EFFECT OF BLAST FURNACE SLAG ADDITION ON MICROSTRUCTURE AND PROPERTIES OF METAKAOLINITE GEOPOLYMERIC MATERIALS

Christina K. Yip  
Ph.D. candidate  
Department of Chemical & Biomolecular Engineering  
The University of Melbourne  
Victoria 3010, AUSTRALIA.

Grant C. Lukey  
Senior Research Fellow  
Department of Chemical & Biomolecular Engineering  
The University of Melbourne  
Victoria 3010, AUSTRALIA.

Jannie S.J. van Deventer  
Dean  
Faculty of Engineering  
The University of Melbourne  
Victoria 3010, AUSTRALIA.

ABSTRACT

Cementitious materials based on Portland cement are the most common materials used in the construction industry. However with increasing energy costs, and environmental and social problems associated with CO₂ emission (greenhouse gas) in the manufacturing of Portland cement, as well as the poor durability of current cement products compared with Ancient materials, an alternative construction material is needed. The increasing acceptance and commercialisation success of geopolymer technology in niche applications in the US and abroad, means that geopolymeric materials could ultimately be used as alternate cost-effective construction materials for the manufacture of precast products such as large-diameter pipes and roofing tiles for instance. Although most applications for geopolymers at present are in the construction industry, it should be noted that these low temperature ceramic materials also exhibit exceptional thermal stability and fire resistance.
The current work postulates that calcium is the key component that distinguishes the chemistry of geopolymerization from that of alkali-activated cements and ordinary Portland Cement. Granulated blast furnace slag is used as the calcium source and the effect of its addition on the microstructure and mechanical properties of a metakaolinite-based geopolymer is investigated. It has been found that the formation of an amorphous calcium-silicate-hydrate (CSH) gel in a geopolymer system is dependent upon the initial alkali concentration. Moreover, it has been established that the coexistence of both CSH and geopolymer phases within the single system enhances the mechanical properties of the resultant binder. This binder is suggested to be the modern version of ancient concrete, whereby the formation of CSH gel within a geopolymeric binder acts as a micro-aggregate, such that the resultant binder is homogeneous and dense, resulting in increased mechanical strength.

INTRODUCTION

Geopolymers, which are sometimes referred to as alkali-activated aluminosilicate binders, represent a group of cement-like materials that can be formed by reacting calcined clay or industrial wastes, such as flyash or ground granulated blast furnace slag (GGBFS), with a solution of alkali or alkali salts. Despite the increasing research effort into geopolymer technology, there is still no universal chemical mechanism that describes the geopolymerization process. The nature of the resultant geopolymeric binder is known to be dependent on the elemental and mineralogical compositions, and physical properties (e.g. particle size distribution) of the aluminosilicate source, the quantity and the nature of the alkaline activator used in activation, and the curing conditions (e.g. humidity and temperature). Through careful modelling, it is possible to utilize a range of starting materials (including industrial waste) in tailoring an environmentally friendly product that will satisfy and meet both commercial and industrial needs. Recent research has shown promising results in the utilization of flyash as an aluminosilicate source to form construction products, or to form geopolymers possessing specific properties such as the ability to immobilize toxic materials. Further application of geopolymer technology, however, will not be possible without on-going research focussed on the development and understanding of the chemical mechanism in geopolymerization.

It is known that geopolymerization involves a chemical reaction between various aluminosilicate oxides ($\text{Al}^{3+}$ in IV-V fold coordination) with silicates under highly alkaline conditions. Due to the coordination of Al, other cations such as $\text{K}^+$, $\text{Na}^+$ and $\text{Ca}^{2+}$ must be present in the structure to maintain electroneutrality. Whether these ions play a charge-balancing role or are actively bonded into the matrix is still unclear, but both scenarios possibly take place. The role of alkali metals in geopolymerization has been the subject of previous investigations. However, the effect of calcium in a geopolymer system has not been studied in any great depth. Moreover, a detailed microscopic investigation to identify phase formation during different curing conditions and the relationship between
microstructure and physical properties such as compressive strength has not been attempted.

In studying the durability of ancient construction materials in comparison to their modern ordinary Portland Cement (OPC) counterparts, Glukhovsky\(^1\) hypothesized that the durability of ancient concrete resulted from the coexistence of calcium-silicate-hydrate (CSH) gel and some forms of alkaline silico-aluminohydrates, which have similar characteristics as geopolymers synthesized today. It is commonly acknowledged that CSH gel and alkali-alumino-silicate gel are responsible for the binding property in ordinary Portland cement and geopolymers respectively\(^2\text{-}^5\). If the hypothesis of Glukhovsky is correct, then it can explain why modern concrete has a much shorter life span than its ancient counterparts, in the sense that the inability of modern concrete to form geopolymeric gel contributes to its poor durability compared to ancient concrete. However, without a detailed understanding of the relationship and interactions between these two phases, it will be difficult to proceed further in developing a new generation of concrete that possesses the durability observed in ancient concrete.

