Dung, N.T., Hooper, T.J.N. and Unluer, C. (2021) Improving the carbonation resistance of Na₂CO₃-activated slag mixes via the use of reactive MgO and nucleation seeding. *Cement and Concrete Composites*, 115, 103832.

(doi: [10.1016/j.cemconcomp.2020.103832](https://doi.org/10.1016/j.cemconcomp.2020.103832))

This is the Author Accepted Manuscript.

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<https://eprints.gla.ac.uk/234075/>

Deposited on: 17 February 2021

Improving the carbonation resistance of Na₂CO₃-activated slag mixes via the use of reactive MgO and nucleation seeding

N.T. Dung^a, T.J.N. Hooper^b, C. Unluer^{c,*}

^a School of Civil and Environmental Engineering, Nanyang Technological University,
50 Nanyang Avenue, Singapore 639798, Singapore

^b Energy Research Institute, Nanyang Technological University, 50 Nanyang Drive, Singapore
637553, Singapore

^c School of Engineering, University of Glasgow, Glasgow G12 8LT, United Kingdom

* Corresponding author. E-mail address: Cise.Unluer@glasgow.ac.uk

Abstract

When exposed to carbonation, Na₂CO₃-activated slag (SCAS) concrete demonstrated 53% mass loss and 57% reduction in compressive strength due to the decalcification of C-(A)-S-H. Improvements in the carbonation resistance of SCAS mixes via the inclusion of hydromagnesite seeds (S) and reactive MgO (M) were reported in this study. The conversion of MgO into hydrated magnesium carbonates (HMCs) and the additional formation of hydrotalcite were observed in the presence of these additives. HMCs contributed to the binding network and limited the diffusion of CO₂ into the sample. The decalcification of C-(A)-S-H was retarded via the absorption of CO₂ in hydrotalcite, producing huntite. These changes in the reaction kinetics of samples involving M and S enabled the retention of hydration products and formation of additional carbonation products, leading to denser microstructures and ~40% increase in compressive strength after carbonation, which was ~10 times higher than the control sample (58 vs. 6 MPa).

Keywords: Slag; MgO; hydration; pH; hydration product; carbonation

1. Introduction

Portland cement (PC) production is associated with high energy use and CO₂ emissions of 1.48 Gt per year, accounting for 8% of total global CO₂ emissions [1]. Nonetheless, the demand for cement is rising in line with the increasing need for civil infrastructure to accommodate the growing world population. Therefore, the development of alternative binders is necessary to reduce the environmental impact. Alkali-activated slag (AAS) systems are considered as an alternative to PC as the use of slag, an industrial by-product, eliminates CO₂ emissions associated with the decomposition of limestone and presents a lower energy demand than PC production.

The activation of slag is initiated by the dissolution of the solid powder in the presence of an alkaline activator, followed by the formation of magnesium aluminum hydrotalcite (i.e. referred to as “hydrotalcite” throughout the manuscript) and the polycondensation of C-(A)-S-H with a low C/S ratio [2-6]. The alkaline activators commonly used in AAS mixes (e.g. alkaline hydroxides and silicates) [7-9] are associated with major environmental impacts [10, 11]. These materials are also known for their high costs, caustic alkalis, high shrinkage and fast setting [12-18]. On the other hand, medium alkaline activators such as sodium carbonate (Na₂CO₃, SC) can provide AAS mixes with lower environmental impacts, while presenting a more economical and less caustic solution with a lower shrinkage [19, 20]. However, despite its promising environmental and mechanical performance, the use of SC has not been widely implemented in AAS systems, partially due to the long setting time and low mechanical performance it results in [11, 21]. Accordingly, while the use of the alkaline hydroxides or silicates as activators results in pastes that set in 3 hours with a 7-day strength of over 40 MPa, SC-activated slag (SCAS) pastes were reported to set over 5 days and produce 7-day compressive strengths lower than 15 MPa [20, 22].

The initially low alkalinity of SC is responsible for the prolonged dissolution of aluminosilicate species, thereby delaying the formation of hydrotalcite, carbonates (i.e. gaylussite and calcium carbonate) and C-(A)-S-H within SCAS samples [21, 22]. To improve the dissolution of slag, a previous study [11] used calcined hydrotalcite to accelerate the absorption of CO₃²⁻ ions from the activator. This increased the pH of the activator within the sample and accelerated the reaction kinetics of the SCAS pastes, enabling setting within 24 hours. Along with increasing the alkalinity of the pore solution, hydrotalcite that formed via recrystallization also played the role of a nucleation site, thus enhancing the formation of hydrate phases. However, the fabrication of

calcined layered double hydroxides is time and energy consuming [23] and requires intensive thermal treatment for the decomposition of synthetic hydrotalcite (i.e. 500°C for 3 hours) [11, 24]. An alternative approach involved the use of slag with high MgO contents, which promoted reaction kinetics and led to faster setting times in SCAS pastes [11, 21].

In addition to the long setting times they suffer from, the durability of SCAS mixes is an important aspect that needs to be considered for these formulations to be used in large-scale applications. AAS systems are vulnerable to carbonation, during which the diffused CO₂ results in the reduction of the pH in the pore solution and decalcification of C-(A)-S-H. The reduction in the alkalinity of the pore solution can lead to the corrosion of steel reinforcement, while the decalcification of C-(A)-S-H can cause the decaying of the binding phase and loss of strength.

In line with these shortcomings, the work presented here aims to improve the hydration mechanism and carbonation resistance of SCAS systems. Accordingly, hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O), a hydrated magnesium carbonate (HMC), was utilized as nucleation seeds to facilitate the increased formation of reaction products such as gaylussite (Na₂Ca(CO₃)₂·5H₂O) and calcite (CaCO₃). Furthermore, reactive MgO was used to improve the formation of hydrotalcite-like phases (M(II)_{1-x}M(III)_x(OH)₂(Aⁿ⁻)_{x/n}·mH₂O, a structure composed of positively charged brucite-type metal-hydroxide layers intercalated with anions (Aⁿ⁻) and water molecules [25], where M(II) and M(III) are Mg²⁺ and Al³⁺ in alkali-activated slag system, and Aⁿ⁻ is CO₃²⁻ in Na₂CO₃ solution [26]). The accelerated formation of calcite, hydrotalcite and gaylussite could promote the consumption of CO₃²⁻ ions from the activator, thereby increasing the alkalinity of the sample and improving the reaction kinetics. These advancements could translate into an increase in the amount of hydration products and an associated densification of the microstructure, which could provide improved resistance against carbonation. Additionally, the formation of a hydrotalcite phase with layered double hydroxides could increase CO₂ absorption [27, 28] and enhance the resistance to carbonation in AAS systems [29, 30]. Furthermore, the reaction between hydrated reactive MgO and CO₂ can form HMC phases [31, 32], which can provide a binding network that fills the pore space and decreases the diffusivity of CO₂, thereby improving the carbonation resistance of SCAS mixes.

With the overall goal of improving the reaction kinetics and enhancing the carbonation resistance of SCAS systems, this paper presents a detailed study on the microstructural and mechanical changes in SCAS samples under carbonation. The influence of hydromagnesite seeds and reactive

MgO on the reaction mechanisms and performance of SCAS mixes was assessed at different periods via pH, setting time and compressive strength tests. X-ray diffraction (XRD), ^{29}Si and ^{27}Al solid-state nuclear magnetic resonance (NMR), thermogravimetry-differential thermogravimetry (TG-DTG), backscattered electron (BSE) and scanning electron microscopy (SEM) analyses were also employed to analyze the influence of hydromagnesite seeds and reactive MgO on the performance of SCAS concrete samples subjected to carbonation.

