Alteration in Molecular Structure of Alkali Activated Slag with Various Water To Binder Ratios Under Accelerated Carbonation

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Abstract

Carbonation of alkali activated materials is one of the main deteriorations affecting their durability. However, current understanding in structural alteration of these materials exposed to an environment inducing carbonation at nano/micro scale remains limited. This study examined the evolution of phase assemblages of alkali activated slag mortars subjected to accelerated carbonation (1% CO₂, 60% relative humidity, up to 28 day carbonation) using XRD, FTIR and ²⁹Si, ²⁷Al, ²³Na MAS NMR. Samples with three water to binder (w/b) ratios (0.35, 0.45, and 0.55) were investigated. The results show that the phase assemblages mainly consisted of C-A-S-H, disordered remnant aluminosilicate binder, and a minor hydrotalcite as a secondary product. Upon carbonation, calcium carbonate is mainly formed as the vaterite polymorph, while no sodium carbonate is found after carbonation as commonly reported. The sodium acts primarily as a charge balancing ion without producing sodium carbonate as a final carbonation product in 28-day carbonated materials. The C-A-S-H structure becomes more cross-linked due to the decalcification of this phase evidenced by the appearance of Q⁴ groups, which replace the Q¹ and Q² ones as observed in the ²⁹Si MAS NMR spectra, and the dominance of Al (IV) in ²⁷Al MAS NMR. Especially, unlike cementitious materials, the influence of w/b ratio on the crystalline phase formation and structure of C-A-S-H in the alkali activated mortars before and after carbonation is limited.

Introduction

Alkali activated materials (AAMs) produced from aluminosilicates and alkaline activators have attracted a lot of attention over the past decades thanks to their environmental and economic benefits compared to ordinary Portland cement (OPC) based materials^{1–3}. Amongst them, alkali activated slag (AAS) formed from granulated blast furnace slag (GBFS), one of the major aluminosilicate sources, and alkaline solutions has been studying intensively^{4–6}. AAMs have illustrated satisfactory performances in several applications⁷. The (long-term) durability of the materials is, however, still uncertain. There is need to further investigate the performance of AAMs under various environmental conditions in order to assess the durability of these materials and to make them more acceptable in various engineering applications⁸.

Carbonation is one of the crucial durability issues of reinforced cement and concrete as the process reduces the pH in the pore solution of materials, leading to the corrosion of reinforcing steel bars due to destroying its passivating layer^{9,10}. Alkali activated materials are also expected to be carbonated during their service life. However, the carbonation mechanism and its effects on the material alteration may be different from OPC systems due to the differences in chemistry and pore structure. Few studies on the carbonation of AAMs have been carried out in recent years to understand the carbonation process and its influence on the performance of the AMMs. For example, several studies^{6,11} showed that AAMs are more vulnerable to carbonation than OPC-based materials. Because of the absence of Ca(OH)₂ that buffers the solution to a high pH and then delays the decalcification of calcium silicate hydrate (C-S-H)¹² in OPC systems, decalcification of aluminosilicate phase C-(N)-A-S-H occurs faster. Bernal *et al.* demonstrated that carbonation of AAS occurred in two stages¹³: (i) carbonation of the pore solution resulting in a reduction of

pH and the Na-rich carbonates precipitation eventually; (ii) decalcification of C-(N)-A-S-H phase and secondary phases leading to the formation of CaCO_3 and probably carbonated hydrotalcite.

Despite a relatively high number of studies^{14–17} on carbonation of AAMs, a systematic approach is still missing to investigate different factors influencing the carbonation process such as precursor type^{18–20}, alkaline activator^{21,22}, CO_2 concentration²³, curing temperature¹⁷, and relative humidity. Amongst these, CO_2 concentration can be considered to play a key role in deciding the process and carbonation products²⁴. Bernal *et al.* reported that the carbonation rate in pore solution and aluminosilicate gel of GBFS/metakaolin based geopolymers at higher CO_2 concentration (3%) seemed significantly different compared to that at 1% CO_2 ¹⁸. They also highlighted that bicarbonate products were favored over carbonates at higher CO_2 concentration. This is in line with the study of Pouhet *et al.*¹⁹ that sodium carbonate was formed in pore solution of metakaolin-based geopolymer under natural carbonation, while sodium bicarbonate was observed at 50% CO_2 . Also, Shi *et al.* found the natural carbonation rate of AAS concrete was only approximately by 1 mm/year, while its carbonation depth under 7% CO_2 was from 13 to 25 mm just after 10 days⁷. Thus, accelerated carbonation at high CO_2 concentration (>1%) was considered to be not representative for the behavior of AAS under atmospheric CO_2 conditions in real service life, because of changes in the carbonate phase equilibrium in pore solution with an increase in CO_2 concentration¹⁹.

The phases and chemistry of gels produced in AASs are also controlled by the chemistry of raw materials^{25,26} and utilized activators^{5,27}, consequently, carbonation of AASs may depend on these factors. Regarding the chemistry of slag described in the quaternary oxide system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, the predominant components CaO and SiO_2 critically control the Ca/Si ratio of the C-A-S-H phase. Under carbonation exposure, this phase leaves a cross-linked and remnant silicate phase resulted from the decalcification of the C-A-S-H and carbonate precipitate²⁸. Ben Haha *et al.*²⁹ identified that an increase in Mg content from 7.7–13.2% leads to additional formation of double-layered hydroxides of hydrotalcite which adsorb CO_2 and thereby reduce the carbonation of C-A-S-H³⁰. An increase in Al_2O_3 content to around 16% combined with a low MgO content (<5%) leads to the formation of zeolites instead of hydrotalcite³¹. Besides slag precursor, the activator is also a crucial parameter on the carbonation process of AASs. An increase in Na_2O concentration of activators enriches Na^+ in C-A-S-H network and forms C-N-A-S-H, reducing the susceptibility to carbonation³².

