Magnesium silicate hydrate (M-S-H) stability under carbonation

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ABSTRACT

This work offers in-depth understanding about the behavior of different M-S-H phases under carbonation. Here, we carbonated 8-year-old M-S-H samples under i) wet carbonation and ii) dried or steamed pressurized CO₂. Both solid and liquids samples were analyzed using various techniques while thermodynamic modelling was coupled to shed light on the response of M-S-H phases under carbonation. We found that M-S-H with Mg/Si = 0.8 showed excellent carbonation resistance in which the phase remained stable in all investigated conditions. M-S-Hs with higher Mg/Si ratios (1.1 and 1.5) released Mg₂⁺ to obtain the stable M-S-H (Mg/Si = 0.8) while the released Mg₂⁺ dissolved in water or formed Mg-carbonates under wet carbonation or pressurized carbonation, respectively. Hence, high temperature and/or pressure are needed to carbonate M-S-H with high Mg/Si ratios to form Mg-carbonates. The remarkable stability of the strength-forming M-S-H phase under carbonation holds promising potential for future applications of such cements.

1. Introduction

Despite some advancements in sustainable cement alternatives, the inherent challenges of reducing the construction industry’s environmental impact persist. Magnesia silicate cements emerge as a promising alternative to replace conventional Portland cement for specific applications, presenting an option to reduce the construction industry’s carbon footprint. These cements could exhibit an effective low environmental impact if the MgO sources originate from non-carbonate Mg-based minerals. Previous studies have demonstrated that the hydration of these reactive MgO-SiO₂ cements leads to the formation of a magnesium silicate hydrate phase (M-S-H) as the main reaction product [1], offering compressive strengths comparable to traditional Ca-based cements [2].

M-S-H is a solid solution where Mg/Si ratio varies from 0.75 to 1.5 [3]. M-S-H structure consists of silicates arranged in tetrahedral layers, similar to phyllosilicate minerals, as observed through ²⁹Si MAS NMR studies showing Q² and Q⁴ signals. Plus, magnesium in M-S-H presents in octahedral layers i.e., similar to Mg(OH)₂ (brucite) [4]. M-S-H also presents some physically and chemically bound water. Therefore, M-S-H phases are hydrated precursors of nanocrystallite phyllosilicates such as talc, serpentinities, chlorites, or even smectites [3–9]. Second, M-S-H can incorporate Al in the silicate layers to form M-A-S-H phase [9,10]. The incorporation rather happens at pH about 10–11 together with the precipitation of hydrotalcite (Mg—Al layered double hydroxide) [11] while the amount of Al incorporation in M-A-S-H seems to be limited to Al/Si ~ 0.15 [10]. Despite the better understanding of the structure and the stability of the M-S-H during the last years, little is known about the stability of M-S-H during natural and pressured carbonation which poses a critical point for the performance of magnesia silicate cements and their uses in service conditions.

At the geology scale, M-S-H precipitation occurs during the serpentinization of olivine-rich rocks. This weathering phenomenon of olivine leads to the formation of serpentine and brucite and results in an equilibrium solution with a high pH, causing partial dissolution of quartz and releasing dissolved Mg and Si, which are available to react and form M-S-H [12]. M-S-H has also been recently detected in Roman concrete [13], likely originating from dolomitic stones and chert-silicate sediment present in the concrete, highlighting its stability over time. Interestingly, no magnesium carbonates are observed in Roman concrete. At the same time, in the Ca-based systems: Ca-silicate rock weathering or Ca-cementitious materials, the natural carbonation and time would result in significant amounts of calcium carbonate with some quartz in the geological case and accompanied by some zeolite phases and Al-totbermorite in the case of Ca-cementitious materials [1–4]. Finally, during the production of reactive MgO and silicates from the Mg silicate minerals via carbonation some persistent M-S-H remained [15].
Therefore, while calcium silicate hydrate (C-S-H), main hydrate of calcium based cement is prone to carbonation which decomposes the phase to CaCO₃ and silica [16], the responses of M-S-H under carbonation remain unclear.

This study investigates the stability of 8-year-old M-S-Hs (Mg/Si = 0.8 and 1.5) and M-A-S-H (Mg/Si = 1.1 and Al/Si = 0.1) versus wet carbonation (bubbling in suspension, for 24 h, but also weekly during 1 month), dry and steamed high-pressure carbonation (directly on solids in autoclave). The reference samples and the resulting carbonated samples were chosen due to the natural composition of the Mg/Si M-S-H samples were characterised by X-ray powder diffraction (XRD), thermogravimetric analysis complemented with Fourier Transformation-Infrared (TGA-FT-IR), attempted total reflectance (ATR) Fourier Transformation-Infrared (FT-IR) and ²⁹Si and ²⁷Al, ¹³C MAS NMR spectroscopy. The solution of the carbonated and non-carbonated suspensions was analysed, and solubility products were calculated and compared to the existing literature. In the last decade, different thermodynamic data were provided in literature [3,17,18]. Additionally, M-S-H was observed experimentally stable from pH 8 to 12.5 [19]. Here, we use thermodynamic modelling with the updated thermodynamic data for relevant species in MgO-SiO₂-C₂H₂O system to further investigate the carbonation of M-S-H.

2. Materials and methods

The M-(A)S-H samples were prepared in a glove box under N₂ to avoid CO₂ contamination using Milli-Q water and a water/solid (W/S) ratio of 45 to ensure a homogeneous suspension. The samples equilibrated at 20 °C were placed on a horizontal shaker. M-S-H with Mg/Si = 0.8 and 1.5 and M-A-S-H Mg/Si = 1.1 and Al/Si = 0.1 were synthesized from reactive MgO, amorphous silica and metakaolin following the proportion given in Table 1. More details on the synthesis and the handling can be found in [10,20]. The compositions M-S-H 0.8 and 1.5 samples were chosen due to the natural composition of the Mg-Si rocks. The M-A-S-H sample with Mg/Si = 1.1 and Al/Si = 0.1 was chosen to ensure the purity of the sample, i.e. without hydrotalcite, as detailed in [10]. The samples were kept in suspension until filtration and wet carbonation for 8 years after the synthesis. The wet carbonations were carried out using 100 % CO₂(g) (controlled flow at 100 cm³/min), bubbling through the suspension at room temperature for 24 h. The pH values were measured every 15 min in the first 8 h of carbonation and at the end of the experiment. In a second experiment, the wet carbonation was carried out weekly (first day: 20 h and then for 6 h weekly) for 1 month using the same CO₂ flow. The one-month suspensions were then let rest for 2 days to re-equilibrate its environment prior to sample collection.

