Intrinsic Differences in Atomic Ordering of Calcium (Alumino)Silicate Hydrates in Conventional and Alkali-Activated Cements

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Abstract

The atomic structures of calcium silicate hydrate (C-S-H) and calcium (-sodium) aluminosilicate hydrate (C-(N)-A-S-H) gels, and their presence in conventional and blended cement systems, have been the topic of significant debate over recent decades. Previous investigations have revealed that synthetic C-S-H gel is nanocrystalline and due to the chemical similarities between ordinary Portland cement (OPC)-based systems and low-CO₂ alkali-activated slags, researchers have inferred that the atomic ordering in alkali-activated slag is the same as in OPC-slag

cements. Here, X-ray total scattering is used to determine the local bonding environment and nanostructure of C(-A)-S-H gels present in hydrated tricalcium silicate (C_3S), blended C_3S -slag and alkali-activated slag, revealing the large intrinsic differences in the extent of nanoscale ordering between C-S-H derived from C_3S and alkali-activated slag systems, which may have a significant influence on thermodynamic stability, and material properties at higher length scales, including long term durability of alkali-activated cements.

Keywords: X-ray Diffraction, Calcium-Silicate-Hydrate (C-S-H), Amorphous Material, Alkali-Activated Cement, Portland Cement

Introduction

With the emergence of alternative cementitious materials in recent decades combined with the massive impact conventional cement production has on the environment, there has been increasing interest in commercialization of low-CO₂ alternative cements. Ordinary Portland cement (OPC) production accounts for 5-8% of man-made CO₂ emissions [1], and the amount produced globally is forecast to double over the next 30 years. Alkali-activated cement, synthesized using industrial by-products including coal-derived fly ash and ground-granulated blast furnace slag (denoted slag), has been shown to emit 80-90% less CO₂ compared to OPC [2], and therefore there is significant push from society to implement this low-CO₂ alternative to traditional concrete in industry.

The atomic structure of OPC-based cements has been the subject of debate over recent decades, however, there is consensus that the main binder phase consists of calcium silicate hydrate (C-S-H) gel with a Ca/Si ratio of 1.7 [3]. Previous investigations have revealed that synthetically-derived C-S-H gel is nanocrystalline, as opposed to amorphous, and therefore possesses medium range ordering up to $\sim 40 \text{ \AA}$, which is the particle size of the gel grains [4]. As was reported by Skinner et al. [4], the atomic structure of a synthetic C-S-H gel with a Ca/Si ratio of 1 ± 0.15 has local and medium range ordering similar to 11 $\text{\AA}$ tobermorite. Due to the large percentage of calcium present in slag, alkali-activated slag cements have been reported to mimic the atomic bonding environments in OPC-based cements, specifically the existence of calcium (-sodium) aluminosilicate hydrate gels (C-(N)-A-S-H) [5-8]. This differs from the known chemistry of alkali-activated fly ash (class F) or metakaolin cements, where calcium is not present in the precursor powders, and therefore calcium-bearing phases do not form during synthesis. Instead,

solely sodium aluminosilicate hydrate gel (N-A-S-H) forms, which is amorphous as seen using X-ray pair distribution function (PDF) [9-12].

Importantly, there are certain long-term degradation processes alkali-activated slag cements can exhibit, specifically microcracking and shrinkage/creep of the binder [13-15], which just may be caused by instabilities at the nanoscale. Hence, it is imperative that the atomic, nanoscale and higher length scale structure and properties of both OPC-based and alkali-activated slag cements are fully understood if durability processes are to be mitigated via controlling the cement chemistry. Here, X-ray PDF analysis is used to investigate the atomic and nanoscale ordering of C-S-H and C-(N)-A-S-H gels present in tricalcium silicate (C_3S), C_3S -slag, alkali-activated slag and blended alkali-activated slag-metakaolin pastes. This experimental technique uses high energy X-rays to probe the local structure of materials in real space by performing a sine Fourier transform of a material's total (Bragg and diffuse) scattering data. Hence, the experimental technique directly distinguishes between materials that are amorphous, nanocrystalline or crystalline while also providing quantitative information regarding the local bonding environment [16]. This powerful technique has been used to gain deeper insight into the structure and mechanisms occurring in numerous materials and processes including electrochemical reactions [17], lead chalcogenides [18], perovskites [19], and oxyhydroxides [20]. By isolating the gel structure in the PDFs via removing crystalline contributions from C_3S and portlandite (calcium hydroxide), we can directly compare the atomic and nanoscale ordering of the C-(N)-A-S-H gel in conventional C_3S -slag cements and alkali-activated slag cements. It should be noted that the C-S-H gels studied here are derived from hydrated- C_3S , and therefore may be different to the C-S-H gel present in OPC-based paste. However, due to the existence of additional phases