2. Materials and Methodology

2.1. Materials

Ground granulated blast furnace (GGBF) slag supplied by Engro Corporation (Singapore) was used as the main binder. Sodium carbonate (Na_2CO_3 , SC), supplied by VWR (Singapore), was used to prepare the activator. Hydromagnesite particles ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, S) with a specific surface area of $43.5 \text{ m}^2/\text{g}$, supplied by Fisher Scientific (UK), were used as nucleation seeds to stimulate the hydration process. Fig. 1 shows the particle size distribution of S. Reactive MgO (M) was obtained from Richard Baker Harrison (UK). The chemical composition and physical properties of slag and M are shown in Table 1.

The XRD patterns of the slag, S and M are presented in Fig. 1. The XRD pattern of slag indicated an amorphous phase at $\sim 25\text{--}35^\circ 2\theta$, along with gehlenite ($\text{Ca}_2\text{Al}(\text{AlSiO}_7)$, PDF # 01-073-6601) and sodium aluminum silicate ($\text{Na}_2\text{Al}_2\text{Si}_{7.2}\text{O}_{18.4}$, PDF # 00-056-0486). The main peaks of S (PDF # 00-025-0513) were observed at 15.1° and $30.7^\circ 2\theta$; and those of M (PDF # 00-043-1022) were observed at 32.6° , 42.8° and $62.3^\circ 2\theta$.

Coarse aggregates used in the prepared concrete mixes were gravel in saturated surface dry condition, with a particle size of 4.7–9.5 mm. Fine aggregates were omitted to avoid any contamination in the identification and quantification of reaction products.

2.2. Sample preparation

Table 2 presents the details of the mix proportions of concrete samples. Samples including 0.5% S and/or 3-10% M (i.e. of the total precursor content including slag, S and M) were prepared in addition to the control sample (CS). The ratio of water to binder (w/b) of all samples was kept at 0.55. The amount of Na_2CO_3 corresponded to 8% by mass of the total binder in all mixes. Prior to mixing, Na_2CO_3 was dissolved with water to serve as the activator, with a pH of 11.8.

For the preparation of concrete samples, S was first dispersed in the activator solution, prior to its addition to the precursor and aggregates mix. After mixing, the fresh concrete was cast into cubic molds (i.e. 50×50×50 mm) and consolidated prior to finishing the surface. After demolding, samples were hydrated under ambient conditions (~30°C and ~80% relative humidity (RH)). In addition to the concrete samples, corresponding pastes with a w/b of 0.55 were also prepared to investigate the influence of S and M on the reaction mechanism of SCAS via pH and setting time measurements.

2.3. CO₂ exposure

After 28 days of hydration, the concrete cubes were exposed to CO₂ for up to 91 days. This exposure took place in an incubator with a controlled environment, during which the temperature, RH and CO₂ concentration were kept constant at ~30°C, 80% and 10%, respectively.

2.4. Methodology

2.4.1. pH

The SCAS pastes were crushed, ground and dispersed in distilled water at a water to powder (i.e. paste sample) ratio of 5 for the measurement of the pH [33, 34]. After 10 min of mixing and vacuum filtration, the filtered solutions were used in the measurement of the pH by using a pH electrode with an automatic titrator. The reported results were the average of three measurements.

2.4.2. Setting time

The setting times of SCAS pastes under ambient conditions (i.e. temperature of $\sim 30^{\circ}\text{C}$ and RH of $\sim 80\%$) were measured by recording the penetration depth of the Vicat needle into each sample [35]. The reported results were the average of two measurements.

2.4.3. Compressive strength

The compressive strengths of SCAS concrete samples before and after carbonation were measured in triplicates at a loading rate of 55 kN/min.

2.4.4. Microstructural analyses

Segments with diameters of $\sim 0.5\text{-}2$ cm extracted from the surfaces of the concrete samples were stored in isopropanol for 3 days and dried in vacuum prior to phase quantification and microstructural analyses. Samples for XRD, NMR and TG-DTG were prepared by grinding dried segments to a particle size smaller than $75\text{ }\mu\text{m}$.

XRD was performed on a Philips PW 1800 spectrometer using $\text{Cu K}\alpha$ radiation (40 kV, 30 mA). The analysis was performed in a 2θ range of $5\text{-}60^{\circ}$ and at a step size of 0.04° 2θ . 5 wt.% fluorite (CaF_2) was included as an internal standard in the analyses samples.

Solid state NMR was performed on a 14.1 T Bruker Avance III HD spectrometer with a 4 mm MAS probe. The ^{27}Al MAS NMR utilized an RF frequency of $\nu_0 = 156.35$ MHz and a MAS frequency of 14 kHz. A one pulse sequence with a $1\text{ }\mu\text{s}$ selective $\pi/6$ pulse length and a 1 s relaxation delay was utilized. A shorter $\pi/6$ pulse length was required in order to satisfy the uniform excitation condition for quadrupolar nuclei, which enabled quantitative ^{27}Al NMR results [36, 37]. Powdered yttrium aluminum garnet ($\delta_{\text{iso}} = 0.7$ ppm w.r.t. $\text{Al}(\text{NO}_3)_3(\text{aq})$, $\delta_{\text{iso}} = 0$ ppm) was used as a secondary reference and to calibrate pulses. The ^{29}Si MAS NMR utilized an RF frequency of $\nu_0 = 119.23$ MHz and a MAS frequency of 12 kHz. A one pulse sequence with a $5.3\text{ }\mu\text{s}$ selective $\pi/2$ pulse length and a 30 s relaxation delay was utilized. Powdered kaolinite ($\delta_{\text{iso}} = -93$ ppm w.r.t. TMS, $\delta_{\text{iso}} = 0$ ppm) was used as a secondary reference and to calibrate pulses. Each of the ^{27}Al and ^{29}Si NMR spectra were completed using 4070 and 1800 scans, respectively. The data was processed using Topspin and DMFIT software packages [38]. Site occupancies were

determined from the NMR data via line-shape integration and spectral simulation for ^{27}Al and ^{29}Si , respectively.

TG-DTG was performed on a Perkin Elmer TGA 4000, operated at a heating rate of $10^\circ\text{C}/\text{min}$ between 30°C and 950°C under N_2 flow. For the quantification of hydrate and carbonate phases, DTG curves were deconvoluted into Gaussian components representing the decomposition of each phase by using the Origin software.

To prepare samples for BSE analysis, the samples, which were vacuum dried, were mounted in epoxy resin for 24 hours in vacuum and polished. The polished samples were cleaned before being exposed to compressed air jet to remove any dust from their surfaces prior to being coated with gold. BSE and SEM imaging was performed on a Zeiss Evo 50 instrument with an accelerating voltage of 15 kV and working distance of 5-10 mm to investigate the phases that formed within the prepared samples. In addition to BSE, SEM imaging was also performed to observe the morphology of the reaction products.

3. Results and Discussion

3.1. pH

Fig. 3 shows the pH values of the SCAS pastes, which were measured by using the filtered solutions obtained after mixing the powder samples with distilled water at a water to powder ratio of 5. While these pH values provided an estimation of the actual pH of the pore solution, the trend observed amongst these values could still indicate the effect of different additives on the pore solution. Accordingly, the pastes using S and/or M demonstrated higher pH values than CS. The inclusion of M could accelerate the absorption of CO_3^{2-} anions from SC, accompanied with the release of NaOH, which increased the initial pH of the pore solution within M3 and M10 samples, in comparison to CS (12.11-12.12 vs. 12.02). As hydration proceeded, the inclusion of S could stimulate the absorption of CO_3^{2-} and increase the pH value of sample S, when compared with sample CS at 2.5 hours (12.70 vs. 12.50). At the same time, the increase in the pH of samples containing M was more obvious when compared with CS (12.76 vs. 12.50). Similarly, the combination of both S and M in samples SM3 and SM10 led to pH values as high as 12.69 and 12.72 at 2.5 hours, respectively.