After the experiments, the suspensions were separated by filtration using pressure (4–5 bars N₂) filtration and nylon filters (0.45 µm). The solids were washed with a 50/50 (volume) water-ethanol mix and a second time with ethanol (94 wt% alcohol) to eliminate dissolved ions and to prevent the precipitation of salts during drying which could perturb the analyses. The samples were dried in the 40 °C oven for 2 h. The solid characterizations were performed after further equilibration in N₂-filled desiccators over saturated CaCl₂ solution for 14 days or longer to ensure ~34 % RH in all the samples. After drying, the samples were gently ground by hand for the solid characterizations. The analyses for 2-year-old M-(A)S-H samples obtained from [20] and [10] were added for comparison. Data for M-S-H 1.5 carbonated for 24 h are partially presented in [21].

The pressurized carbonation was performed using a UOS Lab reactor (RVD-3-2000) in 2 sets of experiments. The first set of samples was carbonated in pCO₂ = 20 bars at room temperature and named dry carbonation (DC) while in the second set, the carbonation was done in pCO₂ = 20 bars and pH₂Osteam = 15 bars (T = ca. 200 °C) and named steamed carbonated (SC). The duration for all experiments was 24 h. Samples were then collected from the reactor, washed with isopropanol, and dried in an oven at 40 °C for 2 h prior to further characterization.

2.1. IC and pH measurements

The composition of the liquid phase was analysed by ion chromatography (IC) immediately after filtration. The dissolved concentrations of Mg, Si, Na, and Cl in undiluted solutions or in solutions diluted by factors 10 or 100 were quantified using a Dionex DP series ICS-3000 ion chromatography system. Independent measurements of solutions with known compositions indicated a measurement error 8 %. All concentrations were determined in duplicates, and hence, the mean values are given. The pH value was measured directly in the suspension as charge balancing anions, such as hydroxides, can be removed during the filtration, as detailed in [5]. Therefore, the pH (±0.1) was measured in the supernatant at ambient temperature (23 ± 2 °C) in an aliquot of the unfiltered suspension where the solid particles had been allowed to settle. The measured pH values were corrected to 20 °C.

2.2. TGA

TGA measurements were carried out using a Netzsch STA 449 F3 Jupiter TGA apparatus coupled with a Bruker Fourier-transform infrared (FT-IR) spectrometer for the analysis of the exhaust gases. Approximately 30 mg of each sample was heated from 30 to 980 °C with a heating rate of 10 °C per minute in 150 µl alumina crucible.

2.3. XRD

X-ray diffraction (XRD) data were collected using a PANalytical XPerT Pro MD3 diffractometer equipped with a rotating sample stage in a theta-2 theta configuration applying CuKa radiation (λ = 1.54 Å) at 45 mV voltage and 40 mA intensity with a fixed divergence slit size and an anti-scattering slit on the incident beam of 1/2° and 1°. The samples were scanned between 5° and 70° 2θ with a X'Celerator detector. Phase identification and Rietveld quantification were performed using PANalytical HighScore (version 5) coupled with PDF 4+ 2022 database. CaF₂ (Sigma-Aldrich, product code: 1.02840.1000) was used as external standard. The refinement included shifted Chebyshev 1 background, scale factors, the lattice constants, and peak profile parameters.

2.4. FTIR

Attenuated total reflectance (ATR) Fourier Transformation-Infrared (FT-IR) spectra were recorded in the mid-region on a Bruker Tensor 27 FT-IR spectrometer between 600 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹ by transmittance on small amounts of powder. Spectra were background corrected and scaled to the maximum of Si–O bonds to ease comparison.

2.5. NMR

The ²⁹Si solid-state magic angle spinning (SS MAS) NMR single pulse experiments were conducted on a Bruker Avance III 400 NMR spectrometer using a 7 mm CP/MAS probe at 79.5 MHz. Ground samples (200–300 mg) were packed into 7 mm zirconia rotors, and Teflon inserts (3 mm thickness) were used to allow smoother sample rotation. The

<table>
<thead>
<tr>
<th>Mg/Si</th>
<th>M-S-H 0.8</th>
<th>M-A-S-H 1.1</th>
<th>M-S-H 1.5</th>
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<tr>
<td>Mg/Si</td>
<td>0.8</td>
<td>1.1</td>
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<tr>
<td>Al/Si</td>
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<td>2.49</td>
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<td>MgO₂·SiO₂ [g]</td>
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Table 1

Starting materials for the different Mg/Si of M-S-H samples (g = grams; Mg/Si = molar magnesium to silica ratio).
filling heights were carefully adjusted so the Teflon spacer was in direct contact with the cap, ensuring equivalent sample volumes for each rotor. The NMR data were recorded under the following conditions: 4500 Hz sample rotation rate, 10 k–20 k scans, 30°–29Si pulse of 2.5 μs, RF field strength of 33.3 kHz during SPINAL64 proton decoupling. The 29Si NMR chemical shifts were referenced to the most intense resonance at ~23 ppm of an external sample of octamethylsilanesoquinoxane (Alrichidron 52,683–5), which was referenced to tetramethylsilane (TMS, δ29Si = 0.0 ppm): details are given in [11]. Relaxation time was 20 s for the 2-year-old samples and 30 s for the 8-year-old samples.

Solid-state 13C CP-MAS NMR spectra were measured on the same equipment, with the rotors prepared as described above. The 13C CP-MAS NMR spectra were recorded at 100.6 MHz, using the following parameters: 6.0 μs 90° excitation pulse on the 1H channel; 2 ms contact time (32.8 kHz spin lock field on 13C channel), applying ramps from 100 to 50 % of power level on the proton channel (spin lock field of 41 to 29 kHz); sample rotation rate of 4000 Hz; 3 s recycle time; and 43 kHz SPINAL 64 proton decoupling, which was applied during acquisition. Appropriate numbers of scans (3000 up to 20,000) were recorded to yield reasonable signal-to-noise ratios. The 13C NMR chemical shifts were referenced to the high frequency signal at 38.5 ppm of an external sample containing adamantane.

The 27Al NMR spectra were measured using a 2.5 mm CP/MAS probe on the same instrument as described above. The 27Al MAS NMR spectra were recorded at 104.3 MHz applying the following parameters: 25,000 Hz sample rotation rate, 3000 to 6000 scans, π/12 pulses of 1.0 μs, and 0.3 s recycle time ensuring quantitative recording of the data (no 1H decoupling was applied during acquisition). The 27Al NMR chemical shifts were referenced to an external sample of Al(acac)3, which in turn was calibrated to the signal from a solution of 1.1 m Al(NO3)3 in D2O at 0.0 ppm. The individual 27Al MAS NMR spectra were analyzed by the line shape fitting software “DMFIT” [22]. Generally, the fitting of the octahedral sites was performed using i) a Lorentzian shape at 9 ppm (FWHM of 4.5–5 ppm) and ii) a quadrupolar broadened shape using the “Czejk simple” [23] model starting with the parameters FWHM CS = 10 ppm (full width at half maximum of the isotropic chemical shift Gaussian distribution), CS = 5.3 MHz (peak value of the quadrupolar coupling of the Czejk/GIM distribution), and d = 5 (exponent of the Czejk distribution). The signals for the pentahedral and tetrahedral Al sites were also fitted with the “Czejk simple” model (FWHM CS = 12 ppm, CS ~ 4–5.5 MHz and d = 5). A detailed description of the fitting procedure used can be found in [11].

