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Impact of chemical variability of ground granulated blast-furnace slag on the phase formation in alkali-activated slag pastes

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ABSTRACT

The influence of ground granulated blast-furnace slag (GGBS) chemical variability on phase formation in sodium hydroxide-activated GGBS pastes has been investigated using X-ray total scattering and subsequent pair distribution function (PDF) analysis. Crystalline phase identification based on reciprocal space analysis reveals that despite large chemical variations in the neat GGBSs the secondary reaction products are quite similar, with the majority of pastes containing a hydrotalcite-like phase. However, PDF analysis reveals considerable differences in short range atomic ordering of the main calcium-sodium aluminosilicate hydrate (C-(N)-A-S-H) gel phase in the pastes. Quantitative analysis of these local structural differences in conjunction with published PDF data identifies the important role calcium plays in dictating the atomic structure of disordered silicate-rich phases in cementitious materials. This study serves as a crucial step forward in linking GGBS chemistry with phase formation in alkali-activated GGBS pastes, revealing key information on the local structure of highly-disordered cementitious materials.

1. Introduction

Ground granulated blast-furnace slag (GGBS) is an industrial by-product of steel manufacturing, and is widely used as a supplementary cementitious material (SCM) in concrete production to partially replace ordinary Portland cement (OPC) [1]. The use of GGBS as a SCM not only reduces the porosity of OPC concrete, via the precipitation of additional calcium-silicate-hydrate (C-S-H) gel [2], but also lowers the carbon footprint of concrete due to the reduced usage of OPC [3]. In addition, GGBS is one of the major precursor materials used in the production of alkali-activated materials (AAMs); a type of alternative cementitious material that exhibits comparable mechanical performance to blended slag cement (i.e., CEM III/B) and similar or even lower global warming potential compared with "the best available concrete technology" [4]. Both applications of GGBS (as a SCM and in AAMs) have a history of over a hundred years (the commercial production of OPC-GGBS blended cement dated back to the late eighteenth century while alkali-activated slag was first patented in 1908 by a German cement chemist and engineer Kuehl [5]) and are still drawing widespread interest from the cements community [6,7].

Although GGBS is currently used in OPC and AAM concrete production, the local atomic structures of GGBS and the main reaction products that form in both types of concrete, which are based on an aluminum substituted calcium-silicate-hydrate gel (commonly denoted as C-A-S-H gel), are still not fully understood [8]. In OPC-based systems the gel is commonly referred to as C-A-S-H gel, whereas in alkali-activated GGBS pastes the gel contains a certain amount of alkalis (typically sodium (N)), and therefore is referred to as C-(N)-A-S-H gel. It is important to note that our recent investigation using X-ray pair distribution function (PDF) analysis revealed that the long range ordering of C-A-S-H and C-(N)-A-S-H gel is different, with the C-A-S-H gel showing nanostructural ordering (nanocrystallinity) whereas C-(N)-A-S-H gel is predominately amorphous [9].

Since C-A-S-H/C-(N)-A-S-H gel in these systems is the main space-filling and strength-giving phase, and largely controls the long-term durability performance of these cementitious systems [6,8], it is crucial to attain a molecular level understanding of these phases. However, elucidation of the local atomic arrangements in these gels is difficult due to the lack of coherent long-range ordering [8,9] that limits the amount of information that can be gained from conventional diffraction techniques. Local structural techniques such as nuclear magnetic resonance (NMR) [8,10] and Fourier transform infrared (FTIR) spectroscopy [10] provide detailed information on the local bonding environment of the silicon (and aluminum) atoms, but the medium range ordering and the effect of calcium on this medium range ordering are not typically assessed using these techniques. What makes it even more challenging is that the atomic structure of C-(N)-A-S-H gel varies with the activation and curing conditions [10,11] (the curing condition also influences the structure of C-A-S-H gel [12] in OPC paste containing GGBS), and the chemical composition of the neat GGBS is different from source to source depending on the iron ore used for steel production and the blast furnace operations adopted [1].