The understanding of the influence of water to binder (w/b) ratio – a factor important for the carbonation of OPC³³ – on the performance of AAMs in general and AASs in particular under carbonation is still limited. The w/b ratio is expected to change the rate of the precursor dissolution and the geopolymerization of AAMs³⁴, which then defines the microstructure of polymerized products. Provis *et al.* pointed out that the water content changes the alkali activator concentration that influences the reaction rate and also the structure of reaction products³⁵. Mobili *et al.* reported that a lower w/b ratio produces AASs with lower total porosity and higher density³⁶. These authors also indicated a linear relation between

w/b ratio and AAS's density, demonstrating an increase of free water results in a more porous matrix. Consequently, AAMs formulated with different w/b ratios can develop different transport properties³⁷, which then affect the diffusion of CO₂ and thereby the carbonation process. Recently, Zhang *et al.* studied the effect of the w/b ratio on the carbonation of alkali activated slag/fly ash and found that a decrease in w/b ratio can reduce the formation rate of Ca-carbonates in alkali activated slag-rich blends, but the crystallinity of Ca-carbonates is higher³⁸. However, the effect of the w/b ratio on the alteration of the gel structure after carbonation is not discussed in details in their study.

This study addresses the gap in understanding of the alteration of the nano/micro structure of AASs under accelerated carbonation conditions (1% CO₂, 60% RH) and the influence of the w/b ratio on the phase evolution of uncarbonated and carbonated materials. Multiple mineralogical characterization techniques have been used including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and high resolution solid state ²⁹Si, ²⁷Al and ²³Na magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy to comprehensively assess the changes in phase assemblages and C-A-S-H structure of AASs. By combining strong experimental evidences and geochemical modelling, a new mechanism for the carbonation process was proposed to better understand the carbonation mechanism of AASs.

Materials And Methods

Materials and mixing procedure

The granulated blast furnace slag was supplied by Ecocem Benelux with chemical compositions as shown in Table 1. Solid NaOH pellets (99% purity, VWR Chemicals) were dissolved in deionized water to reach a solution of 5 mol/L, which was then mixed with a commercial sodium silicate solution from VWR Chemicals (consisting of 8.97% Na₂O, 26.78% SiO₂, 64.25% H₂O) to form the alkali activating solution. The activator dosage was followed the one reported in RILEM TC 247-DTA round robin test (i.e. 4 g NaOH/100 g GBFS and 2.69 g Na₂O.2SiO₂/100 g GBFS)³⁹. The activator was kept in a fume hood for about 24 hours to cool down to room temperature before used. Tap water was added to the activating solution to reach the target w/b ratios of 0.35, 0.45 and 0.55. River sand was used as a fine aggregate with a maximum particle size of 2 mm and a density of 2.67 g/cm³. The volume fraction (relative to total volume of the mortar) of the river sand was fixed at 0.2 (relevant for waste encapsulation context). The mix designs are given in Table 2.

The activating solution and additional water were mixed for 1 minute in a mixing bowl, and then GBFS was added and mixed for 2 minutes by a rotary mixer at a low speed. Afterwards, sand was poured into the mixture and continued the mixing for 2 minutes. The mixer was stopped to scrape the mortar off the wall of the bowl, and was finally mixed at high speed for another 2 minutes. The mortar was then cast in the 40x40x160 mm moulds and kept at room temperature under sealed condition for 24 hours. Finally, samples were demoulded and placed in a curing cabinet at 20 °C and relative humidity higher than 95% RH for 27 days.

Table 1
Chemical compositions of GBFS (wt.%)

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	L.O.I
GBFS	32.4	11.1	0.60	43.40	7.77	0.53	0.27	1.01	2.41	2.08

Table 2
Mix design for AAS mortars

Mortars	w/b	SiO ₂ /Al ₂ O ₃	SiO ₂ /Na ₂ O	H ₂ O/Na ₂ O
AAS 035	0.35	5.23	8.79	32.02
AAS 045	0.45	5.23	8.79	41.17
AAS 055	0.55	5.23	8.79	50.32

Accelerated carbonation test

After 28 days of curing, the samples were conditioned in a 20°C climate chamber until the mass difference of two measurements within 24 hours was less than 0.2% to reach a target RH of 60% (around 4 weeks). Afterwards, two samples of each w/b ratio (reference samples) were still kept at the same conditioning RH and temperature, while the other samples (carbonation samples) were placed in the carbonation chamber for accelerated carbonation tests. The carbonation conditions were set at temperature of 20 °C, RH of 60%, and CO₂ concentration of 1% following EN standard 13295⁴⁰. Carbonated zone was determined by phenolphthalein indicator on samples subjected to accelerated carbonation after 7, 14, and 28 days. Sub-samples were then taken from the carbonated zone within 3 mm from the reactive surface for characterization. Also, sub-samples were taken from the reference samples at the same times.

