% of calcium, while the elemental composition of area B was dominated by silicon and calcium with some sodium and less than 3 wt.% of aluminium. Clearly the phases present in areas A and B are different in terms of their elemental composition.

The concentration of each element was found to be consistent within the areas A and B and there is a narrow interfacial area between the two regions. Area A is suggested to be a geopolymeric binder, which has similar characteristics to the geopolymeric binder formed in the absence of GGBFS as shown in Fig. 5. This observation is in agreement with previous observations by Alonso and Palomo [12,13] that the geopolymer formed as the result of the alkali activation of MK in the presence of $Ca(OH)_2$ has the same characteristics as that formed in the absence of $Ca(OH)_2$. Traces of calcium within this geopolymeric phase (A) originated from and diffused outward from the GGBFS.

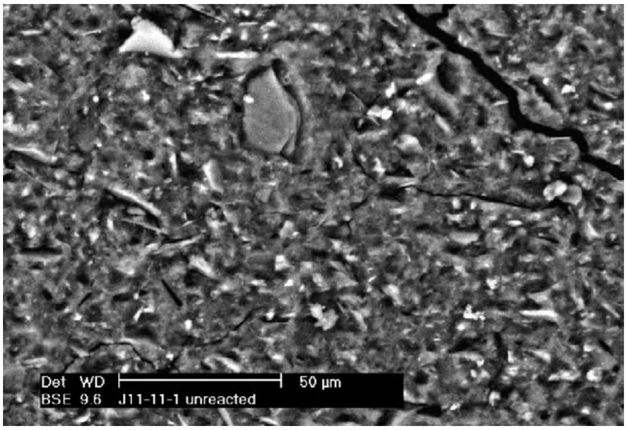

Fig. 5. SEM micrograph of Matrix 7 (100% MK, Ms = 2.0) at 14 days.

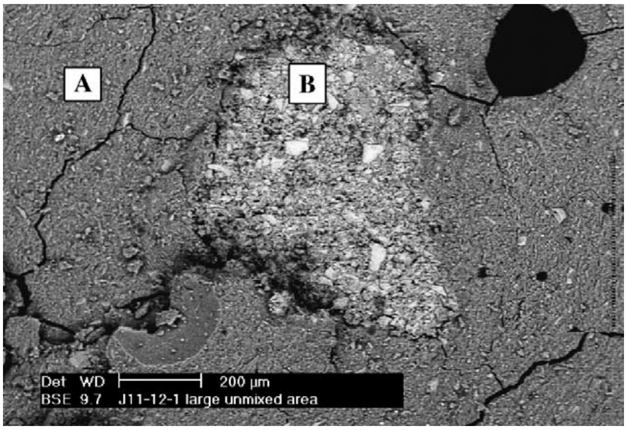

Fig. 6. SEM micrograph of Matrix 8 (20% slag, Ms = 2.0) at 14 days. Identification of the different phases: (A) geopolymeric binder with low content of calcium; (B) calcium silicate hydrate with small proportion of aluminium.

Likewise, the elemental composition of area B is consistent within the region. Calcium and silicon are the main elements in this area, in which aluminium and sodium are of much lower concentrations. It is suggested that the phase present in area B could be some form of CSH (calcium silicate hydrate). However, it is believed that this CSH is different from the one generally resulting from the normal hydration of Portland cement or amorphous calcium silicate in raw slag because of the much lower Ca/Si ratio (ca. 0.98) in phase B. Barnes [25] and Gani [2] suggested that the average bulk Ca/Si ratio of a CSH gel in ordinary cement lies in the range of 1.5–1.7, while Richardson [26] found that the Ca/Si ratio of CSH in neat Portland cement pastes varies from 1.2 to 2.3 with a mean value of ~1.75. Brough and Atkinson [27] found that the CSH formed in a KOH activated slag mortar has a well-defined Ca/Si ratio of ~1.1, which is more similar to the Ca/Si ratio obtained in the current alkaline activated system. As reported widely in the literature [3,27–30], it is likely that some of the aluminium atoms present within the CSH phase in the current system is due to the substitution with silicon atoms. The calculated Al/Ca ratio (~0.25) is less than that of Na/Ca (~0.39) in the CSH phase, subsequently, the amount of sodium present is more than is required to play a charge-balancing role for aluminium to substitute for silicon in the structure. Thus, the excessive sodium present is probably an indication of the presence of other minor constituents in the phase as well as for the possible sodium substituting for calcium in the structure.