in hydrated OPC, such as hydrogarnet, AFm and AFt, it is extremely difficult at present, if not impossible, to quantitatively analyze the local atomic structure of C-S-H gel in situ. Hence, it is important to keep in mind the potential differences that may exist between the structure and behavior of (i) C-S-H gel in OPC pastes and (ii) gels derived from synthetic laboratory processes. Nevertheless, with the emergence of advanced techniques such as tomography coupled with microdiffraction (and PDF analysis), it will be possible to access spatially-resolved local structural information on heterogeneous materials in the future.

Materials and Methods

C-S-H gels of varying Ca/Si ratios (0.83, 1.2, 1.5, 1.7 and 3.0) were synthesized using triclinic tricalcium silicate (C_3S , CTLGroup) and amorphous fumed silica (SiO_2 , Alfa Aesar, 325 mesh). For the samples with Ca/Si ratios ≤ 1.7 , C_3S and fumed silica were mixed together by placing the powders in acetone and sonicating the solution for 5 minutes. After sonication the solutions were left in air for the acetone to evaporate. Once most of the acetone had evaporated, excess acetone was removed by placing the mixtures in a vacuum drying oven at ambient temperature for 12 hrs. The dried mixtures were crushed using a mortar and pestle to remove any agglomerates. The prepared powders were hydrated using D_2O , as the samples were subsequently analyzed using neutron pair distribution function in a complementary study (unpublished work). It is known that the use of D_2O in place of H_2O affects the kinetics of hydration of C_3S [21], however, the use of D_2O does not appear to change the structure of C-S-H. In fact, as will be discussed later, a visual comparison between the data acquired for samples synthesized using D_2O and published PDF data on C-S-H gel reveals that the H/D isotopic substitution does not affect the resulting PDF characteristics (location and peak height of atom-atom correlations). The D_2O /precursor ratios (by weight) used to hydrate the powders were 2.17, 1.53, 1.27, 1.25 and 0.56 for Ca/Si ratios of 0.83, 1.2, 1.5, 1.7 and 3.0, respectively. The higher D_2O /precursor ratios for lower Ca/Si ratio samples were necessary due to the higher water demand of the increasing amount of fumed silica. The D_2O /precursor ratio of 0.56 is equivalent to a H_2O /precursor ratio of 0.50 (weight-correction). Blended C_3S -slag samples were synthesized by mixing equal weights of C_3S and slag powder, and then hydrating the mixed powders with (i) pure D_2O and (ii) 7 w.t. % Na_2O (i.e., 7g of Na_2O for 100g of precursor powder, using NaOD (40 w.t. % NaOD in D_2O from Sigma-Aldrich)), with a D_2O /precursor ratio of 0.56 for both samples. Once the samples were

mixed by hand for 2 minutes, they were sealed in air-tight containers and left to hydrate for 3 months (for the C-S-H gels) and 6 weeks (for the blended slag cements). Prior to X-ray measurements the samples were crushed using a mortar and pestle in an inert environment (to limit the exchange of H/D) and loaded into polyimide tubing.

The synthesis method used to create silicate- and hydroxide-activated (S- and H-activated) slag and slag-metakaolin pastes was previously outlined in White et al. [11]. 7 w.t. % Na₂O was used as the alkali activator (i.e., 7g of Na₂O for 100g of precursor powder) and the alkali source was NaOH (H-activated) or sodium metasilicate (S-activated). The H₂O/precursor ratio was 0.35 for the slag systems and 0.625 for the mixed slag-metakaolin systems due to the higher water demand of metakaolin. The mixed systems were synthesized using 50/50 amounts of slag and metakaolin by weight. Samples were mixed by hand and loaded into polyimide tubing (X-ray sample holders). Initial in-situ measurements were performed for the alkali-activation reactions of slag and slag-metakaolin [11, 22], however, the data reported in this study are from subsequent measurements performed 128 days after initial mixing.

All samples were mounted and aligned on the sample changer on the 11-ID-B beam line at the Advanced Photon Source, Argonne National Laboratory, under ambient temperature conditions (including neat C₃S). The samples were analyzed using a wavelength of 0.2128 Å and a Perkin-Elmer amorphous silicon two-dimensional image plate detector [23]. This wavelength was selected to provide a compromise between high flux (statistics) and a sufficient maximum momentum transfer. The detector was located 164 mm from the sample for C₃S, the C-S-H gels and C₃S-slag blended cements, and 168 mm from the sample for the alkali-activated slag and

slag-metakaolin cements. Data were collected for 30 minutes per sample. The data conversion from 2D to 1D was carried out using the program Fit2D with CeO₂ as the calibration material [24, 25].