X-ray diffraction (XRD)

After freeze drying, samples for quantitative XRD were crushed in a mortar, sieved to a size below 63 µm and mixed with 10% of the internal standard zincite (ZnO)⁴¹. The powders were then measured as quickly as possible (few hours) to prevent atmospheric carbonation. Measurements were performed with a Bruker D8 instrument equipped with a Cu Kα source, a beam knife, a Ni filter and automated divergence slits. Operational settings were set at 40 kV and 40 mA and measurements were done between 5 to 60°2θ at a step size of 0.02°2θ. Quantification was subsequently performed using Rietveld refinement with the Profex software⁴², which is a graphical user interface of the BGMN code.

Fourier-transform infrared spectroscopy (FTIR) measurements

The freeze-dried powder samples were homogenized with KBr in a 0.05 sample to KBr ratio, after which the mixtures were measured by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy on a Bruker Tensor II spectrometer. Measurements were carried out in the wavelength range of 4000-400 cm⁻¹ and a resolution of 4 cm⁻¹ at a total of 50 scans per measurement.

Solid-state ^{29}Si , ^{27}Al and ^{23}Na MAS NMR

High resolution solid-state ^{29}Si , ^{27}Al and ^{23}Na magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired at 25 °C on a Varian Inova 500 MHz wide moreNMR spectrometer ($B_0 = 11.7\text{ T}$) using a single pulse sequence. The resonance frequency of ^{29}Si , ^{27}Al and ^{23}Na were at 99.3 MHz, 130.23 MHz and 132.21 MHz, respectively. The ^{29}Si MAS NMR spectra were obtained using a Chemagnetics 7.5 mm double air bearing CPMAS probe and rotors spinning at 6 kHz with a 90° pulse width of $3.42\text{ }\mu\text{s}$, a recycle delay of 30 s and 1680 scans. High power ^1H decoupling was applied during the acquisition. The ^{27}Al and ^{23}Na MAS NMR spectra were measured using a Chemagnetics 2.5 mm double air bearing CPMAS probe and rotors spinning at 15 kHz with a pulse length of 2 - $2.2\text{ }\mu\text{s}$, a recycle delay of 0.5 s and 1024 up to 2048 scans. All the spectra were measured in ZrO_2 rotors to eliminate the influence from the any Si, Al background. The ^{29}Si MAS NMR spectra were referenced to an external standard sample of tetrakis(trimethylsilyl)silane (TKS). The peak position of ^{27}Al and ^{23}Na MAS NMR spectra were referenced to 1M $\text{Al}(\text{NO}_3)_3$ and 1M NaCl solution, respectively.

Deconvolution of ^{29}Si MAS NMR spectra was performed with the FitYK software⁴³ using Lorentzian functions for the crystalline peaks and Gaussian functions for the broaden peaks. The full width at half height of each peak was constrained within 10 ppm. The minimum number of fitting peaks was chosen to describe the spectra. The peak positions were referenced from literature^{28,44-46}.

Results And Discussion

X-ray diffraction

The XRD patterns (Figure 1) of the uncarbonated alkali-activated slag specimens are dominated by a mixture of amorphous phases with a broad peak at $29.16^\circ 2\theta$, which can be related to a combination of unreacted slag particles and newly formed C-A-S-H phase⁴⁷. The main crystalline phase is quartz, which is associated with the aggregate, as well as smaller amounts of K-feldspar. An AFm-phase with a peak at $11.53^\circ 2\theta$, best modeled by hydrotalcite, is also present in small amounts (1%). Note that with the presence of aggregate in the samples, more attention is needed to interpret the XRD data because aggregate particles are typically not homogeneously distributed in the sample at small scale (few grams for XRD measurement). To eliminate the effect of aggregate, we removed the amount of aggregate and then normalized the rest of phases to 100%. In such way, the phase amounts reported in Table 3 should be understood as the paste level (excluding aggregates). The proportion of amorphous phase at paste level, calculated by the internal standard method, is quite similar (97-98%) for all uncarbonated samples with various w/b ratios as shown in Table 3.

The carbonation of the alkali-activated slag specimens results in the formation of carbonate minerals and a reduction of the amorphous content (due to the reaction with CO_2). As is often the case for accelerated carbonation experiments^{6,24,48}, the metastable vaterite formed instead of its stable polymorph calcite. The

amount of vaterite formed depends on both the water to binder ratio of the mixture and the duration of carbonation as shown in Figure 2 and Table 3. A longer carbonation duration resulted also in a higher vaterite content as observed for AAS 045. The vaterite content after 14 days of carbonation is not much higher than after 7 days. However, this does not mean the carbonation degree of these two carbonation periods are similar because amorphous calcium carbonate is formed from 7 to 14 days of carbonation as proved later by FTIR results. In AAS 035, the carbonation is markedly slower: after 28 days of carbonation only small amounts of vaterite (1.2%) could be observed in the XRD patterns. Overall, the amount of vaterite formed after 28 days of carbonation is the highest in AAS 055 (13.4%), indicating that a higher w/b ratio induces a higher carbonation rate due to a faster diffusion of CO₂⁴⁹.

