Impact of Chemical Variability of Ground Granulated Blast-Furnace Slag on the Phase Formation in Alkali-Activated Slag Pastes

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1 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.

2 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].

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. %), SiO₂ (28-38 wt. %), Al₂O₃ (8-24 wt. %) and MgO (1-18 wt. %) [1], which all influence the resulting alkali-activated GGBS paste. The roles of Al₂O₃ 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 Al₂O₃ (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 Al₂O₃ content leads to lower Mg/Al ratios in hydrotalcite-like phases (these phases have similar LDH structures as hydrotalcite (Mg₆Al₂(CO₃)(OH)₁₆·4H₂O) but with a Mg/Al ratio of ~1.2-2.1). Furthermore, increasing Al₂O₃ content correlates with high aluminum uptake in the C-(N)-A-S-H gel and the formation of strätlingite (Ca₂Al₂SiO₇·8H₂O) 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 ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) and garronite ($\text{Na}_2\text{Ca}_5\text{Al}_{12}\text{Si}_{20}\text{O}_{64} \cdot 27\text{H}_2\text{O}$) 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.

3 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. %), Al₂O₃ (9.0 - 14.7 wt. %), MgO (1.2 - 14.3 wt. %) and SiO₂ (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 and aluminum) with network modifier cations (calcium and magnesium) in the glassy GGBS structure [1]. It is also observed that there is a trend between the network formers and modifiers, where with increasing calcium (and decreasing magnesium) the aluminum content increases while the silicon content decreases.

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	39.6	42.33	33.92	41.16	40.21	39.68
SiO ₂	31.62	35.15	32.25	37.4	35.83	34.11	36.6
Al ₂ O 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 ₂ O ₃	1.07	0.28	0.60	0.4	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	0.5
K ₂ O	0.31	0.51	0.33	0.54	0.41	0.29	0.65
Na ₂ O	0.00	0.14	0.00	0.23	0.03	0.00	0.39
P ₂ O ₅	0.19	0	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

All GGBS powders were activated with a sodium hydroxide solution. This solution was prepared by dissolving NaOH pellets (Sigma-Aldrich, reagent grade) in liquid D₂O (Sigma-Aldrich, 99.9%), with the final mix proportions being: 7g of Na₂O for every 100g of GGBS powder, with a GGBS/D₂O weight ratio of 0.483 for AU-GGBS, 0.482 for IR-GGBS and 0.389 for all the other GGBSs. This higher water content for the Australian (AU) and Ireland (IR) alkali-activated pastes was necessary to achieve a paste mixing consistency similar to the other (lower water content) pastes. All pastes were mixed by hand for 2 minutes and then sealed in air-tight containers and left to cure for approximately 6 months. Prior to measurement, the samples were ground using a mortar and pestle in an inert environment.

Both the neat GGBSs and hydroxide-activated GGBS pastes were measured using X-ray PDF analysis. For each sample, the powder was loaded into a polyimide capillary and measured on the

11-ID-B beam line at the Advanced Photon Source, Argonne National Laboratory, under room temperature conditions. The samples were analyzed using a wavelength of 0.2114 Å and a Perkin-Elmer amorphous silicon two-dimensional image plate detector [37]. The wavelength was selected to provide a compromise between high flux (statistics), Q -resolution and a sufficient maximum momentum transfer. The detector was located 175 mm from the sample. Data were collected for 30 minutes per sample. The data conversion from 2D to 1D was carried out using the program Fit2D [38, 39] with CeO₂ as the calibration material.

The pair distribution function (PDF), $G(r)$, is obtained by taking a sine Fourier transform of the measured total scattering function, $S(Q)$, where Q is the momentum transfer, as outlined by Egami and Billinge [29]. The PDF data were obtained using PDFgetX2 [40], with a Q_{max} of 20 Å⁻¹. The instrument parameters were refined by using a standard calibration material (nickel, Sigma-Aldrich) and the refinement program PDFgui [41]. The refined parameters ($Q_{\text{broad}} = 0.016$ Å⁻¹ and $Q_{\text{damp}} = 0.035$ Å⁻¹) were used for subsequent refinement of crystalline phases during analysis of the PDF data.

4 Results and Discussion

4.1 Reciprocal Space Analysis

Figs. 1a and 1b show the normalized X-ray total scattering patterns for the GGBS powders and the hydroxide-activated GGBS pastes, respectively. The broad diffuse peak centered at ~2.16 Å⁻¹ in Fig. 1a is clearly visible in all the diffraction patterns and is attributed to the amorphous calcium/magnesium-rich aluminosilicate glassy phase in GGBS (in agreement with previous X-ray diffraction studies on GGBSs [14, 20, 23]). It is apparent from Fig. 1a that besides this broad peak there are no observable features in the diffraction patterns for AU, IR, SP and UK-2 GGBSs,