Table 4
The average elemental compositions of Phases A and B as shown in Fig. 6

	Oxygen (O)	Sodium (Na)	Aluminium (Al)	Silicon (Si)	Calcium (Ca)
Phase A	65.9	8.55	7.42	16.2	1.12
Phase B	67.5	4.48	2.86	11.8	11.6

The concentration of aluminium in this phase is abnormally low when it is considered that both MK and GGBFS contain a relatively high level of aluminium (Table 1). Therefore it is thought that some of the aluminium originating from the GGBFS would diffuse outward from the surface of GGBFS and participate in the geopolymerisation. It can also be observed in Fig. 6 that some cracking has occurred in the sample. This is not believed to be due to sample preparation for SEM, but rather due to volume changes that would occur when forming an amorphous to semi-crystalline CSH gel within a partially hardened geopolymer gel.

Although not presented here, the coexistence of a geopolymeric gel and CSH gel was still the prominent feature of the binders (as observed using SEM) when more GGBFS was added to the system (at constant alkalinity). However, the coexistence of the two separate phases disappears or the geopolymeric gel has become too small to be observed when more than 80 wt.% of GGBFS was added. The major products formed under such conditions are various types of calcium silicate hydrate, calcium silicate aluminate and calcium aluminosilicate hydrate. However, due to the highly amorphous nature of the resultant products, it is not possible to determine whether phases such as C_2ASH_8 and C_4AH_{13} were formed.

When the concentration of NaOH in the alkali activation increased (Ms = 1.2), a clear coexistence of geopolymeric gel and CSH gel could not be observed unless a substantial amount of GGBFS (> 50 wt.%) was used initially as shown in Fig. 7. The morphology of the major product formed with < 50 wt.% GGBFS at high alkalinity resembles a geopolymeric gel, which is similar to the one obtained at low alkalinity. The microscopic analysis on such system has also indicated that small calcium precipitates (< 10 μm) are scattered throughout the geopolymeric phase as shown in Fig. 8. The absence of the formation of two separate phases at a highly alkaline condition has indicated that the coexistence is dependent on the alkalinity used as well as the ratio between GGBFS and MK.

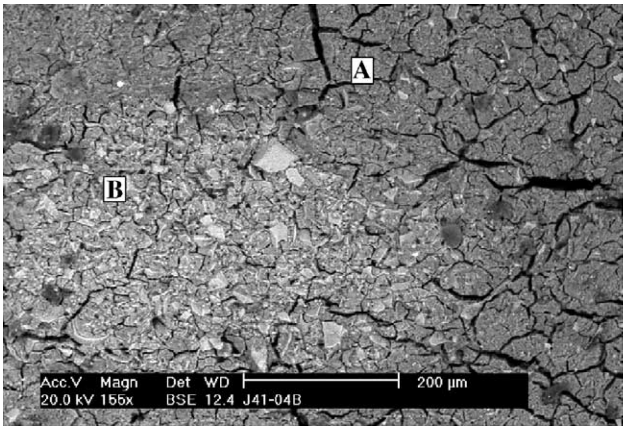

Fig. 7. SEM micrograph of Matrix 4 (60% slag, Ms = 1.2) at 14 days. Identification of the different phases: (A) geopolymeric binder with low content of calcium; (B) calcium silicate hydrate with a small proportion of aluminium.

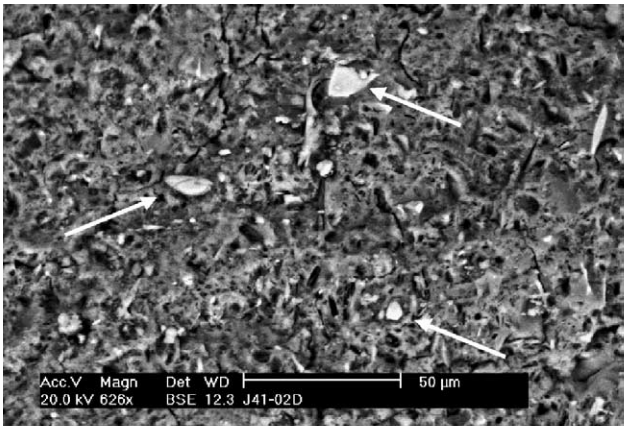

Fig. 8. SEM micrograph of Matrix 2 (20% slag, Ms = 1.2) at 14 days. A clear formation of CSH phase could not be observed in such binder; instead, scattered small calcium precipitates (the white bright islands, < 10 μm) within the binder were observed.