Table 3. Quantitative phase analysis for reference and carbonated AAS specimens at three w/b ratios

Phases	AAS 035		AAS 045				AAS 055	
	Ref	28D	Ref	7D	14D	28D	Ref	28D
Amorphous	98.8	97.6	97.5	92.9	92.4	85.2	97.6	82.9
Hydrotalcite	1.2	1.2	2.5	1.2	1.3	1.2	1.2	1.2
Microcline	0.0	0.0	0.0	0.0	0.0	2.5	1.2	2.4
Vaterite	0.0	1.2	0.0	6.0	6.3	11.1	0.0	13.4
Total	100	100	100	100	100	100	100	100

*Ref: uncarbonated samples

* 7D, 14D, 28D: 7-day, 14-day and 28-day carbonated samples, respectively

Fourier-transform infrared spectroscopy

In uncarbonated samples (Figure 3 (top)), a band at 1643 cm⁻¹ is detected, related to the bending vibration modes of H-OH bonds as chemically bound water in activated slag⁵⁰. The band ranging from 1500 to 1400 cm⁻¹ relates to the asymmetric stretching mode of C-O bonds of carbonate ions, which could be from the CaCO₃ in unreacted slag or the occurrence of natural carbonation during sample preparation as the powdered state is vulnerable to be carbonated. However, the latter may be ignored because samples were controlled to avoid exposing to atmospheric CO₂. The asymmetric stretching vibration of Si-O-T bonds (where T is Si or Al) in C-A-S-H is observed at 984 cm⁻¹. This band position is representative for the environment of SiO₄ (silicate sites) in the C-A-S-H gels³⁸. The increase in w/b ratio does not significantly influence the AAS structure as similar spectra exhibit for all samples with various w/b ratios. Only a slight difference can be observed in AAS 055, which shows a broader band at 1500-1400 cm⁻¹ and a slightly lower intensity of Si-O-T, probably suggesting a lower degree of geopolymerization in AAS 055.

After accelerated carbonation, in the region from 1500 to 1400 cm^{-1} , the right shoulder at approximately 1400 cm^{-1} diminishes, and the left shoulder gravitated toward 1500 cm^{-1} becomes larger. Comparing to the FTIR characteristic frequencies of Ca-carbonates from the report of Andersen⁵¹, a broader band is found in this region (1500 to 1400 cm^{-1}), which suggests the presence of amorphous CaCO_3 . Furthermore, higher wavenumbers in carbonated AAS samples indicate the appearance of vaterite or aragonite. The sharp peak at 875 cm^{-1} can be assigned to calcite or vaterite as the frequency ranges of both CaCO_3 polymorphs overlap with each other. Combining these signals, it is assumed that vaterite is the predominant Ca-carbonate product after 28-day carbonation, which is in line with XRD detection. Furthermore, signals of Na-carbonates are not identified in FTIR spectra, also in agreement with XRD results. In the range between 1200 and 900 cm^{-1} , a remarkable shift of the main Si-O-T vibration band from 954 to around 1027 cm^{-1} is observed, indicating a higher degree of geopolymerization of silicates after carbonation. Li *et al.*⁵² and Zhang *et al.*²¹ also reported the peaks at high wavenumbers similar to those detected in the carbonated samples of this study.

Amongst the three carbonated samples, a specific difference can be found at the main Si-O-T bands, which shift toward a higher wavenumber for samples with higher w/b ratios from around 954 cm^{-1} to 1027, 1035 and 1041 cm^{-1} corresponding to the w/b ratios of 0.35, 0.45, and 0.55, respectively. This suggests that carbonated samples with higher w/b ratio are more cross-linked, and probably polymerized further under carbonation. A higher decalcification of C-A-S-H gels is also expected in these cases. In addition, the degree of polymerization also depends on the carbonation duration, as shown in the Figure 3 (bottom) by the shifting in the spectra of carbonated AAS 045 after 7, 14, and 28 days of carbonation. The centered peaks of the main Si-O-T bands shift to higher wavenumbers with carbonation duration, which indicates an increase in crosslinks in the gels during carbonation. In consistence with XRD results, the intensity of vaterite peaks at 875 cm^{-1} also increases, especially in the first 14 days of carbonation, indicating that the carbonation rate is accelerated in this period.

In order to deeply examine the changes in carbonate products and chemical arrangement, several studies^{21,53} deconvoluted FTIR spectra focusing on the main band of 1300-800 cm^{-1} . They suggested that the appearance of Q^1 , Q^2 , Q^3 , and Q^4 sites corresponds to the signals at 865, 976-1000, 1088, and 1136 cm^{-1} , respectively. In this study, it is assumed that AAS samples contain mostly Q^1 and Q^2 , while Q^3 and Q^4 are preferred in carbonated AAS samples. However, the complex environment around Si centers in AAS structures considerably affects the signals of Si-O vibrations. In that sense, sophisticated NMR technique is more insightful for a better quantification of the C-A-S-H structure compared to the use of FTIR method alone.

