Effect of magnesium on calcium silicate hydrate (C-S-H)

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Abstract

The addition of MgCl_2 to synthetic calcium silicate hydrate (C-S-H) with $\text{Ca/Si}=0.8$ lowers the pH values below 10. Experimental observations and thermodynamic calculations show the destabilization of C-S-H and the precipitation of magnesium silicate hydrate (M-S-H). In contrast, the addition of MgO to C-S-H increases the pH values up to 11.5 and the Ca/Si in C-S-H from 0.8 to ~ 1.0 . At high pH, the formation of M-S-H and brucite is observed experimentally. Less brucite is present at 50 than at 20°C indicating a slow dissolution kinetic of brucite at 20°C. Thermodynamic modelling is in good agreement with the changes in C-S-H and M-S-H formation in the presence of MgO although no brucite is predicted.

M-S-H is observed in the presence of both MgCl_2 and MgO , is stable from pH 7.5 to 11.5 and has a structure comparable to the structure of M-S-H prepared from MgO and SiO_2 only.

Keywords

Low-pH cement, C-S-H, M-S-H, ^{29}Si MAS NMR, thermodynamic modelling

1. Introduction

The possible future disposal of radioactive wastes in deep repository will create interfaces between cementitious materials and clay-rich rocks. In these contact areas the differences in pH and alkali, calcium and magnesium concentrations in the pore solution will result in a transition zone [1-3]. “Low-pH concretes” have been developed to reduce the alkalinity of the cement and the pH of the solution diffusing into the clayey rocks, [4-6].

Decalcification of calcium silicate hydrate (C-S-H), leaching and carbonation have been observed in the hydrated cement paste at the interaction zone with the clayey rocks; all these phenomena decrease the pH at the hydrated cement paste/clay interface and lead to the formation of silica gel in the case of “low pH cements” [1, 7, 8]. In the interstitial solution of the clay, relatively high magnesium concentration (3-40 mmol/L) is present [1, 2, 8]. Magnesium reacts with silica from the cement leading, under water saturated conditions, to the formation of M-S-H (magnesium silicate hydrate) [1, 7] along with possible hydrotalcite [7, 8].

Studies on the formation of synthetic M-S-H from SiO_2 and MgO show that the rate of M-S-H formation is very slow [9-12]. Initially, brucite, $\text{Mg}(\text{OH})_2$, forms from MgO and reacts slowly with amorphous silica. A “transitional M-S-H” [11] is formed initially with a Mg/Si of 0.8-1.0 independent of the total Mg/Si [9-14]. Only after longer equilibration times, the M-S-H composition varies with the initial Mg/Si with a range observed between 0.8 and 1.3 [11, 15, 16]. M-S-H is stable at pH values between 8 to 10.4 [11, 12, 15].

Portlandite and high Ca/Si C-S-H, the most important hydrates in hydrated Portland cement, are generally observed at $\text{pH} \geq 12.5$. Lower pH values between 10 to 12.5 are measured for synthetic C-S-H [17-22] and also in “low pH” cements in the absence of portlandite where a low Ca/Si C-S-H (0.7-1.3) is present [4-6].

The C-S-H solid composition is well investigated and depends mainly on the total Ca/Si and the pH [20, 23-26]. C-S-H consists of calcium oxide layers each sandwiched on both side by silicate chains with the typical dreierketten structure [24]; i.e. with repeating building blocks consisting of two pairing silicate tetrahedra attached to the calcium oxide layer and a bridging position, which can be occupied by a bridging silicate tetrahedra or be empty, depending on the C-S-H composition. Thus, silicate in C-S-H, investigated by ^{29}Si MAS NMR, is either bound to one silicate neighbor (Q^1) at high Ca/Si or to two neighbors, Q^2 at low Ca/Si ratio. In contrast, M-S-H gels have a layered silicate structure [13, 15, 16, 27, 28], similar as in clay minerals, and silicate is bound to two or three neighbors (Q^2 and Q^3).