The pair distribution function (PDF), $G(r)$, is obtained by taking a sine Fourier transform of the measured total scattering function, $S(Q)$, as shown in equation (1), where Q is the momentum transfer given in equation (2) [16].

$$G(r) = \frac{2}{\pi} \int_{Q=Q_{min}}^{Q=Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (1)$$

$$Q = \frac{4\pi \sin \theta}{\lambda} \quad (2)$$

Standard data reduction procedures were followed to obtain the PDF using PDFgetX2 [26], with a Q_{max} of 20 Å⁻¹.

Results and Discussion

Total Scattering Data

The X-ray total scattering functions, $S(Q)$, of the various conventional and alternative cement pastes are displayed in Figure 1. For the C-S-H gels (denoted by their Ca/Si ratios) the presence of distinct Bragg peaks indicate that crystalline phases do exist in the samples. As was discussed by Skinner et al. [4], hydrated C_3S leads to the coexistence of C-S-H gel together with portlandite (CH in cement notation) and unreacted C_3S particles. This is also visible in Figure 1 for the Ca/Si 3 sample, where both CH and C_3S peaks are present in the diffraction pattern. As the Ca/Si ratio decreases so does the CH content, which can be seen by the decrease in intensity of the Bragg peaks (for instance, situated at ~ 1.28 and $2.39 \text{ \AA}^{-1}$). For the blended C_3S -slag samples (hydrated and hydroxide-activated, denoted H-activated) CH and C_3S is also present. In contrast, the alkali-activated slag and alkali-activated slag-metakaolin samples are predominately amorphous or nanocrystalline evidenced by the lack of Bragg peaks. However, for the H-activated slag sample there are crystalline peaks, which may be attributed to akermanite or gehlenite [27]. H-activated metakaolin tends to crystallize more readily than S-activated [28], and the results displayed in Figure 1 show that the same is true for slag-based alkali-activated cements.

Figure 1. X-ray total scattering functions of hydrated C_3S -silica (containing C-S-H gels, denoted by the Ca/Si ratios), blended C_3S -slag cements (hydrated with D_2O , denoted “hydrated”, and hydroxide-activated, denoted “H-activated”), alkali-activated slag (silicate-activated, denoted “S-activated” and H-activated), and alkali-activated slag-metakaolin (S- and H-activated). Crystalline peaks have been identified as portlandite (*) [4], C_3S (†) [4] and akermanite or gehlenite (#) [29], while the C-S-H gel is denoted by $\pm$ [4].

Method to Isolate Nanocrystalline/Amorphous Gel Components

Due to the mixed phases present in the total scattering patterns, both crystalline and nanocrystalline/amorphous phases, the contributions of calcium silicate hydrate (C-S-H) and calcium (-sodium) aluminosilicate hydrate (C-(N)-A-S-H) gels were isolated by removing the crystalline contributions to the X-ray PDFs. As was reported by Skinner et al. [4], the synthetically-derived nanocrystalline C-S-H gel possesses coherent ordering up to ~ 40 Å, whereas the resolution of 11-ID-B instrument provides information past 60 Å (Q_{damp} parameter of 0.038 Å^{-1} , determined by refinement of the calibration material CeO_2) [30]. Hence, the crystalline phases present in Figure 1 will be the only phases contributing to the atom-atom correlations in the region $40 \leq r \leq 60$ Å, which can be fitted to the experiment data and subtracted, leaving only the atom-atom correlations attributed to the nanocrystalline and amorphous gel phases (C-S-H, C-A-S-H, C-(N)-A-S-H and N-A-S-H). Apart from the hydroxide-activated ground-granulated blast furnace slag (H-activated slag) sample which contains a crystalline phase most likely attributed to akermanite or gehlenite [29], all other samples contained varying amounts of tricalcium silicate (C_3S) and portlandite ($\text{Ca}(\text{OH})_2$), denoted CH in cement notation). The relative phase fractions of these crystalline phases were obtained by using (i) the experimental X-ray PDF data set of C_3S measured on 11-ID-B, and (ii) the simulated X-ray PDF of CH from the study of Petch [31]. To ensure experimental feasibility the simulated X-ray PDF of CH was refined against the hydrated C_3S sample (Ca/Si of 3, Figure 1) in the region $40 \leq r \leq 60$ Å using PDFgui [30]. This experimental PDF contained the highest percentage of CH, as seen in Figure 1 for the Bragg peak located at 1.28 Å^{-1} . Parameters that were refined for the CH structure include the lattice parameters (a and c) and the atomic displacement parameters for Ca, O and D atoms (deuterium was used to synthesize the sample),