Solid-state MAS NMR results

²⁷Al MAS NMR

Figure 4 shows the ^{27}Al MAS NMR spectra of AAS samples before and after carbonation. The spectrum of the raw slag shows a broad resonance ranging from 10 to 80 ppm, demonstrating the high disorder of the slag precursor as also indicated by the typical amorphous hump in the XRD pattern (Figure 1). The centered resonance at around 67 ppm is assigned to the tetrahedral Al environments, which indicates that Al exists in the raw material mainly under four-fold coordination, Al (IV). Upon alkaline activation, the reaction products are recognized by two predominant regions centered at ≈ 73 ppm, ≈ 10 ppm, and a very minor contribution around 37 ppm, which correspond to the tetrahedral aluminum Al (IV), octahedral aluminum Al (VI), and pentahedral aluminum Al (V) environments, respectively⁴⁴. Comparing to the spectrum of anhydrous slag, a higher intensity and narrower shape of the Al (IV) resonance is found, suggesting that Al (IV) becomes incorporated in C-A-S-H phase under bridging tetrahedral Al^{45,54}. This Al (IV) region shows two resonances: one at 73 ppm and one at around 68 ppm appearing as a shoulder, which are supposed to be $\text{Q}^2(1\text{Al})$ and $\text{Q}^3(1\text{Al})$ sites^{28,45}, respectively. These sites are charge-balanced with H^+ , Na^+ and with more positive charges such as Ca^{2+} ions. The octahedral Al location with a peak centered at 10 ppm and a small shoulder at 4 ppm is assigned to the layered double hydroxide phases⁵⁴ (LDHs) with mainly hydrotalcite (Mg-Al), which agrees with the detected signal of hydrotalcite in the XRD results. Especially, these peaks are present in both uncarbonated and carbonated samples, meaning that hydrotalcite is not fully carbonated^{45,55}, which is confirmed more conclusively in the ^{29}Si MAS NMR. In addition, the signal of Al (V), shown by a minor intense peak around 37 ppm is observed, which represents the remnant unreacted slag in the materials⁵⁵.

Upon 28-day exposure to CO_2 , the specimens witness a shifting of Al (IV) region from around 73 ppm to 58 ppm, which suggests a higher silicate content than oxyhydroxyl surrounding Al center, leading to a lower electron density and thereby a lower aluminum chemical shift of this region⁴⁵. Combining with the symmetry of this peak after carbonation, it is indicated that the more cross-linked in the C-A-S-H phases is, the more homogeneous the Al sites in this structure are. A significant reduction of Al (VI) is also observed, while the resonance of Al (V) has mostly disappeared. That means the unreacted slag is transformed into aluminosilicate phases, leading to the dominance of only Al (IV) in C-AAS samples compared to both Al (IV) in C-A-S-H and Al (VI) in alumina-rich phase of AAS ones. This is also consistent with the ^{29}Si MAS NMR results (discussed later) that clearly show a decrease in content of unreacted slag after carbonation. Besides, a very small shoulder at 14 ppm is also detected on C-AAS 035 and C-AAS 045. This peak is supposed to be Ca-Al phase belonging to LDHs types such as stratlingite³⁰. The appearance of these phases may attribute to the reduction in the intensity of hydrotalcite at 10 ppm. However, AFm layers or even hydrotalcite types of LDHs are partially ordered forms in the C-A-S-H interlayers²⁸, which make it difficult to be detected and distinguished clearly by XRD.

The water to binder ratio does not remarkably influence the C-A-S-H structure of reference and carbonated AAS as similar characteristics amongst the samples are observed. However, if a relative comparison between the intensity of Al (IV) and Al (VI) is carried out, Al (VI) seems to be more pronounced with an increase of w/b ratio of uncarbonated AAS, while this is not observed in carbonated AAS. This suggests that the lower w/b ratio can allow the formation of more C-A-S-H phase. However, ^{27}Al MAS NMR should be

considered as a qualitative assessment rather than quantitative evaluation⁵⁶, and a quantitative deconvolution of ²⁹Si MAS NMR will quantify the effects (see further).

²³Na MAS NMR

The ²³Na MAS NMR spectra of uncarbonated and carbonated AAS samples are shown in Figure 5 by a single broad resonance. The resonance centered at -3.9 ppm indicates Na in a coordination 6-7, which is associated with Na⁺ in a charge-balancing role in the network of the C-(N)-A-S-H⁵⁷. Upon 28 days of carbonation, this resonance shifts toward a lower chemical shift at about -6.5 ppm, showing an increase in the Na coordination number⁵⁸. This is in line with the results of ²⁷Al MAS NMR and ²⁹Si MAS NMR, which show that AAS is more cross-linked after carbonation. The trend of shifting in ²³Na resonance is similar to that of Al (IV) in ²⁷Al NMR spectra, which again suggests that the primary role of Na⁺ is to reduce the negative charge of Al in the Si-O-Al chain⁵⁹. This is also consistent with XRD results, which show no Na-carbonate precipitation after carbonation. In addition, the similarity amongst the spectrum of samples with various w/b ratios before and after carbonation again illustrates that the role of w/b ratio is less important to the C-A-S-H structure. The only different characteristic that can be observed is that the shoulder around 5 ppm along with the main peak of low w/b ratio sample (AAS 035) appeared with a less coordinated Na (smaller or equal to 5) beside a higher coordinated Na as the main Na state⁵⁸. This indicates a variation of solvated Na⁺ in the hydration state in pore water of the specimens⁴⁴. Therefore, the broader peak toward a higher chemical shift is evident to the low H₃O⁺ in pore solution of AAS 035.

²⁹Si MAS NMR

Figure 6 shows the ²⁹Si MAS NMR spectra of uncarbonated and 28-day carbonated AAS with different w/b ratios. In general, the C-A-S-H structures are not much different either for uncarbonated or carbonated AAS specimens with different w/b ratios, whereas there is a significant evolution of their structure (with the same w/b ratio) due to carbonation. The phases become toward more cross-linked witnessed by a shifting from Q¹ and Q² sites to Q⁴ species. Especially, the resonance of GBFS is observed in all samples when comparing with the spectrum of slag precursor, suggesting the existence of remnant slag in both uncarbonated and carbonated AASs.