It has been suggested that magnesium could be incorporated in calcium silicate hydrate [29-31], although no clear experimental evidence was presented. Very limited Mg-Ca exchange could have occurred at the surface of tobermorite (natural mineral with a structure, stoichiometry and density similar to a low Ca/Si C-S-H) [32, 33] while for natural samples of tobermorite rather the presence of tobermorite with M-S-H and calcite in small veins have been observed [34]. According to Lothenbach et al. [35], the existence of different silicate structure, as described above, prevents the formation of a “M-C-S-H” phase but leads to the presence of separate M-S-H and C-S-H phases in a mix containing both Mg and Ca. However, a small uptake of magnesium in C-S-H and vice versa cannot be excluded. The presence of two solids confirms the conclusions of Brew and Glasser [13] that magnesium calcium silicate hydrate are not stable.

In the present paper, the effect of magnesium on the stability of C-S-H has been investigated by batch experiments where magnesium oxide or magnesium chloride were added to C-S-H with a Ca/Si ratio equal to 0.8.

2. Materials and methods

2.1. Synthesis

The synthesis of the C-S-H suspensions was done in a glovebox under nitrogen gas to minimize CO₂ contamination. Calcium oxide and silica fume (SiO₂, Aerosil 200, 0.9 wt.% HCl) have been chosen as starting materials for the C-S-H synthesis. CaO has been obtained by burning calcium carbonate (CaCO₃, Merck, pro analysis) for 12 hours at 1000 °C as detailed in [36]. 4.27 g of CaO and 5.73 g of SiO₂ were mixed with 225 ml of MilliQ-water in 250 ml PE-HD containers to obtain C-S-H with a Ca/Si of 0.8. The containers were sealed and stored at 20°C on a horizontal shaker (100 rpm) for one month. After one month, the C-S-H suspensions were separated by vacuum filtration using nylon filters (0.45 µm) in a glovebox under nitrogen. Directly following the filtration, the wet C-S-H (2 g of C-S-H with additional pure water of approx. 20 ml) was put in 100 ml PE-HD containers.

MgCl₂ (Anhydrous $\geq 98\%$, Sigma Aldrich) was dissolved in milli-Q water and added to the C-S-H (C-S-H and water) in the containers, resulting a water/solid (W/S) ratio equal to 54 and Mg/Si ratios of 0.05, 0.11, 0.15, 0.26, 0.87 and 1.34.

MgO (Merk, pro analysis, containing 0.18 ± 0.02 wt.% Na₂O) was added directly to C-S-H, as the solubility of MgO in water is low, and 90 ml milli-Q water in the containers to reach W/S equal to 54 and Mg/Si of 0.04, 0.23, 0.59 and 0.86.

After the addition of MgO or MgCl₂ to C-S-H, the samples were again equilibrated for 3 and 12 months at 20 and 50°C. Also, pure C-S-H suspension samples have been prepared and analyzed. The suspensions equilibrated at 20°C were placed on a horizontal shaker (100 rpm) while the

suspensions at 50°C were shaken weekly by hand. The analysis of the solids in this paper is focused on three samples of each set at 20°C after 12 months only as detailed in bold in Table 1.

Table 1: Starting materials for the theoretical 2 g of wet C-S-H with Ca/Si=0.80 and the different additions of MgCl₂ to reach the theoretical Mg/Si of 0.05; 0.26; 0.87; 1.34 and the different additions of MgO to reach the theoretical Mg/Si of 0.04; 0.23; 0.59; 0.86 (g = grams; Mg/Si = molar ratio).