together with the phase fraction of C₃S. The simulated PDF of C₃S was obtained by refining the literature structure [32] against the C₃S experimental PDF over the full range, $1 \leq r \leq 60 \text{ \AA}$, including the scale factor, lattice parameters, and atomic displacement parameters, using PDFgui [30]. Once the simulated PDF of CH was obtained, the percentage of C₃S and CH in the hydrated C₃S-silica and blended C₃S-slag cement samples was obtained by calculating the unweighted *R*-value in the region $40 \leq r \leq 60 \text{ \AA}$ using a purpose designed C++ computer program, and the following equation (3):

$$R = \sqrt{\frac{\sum_{i=1}^N (G(r_i)_{calc} - G(r_i)_{exp})^2}{\sum_{i=1}^N (G(r_i)_{exp})^2}} \quad (3)$$

$G(r)_{calc}$ was calculated by varying the fractional amounts of C₃S and CH from 0.000 to 1.000 in 0.001 increments followed by calculating the corresponding $G(r)_{calc}$ for the given fractional amounts (i.e., $G(r)_{calc} = (\alpha \times G(r)_{C_3S}) + (\beta \times G(r)_{CH})$, where α and β vary between 0.000 and 1.000). The values of α and β that gave the lowest *R*-value were subsequently used to subtract out contributions from the crystalline phases (results given in Table 1). In order to implement this subtraction methodology, the crystalline phases (C₃S and CH) were assumed to be separate to the gel binder, and therefore the surface interactions between the various phases have not been included in the PDF refinement process. As seen via imaging techniques such as scanning electron microscopy, the residual C₃S grains and precipitated CH crystals in hydrated-C₃S samples are readily apparent at the micron length scale [5], so the surface interactions between the crystalline phases and the gel binder will not be detectable in the PDF data (since the bulk interactions dominate), and therefore treating the crystalline phases as separate from the gel will not adversely affect the results. Figure 2 displays the experimental X-ray PDF of the C-S-H gel

(denoted *C-S-H with C₃S (Ca/Si 0.83)*, black line) and after subtraction of the contribution from C₃S (denoted *C-S-H (Ca/Si 0.83)*, thin grey line). Figure 3 shows the crystalline contributions to the X-ray PDF of hydrated C₃S-slag (black line), and the resulting C-A-S-H gel obtained using this method (thin grey line).

Table 1. Fractional amounts of C₃S and CH crystalline phases present in samples synthesized using C₃S, as determined by refining simulated X-ray PDFs to experimental data in the region $40 \leq r \leq 60$ Å. Agreement with data is given by the *R*-value, as defined in equation (3). Ca/Si ratios of the gels were calculated using the known starting Ca/Si ratios of the synthesized samples and by taking into account the refined amounts of C₃S and CH (with known Ca/Si ratios). The Ca/Si ratio of blended C₃S-slag samples was calculated assuming the stoichiometry of slag was $0.09\text{Al}_2\text{O}_3 \cdot 0.35\text{SiO}_2 \cdot 0.49\text{CaO} \cdot 0.07\text{MgO}$ [22].

Sample	C ₃ S	CH	<i>R</i> -value	Ca/Si ratio of gel*
Hydrated C ₃ S (Ca/Si 3.0)	0.407	0.312	0.305	1.42
Hydrated C ₃ S-silica (Ca/Si 1.7)	0.245	0.088	0.454	1.32
Hydrated C ₃ S-silica (Ca/Si 1.5)	0.307	0.046	0.636	1.15
Hydrated C ₃ S-silica (Ca/Si 1.2)	0.324	0.003	0.576	0.93
Hydrated C ₃ S-silica (Ca/Si 0.83)	0.388	0.000	0.453	0.57
Hydrated C ₃ S-slag	0.235	0.106	0.461	1.32
H-activated C ₃ S-slag	0.026	0.093	0.507	1.53
S-activated slag				0.93
S-activated slag-metakaolin				0.32

235 * $\frac{Ca+Mg}{Si+Al}$ ratios are given for samples containing slag. Alkali-activated slag and alkali-activated
 236 slag-metakaolin do not contain any percentage of C_3S and CH , as seen in Figure 1.