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In alkali-activated GGBS pastes, C-(N)-A-S-H gel is almost always accompanied by secondary hydration products (i.e., layered double hydroxides (LDH) with similar structures to hydrotalcite [13–16], AFm-type phases [16–18], strätlingite [14,19], zeolites [20–22]). Variation in the formation of secondary hydration products in these investigations [13–22] is largely attributed to the different activation and curing conditions adopted together with the mineralogical and chemical differences in the neat GGBSs. For instance, hydrotalcite-like phases are commonly found in hydroxide-activated GGBS [13–15], however they are not often identifiable in silicate-activated GGBS using X-ray diffraction (XRD) [22]. Although the formation kinetics of the secondary hydration products are still not clear [6], these products have been shown to play an important role in dictating the durability of the alkali-activated GGBS pastes when exposed to carbonation conditions [20]. Since both the main and secondary reaction products are largely influenced by chemistry of the neat GGBSs (along with the type of activator and curing conditions), there is the need for additional studies to systematically analyze how chemical variabilities in the neat GGBSs influence the phase formation and local atomic structure of the alkali-activated GGBS pastes.

GGBS consists of four major chemical components: CaO (30–50 wt.%), SiO_2 (28–38 wt.%), Al_2O_3 (8–24 wt.%) and MgO (1–18 wt.%) [1], which all influence the resulting alkali-activated GGBS paste. The roles of Al_2O_3 and MgO in the formation of alkali-activated GGBS have been reported in several investigations [14,20,23,24]. Ben Haha et al. [23] studied the impact of Al_2O_3 (7–17 wt.%) on the hydration kinetics and microstructure of GGBS activated with sodium hydroxide and sodium silicate solutions, with the results showing that an increase in Al_2O_3 content leads to lower Mg/Al ratios in hydrotalcite-like phases (these phases have similar LDH structures to hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$) but with a Mg/Al ratio of ~1.2–2.1). Furthermore, increasing Al_2O_3 content correlates with high aluminum uptake in the C-(N)-A-S-H gel and the formation of strätlingite ($Ca_2Al_2SiO_7\cdot 8H_2O$) in the hydroxide-activated pastes [23]. In a similar study [14], Ben Haha et al. examined three GGBS sources with different MgO content (8–13 wt.%) and found that higher MgO content increases the amount of hydrotalcite-like phases and decreases aluminum incorporation in the C-(N)-A-S-H gel. For the GGBSs activated using waterglass, a higher MgO content is correlated with an increase in the total volume of hydrates and an increase in the compressive strength. This is in agreement with an early study by Douglas et al. [25] which showed that the 28-day compressive strength of silicate-activated GGBS was tripled when the MgO content of GGBS increased from 9 to 18 wt.%.

Bernal et al. [20] also studied the effects of GGBS MgO content (1–7 wt.%) on the phase evolution of silicate-activated GGBS, with the results showing that the higher MgO content GGBSs lead to an increase in the amount of hydrotalcite-like phases and a reduction in aluminum uptake in C-(N)-A-S-H gel. In silicate-activated GGBS synthesized with low MgO content GGBS (<5 wt.%), the formation of gismondine ($CaAl_2Si_2O_8\cdot 4H_2O$) and garronite ($Na_2Ca_5Al_{12}Si_{20}O_{64}\cdot 27H_2O$) is seen to be favored over hydrotalcite-like phases [20–22]. The authors [20] also discovered that samples with higher MgO content exhibit better resistance to accelerated carbonation, from which they postulated that the hydrotalcite-like phases are playing a key role in limiting carbonation by being a sink for the carbon dioxide. A related phenomenon has been observed in a recent study [26], where an improvement in the carbonation resistance of alkali-activated GGBS binders containing high MgO for samples exposed to 100% CO_2 gas has been attributed to the formation of magnesium-stabilized amorphous calcium carbonate, which hinders further decalcification of C-(N)-A-S-H gel once formed.