	Mg/Si	Sample name	g		MgCl ₂ ^b	mmol/L		Mg ^b	mmol		Mg ^b
			CaO ^a	SiO ₂ ^a		Ca ^a	Si ^a		Ca ^a	Si ^a	
MgCl ₂	0.05	0.05MgCl₂	0.85	1.15	0.09	138.5	173.3	9.0	15.2	19.1	1.0
	0.26	0.26MgCl₂	0.85	1.15	0.48	138.5	173.3	45.4	15.2	19.1	5.0
	0.87	0.87MgCl₂	0.85	1.15	1.57	138.5	173.3	149.7	15.2	19.1	16.5
	1.34	1.34MgCl ₂	0.85	1.15	2.42	138.5	173.3	231.5	15.2	19.1	25.5
MgO					MgO ^b						
	0.04	0.04MgO	0.85	1.15	0.03	138.5	173.3	6.8	15.2	19.1	0.7
	0.23	0.23MgO	0.85	1.15	0.18	138.5	173.3	40.6	15.2	19.1	4.5
	0.59	0.59MgO	0.85	1.15	0.45	138.5	173.3	101.5	15.2	19.1	11.2
	0.86	0.86MgO	0.85	1.15	1.38	138.5	173.3	149.0	15.2	19.1	16.4

Samples in bold=samples fully analysed

^a theoretical values

^b measured values

After 3 and 12 months the suspensions were separated by vacuum filtration using 0.45 µm nylon filters in the glovebox under nitrogen.

Following the filtration, the liquid phases were recovered and the solids were washed with a 50/50 (volume) water-ethanol mix and then with ethanol (94 wt% alcohol) to remove dissolved ions and to prevent the precipitation of salts during drying. The samples were freeze dried with liquid nitrogen (around 20 min at -195°C) and kept at -40°C at 0.28 mbar pressure (vacuum) for a further 7 days. The solid phase analysis were done after further equilibration in N₂ filled desiccators over saturated CaCl₂ solution for a period of 14 days or longer to ensure ~30% RH in all the samples. Before analysis the samples were gently ground by hand.

2.2. Analytical techniques

The composition of the liquid phase was analyzed by ion chromatography (IC) immediately after filtration. The concentrations of Mg, Ca, Na, Si, Cl, in undiluted solutions or in solutions diluted by factors 10, 100 and 1000 were quantified using a Dionex DP serie ICS-3000 ionic chromatography system. Independent measurements of solution with known compositions indicated a measurement error $\leq 10\%$. All concentrations have been determined as duplicate and the mean is given. The pH values (± 0.1) were measured at ambient temperature ($23 \pm 2\text{ }^{\circ}\text{C}$) in an aliquot of the unfiltered suspension and the measured pH values were corrected to 20 or 50 $^{\circ}\text{C}$. No significant modification in the aqueous phase composition is expected within the 30 minutes used to cool down the solutions from 50 $^{\circ}\text{C}$ to ambient temperature, as M-S-H precipitation occurs only very slowly and as no significant differences in the concentrations measured by IC between diluted and not-diluted solutions were observed.

Thermogravimetric analyses (TGA) were done on ground powder ($\sim 20\text{--}30\text{ mg}$) using a heating rate of 20 $^{\circ}\text{C}/\text{min}$ from 30 to 980 $^{\circ}\text{C}$ with a Mettler Toledo TGA/SDTA 8513 instrument. The amount of $\text{Mg}(\text{OH})_2$ (brucite) was quantified from the water weight loss around 400–420 $^{\circ}\text{C}$ using the tangential method [37] and calculated according to the Equation (1):

$$\text{wt. \% brucite}_{\text{dry}} = \frac{\text{water loss (brucite)}}{100 - \text{water loss}_{(30-550^{\circ}\text{C})}} \times \frac{M_{\text{brucite}}}{M_{\text{H}_2\text{O}}} \times 100 \quad (1)$$

Where wt. % $\text{brucite}_{\text{dry}}$ corresponds to the wt.% of brucite for 100 g of dry mass (g/100 g) and the water losses are in wt.%. M_{brucite} is the molar mass of $\text{Mg}(\text{OH})_2$, equal to 58.32 g/mol and $M_{\text{H}_2\text{O}}$ is the molar mass of the water, equal to 18.02 g/mol. The relative error on the brucite content is $\pm 5\text{--}10\%$ [37, 38].