190 indicating that these four sources of GGBS are amorphous. For the other GGBSs (COL, UK-1 and
191 CAN) the diffraction patterns contain Bragg peaks associated with crystalline phases in addition
192 to the dominant diffuse peak. After alkali-activation (Fig. 1b) the diffuse peak associated with the
193 glassy phase is still present, but is superimposed with a new, more defined peak situated at ~ 2.07
194 $\text{\AA}^{-1}$. Hence, these results imply that some unreacted GGBS remains in the hydroxide-activated
195 GGBS pastes after 6 months of curing. The emergence of the new peak at $\sim 2.07 \text{\AA}^{-1}$ is attributed
196 to the formation of a C-S-H type product (sodium-containing C-(N)-A-S-H gel [26]). This peak
197 appears to have a smaller full width at half maximum (FWHM) compared to the main diffuse peak
198 in GGBS, implying that the resultant gel is slightly more ordered at the atomic level compared to
199 GGBS. However, compared with C-A-S-H and C-S-H gel, which exhibit certain degrees of
200 nanocrystallinity, C-(N)-A-S-H gel is predominately amorphous [9]. It is also observed that several
201 new Bragg peaks emerge in the diffraction patterns after alkali-activation (Fig. 1b) due to the
202 formation of secondary hydration products. These secondary products are rather similar for all the
203 pastes despite the large differences in the chemical compositions of the neat GGBSs.

Fig. 1. X-ray total scattering patterns of (a) GGBSs, and (b) hydroxide-activated GGBS pastes. (c) is a zoom of (b) for Q values below $1.8 \text{ \AA}^{-1}$.

Table 2. Summary of phases identified in GGBSs and hydroxide-activated GGBS pastes using X-ray diffraction phase identification.

Slag origin	Phases in GGBS		Phases in hydroxide-activated GGBS	
	Disordered	Crystalline	Disordered	Crystalline
Colombia		Gehlenite, Calcite, Quartz		Calcium monocarboaluminate hydrate, Gismondine, Gehlenite, Calcite, Quartz,
UK-1		Gehlenite/Åkermanite		Hydrotalcite, Gehlenite/Åkermanite
Canada	Ca/Mg-rich aluminosilicate glass	Merwinite, Gehlenite/Åkermanite	C-(N)-A-S-H gel	Hydrotalcite, Gehlenite/Åkermanite, Merwinite
AU		---		Hydrotalcite
Ireland		---		Hydrotalcite
Spain		---		Hydrotalcite
UK-2		---		Hydrotalcite

Phase identification results based on the X-ray total scattering patterns (Fig. 1) are summarized in Table 2. It is clear that the main phase in all the GGBSs is amorphous, and is attributed to a calcium/magnesium-rich aluminosilicate glassy phase. The COL-, AU- and SP-GGBSs have been studied previously [20], where the amorphous content was shown to exceed 98 % in these GGBSs. In COL-GGBS, crystalline calcite (CaCO_3 , PDF #01-083-0577), quartz (SiO_2 , PDF #00-046-1045), and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$, PDF #00-035-0755) are identified, which is consistent with previous investigations [20, 21] on the same GGBS source. The present of calcite in this source of GGBS has been attributed to a small degree of weathering [20]. UK-1 and CAN-GGBS, both gehlenite and åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$, PDF #01-074-2522) have been identified. Merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$, PDF #00-035-0591) is also detected in CAN-GGBS.

Phase identification of the hydroxide-activated GGBS pastes reveals that a sodium-containing aluminum substituted C-S-H phase (C-(N)-A-S-H gel) is present in the reciprocal space data, with this phase matching the Bragg peaks attributed to poorly ordered C-S-H(I) (CaSiH_2O_4 , PDF #00-034-0002) [42]. However, depending on the chemical composition of GGBS and the type of activator used, the Ca/Si and/or Al/Si ratio of the C-(N)-A-S-H gel may vary [43], which will lead to differences in the atomic structure of the gel, as will be shown later in this study. In addition to the main binder phase (C-(N)-A-S-H gel), a hydrotalcite-like phase with LDH structure has been identified as the secondary hydration product in all but the COL-GGBS-based paste owing to the low MgO content in COL-GGBS (~1.2 wt. %). This is consistent with previous investigations which showed that the hydrotalcite-like phase (LDH) was observed only in alkali-activated GGBSs with relatively high MgO in the neat GGBS (> 5 wt. %) [13, 14, 20, 23, 24, 44, 45]. Although the hydrotalcite-like phase was not detected in the COL-GGBS-based paste, traces of gismondine and a LDH-type calcium monocarboaluminate hydrate phase ($\text{C}_4\text{AcH}_{11}$,

$\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$, PDF #00-054-0848) [46, 47] have been identified. Identification of $\text{C}_4\text{AcH}_{11}$ instead of the hydrotalcite-like phase is apparent in Fig. 1b due to the absence of peaks at ~ 2.43 and $3.21 \text{ \AA}^{-1}$ together with the emergence of a new peak at $\sim 2.52 \text{ \AA}^{-1}$.