### 2.6. Thermodynamic modelling

Thermodynamic modelling of the experiments was carried out using the Gibbs free energy minimization program GEMS [24]. GEMS is a broad-purpose geochemical modelling code that calculates equilibrium phase assemblage and speciation in a complex chemical system based on its total bulk elemental composition. The activities of dissolved species were determined from the measured concentrations in solution and pH values using the geochemical software GEMS v3.3 [25] with the PSI database [26].

The activity of a species i, 〈i〉, was calculated from the measured concentrations considering the formation of different aequous complexes; 〈i〉 = yi·mi, where yi is the activity coefficient, and mi is the concentration in mol/kg H2O. The activity coefficients of the aequous species yi were computed with the built-in extended Debye-Hückel equation with standard ion-size parameter aq = 3.31 Å for NaOH solutions and standard third parameter b by according to the Eq. (1):

$$\log y_i = \frac{A_i \sqrt{\frac{\mu_i}{2 \pi R T_0}}} {1 + B_i \frac{\sqrt{\mu_i}} {T_0^{1/2}}} + b_i I$$  

(1)

where z_i denotes the charge of species i, 〈i〉 is the effective molal ionic strength, b_i is a semi-empirical parameter (~0.098 for NaOH electrolyte at 25 °C), and A_i and B_i are P, T-dependent coefficients. This activity correction is applicable up to ~1 M ionic strength [27].

From the solution analysis presented in this study and the solution analysis presented in [20] solubility products of M-S-H were calculated with respect to 3 end-members with compositions of (MgO)0.67(SiO2)1.42(H2O)1.78, (MgO)0.75(SiO2)(H2O)1.25 and (MgO)1.5(SiO2)(H2O)1.5, respectively [3] (Mg/Si = 0.67, 0.75 and 1.50). The solubility products for talc and antigorite were taken from [28]. From the solubility products calculated at different temperatures, the Gibbs free energy of reaction, ΔG°, and the Gibbs free energy of formation, ΔG°f, at 25 °C can be obtained according to Eqs. (2) and (3):

$$ΔG^° = -RT \ln K = \sum \gamma_i ΔG_i^°$$  

(2)

$$ΔG_i^° = \Delta_r G_{i,f} - S_{T_i}(T - T_0) - \int_0^T \frac{C_i}{T} dT = \Delta_r G_{i,f} - S_{T_i}(T - T_0) - \frac{d}{2} \left[ \ln T_0 - \ln \left( \frac{T - T_0}{2} \right)^2 \right] \sqrt{T_0}$$  

(3)

where γ_i correspond to the stoichiometric reaction coefficients, R = 8.31451 J/mol/K and T is the temperature in K. The apparent Gibbs free energy of formation, ΔG°f, refers to the free energies of the elements at 298 K. A more detailed description of the derivation of the dependence of the Gibbs free energy on temperature is given in [29,30]. The molar volumes were taken from [3] where they were calculated based on the volume of talc or chrysotile and the volume of water bound in brucite. The standard entropy S° and heat capacity C_p of the phases were estimated based on the molar volume as proposed in [31] and [32] where we discussed these approaches in our recent review [17].
For the thermodynamic modelling, the thermodynamic data for aqueous species, brucite and amorphous silica were taken from the PSI-GEMS thermodynamic database [26]. The solid solution model used for M-S-H was developed in this study, and the thermodynamic data for the Mg-carbonate phases were taken from the summary given in [33]. Tentative thermodynamic data for the M-A-S-H phases were taken from [10] and for the hydrotalcite phase from [34].

3. Results and discussions

3.1. Effect of long curing time

Solution analysis of the 2-year-old and 8-year-old samples are presented in Table 2: minimal changes were observed after 8 years, except for a slight decrease in pH values. This small reduction is likely attributed to the gradual carbonation of the solution by atmospheric CO$_2$ over time. While the carbonates were not measured after 2 years, their concentration was about 1.7–3 mmol/L after 8 years of equilibration. Additionally, there was a slight increase in sodium (Na) and magnesium (Mg) concentrations. The slight increase in Mg concentration is presumed to be related to the pH decrease, hence, a rearrangement in the M-S-H structure for a lower Mg/Si M-S-H, decreasing Mg in the solution as already observed in such systems [3, 20]. This is similar to a classical phenomenon in C-S-H for the pH decrease at equilibrium (e.g. [35, 36]).

The concentration of Si stayed rather stable with time. However, the Si concentration of the M-S-H 0.8 sample was below the solubility of the amorphous silica, indicating that the solution was not anymore at equilibrium with respect to amorphous silica, and the solid was potentially free of amorphous silica.

The XRD patterns, the TG analyses, and the FT-IR spectra of the M-(A-)S-H samples after 8 years are compared to the 2 years and the carbonated samples in Fig. 1, Fig. 2, and Fig. 3, respectively. After 2 years, the TGA, XRD, and FT-IR data indicated that the M-S-H 0.8 and...
the M-A-S-H samples contained only M-S-H, while the M-S-H 1.5 sample contained, in addition to M-S-H, some brucite with the characteristic reflection peaks at 32.7, 38.0, 50.9, 58.7° 2θ, the water loss at 420° C and the band at 3690 cm⁻¹. This brucite observation together with a solution undersaturated with respect to brucite is due to a brucite dissolution hindrance as detailed in [20]. After 8 years, the data indicated the presence of brucite in the M-S-H 1.5 sample, but the uncarbonated M-S-H 0.8 and the M-A-S-H 1.1 seemed to be only composed of M-(A-)S-H.

XRD patterns showed the large humps at 19.7, 26.7, 35.0, 60.3° 2θ indicating the presence of M-S-H [3, 4]. The reflection at 59.9° 2θ of the sample 0.8 were shifted to slightly lower angles with time. These reflections are characteristic of the main layer of trioctahedral phyllosilicates. This increase indicates a rather T:O phyllosilicates (talc) structure to a 1:1 phyllosilicates (serpentine) (the 060 is shifting from 1.528 Å to 1.54 Å). This indicates only small changes in the large scale of the arrangement of the sheets. The reflection at 27.2° 2θ corresponds to the (003) distance of talc and was better defined in the M-S-H 0.8 sample after 8 years indicating a rather talc structure as in the hydrothermally treated M-S-H 0.8 from [5]. A reflection closer to 24.9° 2θ can be observed in the M-A-S-H 1.1 and M-S-H 1.5 samples, which could be attributed to the (002) of the serpentine minerals.