A reduction in the pH values was observed after 12 hours of hydration, which could be attributed to the consumption of NaOH in the dissolution reaction. The dissolution of slag, which released silicon and aluminum into the solution, also caused a reduction in the pH. The higher concentrations of silicon and aluminum facilitated the formation of C-(A)-S-H, which increased the alkali uptake and further reduced the pH [39, 40]. Nevertheless, the inclusion of S and/or M led to higher pH values than CS. These higher pH values were due to the accelerated consumption of CO_3^{2-} and the reduction in $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$, $\text{AlSiO}_3(\text{OH})_4^{3-}$ and $\text{Al}(\text{OH})_4^-$ anions as slag was replaced by S and/or M within these samples. The combined use of S and M enabled the reaction between CO_3^{2-} and dissolved Mg-phases, resulting in the formation of HMCs (e.g. nesquehonite, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), as can be seen in Fig. 4. The trends observed in the pH values were an indication of the role of S and M in enhancing the consumption of CO_3^{2-} ions from SC to release NaOH and thereby increase the pH values of SCAS pastes.

3.2. Setting time

Table 3 presents the setting times of the SCAS pastes. The low initial pH of CS resulted in a very long setting time (i.e. 94.3 h and 148.2 h for initial and final setting times, respectively). Alternatively, samples incorporating S and/or M, which were associated with higher pH values, demonstrated significantly shorter setting times. The sole use of S or M shortened the setting times of the prepared samples to 12.2-34.1 h (initial) and 19.2-49.7 h (final). Moreover, the combination of both S and M resulted in the shortest setting times in sample SM10 (i.e. initial setting time of 7.8 h and final setting time of 12.8 h).

3.3. Effect of carbonation on the reaction products

3.3.1. XRD analysis

The XRD patterns of SCAS samples after 28 days of ambient curing are presented in Fig. 5. The internal standard (i.e. fluorite (CaF_2)) had its main peak at $\sim 28.2^\circ 2\theta$. The broad hump at $\sim 25\text{-}35^\circ 2\theta$ was attributed to the unreacted amorphous phase in slag. Relative to the intensity of fluorite, the simultaneous decrease in the amorphous content and increase in the intensities of the peaks

referring to the hydrate phases within samples containing S and M was higher than those observed within CS. This notable change within these phases was an indication of the enhancement of hydration with the introduction of S and M into SCAS mixes, which was consistent with the trends observed in the pH and setting time results.

The XRD patterns indicated the formation of gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$; PDF # 01-072-8410) and calcite (CaCO_3 ; PDF # 01-071-3699) in all samples. In the dissolution of slag, the Ca-O bond could be broken under the polarization effect of OH^- at low alkalinities to form calcite and gaylussite before the formation of hydrotalcite and C-(A)-S-H as this bond is weaker than Al-O and Si-O bonds [41]. Gaylussite is a transient phase and can be dissolved as the concentration of CO_3^{2-} decreases to form more stable CaCO_3 polymorphs (e.g. calcite or aragonite) [11]. Therefore, under their high pH environments, samples including S and/or M demonstrated a faster consumption of CO_3^{2-} ions, leading to higher calcite and lower gaylussite contents than CS. A notable difference was observed in the formation of hydrotalcite ($\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$; PDF # 01-070-2151), where the amount of hydrotalcite was higher in samples incorporating S and/or M than CS. The higher hydrotalcite content of samples including 10% M was especially obvious. Similarly, the higher intensities of C-(A)-S-H ($\text{Ca}_{1.5}\text{SiO}_{3.5}\text{H}_2\text{O}$; PDF # 00-033-0306) and calcite peaks indicated their increased formation in samples containing S and/or M, as opposed to CS.

The XRD patterns obtained after 28 days of exposure to carbonation conditions are shown in Fig. 6. The decrease in the intensity of periclase (MgO , main peak at $42.9^\circ 2\theta$) within samples incorporating M indicated the consumption of Mg-phases in the carbonation reaction. Huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$; PDF # 01-014-0409), whose formation could be associated with the carbonation of hydrotalcite [42], was also identified in samples including M. This was accompanied with a reduction in the intensity of hydrotalcite after carbonation. The formation of huntite via the carbonation of hydrotalcite indicated the role of hydrotalcite in reacting with the dissolved CO_2 during exposure to carbonation conditions. This highlighted the importance of the presence of M in promoting the formation of phases that can react with CO_2 , thereby maintaining a high pH that can alleviate the decalcification of C-(A)-S-H. The increased formation of hydrotalcite led to a higher carbonation resistance in these mixes. Similarly, the increased formation of hydrotalcite in sample S could also explain its improved carbonation resistance when compared with CS. As observed earlier, the disappearance of gaylussite could be associated with its transformation into other stable carbonates. The decrease in the intensity of C-S-H, linked with its decalcification under carbonation, could explain the formation of aragonite (CaCO_3) and vaterite (CaCO_3). The

use of M resulted in higher Mg/Ca ratios in the bulk of the system, which could facilitate the formation of aragonite rather than calcite [43].

3.3.2. ^{27}Al and ^{29}Si NMR analysis

The ^{27}Al and ^{29}Si NMR spectra of the precursor anhydrous slag are presented in Fig. 7 (a) and (b), respectively. Differently coordinated Al sites appeared within distinct ^{27}Al chemical shift ranges (i.e. 80-50 ppm for Al(IV) and 15-0 ppm for Al(VI)) [44]. The ^{27}Al NMR spectra of the precursor material showed a broad amorphous Al(IV) resonance, representing the glass-like structure of slag [11].

In ^{29}Si NMR, different Si(IV) environments could be identified by their chemical shift, covering a range from -60 to -120 ppm. The different Si moieties in aluminosilicate networks were labelled $\text{Q}^n(m\text{Al})$, where n is the amount of oxygen atoms shared with adjacent Si/Al tetrahedral units and m is the number of Al units involved. Corroborating the results of previous studies [11, 45], the precursor material presented broad amorphous resonances at δ_{iso} of -75 ± 3 ppm, corresponding to the monomeric/dimeric Si(IV) units (Q^0/Q^1) in the glassy unhydrated slag [22]. The smaller resonance at δ_{iso} of 110 ± 5 ppm was due to the amorphous silica glass (Q^4 Si(IV) environments) present in the slag precursor [46].

The ^{27}Al NMR spectra of the SCAS samples after 28 days of ambient curing are presented in Fig. 8 (a), whereas the spectra of the same samples after a further 28 days of exposure to carbonation conditions are presented in Fig. 8 (b). The ^{27}Al NMR line-shape of the precursor (presented in black in Fig. 7 (a)) was shown with each spectrum of the SCAS samples to highlight the remnant reactant in the ^{27}Al spectrum, hence revealing the sites produced by hydration. Fig. 8 (a) revealed that the hydration products of SCAS contained both Al(VI) and Al(IV) species. The produced Al(IV) species related to the tetrahedral AlO_4 moieties in the C-(A)-S-H gel, whereas the Al(VI) resonances corresponded to Al in the produced hydrotalcite phase [11], which was also detected in the XRD analysis. Table 4 shows the relative intensity, and hence site occupancy, of AlO_6 and AlO_4 components, determined from the ^{27}Al NMR spectra. These results indicated that the use of S and/or M increased the relative site occupancy of AlO_6 species in comparison to CS (19.1-24.1% vs. 4.8%), which supported the increased hydrotalcite formation shown in the XRD patterns (Fig. 5). This improvement could be due to the additional nucleation sites provided by S, which

promoted the production of hydrotalcite and the hydration of M [11], resulting in more brucite in the metal oxide layer within the hydrotalcite structure [47, 48]. The combination of both S and M in sample SM10 provided the highest AlO_6 relative site occupancy (24.5%) and therefore the highest hydrotalcite content.