Calcium-silicate-hydrate is a gel of hydrated CaO-Si\(_2\)O\(_5\), which is normally non-stoichiometric. It is generally agreed that CSH gel is the major component that contributes to the mechanical strength of cement\(^6\). In contrast, the formation of the three-dimensional amorphous alkali aluminosilicate network with a general formula of \((\text{Na/K})_n-(\text{Si-O})_z-\text{Al-O})_n.n\text{H}_2\text{O}\) is often argued to be the phase that gives the binding property to the geopolymeric gel\(^3\text{-}^5\). The major difference therefore between CSH gel and geopolymeric gel in terms of their elemental composition is calcium. It is anticipated that if enough calcium is added to a geopolymeric system, some form of CSH gel will be obtained, however it is still unclear whether calcium will participate in geopolymerization in a similar way to sodium or potassium as described.

An understanding of the mechanisms that govern the geopolymerization process is essential for developing a new durable concrete, consisting of both geopolymeric and calcium-silicate-hydrate gels. It is generally believed that there are three mechanistic steps: (1) dissolution, (2) transportation or orientation and (3) polycondensation (reprecipitation) involved in geopolymerization\(^2\text{-}^4\text{-}^6\). However, it is still unknown how the presence of calcium species would affect the geopolymerization as described earlier, and more importantly, it is still unclear how the possible formation of calcium-silicate-hydrate gel would interact with the geopolymeric gel.

It is generally acknowledged that CSH will be formed when soluble calcium and silicate species are present in a neutral to mild pH environment (from OPC system to alkaline activated system). It is anticipated that provided sufficient calcium is added to a geopolymeric system, a CSH based cementitious material may also result. However, the nature of this CSH product is expected to be dependent on the type and concentration of the alkaline activator present, as well as the nature and the amount of initial calcium and aluminosilicate sources used\(^3\).
Figure 1 shows the proposed conceptual model of the relationship between natural zeolite, geopolymers, alkaline activated cement and OPC.

The role of calcium in ancient concrete could possibly include (1) the formation of the conventional calcium-silicate-hydrate (CSH), (2) participation in geopolymerization to form a Ca-geopolymer and, (3) bridging the bonding between the calcium-silicate-hydrate and geopolymers or many others. However, there is a lack of documented research involving the chemical mechanisms occurring in such systems. It is probable that both calcium-silicate-hydrate and geopolymers could be forming simultaneously.

This paper will therefore focus on the current mechanistic understanding of geopolymerization, in which it is proposed that calcium is the key species that distinguishes geopolymers from alkali-activated cements and ordinary cement. Granulated blast furnace slag is used as the calcium source and this study will demonstrate the effect of calcium content on the microstructure and ultimate physical properties of the geopolymer. An investigation into the role of calcium in dictating the chemical mechanism will provide answers to the fundamental question as to whether two separate phases will be formed, or a new material will be produced instead. More importantly, this will provide a basic understanding of whether the coexistence of the two phases will benefit the properties of the resultant binder.

EXPERIMENTAL PROCEDURES
Raw Material

Metakaolin (MK) used in the current work was obtained from ECC International under the brand name of MetaStar 402. GGBFS was obtained from Independent Cement Australia. The oxide composition of both materials was...
obtained by X-Ray Fluorescence (XRF) analysis, using a Siemens SRS 3000 instrument. A particle sizing analysis using a Coulter LS130 optical particle size analyzer found that the average particle size of MK and GGBS is 1.895 μm and 21.54 μm respectively and specific surface area of 1265.8 m²/L and 932.7 m²/L respectively. The XRD diffractograms were obtained using a Phillips PW1800 diffractometer using a CuKα anticathode from a scanning rate of 2°/minute from 5 to 70° 2-theta. All SEM and TEM micrographs presented in this paper were captured by Philips XL30 scanning electron microscope and Philips EM420 transmission electron microscope respectively, unless otherwise stated.

The sodium silicate solution used in the experiments was supplied by PQ Australia, under the brand name of Vitrosol N48 (with 28.7 wt.% SiO₂, 8.9 wt.% Na₂O and 62.4 wt.% H₂O; 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% <2mm) 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.

Synthesis

Geopolymers were prepared by mixing metakaolin (MK) with or without the addition of GGBFS in an alkaline activator (sodium hydroxide NaOH + sodium silicate NaSi). Two different sets of alkaline activators were prepared using a different alkalinity (Ms = SiO₂/Na₂O molar ratio = 2.0 and 1.2). The mass ratio between total mass of the dry raw material (MK + GGBFS) and the alkaline activator used was 0.69 and 0.61 for Ms = 2.0 and 1.2 respectively. These ratios were selected in order to maintain consistent water and soluble silicate content in all binders with the amount of sodium hydroxide added being the only variable.

In making the alkaline activators, sodium hydroxide pearl was mixed with the sodium silicate solution to form an alkaline silicate solution with two different molar ratios (Ms = 2.0 and 1.2). The hot solution was then cooled overnight to ambient temperature. Samples were synthesized using a mass ratio between MK and the calcium source, ranging from MK/(MK + GGBFS) = 0 to 1. The mass ratio between the dry mix (MK and GGBFS) and the alkaline mix (NaOH + NaSi) remained constant for a particular alkaline (Ms) condition irrespective of the ratio between MK/(MK + GGBFS) used.