To better understand the structure of samples via their ²⁹Si MAS NMR spectra, each spectrum is deconvoluted, allowing a detailed comparison between component peaks, simulated spectrum and the experimental data as shown in Figure 7. The broad region from approximately -60 to -95 ppm with a maximum at around -75 ppm corresponds to the unreacted slag. In uncarbonated mortars, the peak residing at -74.7 ppm assigns to Q⁰ species which encompass Si in isolated silica tetrahedral in the products⁴⁵. The peaks located around -78 ppm is marked as Q¹, which represents to the chemical environment of Si at the end of a chain of silicate tetrahedral of C-(A)-S-H⁶⁰. Herein, Q¹ sites are represented by two peaks as Q^{1a} and Q^{1b} at -76.8 and -78.5 ppm, respectively, indicating the bonding effect

of Q^1 units with Ca^{2+} , Na^+ or H^+ in the environment. This changes the chemical shift of Q^1 sites²⁸. Three types of Q^2 groups are detected in these alkali activated products including $Q^2(1Al)$ sites assigned at around -81 ppm, Q^{2b} and Q^{2p} sites at approximately -84 ppm and -85 ppm, respectively. These Q^2 groups are indicated to the middle chain silicates of C-(A)-S-H phases^{45,54}. Interestingly, the signals representative to the high cross-linked sites in gels as Q^3 are not well observed although a very small peak of $Q^3(1Al)$ at around -88 ppm is still detected. This is not in line with previous studies^{28,45,54}. One explanation may be the lower activator modulus (M_s) used in this current study ($M_s = 0.45$) as Gao *et al.*⁴⁵ reported that an increase of M_s to 1.7 or higher can accelerate the alkali activation resulting in a higher number of Q^3 groups. Comparing amongst the three AAS with different w/b ratios, it is found that the difference only comes from the quantity of silicate groups in C-(A)-S-H, implying that the w/b ratio does not define the types of Si groups formed in these phases.

After 28 days of accelerated carbonation, remarkable changes in the structure are noticed as shown in Figure 7. After carbonation, the chain structure of C-(A)-S-H containing predominantly Q^1 and Q^2 silicate species shifts into a more cross-linked gel, evidenced by the presence of four-connected silicate units (Q^4) in the deconvoluted spectra of carbonated AAS samples. Similar to AAS mortars, a difference in the spectra of three carbonated AAS corresponding to the three w/b ratios is not clearly observed, implying a less important role of w/b ratio in the formation of C-(A)-S-H structure. In all carbonated mortars, the peaks at approximately -86, -94, -102 ppm are identifiable, assigning for the presence of $Q^4(4Al)$, $Q^4(3Al)$ and $Q^4(2Al)$ units in the gels⁶¹, respectively. This observation is consistent with the lower ppm range and high intensity of Al (IV) sites as indicated by ^{27}Al MAS NMR, showing the formation of Al-rich gel.

The relative intensities of Q^n species (%) from deconvolution results are reported in *Table 4*. Interestingly, the unreacted GBFS in carbonated AAS is significantly reduced compared to the reference AAS, from around 55% to 36% in general, meaning that more than one third of unreacted GBFS has been transformed in C-A-S-H phase and/or carbonated products during carbonation. In particular, the Q^1 and Q^2 units in reference AASs are unidentified in carbonated ones and replaced by plenty of Q^4 groups in which $Q^4(3Al)$ is dominant (over 40%), indicating the presence of an extremely high cross-linked carbonated aluminosilicate C-A-S-H. This alteration is supposed to be the result of the decalcification of C-A-S-H phase²⁸. Especially, the absence of Q^1 and Q^2 groups as representative for reacted products of AAS suggests that both existing and new formed C-A-S-H phases in the materials are fully carbonated during 28 days of carbonation. Regarding to the influence of w/b ratios, there is only a slight difference in the relative intensity amongst Al-substituted silicate sites in AAS, and this is also similar in carbonated AAS. The largest difference is observed in samples with the w/b ratio of 0.35, evidenced by a higher percentage of unreacted slag after carbonation. This could be explained by a denser matrix formed before carbonation, which can diminish the diffusion of CO_2 into the matrix for carbonation.

Table 4. Deconvolution of ^{29}Si MAS NMR results of uncarbonated and carbonated alkali activated slags

Samples	Site type										
	Unreacted GBFS (%)	Reaction products (%)									
		Q ⁰	Q ^{1a}	Q ^{1b}	Q ²	Q ^{2b}	Q ^{2p}	Q ³	Q ⁴	Q ⁴	Q ⁴
					(1Al)			(1Al)	(4Al)	(3Al)	(2Al)
	-75	-75	-77	-78	-81	-84	-85	-88	-86	-94	-102
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
AAS 035	54	6	3	10	18	5	2	2	-	-	-
AAS 045	56	5	3	9	16	5	4	2	-	-	-
AAS 055	55	6	4	10	13	6	5	1	-	-	-
C-AAS 035	39	-	-	-	-	-	-	-	9	41	12
C-AAS 045	36	-	-	-	-	-	-	-	7	44	13
C-AAS 055	36	-	-	-	-	-	-	-	7	44	13