The results presented in Fig. 8 (b) and Table 4 demonstrated that the carbonation process reduced the site occupancy of the AlO_6 species in the SCAS samples. This correlated with the sorption of CO_2 in the hydrotalcite phase, leading to the expulsion of Al and the formation of huntite in the samples. The reduction in the Al(VI) site occupancy in carbonated samples (Table 4) was less severe in samples containing M, which could be associated with the reaction of CO_2 with MgO to form HMCs. The Al(IV) resonances were also altered by the carbonation process, as demonstrated by the loss of the sharper features present in the Al(IV) line-shapes of samples involving S and/or M after hydration (Fig. 8. (a)). The ^{27}Al NMR spectra of these carbonated samples (Fig. 8 (b)) presented amorphous Al(IV) line-shapes that shifted to lower frequencies, indicating that the structure of the C-(A)-S-H gel changed during the carbonation process.

The ^{29}Si NMR spectra of the SCAS samples after 28 days of ambient curing are presented in Fig. 9 (a), whereas the spectra of the same samples after a further 28 days of exposure to carbonation conditions are presented in Fig. 9 (b). The NMR spectra were fitted with up to 6 distinct Gaussian resonances, providing a good simulation of the experimental data (Fig. 9). All of the ^{29}Si NMR spectra in Fig. 9 presented familiar amorphous resonances at δ_{iso} of -76 ± 3 and -110 ± 5 ppm, which were associated with the unreacted remnant precursor material. As seen in Fig. 9, the relative intensity of the -76 ppm component reduced upon curing, demonstrating the reaction of the Q^0/Q^1 species in the slag precursor. Alternatively, the Q^4 environment (-110 ppm) was unchanged, suggesting that the amorphous silica present in slag did not dissolve to participate in the reaction. The combined relative intensities of these remnant precursor components were given in Table 5. It was presumed that the hydration of the precursor slag material was negligible under carbonation. In this respect, the concentration of Si in the remnant precursor material components should be unchanged during the carbonation process. Hence the relative intensity of these components was held constant in the simulation (i.e. within error) of the ^{29}Si spectra for each SCAS mix.

The ^{29}Si NMR spectra of the SCAS samples with S and/or M after 28 days of ambient curing (Fig. 9 (a)) presented three sharp resonances with a mean δ_{iso} of -79.0, -81.8 and -84.7 ppm, correlating to crystalline C-(A)-S-H components $\text{Q}^1(0\text{Al})$, $\text{Q}^2(1\text{Al})$ and $\text{Q}^2(0\text{Al})$, respectively [11]. These

were accompanied with an amorphous product component (-86.0 to -87.5 ppm) relating to Q^2/Q^3 sites in less crystalline portions of the C-(A)-S-H phase. The relative intensity of these ^{29}Si components (Table 5) demonstrated that S and M both enhanced the hydration of slag into C-(A)-S-H, corroborating the pH and setting time results. Accordingly, CS contained the lowest content of Si in hydration products (27.2%); whereas sample SM10, which included both S and M, had the highest content of Si in hydration products (39.4%).

The carbonation process resulted in the loss of crystalline phases ($Q^1(0\text{Al})$, $Q^2(1\text{Al})$ and $Q^2(0\text{Al})$) in all the SCAS samples, as shown by Fig. 9 (b). An additional resonance at δ_{iso} of -73 ± 2 ppm was observed in the majority of carbonated samples, assigned as amorphous monomeric/dimeric (Q^0/Q^1) silicate units produced under carbonation. This component was distinct from the Q^0/Q^1 precursor slag resonance, which was assumed to be unaltered by the carbonation process. These less connected silicate moieties could have formed during the breakdown of the silicate chains, forming the C-(A)-S-H structure upon decalcification. The relative intensity of this degraded (Q^0/Q^1) C-(A)-S-H component, along with those of the amorphous hydration product and precursor components is given in Table 5. The decrease in the site occupancy of the crystalline components resulted in a concomitant increase in both the amorphous Q^2/Q^3 C-(A)-S-H components and the amorphous Q^0/Q^1 carbonation product, revealing the degradation of the C-(A)-S-H structure due to its decalcification by CO_2 . The degradation of C-(A)-S-H in CS explained the loss of strength observed during carbonation. The use of S and/or M enhanced the carbonation resistance of SCAS samples due to the increased formation of hydrotalcite. Furthermore, the presence of MgO in samples containing M enabled the C-(A)-S-H gel to retain its integrity via the reaction of Mg-phases with CO_2 to form HMCs. Therefore, the degradation of the C-(A)-S-H gel was less severe within these samples. In samples S and M10, the crystalline C-(A)-S-H was shown to partially convert into amorphous C-(A)-S-H phases as well as amorphous silicate, thereby facilitating a stable mechanical performance after 28 days of carbonation. Moreover, no amorphous silicate could be observed in the carbonated SM10 sample, with the entirety of the crystalline C-(A)-S-H phases converting to amorphous hydration phases. The change in C-(A)-S-H structure instead of its degradation could be attributed to the higher pH of the pore solution, maintained via the consumption of CO_3^{2-} in the formation of huntite and HMCs.

3.3.3. TG-DTG analysis

Fig. 10 presents TG-DTG curves of SCAS samples after 28 days of ambient curing. Consistent with the pH, XRD and NMR results, the use of S and/or M improved the hydration degree of slag and resulted in higher mass losses in SCAS samples. Each step of mass loss was identified by an endothermic peak in the DTG curves, as listed below:

(i) Dehydration (30-250°C): Mass loss due to the loss of bound water of C-(A)-S-H, gaylussite, hydrotalcite and HMCs (e.g. nesquehonite). The peak at ~80°C corresponded to the water loss of C-(A)-S-H [49, 50], while the peak at ~120°C was due to the water loss of carbonate phases [31, 51]. The shoulder at ~200°C was related to the water loss of hydrotalcite [52].

(ii) Dehydroxylation (250-450°C): Mass loss due to the decomposition of hydroxyl groups of hydrotalcite and magnesium carbonates (e.g. hydromagnesite), corresponding to an endothermic peak at ~350-370°C [31, 32, 52, 53].

(iii) Decarbonation (450-900°C): Mass loss due to the removal of CO₂ from hydrotalcite and carbonates (e.g. nesquehonite, gaylussite, aragonite and calcite). The endothermic peak at ~560°C corresponded to the decarbonation of hydrotalcite and huntite [54, 55], while another peak at ~620-680°C was associated with the decarbonation of carbonate salts (e.g. gaylussite, huntite and calcite) [54, 56].

The TG-DTG curves of SCAS concrete samples after 28 days of carbonation are shown in Fig. 11. The mass loss corresponding to each step of thermal decomposition, obtained from the deconvoluted DTG curves, is summarized in Table 6 for samples cured for 28 days and carbonated for a further 28 days. The mass loss results confirmed the enhanced formation of hydrotalcite and carbonates within samples incorporating S and/or M. While the incorporation of S stimulated the formation of carbonates, the inclusion of M enhanced the formation of hydrotalcite. The associated consumption of CO₃²⁻ ions in the formation of these phases increased the alkalinity of the pore solution, thus accelerating the reaction kinetics of SCAS and the production of C-(A)-S-H. Accordingly, the total mass loss of these samples increased by 25-38% in comparison with CS (21.9-24.2 vs. 17.5%).

As shown in Table 6, the decalcification and the conversion of hydrotalcite to huntite led to a reduction in the mass loss associated with hydrotalcite and C-(A)-S-H in all samples subjected to carbonation. When compared with its mass loss after 28 days of ambient curing, CS exhibited a

significant reduction in its total mass loss after 28 days of carbonation (17.5 vs. 8.2%). Differing from CS, the use of S or M significantly reduced the loss of hydration products during carbonation. When compared with its mass loss after 28 days of ambient curing, the increase in the mass loss of sample S within the temperature range of 450-650°C after 28 days of carbonation (5.4 vs. 3.2%) revealed the role of S in increasing the hydrotalcite content. Alternatively, the ability of M to react with CO₂ compensated for the mass loss due to decalcification within the samples it was incorporated. Accordingly, the decomposition of carbonates was more influential on the mass loss than decalcification within samples involving up to 10% M. This effect could be observed by the higher total mass loss of sample M10 after carbonation (25.6 vs. 24.2%). Reflected by the mass loss associated with decarbonation, the use of both S and M stimulated a higher degree of hydrotalcite and HMC formation during carbonation, when compared with their sole use. In this respect, sample SM10 exhibited the highest mass loss (28.2%) amongst all carbonated samples, accounting for 23% increase after carbonation.