MK and GGBFS were mixed thoroughly at a specified ratio until a uniform mix was produced. The alkaline activator solution was subsequently stirred into the dry mix to form a paste. The paste was mixed for a further 3 minutes to ensure homogeneity. The paste was then poured into PVC cylindrical moulds (50mm diameter and 100mm 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) prior to testing at specified times. For binders subjected to compressive strength testing, washed sand (with mass ratio = sand/(MK + GGBFS) = 3) was gradually added to the homogeneous paste until a uniform mixture was formed before pouring into the mould as described earlier. All samples were cured...
at atmospheric pressure and no attempt was made to control the humidity during curing.

Analysis

Compressive strength testing was performed as per Australian Standard (AS1012.9-1999) using two 50mm diameter cylinders with a 1:2 diameter to length ratio. All compressive strength measurements were taken as the average of strength results of two samples. An ELE International Auto Test Compression Machine was used. Three sets of samples were synthesized to be subjected to the compressive strength testing, one with washed sand added and the other was synthesized without 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 left overnight at room temperature and atmospheric pressure. The compressive test was conducted on the following day.

A Philips XL30 scanning electron microscope, operated at 10keV was used in analysing the surface morphology of the specimen. EDS (Energy Dispersive Spectroscopy) was used to analyze the elemental composition of the surface of a specimen. A DYNAVAC sputter coater was used in coating the specimen with carbon.

Transmission electron micrographs and electron diffraction patterns were obtained from a Philips EM420 transmission electron microscope, operated at 100kV. EDXS (Energy Dispersive X-ray Spectroscopy) was installed to analyze the elemental composition of the specimen. Specimens were prepared by mechanically grinding the powder in ethanol, followed by precipitation on an amorphous carbon film.

RESULTS AND DISCUSSION

Characterization of Metakaolinite and Ground Granulated Blast Furnace Slag

The chemical composition of metakaolinite and ground granulated blast furnace slag is shown in Table I. It should be noted that the commercial metakaolin was purified before calcination, and it had less than 0.1 wt.% of CaO. It is therefore assumed in this study that all calcium would come from ground granulated blast furnace slag (GGBFS).

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

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK</td>
<td>0.10</td>
<td>54.78</td>
<td>40.42</td>
<td>0.76</td>
<td>0.41</td>
<td>2.72</td>
<td>0.07</td>
<td>0</td>
</tr>
<tr>
<td>GGBFS</td>
<td>43.0</td>
<td>34.4</td>
<td>14.1</td>
<td>0.11</td>
<td>6.3</td>
<td>0.33</td>
<td>0.3</td>
<td>0.58</td>
</tr>
</tbody>
</table>

The XRD diffractograms obtained for both materials is shown in Figure 2. MK consisted mainly of glassy phases with low-intensity peaks corresponding to
muscovite (potassium aluminium silicate hydroxide with JCPDS 07-0042) as compared to the diffraction patterns of the Joint Committee on Powder Diffraction Standards (JCPDS) data (Figure 2).

![X-ray diffractograms of raw metakaolin (MK) and ground granulated blast furnace slag (GGBFS)](image)

Figure 2. X-ray diffractograms of raw metakaolin (MK) and ground granulated blast furnace slag (GGBFS) (CuKα radiation).

Figure 3 shows the scanning electron micrograph (SEM) of raw MK using a Philips XL30 scanning electron microscope. The micrograph highlights the glassy structure of the raw MK used.

![Scanning electron micrograph of metakaolin (MetaStar 402)](image)

Figure 3: Scanning electron micrograph of metakaolin (MetaStar 402).

Figure 4 shows transmission electron micrographs of MK using a Philips EM420 transmission electron microscope (TEM). Figure 4a highlights the hexagonal structure of MK, while Figure 4b highlights the small percentage of the fibrillar structure (marked “A” on the micrograph) present in the raw material.
The hexagonal structure is the prominent feature of the MK, even though the hexagonal shape is slightly distorted, it still retains the hexagonal shape of kaolin (the nature mineral – pre-calcined MK). This is in agreement with previous studies that metakaolin is a defect phase in which tetrahedral silicon layers of the original clay structure are largely retained.

![Micrograph A](image1)
![Micrograph B](image2)

Figure 4. Transmission electron micrograph of metakaolin used. A - Highlights the prominent hexagonal particles present in metakaolin. B - region “A” represents the small percentage of fibrillar structure present in metakaolin.

GGBFS consisted mainly of glassy phases with a detectable amount of gypsum (calcium sulphate dihydrate with JCPDS 33-0311) as shown in Figure 2. Figure 5 shows a SEM image of GGBFS, which highlights the heterogeneous nature of the material, which contains several different phases.