Mechanism of carbonation and its influence on AAS gel structure

The changes in gel structure of AAMs with various w/b ratios exposed to accelerated carbonation (1% CO₂, 60% RH) have been thoroughly examined in this study, and it is revealed that calcium carbonate is the dominant crystalline carbonation product, in which vaterite is the main polymorph as observed by XRD. Most of the previous studies^{16,28,52,62,63} reported the formation of stable calcite as the major stable polymorph. However, those samples were carbonated under different conditions such as high relative humidity (more than 80%), with either too low CO₂ concentration of 0.04% (natural carbonation) or high CO₂ concentration (5%) but longtime exposure up to 3 years. In addition, early age curing was chosen (3 or 14 days) and especially some studies were performed on AAM powder. Those testing conditions could result in the transformation of CaCO₃ polymorphs from the metastable to stable state. In this study, carbonation is performed under intermediate conditions of 1% CO₂ and 60% RH on well-cured AAS specimens for a shorter period of 28 days, which could be the reason for the main appearance of vaterite as crystalline carbonate. Also, no sodium crystalline phases is detected. This is also in line with reported data²⁸ as the formation of sodium carbonate is only expected under some specific carbonation conditions. Typically, the Na-rich carbonation product nahcolite can only be observed under a high CO₂ concentration

of 5% or higher²⁸, which is much higher than the one applied in this study. The evidence of crystalline carbonation products is also indicated by FTIR spectra under characterized wavenumber signals of CO_3^{2-} , and particularly from ^{23}Na MAS NMR, which provides a strong proof of the non-presence of Na-carbonate precipitates because Na is only in charge-balancing role for C-(N)-A-S-H phase. Additionally, hydrotalcite is detected as a secondary product of AAS, which still remains after carbonation, proven by XRD and ^{27}Al MAS NMR results.

Carbonation also strongly influences the amorphous aluminosilicate structure of AAS. Results of XRD quantification show the decrease of amorphous content during carbonation, resulting from the decalcification of C-(N)-A-S-H to form calcium carbonate precipitates. In particular, the decalcification allows the aluminosilicate gel to become significantly cross-linked. This is evidenced by FTIR and ^{27}Al MAS NMR results. Furthermore, the ^{29}Si MAS NMR spectra with deconvolutions also show mainly Al-substituted Q^4 species in aluminosilicate gel instead of Q^1 and Q^2 in uncarbonated gels, which are consistent with data from previous studies^{20,46}. However, it is worth noting that the content of unreacted slag in AAS specimens (around 55%) is significantly higher than reported data in literature^{64,65} with approximately 30%. The high amount of unreacted slag can be activated and then carbonated during the carbonation process. As a result, a lower unreacted slag content is observed in carbonated specimens compared to uncarbonated samples.

This study also clarifies the influence of w/b ratio on the evolution of phases and the amorphous gel nanostructure in particular. Overall, the w/b ratio does not influence the type of crystalline reaction products but slightly defines the structure of C-A-S-H, which becomes highly structurally ordered and better resistant to carbonation at a low w/b ratio (e.g. 0.35). Zhang *et al.*³⁸ and Ismail *et al.*⁶⁶ also found a small effect of the w/b ratio on the gel nanostructure of alkali activated materials based on blends of slag and fly ash with the w/b ratio in the range of 0.3-0.6. By using a combination of FTIR, ^{23}Na , ^{27}Al , ^{29}Si MAS NMR, and especially deconvolution of ^{29}Si MAS NMR to assess the gel structures of AASs, this study was able to provide a comprehensive picture on the effect of w/b ratio on the gel structure of AAS, which is typically characterized only by FTIR technique as normally seen in literature³⁸.

Based on the experimental evidences obtained from multiple characterization techniques, it allows us to propose a comprehensive mechanism for a diffusion-driven carbonation process of AAS as follows:

- Diffusion and dissolution of CO_2 gas in pore solution of AAS: This step liberates bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. However, the former is unstable under the high alkalinity ($\text{pH} > 12.5$) in the AAS solution and transforms/converts into carbonate ions (CO_3^{2-}).

- Formation of Na-carbonate products: HCO_3^- and CO_3^{2-} can react with the abundant Na^+ in pore solution to form sodium carbonates including Na_2CO_3 (natron) and $NaHCO_3$ (nahcolite) precipitates as intermediate products.

In order to verify whether natron and nahcolite are stable under our experimental conditions, we have performed a geochemical modelling to examine the saturation indices of nahcolite, natron and calcite in a 3-component system (Ca, Na, C) in 1 liter of water (20°C). The amounts of Ca and Na are expressed as totals in the system, and C as the partial pressure of CO_2 gas. Calculations are done with PHREEQC⁶⁷ with the CEMDATA18.1 database⁶⁸ and additional constants for nahcolite and natron obtained from BRGM Thermodem database⁶⁹. As shown in Figure 8 (top), at 1% CO_2 , natron tends to be dissolved (negative saturation index) even at a very high Na concentration of 7 mol/l in pore solution. Nahcolite is only stable if the Na concentration is higher than 3 mol/l, which is much larger than the typical Na concentration in pore solution of hardened AAS (1-2 mol/l)^{70,71}. The initial Na concentrations calculated from the mix compositions are 3.5, 2.7, and 2.2 mol/l for AAS with w/b ratios of 0.35, 0.45, and 0.55, respectively. The Na concentration is significantly decreased during polymerization (due to the precipitation of Na containing phases)⁷⁰ to reach the average Na concentration of 1-2 mol/l.