The $\text{C}_4\text{AcH}_{11}$ phase has been reported to exist in cementitious systems, especially for tricalcium aluminate cement blended with limestone [48-50] and Na_2CO_3 -activated slag cement [51]. Thermodynamic calculations also predict the formation of $\text{C}_4\text{AcH}_{11}$ in OPC [52] and Na_2CO_3 -activated GGBS [43]. However, it has never before been identified in hydroxide- or silicate-activated GGBS systems, including those reported in refs. [20-22], where sodium silicate-activated COL-GGBS paste was investigated. Hence, our result demonstrates that the hydroxide activator can lead to the formation of a calcium aluminate LDH ($\text{C}_4\text{AcH}_{11}$) in alkali-activated GGBS with low magnesium content (1.2 wt. % MgO in the case of COL-GGBS), potentially due to the presence of calcite in the GGBS.

When comparing the XRD results of AU-GGBS- and SP-GGBS-based pastes presented in ref. [20] with those in the current study, it is found that although a hydrotalcite-like phase was also identified in the silicate-activated system with high MgO content (> 5 wt. %), the XRD peak intensities are much smaller, which is in agreement with other studies [13, 24, 26]. However, SEM-EDX analysis in refs. [13, 14, 23, 24] clearly indicated the presence of a hydrotalcite-like phase finely intermixed with C-(N)-A-S-H gel for both silicate- and hydroxide-activated GGBSs. The apparent discrepancies in XRD results for the silicate- and hydroxide-activated GGBS could be caused by differences in the quantity, size and/or crystallinity of the hydrotalcite-like phases formed. Additional research is required to determine the local atomic structural motifs of the magnesium-rich regions in these pastes and compare the results with bulk hydrotalcite-like phases,

with transmission electron microscopy combined with electron-based radial distribution functions well-suited for acquiring this information.

Fig. 1c compares the reciprocal space low- Q scattering component ($< 1.8 \text{ \AA}^{-1}$) and therefore large d -spacings for the GGBS pastes, which shows visible differences in the position (Q value) of the Bragg peaks. The peak at $\sim 0.82 \text{ \AA}^{-1}$ is attributed to the 003 reflection of the hydrotalcite-like phase and the 002 reflection of $\text{C}_4\text{AcH}_{11}$, whereas the Bragg peak at $\sim 1.65 \text{ \AA}^{-1}$ corresponds to the 006 and 004 reflection for hydrotalcite-like phase and $\text{C}_4\text{AcH}_{11}$, respectively [53, 54]. This gives a layer thickness of $\sim 7.68 \text{ \AA}$ (d_{003} and d_{002}) for the LDH structures, which is in general agreement with the literature [46, 47, 53]. It is clear that these peaks in CAN-GGBS-based paste occur at smaller Q values compared to the other pastes containing the hydrotalcite-like phase, which corresponds to slightly larger layer thickness. According to Bellotto et al. [53], the layer thickness in the $\text{CO}_3\text{-Mg,Al}$ -based LDH system increases with increasing Mg/Al ratio, which implies that the LDH formed in the CAN-GGBS-based paste has a higher Mg/Al ratio than the others in the current study. This interpretation of the diffraction data is reasonable since CAN-GGBS has an Mg/Al ratio at least 2-3 times higher than the other GGBSs. It is also observed in Fig. 1c that $\text{C}_4\text{AcH}_{11}$ formed in the low-Mg COL-GGBS-based system exhibits slightly larger Q values than the hydrotalcite-like phase for the first two peaks (most noticeable in the second $\text{C}_4\text{AcH}_{11}$ peak at $\sim 1.65 \text{ \AA}$), and therefore the $\text{C}_4\text{AcH}_{11}$ phase has a slightly smaller layer thickness [47, 53]. The other small features visible in Fig. 1c are attributed to C-(N)-A-S-H gel and gismondine as well as crystalline phases (quartz, gehlenite and åkermanite) detected in the neat GGBSs.

4.2 Pair Distribution Functions of GGBSs

To discover the local atomic structural arrangements of the glassy phases in the GGBSs, the dominant crystalline phases (calcite and quartz, if present) have been removed from the X-ray PDF data using PDFgui [41]. Details on this subtraction process have been outlined in our previous investigation [9]. Fig. 2 shows the influence of removing calcite and quartz from the PDF of COL-GGBS. It is clear that the medium/long range ordering in this Figure ($> 10 \text{ \AA}$) almost vanished after removing calcite and quartz, indicating that crystalline gehlenite (identified in COL-GGBS, Table 2) does not contribute to the long range ordering in the PDF data owing to its small quantity. Therefore, prior to analysis of the PDF data for the different GGBSs and pastes, contributions to the PDF data from calcite and quartz, if present, have been removed (Table S1 in Supplementary Material contains additional information about the refined parameters). However, contributions from other crystalline phases (i.e., gehlenite, åkermanite and merwinite) have not been removed due to (i) their relatively minor quantities in the GGBSs studied here, and/or (ii) the presence of partial occupancies (leading to erroneous atom-atom correlations in the simulated PDF) that make them difficult to remove using the method outlined in ref. [9]. For the alkali-activated GGBS pastes, it would be desirable to remove the contributions from the crystalline LDHs (hydrotalcite-like phases and $\text{C}_4\text{AcH}_{11}$) and gismondine so that the main binding phase (C-(N)-A-S-H gel) can be isolated and analyzed. However, since the secondary hydration products are often finely intermixed with C-(N)-A-S-H gel [42, 45], and hydrotalcite has partial occupancies in all the structure files available in the ICSD database, it is almost impossible to completely isolate hydrotalcite and related phases in the PDF data using current methods [9]. Therefore, the PDF contributions from all the secondary reaction products have not removed from the pastes.