![SEM micrograph of GGBFS](image3)

Figure 5. SEM micrograph of ground granulated blast furnace slag (GGBFS).
The Effect of GGBFS Addition on Strength of MK-based geopolymer

Figures 6 and 7 show the compressive strength test results of the MK-GGBFS binders synthesized using $Ms = 2.0$ and 1.2 respectively at different time periods following synthesis.

In a low alkaline system ($Ms = 2.0$), the resultant compressive strength of the matrices increased when a moderate amount (20 wt.% of the total mass between MK and GGBFS) of GGBFS (Matrix M2) was added to the system. The compressive strength of Matrix M2 after 720 days is 65.4MPa as opposed to 35.2MPa and 9.8MPa for Matrices M1 (with 100% of MK) and M6 (with 100% GGBFS) respectively. It is important to note that the difference between the compressive strength of Matrices M1 and M2 (with 20 wt.% of GGBFS) was found to increase from 7.2MPa after 1 day to 30.2MPa after 720 days following synthesis.

The compressive strength of matrices containing only MK (Matrices M1 and N1) was found to increase with time, however this gain (from 1 day to 720 days) was only 3.1MPa and 4.5MPa for Matrices M1 and N1 respectively. This improvement in compressive strength for these MK-binders was small, in comparison to over 26MPa increase recorded for Matrix M2 over the same period. The compressive strength development of the matrices containing only MK (Matrices M1 and N1) was limited after 1 day. These results have indicated that moderate addition of GGBFS to a metakaolin-based geopolymeric gel will improve the mechanical property and enhance the durability of the resultant matrix with time.

![Figure 6. Compressive strength of matrices (Matrices M1 to M6) containing various amount of GGBFS synthesized using $Ms = 2.0$ (low alkaline).](image-url)
Figure 7. Compressive strength of matrices (Matrices N1 to N6) containing various amount of GGBFS synthesized using Ms = 1.2 (high alkaline).

As shown in Figure 6, the excessive addition (> 40wt.%) of GGBFS (Matrices M5 and M6) was, however, found to be destructive. The resultant compressive strength of these matrices was found to be significantly less than the other matrices containing more MK. The difference in compressive strength between Matrices M2 (20% of GGBFS) and M5 (80% of GGBFS) increases from 19.3MPa after 1 day to 52.7MPa after 720 days. This indicates that Matrices M5 and M6 rapidly lost their mechanical property after 7 days following synthesis. The compressive strength recorded by these matrices (< 5MPa) fell below the lowest detectable limit for the ELE International Auto Compressive Machine after 90 days before slowly reaching back to approximately 12MPa and 10MPa after 720 days for Matrices M5 and M6 respectively. From the physical observation of these matrices, it was found that cracks had developed (in less than 28 days) within the hardened samples containing substantial a amount of GGBFS. When external force was applied, the whole sample therefore crumbled. The durability of geopolymeric matrices synthesized at low alkalinity and containing a substantial amount of GGBFS is therefore poor.

When an alkaline activator solution of high alkalinity (Ms = 1.2) was used (Figure 7) for synthesis, the addition of a moderate amount of GGBFS (Matrix N2) was also found to give an optimum strength result. By increasing the amount of GGBFS added to the system (> 20wt.%), it is shown by Figure 7 that the resulting binders had a poor compressive strength (i.e. less than 15 MPa). Matrices N5 (80% GGBFS) and N6 (100% GGBFS) become particularly unstable with time. The compressive strength of these matrices decreased rapidly until the matrices deteriorated and crumpled after approximately 240 days.
In order to explain these results, it is important to note that the specific surface area of MK used in this work is higher than that of GGBFS (1265.8 m²/L compared to 932.7 m²/L) and the MK has a considerably smaller particle size (1.895 μm compared to 21.54 μm). When dissolution takes place therefore, it is anticipated that MK will be more reactive than GGBFS due its higher surface area. Subsequently, the viscosity of the initial suspension with more MK will be higher than the one with more GGBFS. In this study, the water content in the all samples was kept constant. Since the same amount of water was used in all binders, the gel resulting from the activation of GGBFS was thinner than the one resulting from the activation of MK. It is therefore believed that if excess water in the thinner gel is not consumed during the hydration process, free water will diffuse out of the matrices with time. Due to the considerable molecular size of water, the diffusion of water out of the matrices may leave behind more inner pores within the structure, which may consequently induce cracking throughout the matrices. This is evidenced by the observed development of cracks, and poor compressive strength values in matrices containing mainly GGBFS (Matrices M5, M6, N5 and N6).

Microstructure of MK-Binder

Electron microscopy was employed in the current work to examine the microscopic effect of GGBFS on the alkali activation of MK. Regardless of the Na₂O/SiO₂ ratio used, previous studies have shown that when metakaolin is activated by an alkaline solution, a geopolymeric binder will be the dominant product formed, with no other phases of substantial quantity being detected by XRD analysis. It is interesting to note that the average \( \frac{Al}{Si} \) molar ratio of the geopolymeric product was found to be ~ 0.26 under the scanning electron microscopy.

