



Evolution of binder structure in sodium silicate-activated slag-metakaolin blends

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ABSTRACT

Structural evolution in pastes produced from alkali silicate-activated granulated blast furnace slag (GBFS)/metakaolin (MK) blends is assessed. In the initial period of the reaction, the addition of MK leads to an increase in the total setting time, reduces the heat release, and affects the reaction mechanism by introduction of a large quantity of additional Al. This effect is more significant when an activating solution with a higher silicate modulus is used, and leads to a slight reduction in the final mechanical strength of mortars but a significant increase in setting time, which is valuable in the development of alkali-activated slag binders as these are known to sometimes harden more rapidly than is desirable. High-energy synchrotron X-ray diffractometry reveals that the main reaction products in alkali-activated GBFS/MK blends are segregated and partially crystalline calcium silicate hydrate and aluminosilicate phases, including a small component with a zeolitic (gismondine) structure. No hydrotalcite-type phases are observed in these samples, which are synthesized from a low-Mg slag. A secondary reaction product (Na-substituted C–S–H) is also identified in pastes activated with a modulus of solution of 2.0. Infrared spectroscopy carried out over a period of 180 days shows the development of the gel structure, with aluminum incorporation leading to an increase in the extent of crosslinking, and higher alkalinity giving a more depolymerized gel structure.

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1. Introduction

Alkali-activated binders are a class of materials that use an alkali activator in conjunction with a solid (usually pozzolanic or cementitious) silicate powder to initiate a reaction sequence which results in the formation of a solid material with properties comparable to traditional hydraulic cements [1]. The possible value of alkali-activated binders has been reported since the 1940s [2,3], although it was not until the 1960s that the understanding of the chemistry of these materials began to be established [3–5]. More recent advances in instrumentation, particularly in the areas of electron microscopy, nuclear magnetic resonance spectroscopy and synchrotron radiation-based analysis [6–11], have provided the ability to understand alkali-activated binders on a detailed level, which is essential to the understanding and prediction of their performance and durability.

Of the different materials that have been subjected to alkali activation, granulated blast furnace slag (GBFS) has been the most

widely studied, and alkali-activated binders based on GBFS have been used in large-scale applications in regions including Eastern Europe and China [1]. The dominant binder phases in these systems are generally identified to be calcium silicate hydrate (C–S–H) gels which are relatively low in Ca. It is also becoming increasingly apparent that a combination of the properties of “geopolymer”-like (alkali aluminosilicate) and GBFS-based systems can show advantages over either of the end-member systems in terms of the formation of desirable microstructures and mechanical properties [12–18], and so this work is focused on one such system: a blend of GBFS with a small amount of MK, activated by sodium silicate (waterglass) solution. The primary reason for blending MK with GBFS in this study is to provide better control of setting time; slag–waterglass binders have a tendency to set extremely rapidly, and it has been observed that the addition of a small amount of MK can retard setting to provide a more convenient period of workability [19].

There exist only a few previous reports regarding the structure and performance of alkali-activated GBFS/MK blends, and these are mainly focused on the MK-rich end of the continuum, where some GBFS is added to a metakaolin-based geopolymer to enhance strength development [14–16,19,20]. Yip et al. and Buchwald et al. [15,16,20] have observed that at low or moderate activator concentrations in alkali silicate-activated GBFS/MK blends rich in MK, the calcium dissolves from the slag and participates in the formation of C–S–H gels (as has also been observed in MK/Ca(OH)₂

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blends [21,22]) instead of contributing to the formation of geopolymer-type gels. Portlandite ($\text{Ca}(\text{OH})_2$) is rarely observed in alkali-activated slag or slag–Portland cement systems beyond early ages, as the high availability of silica in these systems favors instead the formation of C–S–H.

Raw materials with depolymerized siliceous structures, such as GBFS, exhibit higher dissolution rates under high alkalinity conditions when compared with raw materials composed of laminar structures, such as MK. Thus, blending these components can contribute to improving the stability of the system, and potentially also to the durability, when compared to binders prepared from a sole raw material [14,15,19], similar to the advantages in long-term performance provided to Portland cement-based systems by the addition of slower-reacting pozzolans in addition to rapidly-reacting cement.

However, slag-rich GBFS/MK blends have shown quite rapid carbonation under accelerated test conditions [19,23], and so it is necessary to develop a better understanding of the progress of the binder formation reactions and of the final hydration products in these materials to enable binder design for enhanced durability. Different sodium silicate activator compositions, and different degrees of MK substitution into the slag-rich formulations, are analyzed here through the application of calorimetry, synchrotron X-ray diffraction and Fourier transform infrared spectroscopy, to determine the details of phase formation and structural development during 180 days of curing. Compressive strength testing is conducted on mortar samples based on the binders developed, in order to generate a better understanding of the relationship between the structural evolution of the pastes and the mechanical strength at different ages of curing.

2. Experimental program

2.1. Materials

The primary raw material used in this study was a Colombian granulated blast furnace slag (GBFS) obtained from the *Acerías Paz del Río* steelworks. The basicity coefficient ($\text{CaO} + \text{MgO}/\text{SiO}_2 + \text{Al}_2\text{O}_3$) and the quality coefficient ($\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3/\text{SiO}_2 + \text{TiO}_2$) based on the chemical composition (Table 1) were 1.01 and 1.92, respectively. Its specific gravity was 2900 kg/m^3 and its Blaine fineness $399 \text{ m}^2/\text{kg}$. The particle size range, determined through laser granulometry, was $0.1\text{--}74 \mu\text{m}$, with a mean (d_{50}) of $5 \mu\text{m}$.