The TGA curves and the derivative weight losses showed the two water loss regions characteristic of M-S-H: the poorly bound water, also named physically bound water, at 30–200° C and the chemically bound water at 200–900° C [5]. After 8 years, the content of brucite decreased to ~7 wt% (of the dry materials) compared to the 2-year-old samples, which contained ~11 wt%. The weight losses at 800° C are related to the recrystallization of MgSiO₃ as detailed in [3] and are not related to carbonates as confirmed by TGA-FTIR (see Appendix, Fig. S2 and S3).

FT-IR data showed the presence of Q² and Q³ silica species in the M-S-H structure with vibrations at 870–920 cm⁻¹ and 950–1150 cm⁻¹, respectively [20]. While the M-S-H 0.8 aged of 2 years, could still contained trace of amorphous silica with the shift of the main band to 1010 cm⁻¹ a mix from the amorphous silica band at 1035 cm⁻¹ and the M-S-H band at 1000 cm⁻¹. However, the main band of the 8-year-old sample was centered at 989 cm⁻¹, indicating the absence of amorphous silica. In the sample M-S-H 1.5 and the M-A-S-H 1.1, the main band shifted from 995 cm⁻¹ after 2 years to 986 cm⁻¹ after 8 years. With time, the bands at ~660 cm⁻¹ corresponding to the Si-O-Si bending band became narrower, indicating a higher symmetry and more ordered structure.

The M-S-H 1.5 showed some asymmetric stretching of C=O=C around 1450 cm⁻¹, presence also confirmed by the total carbon content of solid samples (see Appendix, Table A1) and the TGA-FTIR (see Appendix, Fig. S3). This could be related to i) CO₂⁻ incorporated into the brucite as detailed in [37] or ii) post-carbonation of the sample after the
## Table 3

|                | Mg/Si = 0.8 | Mg/Si = 1.1 | Mg/Si = 1.5 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 | M-S-H 1.1 |
|----------------|-------------|-------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Q<sub>1</sub>  | 79.0 ± 0.5  | 78.7 ± 0.5  | 78.4 ± 0.5  | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 | 78.4 ± 0.5 |
| Q<sub>2</sub>  | 20.0 ± 0.5  | 21.5 ± 0.5  | 21.5 ± 0.5  | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 | 21.5 ± 0.5 |
| Q<sub>3</sub>  | 6.2 ± 0.5   | 11.7 ± 0.5  | 11.7 ± 0.5  | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 | 11.7 ± 0.5 |
| Q<sub>4</sub>  | 39.4 ± 0.5  | 37.3 ± 0.5  | 37.3 ± 0.5  | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 | 37.3 ± 0.5 |
| Q<sub>5</sub>  | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 | 100.5 ± 0.5 |

Fig. 5. <sup>27</sup>Al MAS NMR spectra of the M-A-S-H samples at 20 °C, after 2 and 8 years, and after 24 h and 1 month of carbonation.

filtration. As no CO\(_2\) was observed in the solids after the wet carbonation and the CO\(_2\) was only observed in the sample containing brucite. The carbonation, i.e. CO\(_2\) in the solid, seemed related to the brucite content in the original sample.

<sup>29</sup>Si MAS NMR spectra of the 2-year-old, the 8-year-old, and the wet-carbonated samples are presented in Fig. 4. The line-shape analysis of the spectra was carried out following the procedure of [20] and is summarized in Table 3, and examples of the simulated NMR spectra are shown in the Appendix (Fig. S1).

The spectra were simulated with five signals attributed to resonances of M-S-H: Q<sub>1</sub> at −78.5 ± 0.5 ppm, Q<sub>2</sub> at −85.5 ± 0.5 ppm, and three Q<sub>3</sub> signals: Q<sub>a</sub> at −92.5 ± 0.3 ppm, Q<sub>b</sub> at −94.4 ± 0.3 ppm, and Q<sub>c</sub> at −96.5 ± 0.5 ppm [3]. Additional Q<sub>3</sub> signals at −100.5 ± 0.5 ppm, and Q<sub>4</sub> at −109.5 ± 0.5 ppm were attributed to the presence of amorphous silica. The 2-year-old and 8-year-old M-S-H 0.8 samples showed similar spectra with a low amount of Q<sub>1</sub> (<3%) and Q<sub>2</sub> slightly lower than 30%. The Q<sub>2</sub> signals accounted for about 70%. The presence of amorphous silica was below the detection limit in both samples. However, the 2-year-old sample solution remained at equilibrium with the amorphous silica. The <sup>29</sup>Si MAS NMR data confirmed the absence of amorphous silica after 8 years, as indicated by the solution analysis.

For simplicity, the M-A-S-H spectra were also deconvoluted with only those five signals, even though the width of the M-S-H Q<sub>1</sub>, Q<sub>2</sub>, and Q<sub>3</sub> signals appeared broader than for the aluminum-free samples, indicating the presence of Q<sub>2</sub>(Al) and Q<sub>3</sub>(Al) at −82 and −91 ppm [10,11]. Similar to the M-S-H 0.8, the deconvolutions of the M-A-S-H and M-S-H 1.5 samples yielded comparable results at both ages: 3.5 ± 0.5% of Q<sub>1</sub>, 41–42.5% of Q<sub>2</sub> and 53% of Q<sub>3</sub> for the M-A-S-H samples, and 5–9% of Q<sub>1</sub>, 44% of Q<sub>2</sub>, and 47–51% of Q<sub>3</sub> for the M-S-H 1.5 samples. Finally, the Q<sub>2</sub>/Q<sub>3</sub> ratio (presented in Table 3) increased with the Mg/Si in the M-A-S-H phases as already observed in [20], indicating a lower polymerization with an increased Mg/Si.