237
 238 Figure 2. X-ray PDF experimental data sets of hydrated C_3S -silica (denoted *C-S-H with C_3S*
 239 (*Ca/Si 0.83*), black line) and C_3S (thick grey line), along with the resulting C-S-H gel PDF (thin
 240 grey line) after subtraction of the contribution from crystalline C_3S . This is achieved by refining
 241 the fractional amount of C_3S , over the region $40 \leq r \leq 60$ Å. The insert frame shows the level of
 242 agreement achieved by this refinement process (see Table 1 for the *R*-value agreement factor).
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Figure 3. X-ray PDF experimental data sets of hydrated C_3S -slag (black line), the summed PDF of crystalline C_3S and portlandite (thick grey line), and the resulting C-A-S-H gel PDF (thin grey line) when the crystalline components are subtracted from the hydrated C_3S -slag sample (by refining the fractional amounts of C_3S and CH over the region $40 \leq r \leq 60$ Å). The insert frame shows the level of agreement achieved by this refinement process (see Table 1 for the R -value agreement factor).

The phase fractions of C_3S and CH obtained using this method are given in Table 1. It is clearly visible that as the silica content in the hydrated C_3S -silica samples decreases, the percentage of CH increases. However, the percentage of unreacted C_3S remains relatively constant (at $\sim 0.33 \pm 0.08$). This residual C_3S content is most likely due to the ongoing hydration reaction of C_3S and

associated C-S-H formation [33], which has been shown to take ~ 20 months when synthesized from CaO and SiO₂ [34] (the hydrated C₃S-silica samples in this investigation were measured 3 months after synthesis). The precipitation of CH in hydrated C₃S (Ca/Si of 3.0) is well known to occur, as has been discussed extensively in the literature [35, 36].

Pair Distribution Functions of C-S-H Gels

The X-ray PDF's for the C-S-H gels for varying Ca/Si ratios are shown in Figure 4a (the initial Ca/Si ratios are given). The presence of features at large r values ($r > 10$ Å) indicates that all C-S-H gels studied in this investigation are nanocrystalline, as opposed to amorphous, and possess the same atom-atom correlations as the synthetic C-S-H gel investigated by Skinner et al, which had a Ca/Si ratio of 1.0 (up to 40 Å, comparison not shown here) [4]. In the total scattering community, a nanocrystalline phase implies that the atomic structure can be roughly described using the bulk crystalline structure (i.e., periodic unit cell) truncated in r -space by the use of a nanosized shape function. More sophisticated techniques now employ the use of finite models that take into account surface relaxation effects and surface chemistry. On the other hand, an amorphous material cannot be described using the bulk crystal phase combined with a shape function (unless the shape function truncates the data below 10 Å, which is infeasible for a nanosized object). Furthermore, it is important to note that since the deuterated C-S-H gels derived here possess the same atomic bonding as the hydrated C-S-H gel synthesized by Skinner et al. [4], it is apparent that the use of deuterium in place of hydrogen has not significantly affected the local structural bonding in the gels studied in this investigation, as seen using PDF analysis. Nevertheless, in general it is well known that the formation of cement-based materials is impacted by the use of D₂O in place of H₂O, particularly the rate of hydration, and therefore,

these potential differences (kinetics and structure) should be taken into account when investigating deuterated samples.

The peaks located at r values below 1.4 Å in Figure 4a are artificial and are due to imperfect corrections and termination errors [16]. It may be possible that some amorphous fumed silica remains unreacted in the pastes, and therefore will be present in the C-S-H gels in Figure 4a. However, the PDF of amorphous silica does not contain atom-atom correlations above ~ 6 Å [12], and will not impact the nanocrystalline ordering of the C-S-H gels (i.e., over the range $6 \leq r \leq 40$ Å). The C-S-H gel derived from hydrated C_3S (without additional silica, Ca/Si of 3.0) does contain additional peaks in the nanocrystalline range (below 40 Å) compared to the other C-S-H gels, which are non-structural in nature as most notable via the sinusoidal ripples between 24 and 40 Å. Given that this sample had the highest percentage of crystalline phases that were removed from the collected experimental PDF data, the remaining information contains a higher level of noise/statistical error. The local atomic correlations for the C-S-H gels are shown in Figure 4b, except for Ca/Si of 3.0 due to the statistical noise present in the data. It is clear that the medium range ordering of these gels are very similar, irrespective of the Ca/Si ratio ($5 \leq r \leq 8$ Å), and the main differences in local atomic bonding (below 4 Å) are attributed to varying Ca/Si ratios, visible in the Si-O, Ca-O, O-O, Si-Si, Si-Ca, and Ca-Ca correlations. The X-ray PDF data is dominated by scattering from the heavier elements present in the material, which are Ca and Si for C-S-H gels (Figure 4b). Therefore, X-ray PDF analysis is well-suited for investigating the local atomic ordering present in the calcium (alumino)silicate framework structure. On the other hand, neutron PDF analysis is dominated by scattering from H/D and O, and will therefore be

301 most sensitive to (i) water in the sample, and (ii) the O-containing correlations attributed to the
302 calcium (alumino)silicate framework structure.