3.4. Effect of carbonation on microstructure

BSE images of SCAS samples after 28 days of curing are presented in Fig. 12. The bright gray tone observed in the images corresponded to unreacted slag grains, while the dark tone surrounding the remnant slag particles was the main hydration products (e.g. C-(A)-S-H and carbonate phases). CS revealed a porous microstructure, which was dominated by unhydrated slag particles with a diameter of 5-45 µm (Fig. 12 (a)). The reduction in the size of the unhydrated slag particles (i.e. 1-13 µm) dispersed in a denser matrix of reaction products (i.e. indicated by the dark gray areas) within samples M10 (Fig. 12 (b)), S (Fig. 12 (c)) and SM10 (Fig. 12 (d)) indicated the role of S and M in improving the hydration process, and thereby the performance of SCAS mixes.

Fig. 13 reveals the formation of HMCs in samples including M after 28 days of carbonation. During carbonation, Mg-phases associated with the use of M in the prepared mixes reacted with the dissolved CO₂, leading to the formation of plate-like hydromagnesite (i.e. diameter of ~0.5-1 µm) and needle-like nesquehonite (i.e. diameter of ~0.4-1.5 µm, length of ~12 µm), as shown in Fig. 13 (a) and (b), respectively [57, 58]. The formation of these carbonate phases not only removed CO₃²⁻ ions to prevent decalcification, but also contributed to the establishment of a continuous binding network within the SCAS system. The densification of microstructure associated with the formation of these HMCs inhibited the diffusion of further CO₂ into SCAS

system by blocking the initially available pore space (Fig. 13 (b)) [31]. The development of a continuous carbonate network as well as the densification of the microstructure could improve the performance of these carbonated samples including M [53, 59].

The microstructure of SCAS samples after 28 days of carbonation is shown in Fig. 14. Since SCAS is associated with a lower shrinkage and the carbonation of Mg-phases leads to the expansive formation of HMCs, the micro-cracks observed in Fig. 12 and 14 could be attributed to the compression and polish processes used during sample preparation. The decalcification, in addition to the low degree of hydration of slag, led to a porous microstructure within CS (Fig. 14 (a)), where the disintegration of slag could be observed. Alternatively, the use of S and/or M significantly improved the microstructure of carbonated SCAS samples. When compared to its microstructure before the carbonation process (Fig. 12 (b)), the carbonated M10 sample, whose pores were partially filled with various carbonate phases, demonstrated a denser microstructure (Fig. 14 (b)). The role of S in improving the CO₂ absorption of hydrotalcite enabled sample S to retain a dense matrix composed of well-dispersed hydration and carbonation products, without any disintegration (Fig. 14 (c)). The reaction of CO₃²⁻ with the Mg-phases provided via the presence of M and the improved CO₂ absorption of hydrotalcite with the use of S led to the highest amount of hydration and carbonation products within sample SM10. This resulted in a very dense microstructure, in which the presence of pores was very limited (Fig. 14 (d)).

3.5. Effect of carbonation on compressive strength

The compressive strength of SCAS concrete samples cured under ambient conditions is shown in Fig. 15 (a). Out of all the samples, CS demonstrated the lowest strength at all ages, which was mainly due to its low initial alkalinity, associated with the low dissolution and reaction of slag. In agreement with the pH, XRD, NMR and TGA results, samples incorporating S and/or M, which were associated with a higher formation of reaction products (i.e. C-(A)-S-H, carbonates and hydrotalcite), gained significantly higher compressive strengths than CS. For example, while CS did not gain any notable strength after 2 days, samples incorporating of S and/or M reached compressive strengths ranging between 19-25 MPa. At 7 days, the compressive strength of CS was 2 MPa, while sample S achieved a compressive strength of 35 MPa. Despite their incomplete hardening after one day of curing, samples including 3% M resulted in an obvious increase in compressive strength at 7 days (22 MPa). The role of M in strength development was more

obvious in sample M10, whose 7-day compressive strength was 32 MPa. Moreover, samples, in which S and M were simultaneously included, gained higher compressive strengths than those involving the sole use of S or M. Accordingly, the highest 7-day strengths were observed in samples SM3 and SM10 (38 MPa). While most of the strength gain was achieved during the first 7 days, samples including S and/or M outperformed CS at all times. At 28 days, CS revealed a strength of 14 MPa, while sample S reached 39 MPa. At the same duration, samples M3 and M10 achieved 28 and 39 MPa, respectively. Out of all samples, sample SM10, with its highest hydrotalcite and C-(A)-S-H contents, revealed the highest 28-day compressive strength of 43 MPa. These results highlighted the significance of the presence of S and M in promoting the hydration reaction and thereby enhancing the performance of SCAS mixes. Increasing the curing duration beyond 28 days (i.e. until 91 days) did not result in any significant strength gain in any of the samples.

As there were not any major changes in strength after 28 days, samples cured for 28 days were subjected to CO₂ environment for up to 91 days. Fig. 15 (b) demonstrates the effect of carbonation on the performance of SCAS samples during this period. Samples incorporating S and/or M demonstrated better carbonation resistance than CS at all times. This improved performance was attributed to the increase in the pH of the pore solution, which provided a better CO₂ buffer capacity and retained higher strengths when compared with CS (26-58 vs. 6 MPa at 28 days of carbonation). The increase in the hydrotalcite content of samples including S and/or M was also associated with the consumption of CO₃²⁻ ions in the formation of huntite and/or HMCs. This led to high pH values in the pore solution, which promoted the precipitation of divalent cations and alleviated the decalcification of C-(A)-S-H. When exposed to carbonation conditions for 28 days, the decalcification of C-(A)-S-H resulted in a decrease in the compressive strength of CS by 57% (14 vs. 6 MPa). The use of 3% M reduced the corresponding strength loss due to the carbonation to 7% (28 vs. 26 MPa). Alternatively, an increase in the amount of M to 10% increased the compressive strength by 10% after 28 days under carbonation (39 vs. 43 MPa). The improvement in the carbonation resistance of samples including M was attributed to the formation of HMCs via the reaction between the dissolved M and CO₂. These HMCs contributed to strength development by forming a continuous carbonate network that filled the pores and reduced the further diffusion of CO₂ into the pore space [32, 60-62], thereby reducing the effects of decalcification. Alternatively, the use of S increased compressive strength from 39 to 46 MPa during the first 7 days of carbonation. A similar outcome was observed with the combination of both S and M,

highlighted by the increase in the strength of sample SM10 from 43 to 58 MPa after 28 days of carbonation.

However, differing from the initial days of exposure to CO₂, most samples revealed a decrease in their strength at longer durations. As carbonation proceeded, the strength loss was mostly prominent in samples containing less than 10% M. Accordingly, the combination of both S and M in sample SM3 reduced the strength loss when compared with their sole inclusion in samples S or M3 (15% vs. 23-36% after 91 days of carbonation). This was partially due to the initial increase in the strength of the former during the first few days of carbonation. Alternatively, samples using 10% M presented higher compressive strengths after 91 days of carbonation than those of uncarbonated samples. For example, despite the slight drop in strength from 58 to 54 MPa after 91 days of exposure, sample SM10 still outperformed all the samples, followed by sample M10, whose strength remained relatively stable at 42 MPa throughout the entire duration of carbonation. Regardless of their composition, all samples visibly outperformed CS, which revealed the lowest strength of 5 MPa after 91 days of CO₂ exposure. Since strength loss was noticeable in samples containing less than 10% M, the use of 10% or higher amounts of M could be adopted to improve the mechanical performance and carbonation resistance of SCAS mixes in the long term.