Fig. 2. X-ray PDFs for COL-GGBS with and without the contributions from quartz and calcite.

Fig. 3a displays the X-ray PDFs for different sources of GGBS after removal of the contributions from calcite and quartz, which shows that the overall PDF profiles appear similar irrespective of the compositional differences. It should be noted that the peaks located at below ~ 1 Å are artifacts arising from statistical noise, imperfect corrections and termination errors [29]. It is clear that there is a lack of distinct atom-atom correlations above ~ 5 Å for AU, IR, SP, UK-1, UK-2 and COL GGBSs, indicating that these six GGBSs are amorphous after the removal of any contributions from calcite and quartz, which is consistent with the reciprocal space analysis. For CAN-GGBS there are distinct crystalline features in the PDF above ~ 5 Å, which are caused by the remaining crystalline phase (i.e., merwinite).

According to the molecular dynamic simulations on the atomic structure of GGBS [55] and calcium aluminosilicate glasses [56] and diffraction studies of calcium-magnesium silicate glasses [57], the correlations positioned between ~ 5 and ~ 8 Å are mainly attributed to the second nearest T-T, T-N and N-N correlations (T = tetrahedral cation (i.e., Al and Si); N = non-tetrahedral cation

(i.e., Ca and Mg)), which aligns with the broad peak between ~ 5 and ~ 8 Å in all PDFs in Fig. 3a. Similarly, the broad peak between 8 and 10 Å in Fig. 3a could be caused by the third nearest T-T, T-N and N-N correlations [56, 57]. The peaks below ~ 5 Å are mainly due to the nearest T-T, T-N and N-N correlations together with T-O, N-O and O-O correlations, which are shown in detail in Fig. 3b. The nearest neighbor atom-atom correlation at ~ 1.65 Å is attributed to Si/Al-O, which is slightly larger than the Si-O distance in tetrahedrally coordinated silica (~ 1.60 Å [58, 59]) due to contributions from tetrahedral alumina (main bonding environment of aluminum in the GGBS glassy phase [8, 60]), located at ~ 1.75 Å [58, 59]. In contrast to the X-ray PDF of metakaolin (alternative alkali-activated paste precursor) [34, 61, 62] which exhibits a shoulder on the main T-O peak at $\sim 1.8 - 2.0$ Å attributed to V-coordinated aluminum [63, 64], the PDFs of GGBS contain no such shoulder, indicating that aluminum atoms in GGBSs are predominantly IV-coordinated, which is consistent with both NMR measurements [8, 60] and molecular dynamic simulations [55].

Fig. 3. X-ray PDFs of the neat GGBSs after removal of quartz and calcite. (a) displays the long data up to 20 Å, (b) the short range ordering (< 5 Å). Peak assignments below 4 Å in (b) have been carried out utilizing refs. [30, 55].

The Mg-O correlation at ~2.00 Å is relatively weak in all GGBS PDFs due to the small amount of magnesium relative to calcium and silicon, and therefore it is possible that this correlation is influenced by the termination ripples associated with the Fourier transformation of a finite diffraction data set (total scattering data) [29]. However, analysis of the PDF data using a range of $Q_{\max}$ values for the Fourier transform reveals that the position of the Mg-O correlation does not move for different $Q_{\max}$ values, indicating that this correlation is sample dependent (i.e., not due to termination ripples). The peak at ~2.35 Å is attributed to the nearest-neighbor Ca-O correlation [55, 56]. The intensities of the first three peaks (Si/Al-O, Mg-O and Ca-O) in GGBSs appear to directly correlate with their chemical compositions. For instance, CAN-GGBS has the highest

magnesium content and the lowest calcium content (Table 1), and the corresponding PDF of CAN-GGBS (Fig. 3b) exhibits the most intense Mg-O correlation and the least intense Ca-O correlation. A quantitative analysis of these first three peaks in GGBSs is presented in Fig. S2 in the Supplementary Material, which reveals that the intensities of the Mg-O and Ca-O correlations in GGBS increase linearly with increasing magnesium and calcium content, as to be expected. The Si/Al-O peak intensity is relatively the same among the different GGBSs due to the similar aluminosilicate content across all GGBSs (< 5 wt. % difference, Table 1).