303

304

(a)

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(b)

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Figure 4. X-ray PDFs of C-S-H gels after removing contributions from crystalline C_3S and CH. The initial Ca/Si ratios are given, prior to removal of crystalline phases. Table 1 provides the updated Ca/Si ratios of the gels. PDFs are displayed over the region (a) $0 \leq r \leq 40 \text{ \AA}$, and (b) $1.2 \leq r \leq 8 \text{ \AA}$.

C-(N)-A-S-H Gels in Blended C_3S -Slag Pastes

The same method for isolating the gel phase has been applied to data for the two blended C_3S -slag pastes. Figure 5a displays the C-A-S-H and C-(N)-A-S-H gels for blended C_3S -slag pastes together with the C-S-H gel with a Ca/Si ratio of 1.7. It is clear that the C-A-S-H and C-(N)-A-S-H gels are nanostructured, and possess atomic bonding arrangements similar to C-S-H gels. Note that for hydrated C_3S -slag, the gel does not contain any alkali (sodium), and therefore is denoted C-A-S-H as opposed to H-activated C_3S -slag, which forms C-(N)-A-S-H. In order to assess the applicability of the $11\text{\AA}$ aluminum-substituted tobermorite structure to C-A-S-H, the X-ray PDFs of C-S-H (Ca/Si of 1.7) and C-A-S-H are provided in Figure 5b. C-S-H with a Ca/Si ratio of 1.7 was chosen for comparison with C-A-S-H due to the similarities in local bonding environments (i.e., relative intensities of the Ca-O and Si-O atom-atom correlations, as seen in Figure 5b). Skinner et al. [4] assessed the nanostructural ordering of a synthetic C-S-H gel (Ca/Si of 1.0), reporting that the atomic bonding of the synthetic C-S-H gel was similar to the crystal structure of $11\text{\AA}$ tobermorite; specifically the crystal structures provided by Hamid [37] and Merlino et al. [38]. The C_3S -derived C-S-H gels with Ca/Si ratios of 0.83 through 1.7 have been compared to the published data of Skinner et al. [4], revealing that all of these C-S-H gels possess the same medium and long-range ordering to their synthetic C-S-H gel over the entire PDF data set ($1 \leq r \leq 40 \text{ \AA}$, nearest-neighbor peak intensities differ according to variations in the Ca/Si ratios).

Therefore, these C-S-H gels can be described using the 11 Å tobermorite model [4]. It is apparent in Figure 5b that the local atomic bonding of C-S-H and C-A-S-H are very similar, especially in the range $1.2 \leq r \leq 5$ Å. Hence, describing the C-A-S-H gel present in C₃S-slag blended pastes as nanocrystalline Al-substituted 11Å tobermorite appears to be appropriate. Furthermore, by comparing the long-range ordering of the gels ($10 \leq r \leq 40$ Å, in Figure 5b) it is clear that C-A-S-H possesses a similar level of nanostructuring to that of the C-S-H gels. Nevertheless, there are subtle differences in the PDFs of C-S-H and C-A-S-H, especially at intermediate ordering for r values above 5 Å, which may be due to the substitution of Al in the C-S-H gel, or could be signaling that there are multiple phases present in the gels. The possibility of unreacted slag in the blended C₃S-slag pastes was not accounted for, and therefore residual slag may be present in the X-ray PDFs. However, given that ground-granulated blast furnace slag is predominately a calcium aluminosilicate glass [39], and therefore mostly amorphous [40], it will not contribute significantly to the atomic ordering beyond ~15 Å. Another possibility is the coexistence of C-S-H and C-A-S-H gels in the blended C₃S-slag pastes, and nanocrystalline regions of hydrotalcite-like structures [41], although crystalline hydrotalcite was not detected in the total scattering data (Figure 1). In general, from these X-ray PDF results it can be stated that the local structure of the C-(N)-A-S-H gel phase(s) in blended C₃S-slag pastes are similar to C₃S-derived C-S-H, and are nanocrystalline in nature.