4. Conclusions

The initially low alkalinity of SC leads to low hydration degrees, very long setting times and consequently low compressive strengths within SCAS mixes. In line with these shortcomings, improvements in the hydration mechanism and mechanical and microstructural performance of SCAS mixes were achieved via the use of S and M. The inclusion of M contributed to the additional consumption of CO₃²⁻ from SC in the formation of HMCs (e.g. nesquehonite) and the high CO₂ uptake of hydrotalcite, which increased the alkalinity in the pore solution within SCAS mixes. Alternatively, the use of S provided additional nucleation sites within SCAS mixes, which facilitated the formation of carbonates and hydrotalcite, thereby increasing the utilization of CO₃²⁻. Overall, the inclusion of M or/and S within SCAS mixes enhanced the dissolution of slag and the subsequent hydration reactions, which led to significantly shorter setting times and improved the microstructure and mechanical performance of the samples.

SCAS concrete was shown to be vulnerable to carbonation as the decalcification of C-(A)-S-H, associated with the expulsion of Al and Si, led to the loss of 53% (i.e. by mass) of hydration products and 57% loss of compressive strength. Accordingly, this study also investigated the use of S and M in enhancing the carbonation resistance of SCAS samples. The higher alkalinity of the pore solution within samples including S and M provided a higher CO₂ buffering capacity. This improvement resulted in the partial conversion of the crystalline C-(A)-S-H into amorphous phases during carbonation, leading to higher compressive strengths when compared to samples that did not involve the use of these additives. The increase in the formation of hydrotalcite within samples incorporating M improved the sequestration of CO₂ via its conversion to huntite, thereby retarding the decalcification of C-(A)-S-H. Furthermore, the formation of HMCs as a result of the reaction between Mg-phases provided by M and CO₂ during the carbonation process contributed to the formation of a continuous network of binding phases. These advancements in the hydration and carbonation reactions facilitated further strength gain within SCAS mixes. Moreover, the additional formation of hydrotalcite on the nucleation sites provided via the presence of S in the pore space increased the absorption of CO₃²⁻, hence alleviating the decalcification of C-(A)-S-H. As a result, the inclusion of 10% M or 0.5% S within SCAS mixes enabled the prevention of strength loss under exposure to carbonation conditions. Moreover, the use of both M and S counteracted the degradation of the hydration products, while enhancing the formation of carbonation products, which resulted in SCAS samples with denser microstructures and improved mechanical performance.

Acknowledgement

The authors would like to acknowledge the financial support from the Singapore MOE Academic Research Fund Tier 1 (RG 95/16) for the completion of this research project.

References

- [1] D.L. Chandler, Researchers have created emissions-free cement, World Economic Forum, 2019.
- [2] O. Burciaga-Díaz, Parameters affecting the properties and microstructure of quicklime (CaO) - Activated slag cement pastes, *Cement and Concrete Composites*, 103, (2019) 104-111.
- [3] J. Zhang, C. Shi, Z. Zhang, Chloride binding of alkali-activated slag/fly ash cements, *Construction and Building Materials*, 226, (2019) 21-31.
- [4] B. Akturk, S. Nayak, S. Das, A.B. Kizilkanat, Microstructure and Strength Development of Sodium Carbonate-Activated Blast Furnace Slags, *Journal of Materials in Civil Engineering*, 31, (2019) 04019283.
- [5] K. Gong, Y. Cheng, L.L. Daemen, C.E. White, In situ quasi-elastic neutron scattering study on the water dynamics and reaction mechanisms in alkali-activated slags, *Physical Chemistry Chemical Physics*, 21, (2019) 10277-10292.
- [6] B. Lothenbach, D.A. Kulik, T. Matschei, M. Balonis, L. Baquerizo, B. Dilnesa, G.D. Miron, R.J. Myers, Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials, *Cement and Concrete Research*, 115, (2019) 472-506.
- [7] H. Ye, Z. Chen, L. Huang, Mechanism of sulfate attack on alkali-activated slag: The role of activator composition, *Cement and Concrete Research*, 125, (2019) 105868.
- [8] A. Ipatti, Solidification of ion-exchange resins with alkali-activated blast-furnace slag, *Cement and Concrete Research*, 22, (1992) 281-286.
- [9] N. Cristelo, J. Coelho, T. Miranda, Á. Palomo, A. Fernández-Jiménez, Alkali activated composites – An innovative concept using iron and steel slag as both precursor and aggregate, *Cement and Concrete Composites*, 103, (2019) 11-21.
- [10] J.L. Provis, S.A. Bernal, Geopolymers and Related Alkali-Activated Materials, *Annual Review of Materials Research*, 44, (2014) 299-327.
- [11] X. Ke, S.A. Bernal, J.L. Provis, Controlling the reaction kinetics of sodium carbonate-activated slag cements using calcined layered double hydroxides, *Cement and Concrete Research*, 81, (2016) 24-37.
- [12] M.S. Kim, Y. Jun, C. Lee, J.E. Oh, Use of CaO as an activator for producing a price-competitive non-cement structural binder using ground granulated blast furnace slag, *Cement and Concrete Research*, 54, (2013) 208-214.
- [13] B. Liu, H. Du, S.-N. Wang, Y. Zhang, S.-L. Zheng, L.-J. Li, D.-H. Chen, A novel method to extract vanadium and chromium from vanadium slag using molten NaOH-NaNO₃ binary system, *AIChE Journal*, 59, (2013) 541-552.
- [14] T. Bakharev, J.G. Sanjayan, Y.-B. Cheng, Alkali activation of Australian slag cements, *Cement and Concrete Research*, 29, (1999) 113-120.
- [15] D. Krizan, B. Zivanovic, Effects of dosage and modulus of water glass on early hydration of alkali-slag cements, *Cement and Concrete Research*, 32, (2002) 1181-1188.
- [16] T. Bakharev, J.G. Sanjayan, Y.B. Cheng, Effect of admixtures on properties of alkali-activated slag concrete, *Cement and Concrete Research*, 30, (2000) 1367-1374.
- [17] A.A. Melo Neto, M.A. Cincotto, W. Repette, Drying and autogenous shrinkage of pastes and mortars with activated slag cement, *Cement and Concrete Research*, 38, (2008) 565-574.