The <sup>27</sup>Al MAS NMR spectra of the M-A-S-H 1.1 after 2 and 8 years are presented, together with the spectra if the carbonated sample in Fig. 5, and the line shape analysis associated is given in Table 4. The <sup>27</sup>Al MAS NMR data indicated the presence of tetrahedrally coordinated Al(IV) between 60 and 70 ppm, as e.g. in saponite [38] and octahedrally...
coordinated Al(VI) environment between 0 and 20 ppm [39,40]. The Al (IV) signal was visible as a broad asymmetric signal, potentially 2 signals, in the M-A-S-H phases. The deconvolution was carried out with an iso chemical shift at 69.5 ± 0.5 ppm. As detailed in [10] the Al(VI) signal could be divided into two Al(VI) signals, a signal centered at ~9 ppm, which seemed symmetric, and a sizeable asymmetric signal at about ~5 ppm. The broad asymmetric shoulder at ~5 ppm is related to the poor ordering of the layers of tri-octahedral phyllosilicates, where all octahedral positions are filled, Al (VI) appears at 5–10 ppm [10,40]. In hydroxalcite-like phases, a symmetric Al(VI) signal centered at ~9–11 ppm [41], and for poorly ordered aluminum hydroxide, an asymmetric signal at around 11 ppm is observed. However, the TGA and XRD data indicated neither hydroxalcite nor aluminum hydroxide presence, making their presence unlikely. The observed chemical shift of the Al(VI) at ~9 ppm indicates that aluminum in octahedral sites is present mainly in a trioctahedral phyllosilicates, where all octahedral positions are filled, Al (VI) seemed to have a reduced amount of hydroxyl group compared to the uncarbonated samples. Additionally, the XRD, TGA, and FT-IR data showed some re-precipitation of the silica during the resting time.

Finally, the calculated Al(VI)/Al(IV) ratios are detailed in Table 4. The 27Al MAS NMR spectra of the M-A-S-H 1.1 after 2 and 8 years showed an increase from 0.6 to 1. A ratio of 0.8 was observed for the sample at synthesized at 50 °C [11], indicating that after 2 years at 20 °C did not reach equilibrium. After 8 years, there is a similar repartition (~half/half) of the aluminum in the samples.

### 3.2. Effect of wet carbonation after 8 years of equilibration

This section compares the uncarbonated M-S-Hs to the wet carbonated samples during 24 h and the repetitive wet carbonation during 1 month. After 24 h of carbonation, the pH values of the M-S-H 0.8, M-A-S-H 1.1, and M-S-H 1.5 suspensions reduced from 8.3 and 7.1, 9.3 to 7.1, and 10.1 to 7.3, respectively. With this pH decrease, the solutions were each saturated with respect to amorphous silica with Si concentrations of 2.1–2.6 mmol/L. Additionally, the concentration of Mg increased to 30.9, 67.4, and 124.7 mmol/L for the M-S-H 0.8, M-A-S-H 1.1, and M-S-H 1.5, respectively. Significant dissolved carbonates were also measured between 54 and 131 mmol/L and were function of the Mg concentrations.

After one month of carbonation, the pH values were observed to be slightly higher (7.7–8) than just after the 24 h of carbonation due to the 2 days resting time which led to some re-equilibration. However, the concentrations of Mg and carbonates were higher, indicating a higher degradation state of the solids. While all the solutions were oversaturated with Si, after 24 h of carbonation, the 1 month carbonated sample M-A-S-H 1.1 and M-S-H 1.5 showed slightly lower concentrations (1.4–1.6 mmol/L), potentially due to some re-precipitation of the silica during the resting time.

The XRD (Fig. 1) and TGA data (Fig. 2 and Appendix, Fig. S1 4 and S1 5) showed no changes in the carbonated M-S-H 0.8 samples. However, the TGA indicated that the carbonated M-A-S-H 1.1 and M-S-H 1.5 seemed to have a reduced amount of hydroxyl group compared to the uncarbonated samples. Additionally, the XRD, TGA, and FT-IR data clearly showed the dissolution of brucite in the M-S-H 1.5 after 24 h or after 1 month of carbonation. This was in accordance with the higher content of dissolved Mg found in the solution. After mass balance, the total amount of dissolved Mg related to the amount of brucite in the sample is estimated to 30 mmol/L, indicating the dissolution of M-S-H and the release of dissolved Mg in every sample.

Surprisingly, in the two wet carbonations, while the carbonates were found in the suspensions, the 27Al MAS NMR data (Appendix, Fig. S8), the TGA-FI-IR (Appendix, Fig. S4 and S5) and the FT-IR data (Fig. 3 and Appendix, Fig. S9) showed no carbonates in the solids after the two carbonations.

The 29Si MAS NMR spectra of the carbonated samples (Fig. 4) were similar to the non-carbonated samples. The deconvolutions (Table 3) showed some residual amorphous silica in the M-S-H 0.8 and M-A-S-H 1.1 samples: ~5 and ~1 %, respectively after 24 h of carbonation. Interestingly, M-S-H 0.8 showed 27 % of amorphous silica after 1 month carbonation. The observation of amorphous silica confirmed the solution analysis where the solutions were found to be at equilibrium with amorphous silica. However, the amorphous silica content did not change in the M-A-S-H potentially indicating that the Al incorporation stabilized the M-S-H. Similarly, the amorphous silica was below the detection limit of the SS MAS Si NMR measurement in the M-S-H 1.5.

### Table 4

Assignments of 27Al MAS NMR chemical shifts and relative amounts of Al signals obtained by simulation of the 27Al MAS NMR spectra shown in Fig. 5. Associated error ± 5 %.

<table>
<thead>
<tr>
<th></th>
<th>Al(IV)</th>
<th>Al(IV)</th>
<th>Al(IV)</th>
<th>Al(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[ppm]</td>
<td>%</td>
<td>[ppm]</td>
<td>%</td>
</tr>
<tr>
<td>2 years M-A-S-H 1.1</td>
<td>69.0</td>
<td>38</td>
<td>9.8</td>
<td>21</td>
</tr>
<tr>
<td>8 years M-A-S-H 1.1</td>
<td>70.0</td>
<td>49</td>
<td>6.9</td>
<td>9</td>
</tr>
<tr>
<td>24 h carbonated M-A-S-H 1.1</td>
<td>69.2</td>
<td>51</td>
<td>60.1</td>
<td>12</td>
</tr>
<tr>
<td>1 M carbonated M-A-S-H 1.1</td>
<td>68.6</td>
<td>58</td>
<td>58.2</td>
<td>7</td>
</tr>
</tbody>
</table>

### Table 5

Experimentally determined Mg/Si in M-S-H phases synthesized after 2 and 8 years of equilibration and after the wet carbonation for 24 h or 1 month by mass balance, i.e. taking into account the dissolved ions and corrected for the amount of brucite quantified by TGA and amorphous silica by 29Si MAS NMR.