XRD data were collected using a PANalytical X'Pert Pro MPD diffractometer equipped with rotating sample stage in a theta-2theta configuration applying CuK α radiation ($\lambda=1.54$ Å) at 45 mV voltage and 40 mA intensity with steps of 0.03° 2theta and 450.2 s per step with a fixed divergence slit size and an anti-scattering slit on the incident beam of 0.5° and 1° 2theta. The samples were scanned between 5° and 75° 2theta with a X'Celerator detector.

Attenuated total reflectance (ATR) Fourier Transformation-Infrared (FTIR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer by transmittance between 600 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹ on ~ 3 mg of powder.

The ²⁹Si MAS NMR experiments were recorded on a Bruker Avance III NMR spectrometer using a 7 mm CP/MAS probe at 79.5 MHz applying the following parameters: 4500 Hz sample rotation rate, minimum of 3072 scans or more, 90 ° ¹H pulse of 7.5 μ s, 20 s relaxation delays, RF field strength of 33.3 kHz during SPINAL64 proton decoupling. The ²⁹Si chemical shifts NMR spectra were referenced to the Aldrich external sample of tetramethylsilane (TMS) with ²⁹Si a chemical shift at -2.3 ppm. The observed ²⁹Si resonances were analysed using the Qⁿ classification, where a Si tetrahedron is connected to n Si tetrahedra with n varying from 0 to 4. The quantification was performed by non-linear least-square fits using the software “DMFIT” developed by Massiot et al [39]. Silica fume was quantified taking into account the shift at -100.9 ppm ((SiO)₃Si-OH from the surface of the amorphous silica [15, 27]) and the Q⁴ shift at -110 ppm. However, the relaxation time T₁ of amorphous silica can be very long and it could be that the amount of silica fume is slightly underestimated.

The deconvolutions of the signals attributed to C-S-H were done following the procedure outlined in [40], with a constant Lorentzian/Gaussian ratio equal to 0.5 and by keeping constant the ratio between bridging and pairing silicate tetrahedra following the Equation (2):

$$\frac{Q_b^2 + Q_u^2}{Q_p^2} = 0.5 \quad (2)$$

Where Q_b^2 is the bridging silicate tetrahedra with one calcium neighbor in the interlayer, Q_u^2 is the bridging tetrahedra with one H^+ neighbor in the interlayer and finally Q_p^2 is the pairing tetrahedra. The mean chain length (MCL) of the silicate chains in C-S-H was calculated following the Equation (3):

$$MCL = \frac{2(Q^1 + Q_b^2 + Q_u^2 + Q_p^2)}{Q^1} \quad (3)$$

M-S-H deconvolutions were done with the The Q^1 and Q^2 environments were deconvoluted using mainly Lorentzian while the Q^3 environment was deconvoluted with Gaussian following the procedure outlined by [11]. Based on the available M-S-H deconvolutions in literature [11, 15, 16, 28], the Q^2/Q^3 ratio was kept between 0.4 [28] and 1 [11].

The Raman spectra were measured with a Bruker Senterra instrument of 5 cm^{-1} spectral resolution, using a 532 nm laser (20 mW) at room temperature and with $\times 50$ objective lens. The spectral acquisition time was 40 s and 5 spectra were accumulated for each sample in the frequency ranges of 110–1560 cm^{-1} .

After quantification of brucite by TGA, and amorphous silica by ^{29}Si MAS NMR, the composition of the solids was calculated by mass balance including the solution composition based on the IC results. The composition of some solids has been also determined directly by dissolving 20 mg of the solid sample in 10 ml of 0.1 mol/l hydrochloric acid. This was repeated 3 times and the mean values are given.

The pure M-S-H reference samples used for comparison in the present paper were synthesized from MgO and SiO₂ and are fully detailed in [11].