The peaks at ~ 3.1 Å, ~ 3.4 Å and ~ 3.6 Å are assigned to Si-Si/Al, Mg-Si/Al and Ca-Si/Al correlations, respectively. The Si-Si/Al peak intensity represents the connectivity between silica and aluminum tetrahedra in GGBSs, which shows that there are slight differences between the various GGBSs. A systematic analysis of these differences will be performed in Section 4.4. The Mg-Si/Al correlation is most noticeable in CAN-GGBS due to its high magnesium content, whereas in COL-GGBS the magnesium content is negligible and the corresponding peak is almost invisible. The Ca-Si/Al correlation for CAN-GGBS is less intense than the other GGBSs due to its lower calcium content (Table 1). The peaks between 4 and 5 Å are difficult to assign due to overlapping atom-atom correlations in this region, although the peak at ~ 4.3 Å (most intense for SP-GGBS) may be attributed to the second Si/Al-O atom-atom correlation [55].

4.3 Pair Distribution Functions of Hydroxide-Activated GGBS Pastes

The X-ray PDFs for the hydroxide-activated GGBS pastes are shown in Fig. 4a. Compared with the PDFs of the neat GGBSs in Fig. 3a, the PDFs of the pastes display more coherent atom-atom correlations due to an increase in atomic ordering for the reaction products (especially the secondary reaction products crystalline LDHs). In addition, the PDFs for the different pastes

appear to possess similar atomic ordering despite the differences in the chemical compositions of the neat GGBSs, which is due to the fact that the primary and secondary reaction products formed in the pastes are similar, as already discussed in the phase identification results in Section 4.1. It is also clear that all the pastes display some degree of ordering below ~ 20 Å, above which few features can be observed. The result agrees with our recent X-ray PDF study on the nanostructure of alkali-activated material gels [9], which showed that binder gel (C-(N)-A-S-H and/or N-A-S-H) is predominantly amorphous with atomic ordering present below ~ 15 Å. Comparing the paste PDFs in this study (hydroxide-activated) to the PDF of silicate-activated GGBS (see Fig. S3 in the Supplementary Material) reveals that hydroxide-activated pastes are slightly more ordered; due to the more extensive formation of crystalline secondary products (such as hydrotalcite-like phases) [13, 24, 26], as already discussed in Section 4.1. In either case (hydroxide- or silicate-activated), the C-(N)-A-S-H gels formed in alkali-activated GGBSs are intrinsically less ordered than synthetic C-S-H gels (model system for OPC pastes), which exhibit long range ordering up to ~ 40 Å [9, 31], although synthetic C-A-S-H gel is seen to become more ordered via the uptake of alkali cations (as determined by XRD analysis).

The atom-atom correlations below 5 Å in the hydroxide-activated GGBS pastes are shown in Fig. 4b. The peaks at ~ 1.64 Å, ~ 2.00 Å and ~ 2.38 Å are assigned to Si/Al^{IV}-O, Mg-O/Al^{VI}-O and Ca-O correlations, respectively, and, as with the GGBS PDFs, they represent the nearest-neighbor bonding environments in alkali-activated GGBS pastes. From the peak position and shape of the Si/Al-O correlation it is clear that both silicon and aluminum in the pastes are predominantly in tetrahedral coordination. While the intensities of the Si/Al-O correlation are similar for the different pastes, there are noticeable differences in the Mg-O/Al^{VI}-O and Ca-O correlations. In particular, the Mg-O/Al^{VI}-O correlation appears to be more intense in the pastes compared with

384 the neat GGBSs owing to the contribution from the Al-O correlation in VI-coordination (at ~ 2.02
 385 $\text{\AA}$) in the hydrotalcite-like phase [8, 53], as shown in Fig. 5. Also, the Mg-O/ Al^{VI} -O correlation in
 386 the COL-GGBS-based paste is positioned at a slightly smaller r spacing compared to those in the
 387 other pastes, which is attributed to VI-coordinated aluminum in $\text{C}_4\text{AcH}_{11}$ phase [47] located at
 388 $\sim 1.91 \text{ \AA}$ (Fig. 5). Similar to the neat GGBSs, the atom-atom correlations for the nearest-neighbor
 389 bonding environments are directly related to the chemical composition of the neat GGBSs, as
 390 shown quantitatively in Fig. S2 in the Supplementary Material.

Fig. 4. X-ray PDFs of the hydroxide-activated GGBS pastes after removal of quartz and calcite. (a) displays the long range data up to 40 Å, (b) the short range ordering (< 5 Å). Peak assignments below 4 Å in (b) are based on refs [9, 26]. The Ca-Al correlation is attributed to calcium LDH (C₄AcH₁₁) phase, whereas Ca-Si/Al correlation is attributed to the C-(N)-A-S-H gel.

The peak at ~3.07 Å, attributed to Si-Si/Al in C-(N)-A-S-H gel and Mg-Al in the hydrotalcite-like phase, displays considerable differences in peak intensity, which is inversely related to the intensity of the Ca-O correlation at ~2.38 Å. For instance, CAN-GGBS-based paste has the lowest intensity Ca-O correlation together with the highest intensity Si-Si/Al + Mg-Al peak, while in contrast the COL-GGBS-based paste has the highest intensity Ca-O correlation along with the least intense Si-Si/Al + Mg-Al peak. The intensity of the Si-Si/Al correlation in C-(N)-A-S-H gel represents the connectivity of the silica and alumina tetrahedral, however, due to the overlap with

the Mg-Al correlation in the hydrotalcite-like phase it is not straightforward to interpret the PDF data. Additional analysis of the data will be discussed in the next section.