Formation of Ca-carbonate products: The dissolution of natron and nahcolite in the presence of Ca^{2+} (from decalcification of C-A-S-H) could induce further carbonation reactions to form a stable precipitate $CaCO_3$ as illustrated in Eqs. (7) and (8). As shown in Figure 8 (top), calcite is oversaturated under our testing conditions. Even with very low Ca concentration of 10^{-5} mol/l (much lower than the average one of $5 \cdot 10^{-4}$ mol/l⁷¹), calcite is still stable regardless of Na concentration (Figure 8 (bottom)). The reactions (7) and (8) also increase the alkalinity in the pore solution with the formation of NaOH. With the high alkalinity and an abundance of unreacted slag in the matrix, the geopolymerization can continue to

form additional C-A-S-H phase, which may be then carbonated. In this study, because of the high amount of unreacted slag in AAS, new products (C-A-S-H) could be formed continuously during carbonation, of which the dissolution provides Ca^{2+} in solution to react with carbonate ions and form calcite, while Na-carbonate products are absent as follows.

Conclusions

The alteration of mineralogy and C-A-S-H structure of alkali activated slag under accelerated carbonation with 1% CO_2 , 20°C and 60% RH were investigated in this work. The combination of multiple characterization techniques including XRD, FTIR and sophisticated solid state ^{29}Si , ^{27}Al , ^{23}Na MAS NMR allows accessing insights into the evolution of material structure at the nano scale. The results revealed that vaterite representative to calcium carbonate is the predominant carbonated crystalline phase of carbonated AAS, which results in a decrease in C-(A)-S-H content. No trace of sodium carbonate is found as commonly reported in literature. The FTIR and solid state MAS NMR in particular highlight an intensively cross-linked structure of the gel upon carbonation, in which Q^4 species is dominant in the carbonated aluminosilicate gels instead of Q^1 and Q^2 sites in uncarbonated specimens. Furthermore, similar characteristics amongst samples with various w/b ratios suggest a limited role of w/b ratio on the structure of AAS before and after carbonation. The w/b ratio only influences the formation of sub-components in the amorphous C-(A)-S-H phase without contributing to the formation of new crystalline and amorphous phases in both uncarbonated and carbonated AASs.

Based on experimental observation and geochemical modelling, for the first time, we propose a carbonation process of AAS including (i) diffusion and dissolution of CO_2 ; (ii) formation of immediate Na-carbonate products, which are not stable in Ca-rich solution due to C-A-S-H decalcification; and (iii) the formation of calcite as the stable CaCO_3 polymorph, which also increases the alkalinity in the pore solution induced further geopolymerization to form additional C-A-S-H to be carbonated later. This proposed process allows to better understand the carbonation mechanism of AAS and to explain well the absence of sodium carbonates and the reduction of unreacted slag under carbonation as experimentally observed.

Declarations

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Author information

Contributions

T.N.N, L.F, Q.T.P conceived and performed the experiments, analysed experimental data analysis and wrote the manuscript. Y.P, J.E, D.J, A.D provided work conception and critical manuscript revision. Z.Y, D.S were involved in NMR measurement and interpretation. All authors have discussed the results and commented on the manuscript.

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Additional information

Competing interests

The authors declare that they have no competing interests.

Data availability

The raw datasets generated during and/or analysed during the current study are available from the corresponding authors on request.

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Figures

Figure 1

XRD patterns of the reference specimens of each water to binder ratio: ZnO = zincite internal standard; Qz = quartz; HT = hydrotalcite.

Figure 2

XRD patterns of specimen AAS 045 in a reference state and after each stage of carbonation. ZnO = zincite internal standard; V = vaterite; Qz = quartz; HT = hydrotalcite.

Figure 3

FTIR spectra of uncarbonated (AAS), 28-day carbonated alkali activated slag (C-AAS) at different w/b ratios (top) and C-AAS with w/b ratio of 0.45 (C-AAS 045) at 7, 14 and 28 days of carbonation (bottom).

Figure 4

^{27}Al MAS NMR spectra of anhydrous slag (GBFS), uncarbonated alkali activated slags at 28 days of curing (AAS), and carbonated alkali activated slag after 28 days of carbonation with 1% CO_2 and 60% RH (C-AAS) at different water to binder ratios.

Figure 5

^{23}Na MAS NMR spectra of uncarbonated alkali activated slags at 28 days of curing (AAS), and carbonated alkali activated slag after 28 days of carbonation with 1% CO_2 and 60% RH (C-AAS) at different water to binder ratios.

Figure 6

^{29}Si MAS NMR spectra of anhydrous slag (BFS), uncarbonated alkali activated slags at 28 days of curing (AAS), and carbonated alkali activated slag after 28 days of carbonation with 1% CO_2 and 60% RH (C-AAS) at different water to binder ratios.

Figure 7

Deconvoluted ^{29}Si MAS NMR spectra of uncarbonated alkali activated slags at 28 days of curing (A column), and carbonated alkali activated slag after 28 days of carbonation with 1% CO_2 and 60% RH (B column) at different water to binder ratios.

Figure 8

Saturation indices of nahcolite (left), natron (middle) and calcite (right) in 1 liter of water (20°C) for 5 different amounts of Na in the system. Top figures show the saturation indices as a function of the partial pressure of CO₂ at a constant Ca amount of 5×10^{-4} mol – vertical dashed lines indicate the CO₂ concentration used in accelerated carbonation. Bottom figures show the saturation indices as a function of amount of Ca in the system at a constant partial pressure of CO₂ of 10^{-2} atm (i.e. 1% CO₂) – vertical dashed lines indicate the average Ca concentration in pore solution.