The presence of calcium in GGBS tends to increase the framework disorder and degree of depolymerization in the calcium/magnesium aluminosilicate glassy phase [15], which is largely responsible for the higher reactivity of GGBS during alkali-activation compared with its low-Ca counterparts (i.e., class F fly ash and metakaolin) [15,27]. Calcium is also important in determining the stoichiometry and atomic structure of the precipitated C-(N)-A-S-H/N-A-S-H gel [6,15]. For precursor materials with low calcium contents (i.e., class F fly ash and metakaolin), the alkali-activation reaction results in a N-A-S-H gel possessing a three dimensional aluminosilicate structure with predominately Q^4 silica units [6,15]. On the other hand, when the precursor material contains high calcium contents (as is the case for GGBS and class C fly ash), the resulting binder consists of C-(N)-A-S-H gel with a depolymerized chain-like silica structure (Q^1 and Q^2 silica units) [8,10,18,28]), although Q^3 and Q^4 units are detected using high resolution NMR [8,28], and are associated with cross-linking in the C-(N)-A-S-H gel (Q^3) and an additional highly polymerized aluminosilicate gel (Q^4) [8].

Although some studies have explored the influence of aluminum and magnesium on the phase formation and aluminum uptake in C-(N)-A-S-H gel [14,20,23,24], together with impact of magnesium on the mechanical and carbonation resistance performance [14,20,25,26], there are a limited number of investigations that have assessed the impact of GGBS chemical composition on the nanostructural ordering of the resulting alkali-activated GGBS paste (short-, medium- and long-range atomic ordering). In this investigation PDF analysis is employed due to its ability to probe the local atomic structure of disordered materials [29]. This technique has already been applied to a range of cementitious systems including synthetic C-S-H gel [9,30–32] and alkali-activated metakaolin [30,33–36], fly ash [30] and GGBS [9,33], revealing additional quantitative information on the complex local structures in these materials. Here, X-ray PDF analysis is used to investigate the impact of GGBS chemical variability on the local structure of the resulting hydroxide-activated GGBS pastes. Via analysis of specific atom-atom correlations in the pastes, including Si-Si/Al and Ca-O, the impact of GGBS chemistry on the structure of the C-(N)-A-S-H gel is assessed. Furthermore, by analyzing existing PDF data available in the literature for a range of C-S-H and C-(N)-A-S-H gels in conjunction with the PDF data presented here, the influence of calcium and aluminum on the intensity of the Si-Si/Al correlation relative to intensity of Si/Al-O correlation is elucidated, providing information on the competing behavior between calcium and aluminum in dictating the local structure of the resulting C-(N)-A-S-H gel.

2. Materials and methods

In total, seven sources of GGBS from six different nations were studied in this investigation. Their chemical compositions obtained by X-ray fluorescence spectroscopy (XRF) are summarized in Table 1, which shows that there are sizable differences in the amount of CaO (33.9–42.9 wt.%), Al_2O_3 (9.0–14.7 wt.%), MgO (1.2–14.3 wt.%) and SiO_2 (31.6–37.4 wt.%). The relationship between the four main chemical constituents in GGBS has been analyzed with the results presented in Fig. S1 in the Supplementary material. Fig. S1 shows that as the magnesium content increases the calcium content decreases, and as the aluminum content decreases the silica content is seen to increase. This behavior is expected due to need to charge balance the network formers (silicon

Table 1
Chemical composition of neat GGBS from different regions (in wt.%) obtained using XRF.

Oxide component	Slag origin						
	Colombia (COL)	UK-1	Australia (AU)	Canada (CAN)	Ireland (IR)	Spain (SP)	UK-2
CaO	42.86	39.60	42.33	33.92	41.16	40.21	39.68
SiO_2	31.62	35.15	32.25	37.04	35.83	34.11	36.60
Al_2O_3	14.65	13.07	13.29	8.95	10.93	12.38	12.15
MgO	1.17	8.47	5.21	14.32	7.84	7.44	8.35
SO_3	2.01	0.17	2.86	0.74	1.60	2.04	–
Fe_2O_3	1.07	0.28	0.60	0.40	0.81	0.32	0.43
TiO_2	0.44	0.66	0.49	0.38	0.61	0.57	0.84
MnO	0.29	0.44	0.19	0.99	0.44	0.38	0.50
K_2O	0.31	0.51	0.33	0.54	0.41	0.29	0.65
Na_2O	0.00	0.14	0.00	0.23	0.03	0.00	0.39
P_2O_5	0.19	0.00	0.03	0.05	0.01	0.01	0.05
Others	5.39	1.51	2.42	2.08	0.33	2.25	0.36