A similar observation was found by Alonso and Palomo [13] when they studied the alkali activation of MK in the presence of calcium hydroxide using thermal analysis. They found that when MK and calcium hydroxide were alkali activated by sodium hydroxide, CSH gel was found to be the main product. However, amorphous alkaline aluminosilicate (geopolymers) was the dominant product with CSH gel being the secondary phase when the concentration of NaOH increased from 5 to 10 M. The system currently investigated is more complex with amorphous calcium silicate mineral (slag) being used as the calcium source and soluble silicate source being added. However the results have reconfirmed the fact that given the right condition, the formation of CSH gel and geopolymers can take place simultaneously. The nature and the amount of end products depend on many factors, of which the ratio between aluminosilicate and calcium sources and the alkalinity of alkali activators are the dominant ones.

It is suggested that calcium dissociated from the surface of GGBFS will precipitate from the alkaline medium as $Ca(OH)_2$. Dissolved calcium that does not precipitate as $Ca(OH)_2$ will participate in the formation of CSH gel in preference to the formation of calcium based geopolymers. Since there is a significant difference between the calcium concentration in the geopolymeric gel and CSH gel, it is anticipated that a small amount of calcium from GGBFS will diffuse outwards into the geopolymeric gel, which may explain why traces of calcium could be detected in the rich aluminosilicate phase. However, it is still unclear how the calcium is structurally bound within the aluminosilicate phase. Moreover, it is suggested that the silicate species will preferentially react with dissolved calcium rather than polymerise with soluble aluminate. Subsequently, excess aluminate species will have to diffuse outward from the calcium rich area into the geopolymeric gel as observed in this study.

3.4. Effect of coexistence of geopolymeric gel and calcium silicate hydrate on compressive strength of binders

The increased compressive strength of the binder with the addition of moderate amounts of GGBFS can be attributed to the formation of two separate phases (Table 2). Although no experimental evidence is provided at this stage, it is proposed that the simultaneous formation of geopolymeric gel and CSH gel may help to bridge the gaps between the different hydrated phases and unreacted particles; thereby resulting in a matrix which is more dense and homogeneous. The formation of CSH gel within a geopolymeric binder could work as a micro-aggregate. Thus the compressive strength of the binders will increase.

Depending upon the alkalinity of the system, it is possible that as the calcium concentration increases, the formation of geopolymeric gel and CSH gel could compete against each other. Therefore, instead of having one phase acting as a micro-aggregate to fill voids and holes of the binder, the two reactions are competing for soluble silicates and available space for growth. Consequently, the resultant binder will be disordered with two phases of similar size, and more residual holes are produced resulting in strength reduction.

4. Conclusion

It was found that the geopolymeric binder formed in the presence of GGBFS is similar to the geopolymeric binder found in the absence of GGBFS. When the concentration of NaOH used is low, calcium dissolved from the GGBFS will take part in the formation of amorphous CSH gel, in preference to the formation of a calcium based geopolymer. CSH gel can be formed within a geopolymeric binder if soluble calcium is available in the mixture. However, if there is excess amount of hydroxides present in the system, the precipitation of calcium hydroxide will be promoted. Subsequently, the precipitation of calcium hydroxide will inhibit any possible formation of CSH gel within a geopolymeric binder unless a significant amount of calcium is present initially.

It is suggested that the coexistence of geopolymeric gel and CSH gel is responsible for the strength increase in matrices containing a moderate amount of GGBFS. The formation of CSH gel within a geopolymeric binder is thought to work as a micro-aggregate, such that the resultant binder is homogeneous and dense, resulting in increased mechanical strength.

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