Comparing Fig. 4b with Fig. 3b reveals that the shoulder at ~ 3.4 Å (Mg-Si/Al) in the GGBS PDFs with high MgO level (> 5 %) disappear in the corresponding paste PDFs. This is because magnesium is known to be incorporated in the hydrotalcite-like phase due to alkali-activation reaction (as opposed to ending up in the C-(N)-A-S-H gel) [20], leading to a slight shift of the Mg-Al correlation to ~ 3.07 Å (Fig. 5). The shift in Mg-Al correlation is due to the different arrangement of magnesium and aluminum polyhedral in the hydrotalcite-like phase compared with the glass phase in the neat GGBSs together with the change in aluminum coordination. In contrast, in the COL-GGBS-based paste, where no hydrotalcite-like phase formed, a minor shoulder at ~ 3.4 Å emerges, which is attributed to the Ca-Al correlation in C_4AcH_{11} (as shown in Fig. 5). The emergence of this shoulder may also have led to the slight shift of the Ca-Si/Al peak to lower r spacing compared with the other pastes. As verified in Fig. S4 in the Supplementary Material, after removal of the atom-atom contributions from the C_4AcH_{11} phase, the minor shoulder at ~ 3.4 Å disappears together with a slight shift of the Ca-Si/Al peak to higher r spacing along with a reduction in the Ca-O peak intensity. The fact that the Ca-O correlation only reduces slightly in intensity due to this subtraction process indicates that the amount of C_4AcH_{11} in COL-GGBS-based paste is relatively small compared with the C-(N)-A-S-H gel.

Fig. 5. Simulated X-ray PDFs for hydrotalcite-like phase (Mg/Al LDH) and C_4AcH_{11} (Ca/Al LDH) using PDFgui software, based on cif files from ref. [65] (this file is used due to the least amount of partial occupancies in the structure) and ref. [47], respectively. The experimentally-derived instrument parameters ($Q_{broad} = 0.016 \text{ \AA}^{-1}$ and $Q_{damp} = 0.035 \text{ \AA}^{-1}$) have been used. Atomic displacement parameters were set at $0.003 \text{ \AA}^2$.

4.4 Quantitative Analysis of Atom-Atom Correlations

As mentioned in the previous section, there appears to be an inverse relationship between the Ca-O and Si-Si/Al peak in the alkali-activated pastes in Fig. 4. The intensity of the Si-Si/Al correlation reflects the silica/alumina tetrahedral connectivity combined with the relative percentage of silicon and aluminum in the sample. The Ca-O is a direct measure of the percentage of calcium in the sample. The correlation between the amount of calcium in the system (assumed to be mostly present in the C-(N)-A-S-H gel) and the aluminosilicate polyhedral connectivity (i.e., amount of Si-O-Si and Si-O-Al linkages in the gel) gives an indication of the influence of calcium on the degree of polymerization of the C-(N)-A-S-H gel. However, to isolate the information relating to

the polyhedral connectivity, the Si-Si/Al intensity has been normalized to the relative amount of silicon and aluminum in the sample by dividing by the intensity of the Si/Al-O correlation.

Fig. 6 displays the results for the polyhedral connectivity of C-(N)-A-S-H in the hydroxide-activated GGBS pastes. This analysis assumes a single gel phase is present, although recent literature has revealed that a small percentage of alkali aluminosilicate gel can be present in alkali-activated GGBS pastes along with the presence of unreacted GGBS (see the Supplementary Material for information on how unreacted GGBS impacts the results given in Fig. 6) [8]. To gauge the level of polyhedral connectivity in the neat GGBSs, the same analysis of the Ca-O and Si-Si/Al correlations has been carried out and is displayed in Fig. 6. Additional data is provided for other cementitious systems studied in the literature, including synthetic C-S-H gel [9, 66], Na₂SiO₃-activated GGBS [9, 26] and NaOH-activated GGBS [26, 33]. It should be noted that the contribution to the Mg-Al correlation from the hydrotalcite-like phase and the Ca-O correlation from C₄AcH₁₁ phase have not been removed from the Si-Si/Al and the Ca-O correlations, respectively, if present in the samples. It is reasonable to believe that this would not change the general trend clearly observed in Fig. 6 where the alumina/silica polyhedral connectivity is seen to decrease monotonically with increasing calcium content, because it has been shown in Fig. S3 in the Supplementary Materials that removing PDF contribution of C₄AcH₁₁ phase does not cause much change to the PDF of the COL-GGBS-based paste. This behavior indicates that the degree of polymerization in these system (i.e., C-S-H, C-(N)-A-S-H and GGBS) decreases with increasing calcium content. This is due to the presence of calcium, which increases the tendency of framework disorder leading to the rupture of tetrahedron linkages [15, 67]. These results clearly demonstrate the influence of calcium in dictating the atomic structure of these disordered glassy and cementitious phases.