<table>
<thead>
<tr>
<th>Mg/Si</th>
<th>H2O/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M-S-H 0.8</td>
</tr>
<tr>
<td>2-year-old</td>
<td>0.8</td>
</tr>
<tr>
<td>8-year-old</td>
<td>0.8</td>
</tr>
<tr>
<td>24 h carbonated</td>
<td>0.7</td>
</tr>
<tr>
<td>1 M carbonated</td>
<td>0.7</td>
</tr>
</tbody>
</table>
which would also indicate that the high Mg/Si retards the dissolution of M-S-H by a first removal of Mg from the M-S-H structure. When the equilibrium of the solution is disturbed with the forced CO$_2$ in the solution, M-S-H presents a lower Mg/Si and is partially dissolved resulting in dissolved silicon release that leads in the solution’s supersaturation with respect to amorphous silica, leading to the precipitation of amorphous silica together with the release of Mg (24 h-carbonated samples). From the M-S-H 0.8, it seems that 1 M-carbonated samples underwent stronger dissolution due to the presence of more amorphous silica and more dissolved Mg in the system, even with a higher pH of the solution. However, in the M-A-S-H 1.1, while the pH values and the dissolved Mg were also higher, amorphous silica was observed even if the solution was undersaturated with respect to amorphous silica. This is potentially associated to i) the error of the measurement, or ii) to the reformation of M-S-H due to the release of CO$_2$ into the atmosphere during the resting period. As explained in [33], in the absence of other anions, but at a set pH value, the concentration of Mg in solution can be increased by the presence of dissolved CO$_2$, due to complexation, meaning that if CO$_2$ degases, magnesium precipitates and pH increases. Table 5 shows the experimentally observed Mg/Si in the uncarbonated and carbonated M-S-H obtained mass balance. The Mg/Si in the M-S-H decreased to 0.8–0.7 in every M-S-H phase. This is in accordance with the lowest composition observed in natural phyllosilicate where sepiolite presents a Mg/Si ratio of 2/3.

In the M-S-H phase left, the amounts of Q$^1$ and Q$^2$ were reduced in favor of Q$^3$ amount, as indicated by the Q$^2$/Q$^3$ reduction. This indicated a higher polymerization degree in the silicate layers, and confirmed the lower Mg/Si in the M-S-H. The $^{27}$Al MAS NMR spectra of the carbonated M-A-S-H samples showed a lower amount of Al(VI) and a shoulder in the Al(IV) environment (Fig. 5). The deconvolution was done with an extra iso chemical shift at 60.1 ppm to mimic this shoulder; the line shape analysis is given in Table 4. In the 24 h-carbonated sample, the amount Al(IV) at 69.5 ± 0.5 ppm remains the same between the non-carbonated and the carbonated samples, about 50% while the sample carbonated for 1 month seemed to show a slightly higher content. The Al(IV) shoulder in the carbonated samples was about 10% leading to a higher amount Al(IV) than Al(VI), with a Al(IV)/Al(VI) of 1.4 and 1.7 in the 24 h-carbonated and 1 M-carbonated, respectively. The larger amount of Al(IV) is consistent with higher silica polymerization observed by $^{29}$Si MAS NMR in the carbonated samples.

To conclude, the wet carbonation leads to a pH decrease, the M-S-H are decalcified and present Mg/Si to 0.7 confirmed by the higher polymerization in silicate sheets. However, the low Mg/Si M-S-H are not fully dissolved. Additionally, no carbonate phases could be observed in the solids after carbonation.

### 3.3. Effect of high-pressured carbonation

Fig. 6 and Fig. 7 show the XRD and TGA data of M-S-H 0.8, M-A-S-H 1.1, and M-S-H 1.5 after high-pressured carbonation in dry (DC) and stream conditions (SC). M-S-H 0.8 exhibited great resistance toward carbonation in both tested conditions where the M-S-H phase remained unchanged with no trace of Mg-carbonate phases formed in the samples as observed via XRD (Fig. 6a and 7a). The M-S-H 1.5 shared similar resistance to carbonation to that of M-S-H 0.8 in which only brucite in the sample was carbonated to form nesquehonite (37 wt%) and magnesite (27 wt%) under DC and SC, respectively. The formation of different carbonates from brucite carbonation was due to the carbonation conditions. Although nesquehonite is a metastable phase [42], it is...
The presence of nesquehonite was confirmed in M-S-H 1.5 and M-A-S-H 1.1 under DC where a series of bands at 1518, 1473, and 1411 cm$^{-1}$ were observed. In M-S-H 0.8 under SC condition with a band at 1072 cm$^{-1}$, there was absence of out-of-plane and in-plane CO$_3^{2-}$ vibration at 884 and 742 cm$^{-1}$, respectively. Finally, the M-S-H showed its presence in all samples in both carbonation conditions with the typical symmetric and asymmetric Si–O stretching between 1200 and 800 cm$^{-1}$ as well as the Si–O–Si and H–O–H bending around 630 cm$^{-1}$ and 1640 cm$^{-1}$, respectively [20]. The presence of γ-AlO(OH) showed a trace in M-A-S-H 1.1 under SC condition with a band at 1072 cm$^{-1}$ corresponding to the symmetric and asymmetric bending of Al-O-H in boehmite [50,51].

The $^{29}$Si MAS NMR spectra of the DC and SC samples are presented in Fig. 9, along with the deconvolutions presented in Table 6. The $^{29}$Si MAS NMR spectra of the DC M-A-S-H samples and the M-S-H 1.5 DC and SC indicate a Q$^3$/Q$^2$ ratio lower than that of the 8-year samples (refer to Table 3), signifying the formation of M-S-H with a reduced Mg/Si ratio, aligning with the presence of nesquehonite or magnesite as observed by TGA and XRD.

The $^{27}$Al MAS NMR spectra of the DC and SC M-A-S-H samples are compared to the 24 h carbonated sample in Fig. 10, while the deconvoluted data are presented in Table 7. The DC M-A-S-H exhibits signals akin to the sample acquired through wet carbonation, albeit with a less pronounced shoulder at 60 ppm, resulting in an Al(IV)/Al(VI) ratio of 1.4. In contrast, the SC M-A-S-H sample displays an Al(IV)/Al(VI) ratio of 0.9, indicating a higher Al(VI) content, likely owing to the presence of γ-AlO(OH), as observed by XRD, which predominantly features Al(VI) [52].

Fig. 11 displays the $^{13}$C CP-MAS NMR spectra of the autoclaved samples. All samples exhibited traces of solvant, indicated by signals ranging from 0 to 50 ppm. The presence of solvant can be attributed to the washing step. It is worth noting that not all of it was evaporated, suggesting significant sorption by the M-S-H surface. As expected, from the other analyses, the autoclaved M-S-H 0.8 (DC or SC) and M-A-S-H 1.1 SC contained no carbonates, as only M-(A-)S-H were present in the sample. Traces of carbonates may be observed around 165–167 ppm, but these fall within the range of the measurement’s noise. The spectra of the M-A-S-H 1.1 and M-S-H 1.5 DC samples displayed a single signal at 165.3 ppm, corresponding to the carbonate in the nesquehonite [53]. The M-S-H 1.5 DC spectrum showed a shoulder at 163 ppm (about 15 %, deconvolution not shown) potentially related to the transformation of the nesquehonite to hydromagnesite.
Notably, the $^{13}$C CP-MAS NMR spectrum of the M-S-H 1.5 SC did not reveal a signal in the carbonate range, potentially due to i) the absence of neighboring protons of the magnesite or ii) some issue in the measurement (as for example, some paramagnetic nuclei near the carbons in the magnesite).