- [18] H. Ye, A. Radlińska, Shrinkage mechanisms of alkali-activated slag, *Cement and Concrete Research*, 88, (2016) 126-135.
- [19] H. Maghsoodloord, A. Allahverdi, Developing Low-Cost Activators for Alkali-Activated Phosphorus Slag-Based Binders, *Journal of Materials in Civil Engineering*, 29, (2017) 04017006.
- [20] C. Duran Atiş, C. Bilim, Ö. Çelik, O. Karahan, Influence of activator on the strength and drying shrinkage of alkali-activated slag mortar, *Construction and Building Materials*, 23, (2009) 548-555.
- [21] B. Susan Andrea, Advances in near-neutral salts activation of blast furnace slags, *RILEM Technical Letters*, 1, (2016).
- [22] S.A. Bernal, J.L. Provis, R.J. Myers, R. San Nicolas, J.S.J. van Deventer, Role of carbonates in the chemical evolution of sodium carbonate-activated slag binders, *Materials and Structures*, 48, (2015) 517-529.
- [23] M.J. Climent, A. Corma, S. Iborra, K. Epping, A. Velty, Increasing the basicity and catalytic activity of hydrotalcites by different synthesis procedures, *Journal of Catalysis*, 225, (2004) 316-326.
- [24] L. Lv, J. He, M. Wei, D.G. Evans, X. Duan, Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: Equilibrium and kinetic studies, *Water Research*, 40, (2006) 735-743.
- [25] R.k. Allada, A. Navrotsky, H.T. Berbeco, W.H. Casey, Thermochemistry and Aqueous Solubilities of Hydrotalcite-Like Solids, *Science*, 296, (2002) 721-723.
- [26] S. Miyata, The Syntheses of Hydrotalcite-Like Compounds and Their Structures and Physico-Chemical Properties—I: the Systems Mg^{2+} - Al^{3+} - NO_3^- , Mg^{2+} - Al^{3+} - Cl^- , Mg^{2+} - Al^{3+} - ClO_4^- , Ni^{2+} - Al^{3+} - Cl^- and Zn^{2+} - Al^{3+} - Cl^- , *Clays and Clay Minerals*, 23, (1975) 369-375.
- [27] G.N. Muriithi, L.F. Petrik, F.J. Doucet, Synthesis, characterisation and CO₂ adsorption potential of NaA and NaX zeolites and hydrotalcite obtained from the same coal fly ash, *Journal of CO₂ Utilization*, 36, (2020) 220-230.
- [28] E. Papa, V. Medri, C. Paillard, B. Contri, A. Natali Murri, A. Vaccari, E. Landi, Geopolymer-hydrotalcite composites for CO₂ capture, *Journal of Cleaner Production*, 237, (2019) 117738.
- [29] Z. Zhang, S. Chen, Y. Zhang, Effect of hydrotalcite-like compounds with high specific surface area on mechanical properties and carbonation resistance of cementitious composites, *Materials Research Express*, 6, (2019) 115099.
- [30] S.Y. Ying-Hua Bai, C. Wei, Experimental Study of Carbonation Resistance of Alkali-Activated Slag Concrete, *ACI Materials Journal*, 116.
- [31] N.T. Dung, A. Lesimple, R. Hay, K. Celik, C. Unluer, Formation of carbonate phases and their effect on the performance of reactive MgO cement formulations, *Cement and Concrete Research*, 125, (2019) 105894.
- [32] N.T. Dung, C. Unluer, Influence of accelerated hydration and carbonation on the performance of reactive magnesium oxide concrete, *Advances in Cement Research*, 32, 78-90.
- [33] V. Räsänen, V. Penttala, The pH measurement of concrete and smoothing mortar using a concrete powder suspension, *Cement and Concrete Research*, 34, (2004) 813-820.
- [34] S. Manso, A. Aguado, A review of sample preparation and its influence on pH determination in concrete samples, *Materiales de Construcción*, 67, (2017) e108.

- [35] ASTM C191 –13, Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle, ASTM Committee C01, PO Box C700, West Conshohocken, PA 19428-2959. United States, 2013, pp. 8.
- [36] K. Hoffmann, T.J.N. Hooper, H. Zhao, U. Kolb, M.M. Murshed, M. Fischer, H. Lührs, G. Nénert, P. Kudějová, A. Senyshyn, H. Schneider, J.V. Hanna, T.M. Gesing, R.X. Fischer, Crystal chemical characterization of mullite-type aluminum borate compounds, *Journal of Solid State Chemistry*, 247, (2017) 173-187.
- [37] K. Hoffmann, T.J.N. Hooper, M.M. Murshed, O. Dolotko, Z. Révay, A. Senyshyn, H. Schneider, J.V. Hanna, T.M. Gesing, R.X. Fischer, Formation, stability and crystal structure of mullite-type $\text{Al}_{6-x}\text{B}_x\text{O}_9$, *Journal of Solid State Chemistry*, 243, (2016) 124-135.
- [38] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Modelling one- and two-dimensional solid-state NMR spectra, *Magnetic Resonance in Chemistry*, 40, (2002) 70-76.
- [39] A. Vollpracht, B. Lothenbach, R. Snellings, J. Haufe, The pore solution of blended cements: a review, *Materials and Structures*, 49, (2016) 3341-3367.
- [40] E. L'Hôpital, B. Lothenbach, K. Scrivener, D.A. Kulik, Alkali uptake in calcium alumina silicate hydrate (C-A-S-H), *Cement and Concrete Research*, 85, (2016) 122-136.
- [41] C. Shi, R.L. Day, A calorimetric study of early hydration of alkali-slag cements, *Cement and Concrete Research*, 25, (1995) 1333-1346.
- [42] J. Zhang, C. Shi, Z. Zhang, Carbonation induced phase evolution in alkali-activated slag/fly ash cements: The effect of silicate modulus of activators, *Construction and Building Materials*, 223, (2019) 566-582.
- [43] J.B. Ries, Review: geological and experimental evidence for secular variation in seawater Mg/Ca (calcite-aragonite seas) and its effects on marine biological calcification, *Biogeosciences*, 7, (2010) 2795-2849.
- [44] Chapter 5 - ^{27}Al NMR, in: K.J.D. MacKenzie, M.E. Smith (Eds.) *Pergamon Materials Series*, Pergamon, 2002, pp. 271-330.
- [45] J. Schneider, M.A. Cincotto, H. Panepucci, ^{29}Si and ^{27}Al high-resolution NMR characterization of calcium silicate hydrate phases in activated blast-furnace slag pastes, *Cement and Concrete Research*, 31, (2001) 993-1001.
- [46] W.J. Malfait, W.E. Halter, R. Verel, ^{29}Si NMR spectroscopy of silica glass: T1 relaxation and constraints on the Si–O–Si bond angle distribution, *Chemical Geology*, 256, (2008) 269-277.
- [47] F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-type anionic clays: Preparation, properties and applications, *Catalysis Today*, 11, (1991) 173-301.
- [48] W.T. Reichle, Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite), *Solid State Ionics*, 22, (1986) 135-141.
- [49] R.J. Myers, E. L'Hôpital, J.L. Provis, B. Lothenbach, Effect of temperature and aluminium on calcium (alumino)silicate hydrate chemistry under equilibrium conditions, *Cement and Concrete Research*, 68, (2015) 83-93.
- [50] N.T. Dung, T.-P. Chang, C.-T. Chen, T.-R. Yang, Cementitious properties and microstructure of an innovative slag eco-binder, *Materials and Structures*, 49, (2016) 2009-2024.
- [51] A.M. Chaka, A.R. Felmy, Ab Initio Thermodynamic Model for Magnesium Carbonates and Hydrates, *The Journal of Physical Chemistry A*, 118, (2014) 7469-7488.

- [52] L. Pesic, S. Salipurovic, V. Markovic, D. Vucelic, W. Kagunya, W. Jones, Thermal characteristics of a synthetic hydrotalcite-like material, *Journal of Materials Chemistry*, 2, (1992) 1069-1073.
- [53] N.T. Dung, C. Unluer, Improving the Carbonation of Reactive MgO Cement Concrete via the Use of NaHCO₃ and NaCl, *Journal of Materials in Civil Engineering*, 30, (2018).
- [54] L.A. Hollingbery, T.R. Hull, The thermal decomposition of huntite and hydromagnesite—A review, *Thermochimica Acta*, 509, (2010) 1-11.
- [55] L.A. Hollingbery, T.R. Hull, The thermal decomposition of natural mixtures of huntite and hydromagnesite, *Thermochimica Acta*, 528, (2012) 45-52.
- [56] Z. Tu, M.-z. Guo, C.S. Poon, C. Shi, Effects of limestone powder on CaCO₃ precipitation in CO₂ cured cement pastes, *Cement and Concrete Composites*, 72, (2016) 9-16.
- [57] V. Ferrini, C. De Vito, S. Mignardi, Synthesis of nesquehonite by reaction of gaseous CO₂ with Mg chloride solution: Its potential role in the sequestration of carbon dioxide, *Journal of Hazardous Materials*, 168, (2009) 832-837.
- [58] Q. Gautier, P. Bénézech, V. Mavromatis, J. Schott, Hydromagnesite solubility product and growth kinetics in aqueous solution from 25 to 75°C, *Geochimica et Cosmochimica Acta*, 138, (2014) 1-20.
- [59] N.T. Dung, C. Unluer, Carbonated MgO concrete with improved performance: The influence of temperature and hydration agent on hydration, carbonation and strength gain, *Cement and Concrete Composites*, 82, (2017) 152-164.
- [60] N.T. Dung, C. Unluer, Development of MgO concrete with enhanced hydration and carbonation mechanisms, *Cement and Concrete Research*, 103, (2018) 160-169.
- [61] N.T. Dung, C. Unluer, Performance of reactive MgO concrete under increased CO₂ dissolution, *Cement and Concrete Research*, 118, (2019) 92-101.
- [62] L.J. Vandeperre, A. Al-Tabbaa, Accelerated carbonation of reactive MgO cements, *Advances in Cement Research*, 19, (2007) 67-79.