Fig. 6. Relationship between the Ca-O peak intensity and the Si-Si/Al peak intensity normalized by the amount of silicon and aluminum in the sample (given by the Si/Al-O peak intensity). This relationship provides an indication of the (alumino)silicate polyhedral connectivity, and therefore the degree of (alumino)silicate polymerization in the sample as a function of the calcium content.

A comparison of the data in Fig. 6 for the various systems (neat GGBSs, hydroxide-activated GGBS, silicate-activated GGBS and synthetic C-S-H gel) reveals that there are noticeable differences between the gels/glasses according to the stoichiometry. It should be noted that the lines drawn on the figure are for the purpose of guiding the eye. It is evident that the gel connectivity (degree of polymerization) of the C-S-H gel decreases with increasing Ca-O intensity and is consistently lower than that found in alkali-activated GGBSs. This is in agreement with previous studies on the C-S-H gel structure using ^{29}Si NMR [68-70], Raman spectroscopy [71], near-, mid-, and far-infrared spectroscopy [72] as well as molecular dynamic simulations [73, 74], which all showed that increasing the Ca/Si ratio leads to a reduction in the degree of polymerization.

It is generally agreed in the literature [28, 71, 75, 76] that C-(N)-A-S-H gel in alkali-activated GGBS exhibits higher degrees of polymerization compared with the C-S-H gel. This is attributed to the generally lower calcium content in C-A-S-H gel. However, even at similar intensities for the Ca-O correlation as shown in Fig. 6, the gel connectivity in the alkali-activated GGBS binders is noticeably higher than that in the C-S-H gel, indicating that aluminum is also playing a key role. In fact, the impact of aluminum uptake on the structure of C-S-H has been analyzed in a number of investigations [8, 75-77], which showed that aluminum incorporation tends to increase the degree of gel polymerization. This is likely due to the restrictions in where aluminum substitution can occur in C-S-H gel (aluminum preferentially substitutes into bridging sites in silica chain [75, 77-79] especially at Ca/Si ratios below 1.4 [76]) that necessitate the development of longer chains to accommodate the aluminum [80], along with the emergence of a significant amount of cross-linking between the silica chains [8]. Hence, the higher gel connectivity of C-(N)-A-S-H in alkali-activated GGBS compared with C-S-H is more likely due to the combined effect of aluminum substitution and lower calcium content.

Previous literature has shown that an increase in the aluminum content of GGBS leads to higher aluminum uptake in the resulting C-(N)-A-S-H gel after alkali-activation [23]. Given that aluminum incorporation in C-(N)-A-S-H increases the gel connectivity, this means that GGBS with a higher aluminum content is likely to result in a higher gel connectivity in the C-(N)-A-S-H. To investigate this behavior, the aluminosilicate gel connectivity ($((\text{Si-Si}/\text{Al}) \div (\text{Si}/\text{Al-O}))$ value) of the hydroxide-activated GGBS pastes has been plotted against the Al_2O_3 and CaO content (in molar fractions) of the neat GGBSs, as shown in Fig. 7. Fig. 7a clearly shows that the gel connectivity in the paste decreases with increasing aluminum content in the GGBS. Meanwhile, Fig. 7b shows that increasing calcium content in GGBS reduces the gel connectivity of the

corresponding C-(N)-A-S-H. This demonstrates that while both aluminum and calcium influence the gel connectivity of the C-(N)-A-S-H gel, calcium is seen to dominate the gel connectivity behavior in this investigation. This is due to the correlation between the aluminum and calcium content in the neat GGBSs, where Fig. S2 in the Supplementary Material shows that as the calcium content increases in the GGBS source so does the aluminum content.

Fig. 7. Correlation between the aluminosilicate gel connectivity $\frac{(\text{Si-Si/Al})}{(\text{Si/Al-O})}$ ratio) in hydroxide-activated GGBS paste and the elemental composition of the GGBS powder. (a) Influence of the GGBS alumina content and (b) the calcium content (in fractional molar units) on the gel connectivity.

Another interesting point to note in Fig. 6 is that the $\frac{(\text{Si-Si/Al})}{(\text{Si/Al-O})}$ ratio in hydroxide-activated GGBS paste appears to be higher than that in silicate-activated GGBS paste. This appears to contradict previous investigations [10, 18, 28] where it was found that the C-(N)-A-S-H gel in silicate-activated GGBS is more polymerized compared with the gel formed in hydroxide-activated GGBS. However, as shown in the Supplementary Material, once unreacted GGBS is removed from the hydroxide-activated GGBS pastes, the ratio is seen to coincide with neat GGBS (and also the silicate-activated GGBS pastes). Therefore, any difference in gel connectivity between hydroxide- and silicate-activated GGBS cannot be elucidated from Fig. 6. It is also

important to note that, as outlined in the Supplementary Material, removal of contributions from unreacted GGBS in the data presented in Fig. 6 reveals that hydroxide-activated GGBS paste without the unreacted GGBS behaves in a similar manner to hydroxide-activated GGBS paste when assessing the $(\text{Si-Si/Al}) \div (\text{Si/Al-O})$ versus Ca-O peak height correlation.