Figure 8 shows a representative TEM image of a geopolymeric binder (Matrix M1), which was found to consist of the following four different micro-phases:

(A) Undissolved metakaolin particle, which retained the original hexagonal shape as identified in Figure 4a. The elemental composition of this phase was found to be similar to the original hexagonal MK plate under the SEM examination;

(B) Undissolved fibrillar metakaolin particle similar to those identified in Figure 4b, having a similar morphology and elemental composition;

(C) Some weakly crystalline sodium aluminosilicate particles, which are proposed to be a constituent of the geopolymeric product. These particles were identified through an elemental analysis conducted randomly across the specimen. They were found to be crystalline to semi-crystalline through the electron diffraction patterns presented in Figure 9. These particles were commonly found as circular plates with an average diameter of ~ 0.2 μm to ~0.5 μm, which have a similar \( \frac{Al}{Si} \) molar ratio as raw MK hexagonal...
plates and particle "A" as identified in Figure 8, but with a much higher sodium content. These particles are proposed to be the result of the alkaline activation of the surface of MK, and that the original hexagonal plate is believed to transform into its circular shape as the result of alkaline activation, before being fully dissociated into different silicate and aluminate species; and

(D) Amorphous aluminosilicate, which is believed to be the other constituent of the geopolymeric product. This phase was found to have no regular shape or morphology under the TEM. It is characterized by a 2-ring electron diffraction pattern that is highly diffused (slightly distorted and poorly defined) as shown in Figure 10. This kind of structure is often resembled by a short-range order where any order present in the structure involves less than 20 atoms in length. The elemental composition of this amorphous aluminosilicate phase was found to vary substantially across the phase, in which the average molar ratio between $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ varied from $\sim 0.11$ to $0.37$.

![Image of Transmission electron micrograph of Matrix M1 after 28 days. Identification of the different phases: A-undissolved metakaolin particle, B-undissolved metakaolin particle, C-crystalline aluminosilicate and D-amorphous aluminosilicate. (Original magnification: x22600).]
Figure 9. Electron diffraction pattern of particle “C” in Figure 8, which is believed to be a crystalline or semi-crystalline sodium aluminosilicate. (CAM length = 1040 mm with a corresponding CAM constant = 35 and rotation of $-92^\circ$).

Figure 10. Electron diffraction ring pattern of particle “D” in Figure 8, which is believed to be a semi-crystalline to amorphous constituent of a geopolymeric gel. (CAM length = 1040 mm with a corresponding CAM constant = 35 and rotation of $-92^\circ$).
Comparing Figure 8 to the TEM image of raw MK as shown in Figure 4, it can be seen that most of the hexagonal particles of raw MK have reacted and thus, disappeared as the result of alkaline activation. The geometric shape of the alkaline activated product of MK was therefore found to be more “rounder” (Figure 8 particle “C”), as discussed earlier. Hence, the alkaline activation of MK is believed to be a surface reaction, with silicate and aluminate species dissociated from the surface of metakaolin. This is the possible reason why then particle “C” in Figure 8 is observed in the resultant product, and that the average diameter of these particles is smaller than the particle size of the hexagonal plate in MK. The silicate and aluminate species dissociated from MK will undergo polymerization to form higher ordered oligomers and thus the geopolymeric gel (amorphous sodium aluminosilicate network). This geopolymeric gel is identified as particle “D” in Figure 8. The current TEM result and observations are in agreement with the chemical mechanism proposed by Xu and van Deventer. Subsequently, the different degree of polymerization that has taken place in the system may also explain why there exists a large variation of the Al₂O₃ to SiO₂ molar ratio for particle “D” throughout the resultant product. This observation also highlights the fact that geopolymerization is an on-going process.

Microstructure of MK-GGBFS Binder

Figure 11 shows a representative scanning electron micrograph of a resultant binder (Matrix M2) containing 80 wt.% of metakaolin and 20 wt.% of GGBFS with Ms = 2.0.

![Figure 11. Scanning electron micrograph of Matrix M2 (20% slag, Ms = 2.0) after 240 days. Identification of the different phases: A – geopolymeric binder with low content of calcium; B – calcium-silicate-hydrate with a small proportion of aluminium.](image)
Figure 12 is representative of the microstructural features found in such systems. Two separate phases (Areas A and B) were formed as a result of the alkali activation of metakaolin in the presence of GGBFS. The formation of two separate phases within a single binder can be clearly observed from the vast difference between the optical contrast of the two regions, in which it is commonly acknowledged that the intensity of reflected electrons is proportional to the atomic number in the object. The brighter region (Area B) is anticipated to contain atoms with atomic number much higher than that of the darker region (Area A).

Moreover, elemental analysis was conducted on the sample after 14 days following synthesis. 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. It is therefore confirmed that areas A and B are different in composition. The brighter contrast observed in area B is the result of the high concentration of atoms with higher atomic number (i.e. calcium) present in the region.

The concentration of each element was found to be consistent within areas A and B and there is a narrow interfacial area between the two regions. Area A is proposed to be a geopolymeric binder, which has similar characteristics to the geopolymeric binder formed in the absence of GGBFS. This result is in agreement with previous observations by Alonso and Palomo\(^1\), whereby 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 the geopolymeric phase (Area A) originated from and diffused outward from the GGBFS.