3.4. Thermodynamic modelling

3.4.1. Thermodynamic data

Nied et al. [3] developed a solid solution model for M-S-H using two end members, Mg$_3$SiH$_2$ and Mg$_3$SiH$_5$ representing Mg/Si ratios of 0.75 and 1.5. The solubility products of the end-members are plotted in Fig. 12 together with the ion activity product calculated following the same procedure with the solution analysis presented in this present study. In this work, we revisited the thermodynamic data of M-S-H.
considering the solubility products of these synthesized phases after 2 and 8 years, with and without carbonates in solution (Fig. 12). Additionally, we considered a M-S-H 0.67 phase as the carbonated M-S-H presented a lower Mg/Si than 0.75. This new phase was created following the composition of sepiolite containing extra water: Mg$_4$Si$_6$O$_{15}$(OH)$_2$·6H$_2$O (see Table 5).

As seen in Fig. 12, the ion activity product of the M-S-H 0.67 and M-S-H 0.75 are not affected by the presence of carbonates in the solution (points on each other), while for the M-S-H 1.5, the carbonates in

![Fig. 9. $^{29}$Si MAS NMR spectra of the 8 years samples (plain colour), and after dry carbonation (DC in grey lines) and steamed carbonation (SC in black lines).](image)

![Fig. 10. $^{27}$Al MAS NMR spectra of samples after dry carbonation (DC in grey line) and after steamed carbonation (SC in black line) compared to the 24 h-carbonated sample.](image)

Table 6
Assignments of $^{29}$Si NMR chemical shifts and relative amounts of Qn silicon species obtained by simulation of the $^{29}$Si MAS NMR spectra shown in Fig. 4. Associated error = 1.5 %.

<table>
<thead>
<tr>
<th>Mg/Si</th>
<th>Q1 Relative amount</th>
<th>Q2 Relative amount</th>
<th>Q3 Relative amount</th>
<th>Q4 Relative amount</th>
<th>Total Q3</th>
<th>Q2/Q3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-S-H 0.8</td>
<td>–</td>
<td>–85.6</td>
<td>22.2</td>
<td>–92.6</td>
<td>16.8</td>
<td>–96.0</td>
</tr>
<tr>
<td>M-S-H 0.8</td>
<td>–79.3</td>
<td>0.2</td>
<td>–86.1</td>
<td>21.7</td>
<td>–94.6</td>
<td>52.6</td>
</tr>
<tr>
<td>SC</td>
<td>Mg/Si = 1.1, Al/Si = 6.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-A-S-H 1.1</td>
<td>–79.6</td>
<td>1.2</td>
<td>–85.7</td>
<td>29.6</td>
<td>–93.0</td>
<td>51.8</td>
</tr>
<tr>
<td>M-A-S-H 1.1</td>
<td>–</td>
<td>–86.1</td>
<td>28.7</td>
<td>–92.6</td>
<td>45.1</td>
<td>–96.0</td>
</tr>
<tr>
<td>SC</td>
<td>Mg/Si = 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-S-H 1.5</td>
<td>–79.4</td>
<td>4.8</td>
<td>–85.7</td>
<td>32.2</td>
<td>–93.7</td>
<td>48.5</td>
</tr>
<tr>
<td>M-S-H 1.5</td>
<td>–79.0</td>
<td>2.0</td>
<td>–85.8</td>
<td>30.8</td>
<td>–92.9</td>
<td>51.8</td>
</tr>
</tbody>
</table>
solution are stabilizing the ion activity product by 0.2–0.4 log unit. The decrease could be caused by the complexation of carbonate ions with dissolved Mg. More generally, the ion activity products are more stable with time, and the latest ion activity products are taken as solubility product. In addition, the solubility product is proportional to the Mg/Si ratio (and the OH/Si) as shown in Fig. 12 (for one Si per unit).

In addition, the value for standard entropy $S^\circ$ and heat capacity $C^\circ_p$ of the phases were estimated based on the molar volume as described in Section 2. Table 8 shows the standard thermodynamic properties at 25 $^\circ$C of M-S-H used in this study.

### 3.4.2. Thermodynamic modelling

Fig. 13 shows the modeled concentrations of Si and Mg relative to the pH, and the Mg/Si using the model solution developed by Nied et al. [3] in an inert system (i.e., no CO$_2$, depicted by dotted lines). The new model is also shown on Fig. 13, the calculations were done in a system with a small amount of dissolved CO$_2$, as observed experimentally in the suspension after 8 years (shown by solid lines). Furthermore, the dissolved Mg and Si measured in both this study and [5, 20] are included for comparison. The increase in dissolved CO$_2$ raises the Mg concentration by more than a log unit and decreases the Si concentration by a log unit. The experimental data are positioned between the two models (carbonated and non-carbonated), indicating that the suspensions are consistently slightly carbonated.

Fig. 11. a) $^{13}$C CP-MAS NMR spectra of the dried carbonated (DC) and steamed carbonated (SC) samples, $^* =$ denotes the spinning sidebands; b) Expanded view of $^{13}$C CP-MAS NMR spectra.

- **Table 7** Assignments of $^{27}$Al MAS NMR chemical shifts and relative amounts of Al signals obtained by simulation of the $^{27}$Al MAS NMR spectra shown in Fig. 10. Associated error = 5%.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>DC</th>
<th>SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-A-S-H</td>
<td>69.2</td>
<td>69.2</td>
</tr>
<tr>
<td>M-A-S-H/Al(OH)$_3$</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>M-A-S-H/hydrotalcite</td>
<td>6.5</td>
<td>7.7</td>
</tr>
</tbody>
</table>

The thermodynamic modelling aligns well with the experimental observations, demonstrating the pH decrease, reduction in Mg/Si, and the presence of amorphous silica. However, the experimental precipitation of hydromagnesite was not observed. Similarly, the precipitation of hydromagnesite was already thermodynamically predicted from M-S-H in presence of Na$_2$CO$_3$, but not experimentally observed [38]. It might be due to i) the presence of silicon in solution inhibiting the precipitation of hydrated magnesium carbonates or/and ii) the dilute systems but these hypotheses would need to be verified.

The thermodynamic modelling for the DC and SC conditions (Fig. 17) confirmed that M-S-H 0.8 was highly durable under carbonation and the phase composition of carbonated samples was in-line with experimental
observation. The M-S-H 0.8 remained stable in both DC and SC conditions with the calculated Mg/Si atomic ratio in the M-S-H was stable around 0.75–0.8 while there was a minor fraction (ca. 3 wt%) of hydromagnesite formed from the carbonation of this M-S-H phase. With higher Mg/Si ratio (in M-A-S-H 1.1 and MSH 1.5 samples), the steam led to the formation of magnesite where the source of MgO came partially from M-S-H causing to the reduction in Mg/Si ratio after carbonation.