2.3. Thermodynamic modelling

Thermodynamic modelling of the experiments was carried out using the Gibbs free energy minimization program GEMS [41]. GEMS software is a broad-purpose geochemical modelling code which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. The thermodynamic data for aqueous species as well as for SiO₂, brucite and portlandite were taken from the PSI-GEMS thermodynamic database [42], the data for C-S-H (CSHT model) from [43] and the data for the M-S-H were taken from [11]. A summary of the data used is given in Table 2.

Table 2 : Standard thermodynamic properties at 25 °C.

	*	LogK _{S0} ^a	Δ _f G° [kJ/mol]	V° [cm ³ /mol]	density [g/cm ³]
Brucite [42]	MH	-11.16	-832.23	24.6	2.37
M-S-H [11]					
Mg/Si = 0.78	M _{0.78} SH _{1.48}	-14.59	-1682.2	57	2.1 ^b
Mg/Si=1.30	M _{1.3} SH _{1.80}	-21.44	-2073.5	71	2.0 ^b
Portlandite [42]	CH	-5.2	-897.01	33.1	2.24
C-S-H [43]					
Ca/Si = 0.67	C _{0.67} SH _{1.60}	-10.24	-1707.3	56.6	2.25
Ca/Si = 1.0	C _{1.00} SH _{2.00}	-13.41	-2014.5	63.4	2.4
Ca/Si = 1.5	C _{1.5} SH _{2.50}	-16.61	-2466.0	80.6	2.35
SiO_{2,am} [42]	S	-2.71	-848.9	29	2.07

*cement short hand notation: C= CaO; H =H₂O; M = MgO; S = SiO₂.

^aAll solubility products refer to the solubility with respect to the species Mg²⁺, Ca²⁺, SiO₂⁰, OH⁻, or H₂O.

^b experimental data from [44]

3. RESULTS AND DISCUSSION

3.1. C-S-H + MgCl₂

The addition of MgCl₂ to pre-synthesized C-S-H lowers the pH values (as discussed below) and destabilizes the C-S-H. The TGA curves of M-S-H, C-S-H and C-S-H plus MgCl₂ and the derivative weight losses are shown in Figure 1. The first water loss region between 30 °C and 250 °C is characteristic for both C-S-H [17, 37, 45] and M-S-H [11, 15, 37, 46] and has been related to poorly bound water on the surface or in the interlayer. In the case of pure C-S-H, the second water loss between 250 °C and 800 °C is related to the calcium or silanol hydroxyl group [37, 45]. In M-S-H this second water loss corresponds to magnesium and silanol hydroxyl group in M-S-H [11, 15, 16, 37, 46], is more distinct and centered at 570 °C (Figure 1) as already reported by [35]. The TGA data indicate the presence of hydrates (C-S-H or M-S-H) in the samples, while no brucite (water loss in a narrow range at around 400 °C [11, 15, 16, 46]), nor portlandite (water loss in a narrow range at around 550 °C [37]) are detected, indicating their absence. Traces of calcite (< 1 wt.%) are observed (weight loss at around 750-800 °C [37]). The presence of M-S-H is clearly detected in the sample with the maximum of MgCl₂ addition, while at lower MgCl₂ additions mainly C-S-H and only small quantities of M-S-H seem to be present.

Figure 1: Thermogravimetric analysis (TGA) of C-S-H samples where $MgCl_2$ has been added: $0.05MgCl_2$, $0.26MgCl_2$ and $0.87MgCl_2$ (solid lines) after 1 year of curing at $20^\circ C$, TGA of M-S-H 0.8 and C-S-H 0.8 (dashed lines) are shown as references.