List of Tables

Table 1 Composition and properties of slag and M.

	Chemical composition (% mass)							Physical properties	
	MgO	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	R ₂ O ^a	LOI	Specific gravity (g/cm ³)	Specific surface area (m ² /g)
Slag	9.3	32.3	37.8	14.6	0.5	0.9	-	-	1.1
M	>91.5	2.0	1.6	1.0	-	-	4.0	3.0	16.3

^a R₂O: Na₂O, K₂O

Table 2 Compositions of SCAS concrete mixes.

Mix	Precursor ^b (% mass)				Mixture composition (kg/m ³)					
	Slag	S	M	W/B	Slag	S	M	SC	Coarse aggregates	Water
CS	100	0	0		600	0	0			
M3	97	0	3		582	0	18			
M10	90	0	10		540	0	60			
S	99.5	0.5	0	0.55	597	3	0	48	1050	356.4
SM3	96.5	0.5	3		579	3	18			
SM10	89.5	0.5	10		537	3	60			

^b Precursor: Combination of slag, S and M

Table 3 Initial and final setting times of SCAS pastes.

Mix	Setting time (h)	
	Initial	Final
CS	94.3	148.2
M3	34.1	49.7
M10	12.2	19.2
S	13.1	19.7
SM3	9.6	16.5
SM10	7.8	12.8

Table 4 The relative intensities of the ^{27}Al NMR resonances relating to AlO_6 and AlO_4 components within the samples initially cured under ambient conditions for 28 days and samples subjected to carbonation for a further 28 days, following the initial curing. The relative intensities of each site were determined via line-shape integration using Topspin.

Curing condition	Mix	^{27}Al NMR relative intensity (%)	
		AlO_6	AlO_4
28 days of ambient curing	CS	4.8	95.2
	S	19.1	80.9
	M10	24.2	75.8
	SM10	24.5	75.5
28 days of carbonation	CS	0.0	100.0
	S	4.0	96.0
	M10	14.2	85.8
	SM10	17.6	82.4

Table 5 The relative intensities of the deconvoluted ^{29}Si components within the samples initially cured under ambient conditions for 28 days and samples subjected to carbonation for a further 28 days, following the initial curing. The relative intensities of each site were determined via line-shape simulation using DMFIT.

Curing condition	Mix	^{29}Si NMR relative intensity							
		Precursor Si components ^c	Crystalline C-(A)-S-H				Amorphous	Total	Degraded
			Q ¹	Q ² (1Al)	Q ²	Total	C-(A)-S-H (Q ² /Q ³)	C-(A)-S-H	C-(A)-S-H (Q ⁰ /Q ¹)
28 days of ambient curing	CS	72.9	0	0	0	0	27.1	27.1	-
	S	63.4	1.3	7.1	11.3	19.7	16.9	36.6	-
	M10	62.4	3.2	9.1	13.0	25.3	12.3	37.6	-
	SM10	60.6	4.7	7.7	15.3	27.8	11.6	39.4	-
28 days of carbonation	CS	72.7	0	0	0	0	20.9	20.9	6.4
	S	63.0	0	0	0	0	25.8	25.8	11.2
	M10	61.9	0	0	0	0	30.9	30.9	7.3
	SM10	61.4	0	0	0	0	38.6	38.6	0.0

^c sum of the precursor components at $\delta_{\text{iso}}(^{29}\text{Si})$ of -76 ± 3 and -110 ± 3 ppm

Table 6 Mass loss of all samples cured for 28 days under ambient conditions (i.e. values outside the parentheses) and further carbonated for 28 days (i.e. values inside the parentheses), obtained by TGA.

Mix	Mass loss (%)						Total
	Dehydration		Dehydroxylation		Decarbonation		
	(30-250°C)		(250-450°C)		(450-650°C)	(650-900°C)	
	C-(A)-S-H	Cb ^d	Ht ^e	Ht & Cb	Ht & Cb	Cb	
CS	1.3 (0.3)	2.5 (1.3)	2.4 (0.5)	5.1 (0.5)	4.0 (2.4)	2.2 (3.2)	17.5 (8.2)
M3	5.6 (1.3)	2.8 (3.6)	3.1 (0.7)	3.9 (3.6)	4.6 (3.5)	2.6 (3.9)	22.6 (16.2)
M10	6.3 (3.7)	3.0 (3.7)	4.0 (2.7)	3.5 (6.6)	4.6 (4.3)	2.8 (4.6)	24.2 (25.6)
S	6.2 (1.9)	1.6 (2.6)	4.2 (2.2)	3.4 (2.6)	3.2 (5.4)	3.3 (3.7)	21.9 (18.4)
SM3	6.7 (2.9)	3.5 (2.3)	2.9 (2.8)	3.2 (4.2)	3.6 (5.4)	3.2 (4.6)	23.1 (22.2)
SM10	6.4 (5.7)	3.4 (4.6)	3.0 (2.2)	3.2 (5.5)	3.3 (5.4)	3.6 (4.8)	22.9 (28.2)

^d Cb: Carbonates

^e Ht: Hydrotalcite

List of Figures

Fig. 1 Particle size distribution of hydromagnesite (S)

Fig. 2 XRD patterns of slag, hydromagnesite seed (S) and reactive MgO (M)

Fig. 3 pH values of SCAS pastes

Fig. 4 BSE image of nesquehonite in sample SM10 after 28 days of curing

Fig. 5 XRD patterns of all samples after 28 days of ambient curing

Fig. 6 XRD patterns of all samples cured for 28 days under ambient conditions, followed by 28 days of accelerated carbonation

Fig. 7 The (a) ^{27}Al and (b) ^{29}Si MAS NMR spectra of anhydrous slag

(Experimental spectra, simulated line shapes and deconvoluted simulation components are indicated by black, red and blue lines, respectively. Spinning sidebands are marked with *)

Fig. 8 The ^{27}Al MAS NMR spectra of samples: (a) initially cured under ambient conditions for 28 days and (b) carbonated for 28 days (i.e. following the initial 28 days of curing)

(Experimental spectra and the representative spectra of the slag precursor are in black and grey, respectively. Spinning sidebands are marked with *)

Fig. 9 The ^{29}Si MAS NMR spectra of samples: (a) initially cured under ambient conditions for 28 days and (b) carbonated for 28 days (i.e. following the initial 28 days of curing)

(Experimental spectra, simulated line shapes, deconvoluted simulation product components and deconvoluted simulation precursor components are given by black, red, blue and grey lines.

Spinning sidebands are marked with *)

Fig. 10 TG-DTG results after 28 days of ambient curing of samples: (a) without S and (b) with S

Fig. 11 TG-DTG results after 28 days of carbonation of samples: (a) without S and (b) with S

(a)

(b)

(c)

(d)

Fig. 12 BSE images after 28 days of ambient curing of samples: (a) CS, (b) M10, (c) S and (d) SM10

(a)

(b)

Fig. 13 BSE images of HMCs' formation after 28 days of carbonation of samples: (a) M10 and (b) SM10

(a)

(b)

(c)

(d)

Fig. 14 BSE images of samples cured for 28 days under ambient conditions, followed by 28 days of accelerated carbonation: (a) CS, (b) M10, (c) S and (d) SM10

Fig. 15 Compressive strength of SCAS concrete samples under: (a) ambient conditions and (b) carbonation condition