Likewise, the elemental composition of area B is consistent within the region. Calcium and silicon have been found to be the main elements in this area, in which aluminium and sodium are of much lower concentrations. Therefore it is suggested that the phase present in area B could be some form of CSH (calcium-silicate-hydrate). However this CSH phase is different from the one generally formed from the hydration of Portland cement, or amorphous calcium silicate in raw slag with a much lower CaO/SiO\(_2\) ratio than that in phase B. The concentration of aluminium in this phase is unexpectedly low when it is considered that both MK and GGBFS contain a relatively high amount of aluminium (Table I). Therefore it is anticipated that some of the aluminium originating from the GGBFS would diffuse outward from the surface of GGBFS and participate in the geopolymerization. In fact the coexistence of the separate geopolymeric gel and CSH gel within a single binder remains the dominant feature of the alkaline activated MK-GGBFS system even after an extended period. The clear coexistence of two separate phases was indeed found in a geopolymeric binder with moderate amount of GGBFS added from an early age (1 day) to more than 2 years after synthesis. Table II highlights the oxide ratio of...
the element of interest for the two separate phases formed in Matrix M2 after 14 and 240 days of synthesis (Figure 11).

Table II. SEM EDS analysis (atomic ratios, $x \pm \sigma_{n-1}$) for rich aluminosilicate phase and rich calcium phase in 14 and 240 days old MK-GGBFS binders synthesized using $Ms = 2.0$. ($x = \text{average atomic } \%$, $\sigma = \text{standard deviation in } \%$ and $n = \text{number of sample size}$).

<table>
<thead>
<tr>
<th>Days after Synthesis</th>
<th>Rich Aluminosilicate Phase (Area A)</th>
<th>Rich Calcium Phase (Area B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14</td>
<td>240</td>
</tr>
<tr>
<td>CaO/SiO$_2$</td>
<td>0.069 $\pm$ 26%</td>
<td>0.186 $\pm$ 30%</td>
</tr>
<tr>
<td>Al$_2$O$_3$/Na$_2$O</td>
<td>0.868 $\pm$ 14%</td>
<td>1.420 $\pm$ 18%</td>
</tr>
<tr>
<td>Al$_2$O$_3$/SiO$_2$</td>
<td>0.230 $\pm$ 15%</td>
<td>0.258 $\pm$ 20%</td>
</tr>
</tbody>
</table>

Figure 12 shows a representative transmission electron micrograph, which is obtained from the alkaline activation of a binder consisting of 60% metakaolin and 40% GGBFS (Matrix M3).

![Transmission electron micrograph of Matrix M3](image)

Figure 12. Transmission electron micrograph of Matrix M3 (40% GGBFS, $Ms = 2.0$) 28 days following synthesis. Identification of the different phases: A - synthetic crystalline aluminosilicate (constituent of a geopolymeric binder), B - amorphous aluminosilicate and C - calcium-silicate-hydrate with a small proportion of aluminium. (Original magnification: x36300).
By comparing the TEM images obtained for Matrices M1 and M3 (Figures 8 and 12), it can be seen that the most notable difference is the absence of undissolved metakaolin particles (particles “A” and “B” as identified in Figure 8) in the M3 binder (Figure 12). Most of the metakaolin particles in Matrix M3 have been dissolved or the concentration of undissolved MK has become too low to enable detection using TEM. The rate of dissolution is postulated to be dependent on the alkaline concentration used in activating both MK and GGBFS, and the compressive strength of resultant binder is postulated to be dependent on the extent of the dissolution of both starting materials. This postulate was confirmed with previous work on the dissolution of various calcium silicate materials, including GGBFS, in a geopolymeric system\textsuperscript{12}.

Recent research by Yip and Van Deventer\textsuperscript{8} has shown using XRD that there is no detectable amount of new phase which is formed as the result of the alkaline activation of MK in the presence of GGBFS. However, based on the electron diffraction analysis conducted randomly over specimens with different amount of GGBFS added in the current study (Figure 13), some undefined crystalline phases do form as the result of alkaline activation. These crystalline phases were found to increase with increasing GGBFS being added to the system. However, it should be noted that despite the increase in quantity of these crystalline phases in the resultant matrix, they remain to be the minor constituents. Due to the low concentration, it is reasonable to believe that these crystalline phases cannot be detected through XRD.

![Electron diffraction of the crystalline phase present in Matrix M3 (40%GGBFS, Ms = 2.0) after 28 days (CAM length = 1510mm with a corresponding CAM constant = 50.7 and rotation of -87°).](image)

Figure 13. Electron diffraction of the crystalline phase present in Matrix M3 (40%GGBFS, Ms = 2.0) after 28 days (CAM length = 1510mm with a corresponding CAM constant = 50.7 and rotation of -87°).
While Figure 13 shows the electron diffraction pattern of a crystalline phase present in Matrix M3, Figure 14 shows a well-defined electron diffraction ring pattern of a semi-crystalline phase present commonly found in the resultant binder with substantial amount of GGBFS added.