The XRD measurements are shown in Figure 2. The patterns of pure C-S-H and M-S-H show broad reflections related to the nanosize of the particles [16, 47-49]. The characteristic reflections of C-S-H are located at 16.3 , 29.2 , 32.0 and $43.0^\circ 2\theta$ [35] as detailed in Figure 2. With the addition of $MgCl_2$, the reflections of C-S-H decrease while M-S-H is observed by the additional broad reflections at 19.7 and $35.0^\circ 2\theta$ [15] in the samples $0.26MgCl_2$ and $0.87MgCl_2$. Peak shifts relative to pure phases, i.e. M-S-H or C-S-H, are not observed confirming the presence of C-S-H and/or M-S-H as separate phases, as previously observed by a few authors [34, 35].

Figure 2: XRD patterns of C-S-H samples where MgCl_2 has been added: 0.05MgCl_2 , 0.26MgCl_2 and 0.87MgCl_2 (solid lines) after 1 year of curing at 20°C , patterns of M-S-H 0.8 and C-S-H 0.8 (dashed lines) shown as references, C= calcite. The area of the main reflections of C-S-H and M-S-H are shaded (+ = C-S-H, * = M-S-H).

The FTIR spectra of these samples are shown in Figure 3. The characteristic bands of C-S-H with a Ca/Si equal to 0.8 are centered at $\sim 950\text{-}980\text{ cm}^{-1}$ and at $800\text{-}825\text{ cm}^{-1}$ and are assigned to Si–O stretching vibrations of the Q^2 and Q^1 respectively [50], while the bands centred at $\sim 990\text{-}1000\text{ cm}^{-1}$ and $\sim 870\text{-}880\text{ cm}^{-1}$ correspond to the Q^3 and Q^2 of the M-S-H [11, 15] as detailed in Figure 3. The Raman bands characteristic of C-S-H [51-54] are given in Figure 4. Raman bands of M-S-H [15, 35] attributed by [15] by comparison with spectra of talc [54] and antigorite [55] are detailed in Figure 4 as well. The Si-O-Si bending of M-S-H is at a higher wavenumber (675 cm^{-1}) than the one of C-S-H (660 cm^{-1}). A broadening of the C-S-H bands due to the appearance of M-S-H (675 cm^{-1}) is already observed at the smallest MgCl_2 addition. At higher

MgCl₂ additions, a clear band at 1000 cm⁻¹ is visible. Similar to the XRD data, FTIR and Raman measurements indicate the absence of any significant amount of C-S-H in the 0.87MgCl₂ sample.

Figure 3: FTIR spectra of C-S-H samples where MgCl₂ has been added: 0.05MgCl₂, 0.26 MgCl₂ and 0.87 MgCl₂ after 1 year of curing at 20 °C, spectra of M-S-H 0.8 and C-S-H 0.8 shown as references (the vertical line indicates the shoulder due to the Q³ silicate sites in M-S-H).

Figure 4: Raman spectra of C-S-H samples where $MgCl_2$ has been added: $0.05MgCl_2$, $0.26 MgCl_2$ and $0.87 MgCl_2$, C-S-H and M-S-H, after 1 year of curing at $20^\circ C$, assignments of the band according to [31-34] for C-S-H and [10, 21] for M-S-H.

The ^{29}Si MAS NMR spectra of these samples are shown in Figure 5. The structure of C-S-H is well investigated [26, 36, 56-59]: the characteristic shifts at ≈ -79.7 , -82.9 , -85.5 and -88.4 ppm, which correspond to Q^1 (end of chains), Q^2_b (bridging position), Q^2_p (pairing position) and Q^2_u (bridging position with binding to H^+ [36, 60, 61]) of the silicate tetrahedra in C-S-H are visible in Figure 5. ^{29}Si MAS NMR studies have shown that at high Ca/Si, no cross linked silicate groups (Q^3) exist in pure C-S-H, while very small quantities of Q^3 with a chemical shift between -95 and -97 ppm [40, 60] have been reported for C-S-H with low Ca/Si. Our C-S-H reference sample contains approximately 4 % (quantification detailed below) of the total silica in a broad