The metakaolin (MK) used was generated in the laboratory by calcination of a Colombian kaolin (containing minor quartz and dickite impurities) at $700 \text{ }^\circ\text{C}$ in air, for 2 h. The particle size range of the MK was $1.8\text{--}100 \mu\text{m}$, with a d_{50} of $13.2 \mu\text{m}$ and 10% of particles finer than $4 \mu\text{m}$.

Mineralogical analysis of the anhydrous raw materials was conducted by synchrotron X-ray diffractometry (Fig. 1).

It can be seen from Fig. 1 that the slag is mainly amorphous, as seen by the broad feature in the diffraction pattern at Q values between 1 and 3 \AA^{-1} . Traces of some crystalline phases such as gehl-

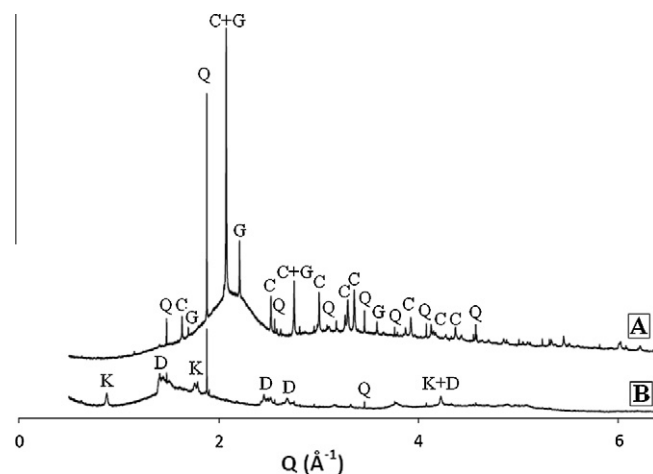


Fig. 1. High resolution synchrotron X-ray diffraction patterns of: (A) GBFS, and (B) MK ($\lambda = 0.401738 \text{ \AA}$), where peaks marked with K are due to kaolinite, D is dickite, Q is quartz. C is calcite and G is gehlenite.

enite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) (Powder diffraction file (PDF) # 035-0755), quartz (SiO_2) (PDF# 046-1045) and calcite (CaCO_3), (PDF# 05-0586) are also observed. In this case akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), a mineral often reported in slags used for alkali-activation purposes, is not identified. This is probably a consequence of the low (<3%) content of magnesium in the slag assessed here.

In the diffraction pattern of the MK, the main crystalline phases accompanying the amorphous component of the MK are traces of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (PDF# 014-0164), dickite (also $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (PDF# 010-0446) and quartz (SiO_2) (PDF# 046-1045), being characteristic of clays of moderate purity. It is important to note that the characteristic peaks associated with kaolinite are weak, indicating a high degree of disorder as a consequence of the conversion from kaolin to MK under the heating conditions used to prepare the material in this study [24–27]. Muscovite, feldspars and anatase, which are typically observed in MK with low purity, are not detected in this material.

Alkaline activating solutions were formulated by blending a commercial sodium silicate solution with 32.4 wt.% SiO_2 , 13.5 wt.% Na_2O and 54.1 wt.% H_2O , together with 50 wt.% NaOH solution, to reach the desired modulus ($M_s = \text{molar } \text{SiO}_2/\text{Na}_2\text{O}$ ratio) of 1.6, 2.0 or 2.4. A constant activator concentration of 5% Na_2O by mass of GBFS + MK was used.

2.2. Sample synthesis and test procedure

2.2.1. Pastes

Pastes with a constant water/(GBFS + MK + anhydrous activator) ratio of 0.23 were produced in accordance with the standard procedure ASTM C305-06. In fresh pastes, setting time was determined using the Vicat apparatus by following the standard procedure ASTM C191-08. The setting process of these mixes was also assessed by isothermal calorimetry (JAF calorimeter) at $25 \text{ }^\circ\text{C}$ over the first 40 h of reaction.

For the study of hardened pastes, the specimens were cast in cylindrical molds and stored in sealed containers with a relative humidity of 90% and a temperature of $27 \pm 2 \text{ }^\circ\text{C}$ for up to 180 days. The reaction process was stopped at different ages of curing by crushing the samples to pass a $74 \mu\text{m}$ sieve, submerging the samples in acetone for 15 min, filtering and drying. To prevent the absorption of water or CO_2 from the atmosphere, samples were stored in a desiccator until testing.

X-ray diffractometry was carried out using a high-resolution high-throughput synchrotron powder X-ray diffractometer with a

Table 1

Oxide composition of the GBFS and MK used, from X-ray fluorescence analysis. LOI is loss on ignition at $1000 \text{ }^\circ\text{C}$.

Component (mass% as oxide)	GBFS	MK
SiO_2	32.29	50.72
Al_2O_3	16.25	44.63
CaO	42.45	2.69
Fe_2O_3	2.35	–
MgO	2.87	–
Other	1.88	0.94
LOI	1.91	1.02

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