**Figure 14.** A common semi-crystalline phase (as shown with a defined electron diffraction ring pattern) present in the resultant binder with a substantial amount of GGBFS. This particular electron diffraction was taken for Matrix M5, 80% of GGBFS and Ms = 2.0 after 28 days (CAM length = 1510mm with a corresponding CAM constant = 50.7 and rotation of −87°).

Comparing Figure 14 with Figure 10, it can be seen that the former contains 2 sharper and well-defined rings. Moreover, some of the individual electron dots making up the electron ring can be clearly observed in Figure 14, which indicates the individual crystals are getting bigger along with the bigger grain size in the resultant product containing a greater amount of GGBFS. This therefore indicates that the resultant product in the binder containing a greater amount of GGBFS is more crystalline.

In summary, for the same alkalinity conditions it has been found that when GGBFS is added to a MK system, the coexistence of geopolymeric gel and CSH gel was still the prominent feature as observed through the SEM examination. However, the coexistence of these two separate phases disappears or the geopolymeric gel has become too small to be observed when more than 80 wt.% of GGBFS was added to the system (Matrix M4). 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 C₂ASH₈ and C₄AH₁₃ were formed.
Effect of Alkalinity

Although all the SEM/TEM images are not shown, when the concentration of NaOH in the alkaline activator was increased (from Ms = 2.0 to Ms = 1.2), a coexistence of geopolymeric gel and CSH gel could not be observed unless a substantial amount of GGBFS (>50 wt.%) was used initially. The morphology of the major product formed with <50 wt.% GGBFS under high alkalinity resembles a geopolymeric gel, which is similar to the one obtained under low alkalinity (Figure 11, Area A). The microscopic analysis on such systems has also indicated that small calcium precipitates (<10 microns) are scattered around the geopolymeric phase. The absence of the formation of two separate phases in highly alkaline condition has indicated that the coexistence is dependent on the alkalinity used as well as the ratio between GGBFS and MK. In fact, it has been found that as the concentration of GGBFS added increases, the clear phase separation between CSH gel and geopolymeric gel is no longer the prominent feature, even in the low alkaline condition. Instead, an increasing amount of crystalline or semi-crystalline calcium product can be observed over the binder. This has indeed confirmed the observation from the TEM presented earlier (Figure 14) that the crystalline calcium phases were found to increase with increasing GGBFS being added to the system.

A similar observation was found by Alonso and Palomo\textsuperscript{11} 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 5M to 10M. The system currently investigated is more complex with amorphous calcium silicate mineral (GGBFS) being used as the calcium source and soluble silicate source being added. However the results have reconfirmed the fact that given the correct synthesis conditions, the formation of CSH gel and geopolymers can take place simultaneously.

It is proposed in the current work that calcium dissociated from the surface of GGBFS will precipitate out of the alkaline medium as Ca(OH)\textsubscript{2}. Dissolved calcium that does not precipitate as Ca(OH)\textsubscript{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.
From both SEM and TEM analysis, it has been shown in the present work that dissolved calcium from GGBFS does not participate in geopolymerization. These results confirm what has been observed recently from XRD analysis, which showed that both metakaolin and GGBFS are independently activated by alkali and that there was no calcium migration from GGBFS to metakaolin to form a geopolymeric binder. The calcium species therefore does not play a significant, if any, charge-balancing role similar to that of sodium or potassium in a geopolymer system. These results demonstrate that it would require more than simply adding a calcium source to an aluminosilicate source to form a calcium-based geopolymer. It is proposed that soluble calcium, either from the dissolution of a chemical reagent or a mineral (e.g. GGBFS), would participate in the formation of calcium-silicate-hydrate rather than participating in the formation of a geopolymer in a low temperature alkaline activated system.

Proposed Mechanism of Alkaline Activation of MK in the Presence of GGBFS

The results presented in the current work indicate that the alkali activation of MK in the presence of GGBFS is dependent on the mass ratio between MK and GGBFS, and also the alkalinity of the alkali activator (Figure 2 and Figure 3). The microscopic analysis has shown that given the right conditions, two separate phases - a calcium silicate phase and a sodium aluminosilicate will be formed simultaneously in the alkali activated system.

It is often argued that dissolution of aluminosilicate minerals is the first step of geopolymerization. It is thought that when both MK and GGBFS are mixed with the alkali activator, dissolution is also the first reaction to take place. Silicon and aluminium will be dissolved from the surface of MK, along with silicon, aluminium and calcium from the surface of GGBFS. As shown previously, the rate of dissolution from each mineral is dependent on the concentration of sodium hydroxide. Subsequently, the nature and amount of dissolved species present in the suspension will determine the subsequent reaction or reactions to take place, which are expected to include polymerization and various other precipitation processes.