Between M-A-S-H 1.1 and M-S-H 1.5, the fraction of magnesite was higher in the latter due to the full carbonation of brucite presented in the M-S-H 1.5 samples. In contrast, in the absence of steam pressure, hydromagnesite formed under DC condition which explained for the need of high temperature in magnesite formation. Overall, the modeling predicted well the carbonation behavior of M-S-H samples under both DC and SC conditions. M-S-H is most stable at Mg/Si = 0.75–0.8 while the higher Mg/Si ratio might be more prone to carbonation. Furthermore, the carbonation conditions affect the carbonate species formed in the samples. Nesquehonite was observed in experiment condition, where hydromagnesite was directly modeled to form. However, the $^{13}$C CP MAS NMR data tends to indicate a potential small conversion to hydromagnesite. This can be due to the high sensitivity of these HMCs in relation to temperature [43].

4. Conclusions

In conclusion, this study investigates the stability and the behavior of M-S-H under carbonation, along with the similar aluminum-containing phase, M-A-S-H, over extended periods. The investigation employed a combination of solution analyses, X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier-transform infrared (FT-IR)
We found that the fundamental integrity of M-S-H phase remained largely intact over the eight years, despite a slight decrease in pH. The wet carbonation (CO$_2$ bubbling) led to the pH of the suspension near to neutral pH. During the carbonation of M-S-H at low Mg/Si (i.e. Mg/Si = 0.8), M-S-H partially dissolved resulting in dissolved Mg while the released Si led to the precipitation of amorphous silica. At higher Mg/Si, no significant amount of amorphous silica was detected after the carbonation while the dissolved Mg was observed to increase, indicating a decrease of Mg/Si in the M-S-H. The decrease of the pH values, the $^{29}$Si MAS NMR analyses revealed a reduction in Q$_1^1$ and Q$_2^2$ with a concurrent increase in Q$_3^3$ signals, pointing toward a higher degree of silicate polymerization and a lower Mg/Si ratio in the M-S-H during wet carbonation. In fact, the experimental Mg/Si in the remaining M-S-H was observed to be about 0.7–0.8. At high Mg/Si (i.e. M-S-H 1.5), the brucite, still present after 8 years, is rapidly destabilized in the presence of CO$_2$ which dissolved and reduced the pH. The dissolution of the brucite leads to the release of Mg in solution but did not lead to the precipitation of Mg-carbonates. In each sample, the TGA(-FTIR), FTIR, and $^{13}$C CP MAS NMR indicated that no carbonates were detected in the solid phase assemblage of the wet carbonated samples, while the thermodynamic modelling predicted the precipitation of hydromagnesite for the M-A-S-H 1.1 and the M-S-H 1.5. The absence of Mg-carbonates is not yet elucidated, but one hypothesis is that the presence of dissolved silica which blocks the nucleation of such magnesium carbonate phases or it also be related to the largely diluted system. The $^{27}$Al MAS NMR data indicated that the amount of Al(IV), i.e. the amount of the Al incorporated in the silicate layers of M-A-S-H was larger after 8 years compared to the 2-year-old samples. The carbonation, and supposedly the pH decrease, slightly modify the structure, less Al is found in the octahedral layers while the Al incorporation in the silicate layers is increased.

Under steam and dry high-pressure carbonation, some M-(A-)S-H remained in all samples. The M-S-H 0.8 exhibited remarkable resistance to the steamed carbonation, with no discernible changes observed in the samples. However, the dried carbonation led to a partial formation of amorphous silica, indicating that the Mg/Si in M-S-H is lower, similar to the wet carbonation. The steamed carbonated M-A-S-H 1.1 sample demonstrated an excellent resistance as well, but the dry carbonation showed partial carbonation observing through the formation of nesquehonite. M-S-H 1.5 showed some carbonation under the investigated carbonation conditions. The sample (consisting of M-S-H 1.5 and brucite) forms nesquehonite and magnesite in the dry and steamed carbonation, respectively. Therefore, both M-A-S-H 1.1 and M-S-H 1.5 samples highlight the influence of the Mg/Si on the carbonation process.

Furthermore, thermodynamic modelling confirmed the experimental observations, elucidating the stable behavior of M-S-H with an Mg/Si ratio of 0.7–0.8 under both dry and steam pressure carbonation conditions. The model predicted the formation of hydromagnesite and magnesite. Nesquehonite is usually metastable and converts to
hydromagnesite at elevated temperature. Hence, the modelling is rather in line with the experimental results. The modelling confirmed the impact of Mg/Si ratios in M-S-H on the carbonation process.

In this study, we showed that M-(A-)S-H phase exhibits great resistance toward carbonation compared to that of C-(A-)S-H phase. While the former remained stable at Mg/Si ~0.7–0.8 under various carbonation conditions investigated in this study, at pH 8, C-S-H becomes unstable and would be greatly dissolved in which the dissolved Si would lead to the precipitation of amorphous silica [36, 54, 55] and the dissolved calcium will precipitate with the dissolved carbonate in CaCO$_3$ [56, 57]. In contrast, our work indicates that while the pH is reduced, no carbonates precipitate during the wet carbonation. Only the high CO$_2$ pressure led to the partial precipitation of the Mg-carbonates. Findings reported here contribute significantly to understanding the durability and stability of M-S-H phases, providing crucial insights for developing sustainable cementitious materials with reduced environmental footprints. By having an excellent resistance toward carbonation, binder based on M-(A-)S-H offer great opportunities to be used in various applications in construction where carbonation resistance is critically required.

![Fig. 15. Thermodynamic modelling of the direct CO$_2$ bubbling of the M-(A-)S-H 1.1 suspensions, a) Repartition of the solid phases and CO$_2$ gas, and b) solution composition and Mg/Si in the M-S-H. Note that the Al concentration is below 1e-5 mmol/L, hence is not plotted.](image1)

![Fig. 16. Thermodynamic modelling of the direct CO$_2$ bubbling of the M-S-H 1.5 suspensions, a) Repartition of the solid phases and CO$_2$ gas, and b) solution composition and Mg/Si in the M-S-H.](image2)

![Fig. 17. The predicted phase composition of M-S-H samples under both SC and DC conditions and the Mg/Si atomic ratios (dots) in the M-S-H after carbonation. Mc = Magnesite, Hydro-Mgs = hydromagnesite.](image3)
CRediT authorship contribution statement

Ellina Bernard: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing – original draft. Hoang Nguyen: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing – original draft.

Declaration of competing interest

E. Bernard and H. Nguyen declare that they have no conflicts of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References