signal at -93.5 ppm. The presence of Q^3 signals in higher quantities between -92 and -97 ppm indicates the formation of M-S-H [11, 13, 15, 16, 27, 28] even at very low $MgCl_2$ addition (0.05 $MgCl_2$) (Figure 5). At higher $MgCl_2$ addition the intensity of the chemical shifts of the C-S-H decreases while the amount of Q^3 tetrahedra sites, indicating the presence of M-S-H, increases. Although the peaks decrease, the relative intensity and the position of the chemical shifts of C-S-H, when present, do not change significantly, indicating that the polymerization of the silicates in the C-S-H remains constant. The 0.87 $MgCl_2$ sample spectrum, similar to M-S-H spectra ($Mg/Si=0.80$ and 1.0), indicates no or very little C-S-H. However the shift of the Q^2 signal to less negative values could indicate the persistence of some C-S-H in the 0.87 $MgCl_2$ sample.

The deconvolutions of the ^{29}Si MAS NMR spectra were done following the procedure outlined in [11, 15, 17] and are presented in Table 3. The deconvolutions of the samples with additional $MgCl_2$ are associated with considerable ($\pm 10\%$) error due to the overlapping of the chemical shifts of ^{29}Si for M-S-H and C-S-H. The Q^3 tetrahedra sites have been attributed to M-S-H with the exception of the 3-4 % at -93.5 ppm which was already present in pure C-S-H. The attribution of the Q^2 tetrahedra signal of M-S-H has been made with keeping the ratio Q^2/Q^3 in M-S-H low (0.4-0.6), respecting Equation (2) and allowing a high MCL (>20) in the structure of C-S-H.

Deconvolutions of the ^{29}Si MAS NMR data indicate that approximately 7 % $\pm$ 3 % is attributed to silica in M-S-H in the sample 0.05 $MgCl_2$, 44 % $\pm$ 7 % in the sample 0.26 $MgCl_2$ while 87 % $\pm$ 11 % and 53 % $\pm$ 8 % are attributed to C-S-H in the samples 0.05 $MgCl_2$ and 0.26 $MgCl_2$. The silica content in C-S-H decreases as M-S-H is formed. All the silica (98 %) has been attributed to M-S-H in the sample 0.87 $MgCl_2$ although the Q^2 signal is broader than in pure M-S-H. The Ca/Si in C-S-H, when present, have been estimated from the MCL [20] and is detailed in Table 3.

Figure 5: ^{29}Si MAS NMR spectra of C-S-H samples where MgCl_2 has been added: 0.05MgCl_2 , 0.26 MgCl_2 and 0.87 MgCl_2 after 1 year of curing at 20°C , (C-S-H and M-S-H shown as references).

Table 3 : Peak shifts and relative intensities (quantifications) of different silicon shifts obtained from the deconvolution of the ^{29}Si MAS NMR spectra for C-S-H samples where MgCl_2 has been added: 0.05MgCl_2 , 0.26 MgCl_2 and 0.87 MgCl_2 after 1 year of curing at 20°C (C-S-H and M-S-H shown as references) ($\delta^{29}\text{Si}$ in $\text{ppm} \pm 0.3 \text{ ppm}$).

$\delta^{29}\text{Si}$ (C-S-H)							$\delta^{29}\text{Si}$ (M-S-H)							Am. silica	Total in	
Q ¹	Q ^{2b}	Q ^{2p}	Q ^{2u}	MCL	Ca/Si	Q ³	Q ¹	Q ²	Q ^{3a}	Q ^{3b}	Q ^{3c}		Q ³ (SiO ₂)	C-S-H	M-S-H	
-79.6	-82.8	-85.8	-88.2			-93.5	-78.3	-85.5	-92.7	-94.7	-96.7	Q ² /Q ³	-100.9			
														% of silica		
C-S-H 0.8	8	22	59	7	25	4	-	-	-	-	-	-	-	96	-	
0.05 MgCl ₂	8	25	53	2	22	0.77	1	2	1	2	1	0.6	1	87	7	
0.26 MgCl ₂	5	12	32	3	21	0.78	2	11	14	8	9	0.4	1	53	44	
0.87 MgCl ₂	-	-	-	-	-	-	2	42	22	20	11	0.8	2	-	98	
M-S-H 0.8	-	-	-	-	-	-	2	34	23	8	27	0.6	6	-	94	
M-S-H 1.0	-	-	-	-	-	-	5	43	17	9	26	0.8	-	-	100	