When alkaline solution activates the surface of the GGBFS, it is reasonable to assume that calcium and silicon dissolve from the GGBFS surface. It was found from the current study that dissolved calcium from GGBFS would take part in the formation of CSH gel in preference to participating in the polymerization with aluminosilicate. It can be concluded that dissolved calcium from GGBFS plays a similar role to the calcium hydroxide as suggested by Alonso and Palomo in the alkaline activation of MK, that leads to the formation of amorphous and semi-crystalline sodium aluminosilicate with some forms of CSH gel as a secondary product.

In the presence of sodium hydroxide in the solution phase, the surface of GGBFS particles will be saturated with the hydroxyl ion. It is therefore reasonable to suggest that when calcium dissolves from GGBFS, it will diffuse out of the GGBFS grain and will further react with hydroxyl ions and precipitate as Ca(OH)$_2$. 

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When there is a substantial amount of calcium hydroxide present around the surface of GGBFS, it will make the diffusion of dissolved calcium out of the GGBFS even more difficult. Since the diffusion of calcium from GGBFS to aluminosilicate is restricted, excess dissolved calcium will remain intact within the GGBFS grain and form a new nucleation centre, in which amorphous calcium-silicate-hydrate will be produced and grown within the region. The lack of dissolved calcium present in the aluminosilicate body will inhibit any formation of calcium aluminosilicate hydrate. It is suggested that the presence of the small amount of dissolved calcium will react with soluble silicate and precipitate on the surface of a geopolymeric gel. As a result, two distinct phases will be produced in such a system and substantial amounts of calcium hydroxide or various other types of calcium precipitate will be formed along the interfacial area as shown in the current investigation.

For systems with a low NaOH concentration, layers of hydroxyl ions and calcium hydroxide will not be too thick along the interfacial area, so that a small amount of dissolved calcium will be able to diffuse out of the layers if there is a relatively high amount of dissolved calcium present in the system. Phair and van Deventer\textsuperscript{14} showed that the solubility of calcium decreased with increasing pH owing to the formation of calcium hydroxide. With a decreased amount of calcium hydroxide formed in the system, more calcium will be available to react with soluble silicate to form calcium-silicate-hydrate. Previous findings from Xu and van Deventer\textsuperscript{4} showed that the dissolution of silicon and aluminium from various aluminosilicate minerals is slower in alkali activator of lower OH\textsuperscript{−} concentration. Hence the formation of calcium-silicate-hydrate is favoured as the initial amount of dissolved aluminate is not enough to promote the formation of calcium aluminosilicate. In addition, since the layers of hydroxyl ions and calcium hydroxides around the surface of the rich calcium silicate region are weak, more space is available for the nucleation growth of CSH in the region. Thus, the growth of CSH will be promoted and a clear region of calcium rich area could be distinguished microscopically.

In contrast, when more sodium hydroxide is added to the system, dissolved calcium species will not participate in the formation of calcium silicate hydration, or only a limited amount of dissolved calcium will participate in the formation of CSH, which makes its presence difficult to be observed microscopically. Instead, calcium hydroxide will precipitate, and this will inhibit any possibility for dissolved calcium to participate in the formation of CSH. With decreasing amounts of dissolved calcium present, the formation of CSH gel is not possible unless a higher amount of calcium source is added to the system initially. Thus, when GGBFS was added in the current study (Matrix M2), a coexistence of the two phases could be observed. Moreover, as the layers of calcium hydroxide and hydroxyl ions are much thicker in systems where high alkalinity was used, the lack of physical space around the GGBFS grain has also restricted any possible growth of CSH. Subsequently, scattering of small calcium precipitates (<10 microns) around the sodium aluminosilicate phase has been observed.
Effect of Coexistence of Geopolymeric Gel and Calcium-Silicate-Hydrate on Durability of Resultant Binders

The increased compressive strength of the binder with the addition of moderate amounts of GGBFS as noted in Matrix M2, can be attributed to the formation of two separate phases in a mildly alkaline condition. The results found in the current study have shown that given the right condition, it is possible to have both amorphous alkali aluminosilicate and CSH gel forming simultaneously within the same system. As suggested by Glukhovsky, the long-term stability of concrete results from the presence of analcime (alkaline silico-aluminohydrates) and CSH gel rather than CSH gel alone. It is suggested that analcime (alkaline silico-aluminohydrates) is similar to the alkali aluminosilicate (geopolymer) produced as a result of the alkali activation of MK. This binder is suggested to be the modern version of ancient concrete.

It is anticipated that voids and pores within the geopolymeric binder become filled with the CSH gel, which helps to bridge the gaps between the different hydrated phases and unreacted particles. The formation of CSH gel within a geopolymeric binder could work as a micro-aggregate. Thus the compressive strength of the binders will increase (Figure 2 and Figure 3). However, as the calcium concentration increases, the formation of geopolymeric gel and CSH gel could compete against each other. Instead of having one phase acting as a micro-aggregate in filling up voids and holes of the resultant 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.

CONCLUSIONS

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. This binder is suggested to be the modern version of ancient concrete. The formation of CSH gel within a geopolymeric binder is working as a micro-aggregate, such that the resultant binder is homogeneous and dense, resulting in increased mechanical strength.
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