(a)

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(b)

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Figure 5. (a) X-ray PDFs of C-S-H, C-A-S-H and C-(N)-A-S-H gels derived from C_3S , after removing contributions from crystalline C_3S and CH. Table 1 provides approximate Ca/Si ratios of the gels after taking into account the relative amounts of C_3S and CH. (b) X-ray PDFs of C-S-H and C-A-S-H gels derived from C_3S , after removing contributions from crystalline C_3S and CH, shown over the region $1.2 \leq r \leq 8 \text{ \AA}$. The insert frame shows the amount of nanostructural ordering present in gels (up to $40 \text{ \AA}$).

C-(N)-A-S-H Gels in Alkali-Activated Pastes

The X-ray PDFs of alkali-activated slag and slag-metakaolin pastes (S-activated) are shown in Figure 6a, together with the C-A-S-H gel in blended hydrated C_3S -slag. S-activated slag was selected for comparison (instead of H-activated slag) since the H-activated sample contained a crystalline phase (as seen in Figure 1). Furthermore, the C-A-S-H gel in hydrated C_3S -slag was chosen for comparison with the alkali-activated gels since the Ca+Mg/Si+Al ratio of C-A-S-H in hydrated C_3S -slag is closer to that of S-activated slag than C-(N)-A-S-H in H-activated C_3S -slag (Table 1). Figure 6a shows that the nanostructure of C-(N)-A-S-H in S-activated slag is different than that of C-A-S-H in blended C_3S -slag, and is more amorphous than C_3S - and blended C_3S -slag-based gels. Figure 6b displays the local atomic ordering of C-A-S-H in hydrated C_3S -slag and C-(N)-A-S-H in S-activated slag. It is apparent that the local atomic structure of alkali-activated slag is similar to C-A-S-H in blended C_3S cements (at r values below $8 \text{ \AA}$), although the relative amounts of calcium and silicon are different, impacting the peak intensities of the nearest-neighbor correlations (Si/Al-O, Ca-O, O-O, Si-Si, Si-Ca and Ca-Ca being the dominant correlations in this region, see Figure 4b for peak assignments). When compared with the X-ray PDF of pure slag precursor powder (not shown here), the atom-atom correlations present in S-

activated slag in the region $6 \leq r \leq 15 \text{ \AA}$ are similar to those present in neat slag, indicating that a percentage of unreacted slag remains in the alkali-activated slag paste. However, without having an accurate structural representation of the C-(N)-A-S-H gel in the paste it is difficult to quantify to amount of slag remaining, since both phases are predominately amorphous. Nevertheless, it is clear that C-(N)-A-S-H gel in S-activated slag does not contain anywhere near the same extent of nanostructural ordering that is present in C-A-S-H gels derived from C_3S -slag blended pastes.

For alkali-activated slag-metakaolin pastes the extent of atomic ordering at the nanoscale is even less than the ordering found in alkali-activated slag. Figure 6a shows that for S-activated slag-metakaolin there is no structural ordering present beyond $\sim 8 \text{ \AA}$, and therefore this sample is predominantly amorphous. It is known that alkali-activated aluminosilicates (synthesized using metakaolin, fly ash or other aluminosilicate sources) consist of N-A-S-H gels, which are amorphous [9-11, 28, 42], and therefore the S-activated slag-metakaolin will consist of both C-(N)-A-S-H and N-A-S-H gels together with unreacted slag and metakaolin.

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Figure 6. (a) X-ray PDFs of (i) C-A-S-H gel derived from C_3S and slag, (ii) C-(N)-A-S-H gel (denoted S-activated slag) in alkali-activated slag, and (iii) N-A-S-H in alkali-activated slag-metakaolin. The C-A-S-H gel was obtained by removing contributions from crystalline C_3S and CH for the hydrated C_3S -slag blended paste. Table 1 provides approximate Ca/Si ratios of the gels after taking into account the relative amounts of C_3S and CH. (b) X-ray PDFs of (i) C-A-S-H gel derived from C_3S and slag, (ii) C-(N)-A-S-H gel (denoted S-activated slag) in alkali-activated slag, shown over the region $1.2 \leq r \leq 8 \text{ \AA}$. The insert frame shows the amount of nanostructural ordering present in gels (up to $40 \text{ \AA}$).