As is the case for C-S-H and C-(N)-A-S-H gel, the structure of neat GGBS can be considered as a depolymerized aluminosilicate network charge balanced by network modifiers [60]. According to Shimoda et al. [60], a GGBS with a chemical composition of $(\text{Ca}_{3.61}\text{Mg}_{0.82})(\text{Al}_{1.38}\text{Si}_{2.75})\text{O}_{12.00}$, similar to that of the AU-GGBS in the current study, contains silica with an average connectivity of $Q^{2.2}$. This connectivity value of 2.2 for the glassy structure in GGBS is similar to that of the C-(N)-A-S-H gel in silicate-activated GGBSs [10, 18, 28], which explains the similar $(\text{Si-Si/Al}) \div (\text{Si/Al-O})$ ratios exhibited by GGBS and C-(N)-A-S-H gel (in the silicate-activated GGBS pastes) in Fig. 6. It is also observed for GGBS that there is a decrease in connectivity of the glass network with increasing Ca-O intensity (black triangles in Fig. 6) except for CAN-GGBS. On the one hand, this clearly illustrates the impact of calcium on GGBS glass structures, consistent with investigations on calcium and/or magnesium containing aluminosilicate glasses which showed that increasing calcium content decreases the degree of polymerization in the glassy structure [56, 81]. On the other hand, the exception for the CAN-GGBS indicates that while magnesium in alkali-activated GGBS paste is mainly incorporated in hydrotalcite-like phase [20] it plays a key role as a network modifier cation (together with calcium) in the aluminosilicate network of GGBS.

5 Conclusions

The mineralogy and chemical composition of ground granulated blast-furnace slag (GGBS) is known to vary considerably from source to source. This variability makes it challenging to fully understand

the structural mechanisms occurring at the nanoscale during the alkali-activation reaction and the subsequent development of the calcium-sodium aluminosilicate hydrate (C-(N)-A-S-H) gel together with the formation of secondary phases. Here, X-ray total scattering and subsequent pair distribution function (PDF) analysis have been used to investigate the influence of chemical variations in neat GGBSs on the resulting phase formation and local atomic structures of the sodium-based hydroxide-activated GGBS pastes.

Reciprocal space analysis of different GGBS sources showed that the GGBSs from Colombia, Canada and UK-1 contain small amounts of crystalline phases (mainly åkermanite/gehlenite/merwinite depending on the chemical composition of the GGBS, and traces of calcite and quartz) whereas the other four GGBS samples were amorphous. However, regardless of the mineralogical and chemical variability in the neat GGBSs, the primary reaction product after alkaline-activation was C-(N)-A-S-H gel with a structure resembling highly disordered C-S-H (I). A hydrotalcite-like phase formed in the majority of the pastes as the main secondary reaction product except for the Columbia GGBS-based paste, where a monocarboaluminate hydrate (C_4AcH_{11}) phase was detected due to the low MgO content of the corresponding GGBS.

PDF analysis confirmed the formation of the hydrotalcite-like and C_4AcH_{11} phases as a result of the alkali-activation reaction, and demonstrated that all the pastes exhibit a similar degree of ordering up to ~ 20 Å despite the differences in GGBS chemical composition. Analysis of the local atomic structure (< 5 Å) revealed that the atomic arrangements in the C-(N)-A-S-H gel varies considerably depending on the chemical compositions, especially the calcium content of the raw GGBSs. Specifically, the results indicate that the gel connectivity (degree of polymerization) of the C-(N)-A-S-H gel in hydroxide-activated GGBS paste increases with decreasing calcium content, with similar trends observed via analysis of published PDF data for synthetic C-S-H gel

and silicate-activated GGBS pastes. Comparison of the C-S-H gel and the alkali-activated GGBS pastes showed that aluminum uptake in C-(N)-A-S-H gel tends to increase gel connectivity which is consistent with previous investigations. However, it appears that calcium has a more prominent influence than aluminum in dictating the atomic structure of these cementitious gel. These results clearly demonstrate the ability of PDF analysis to analyze the gel connectivity (degree of polymerization) in complex aluminosilicate systems.

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7 Supplementary Material Available

Fractional amounts of calcite and quartz in the COL-GGBS and COL-GGBS-based paste, determined by refining simulated X-ray PDFs against experimental data in 40-60 Å. Compositional relationship between the major elements present in the GGBSs. Relationship between the chemical composition of the neat GGBSs and peak height of the nearest atom-atom correlations in the GGBSs and pastes. Comparison of the X-ray PDF of the hydroxide-activated AU-GGBS paste with a silicate-activated GGBS paste reported in a previous study [9]. Influence of removing contributions from calcite, quartz and Ca/Al LDH (C_4AcH_{11}) on the X-ray PDF data

of hydroxide-activated COL-GGBS paste. Impact of removing unreacted GGBS from the PDF data for hydroxide-activated GGBS on the relationship between $(\text{Si-Si/Al})/(\text{Si/Al-O})$ and Ca-O peak height correlation. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

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