Nanostructural Ordering and Gel Stability: Implications for Alkali-Activated Cements

The general consensus regarding the C-(N)-A-S-H gel phase in alkali-activated slag is that it possesses similar atomic and nanostructural ordering to C-A-S-H gels found in C_3S blended cements. Puertas et al. constructed an atomic structural representation of C-(N)-A-S-H gel applicable to alkali-activated slag, which is visually depicted as (nano)crystalline in nature [8], with the C-(N)-A-S-H gel present in S-activated slag consisting of both $11 \text{ \AA}$ and $14 \text{ \AA}$ tobermorite structures. Lothenbach and Gruskovnjak used thermodynamic modeling and their Gibbs free energy minimization program (GEMS) to predict the concentration of dissolved species and amount of precipitated solid phases for various alkali-activated slag systems (H- and S-activated) [6]. The modeling is carried out using thermodynamic data originally compiled and verified for OPC-based systems. Hence, assumptions are made regarding the applicability of C-S-H gel formation to alkali-activated systems (i.e., C-(N)-A-S-H gels) to enable the modeling to proceed. However, given that the thermodynamics (including solubility) of amorphous phases are known to differ significantly from their (nano)crystalline counterparts [43-45], and our

results showing that the structure of C-(N)-A-S-H gel in alkali-activated slag is mostly amorphous (as opposed to nanocrystalline), it is clear all alkali-activated gel phases must be fully understood across length scales independent of the structure and behavior of C-S-H and C-A-S-H gels. To rely on the structural and thermodynamic behavior of C-S-H and C-A-S-H gels derived from conventional cement systems for interpretation of alkali-activated cements (assuming C-(N)-A-S-H is the same as C-A-S-H) may lead to significant misinterpretations and erroneous results. Only once the structure and thermodynamics of alkali-activated gels are treated independently will it be possible to accurately simulate the short- and long-term behavior of these systems under a variety of conditions, including phase dissolution/precipitation.

Apart from bringing into question the applicability of C_3S and blended C_3S -slag-based phases for alkali-activated slag cements, including C-S-H and C-A-S-H experimental and theoretical data, this investigation has shown that the gels in alkali-activated slag and alkali-activated slag-metakaolin pastes are predominantly amorphous. Alkali-activated slag cements are known to be susceptible to a number of detrimental degradation phenomena (as are certain OPC-based cements), including microcracking, shrinkage and creep [13-15]. Hence, given we have shown that gels in alkali-activated cements are mostly amorphous, it is highly likely that the stability of these amorphous gels may contribute in part to these degradation mechanisms. From a thermodynamics viewpoint, the gels are more stable when (nano)crystalline compared to amorphous, and therefore the alkali-activated gels are intrinsically less thermodynamically stable than C_3S -based gels. However, many amorphous phases exist in nature without crystallizing or undergoing amorphous-amorphous phase transitions, including silica glass and biogenic amorphous calcium carbonate. Given that we now know the nanostructure of C-(N)-A-S-H gel in

alkali-activated slag is intrinsically different to C-A-S-H in blended C_3S -slag (and C-S-H in hydrated C_3S) cements, we need to investigate whether this difference is responsible for certain degradation phenomena manifested at the higher length scales (microns to macroscale). Then it will be possible to investigate if we can tailor the structure of alkali-activated cements to be more nanocrystalline, such as by seed nucleation using nanoparticles [46], to obtain more thermodynamically stable C-(N)-A-S-H gels.

Conclusions

In summary, the atomic and nanostructure of alkali-activated cement gels have been investigated using X-ray pair distribution function analysis, revealing the intrinsic difference in nanoscale ordering between C-(N)-A-S-H gel in alkali-activated slag pastes, and C-S-H and C-A-S-H in C_3S -based pastes. C-S-H and C-A-S-H gels derived from C_3S pastes are nanocrystalline in nature, and contain coherent atom-atom correlations up to $\sim 40 \text{ \AA}$, which is the particle size of the gel grains. On the other hand, C-(N)-A-S-H gel in alkali-activated slag paste is predominately amorphous, and therefore only contains coherent atom-atom correlations up to $\sim 15 \text{ \AA}$, with the medium range correlations attributed to unreacted slag particles in the paste. Nevertheless, the local bonding environments of C-(N)-A-S-H, C-A-S-H and C-S-H are very similar up to $\sim 8 \text{ \AA}$. These results stress the need to further understand the atomic structure and bonding of alkali-activated gels, and to link gel stability to macroscopic degradation phenomena, which will help to convince industry that there are viable durable alternatives to OPC-based concrete that can assist greatly in promoting sustainable building practices around the globe.

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Figure1

Figure2

Figure3

Figure4a

Figure4b

Figure5a

Figure5b

Figure6a

Figure6b