Quantification error $\approx \pm 10\%$ of absolute amounts of (%Si) $+2.5\%$

The pH values and measured concentrations of the solution for samples cured for 3 months and 1 year at 20 °C are plotted in Figure 6 and detailed with the additional results at 50°C in Table 4. The addition of MgCl_2 to C-S-H decreases the pH value from 10.5 in the solution equilibrated with C-S-H only ($\text{Ca/Si} = 0.8$) to pH 7.7 at the maximum MgCl_2 addition (1.34 MgCl_2 sample). The calcium concentrations increase with the addition of MgCl_2 up to 130 mM [Ca] at 20°C and up to 140 mM [Ca] at 50°C and reach a plateau at $\text{Mg/Si} \geq 0.87$. Thus 93 to 100 % of the initially present calcium (Table 1) is in the solution indicating the dissolution of C-S-H and possibly the uptake of some calcium in the M-S-H. This is in agreement with the ^{29}Si MAS NMR results in Figure 5, where only M-S-H was clearly observed. The destabilization of C-S-H at pH values below 9.5 is in agreement with studies on the stability of C-S-H upon leaching [62-65]. The silicon concentrations, however, remain below the concentrations in equilibrium with respect to amorphous silica (1-2 mM), which indicates the formation of another silica containing solid, i.e. M-S-H.

Figure 6: Measured silicon, magnesium, and calcium as a function of pH (diamond: 3 months, circles: 12 months) and calculated solubility curves of C-S-H and M-S-H using the solid-solution's models. Solubility's of brucite and amorphous SiO_2 are indicated in grey.

The magnesium concentrations are very low in the case of low MgCl_2 additions (samples 0.05MgCl_2 up to 0.26MgCl_2) at the pH values ≥ 9.7 , indicating that the magnesium initially added reacts directly with the amorphous silica from the dissolution of C-S-H, consistent with the observation of M-S-H by ^{29}Si MAS NMR. Only for relatively high MgCl_2 additions (0.87MgCl_2 , 1.33MgCl_2) at pH values lower than 8.3, higher magnesium concentrations are observed. The magnesium concentrations increase with the MgCl_2 addition up to ≈ 80 mM at pH 7.7, i.e. up to

one third of the total magnesium present (see Table 1). The strong increase of magnesium could indicate that M-S-H is expected to be not stable below a pH of ~ 7.5 . The measured concentrations show little variations between 3 and 12 months indicating that the formation of M-S-H is relatively fast under these lower pH conditions, while the formation of M-S-H from MgO and SiO₂ needs several months to years to reach equilibrium [9-12, 15].

Table 4: Summary of the presence of brucite and unreacted silica in the solid composition, the measured dissolved concentrations, pH values in the solutions in equilibrium with the C-S-H and the magnesium additions samples at 20°C and 50°C after 3 months and 1 year. M-S-H samples from [11] have been added as references (bold samples indicate that the solid has been analyzed in detail).

			Mg/Si	time [months]	brucite ^a	unreacted silica ^b	[OH] ^c	[Ca]	[Mg] mM	[Si]	[Cl]	pH	
20°C	C-S-H	Ca/Si=0.8	references	3			0.239	0.91	---	2.16	0.18	10.5	
				12			0.136	1.04	---	2.19	0.01	10.3	
	M-S-H	Mg/Si=0.8		3	✓	✓	0.028	---	0.28	1.54	0.02	9.6	
				12		✓	0.0022	---	0.33	1.36	0.03	8.5	
	50°C	C-S-H		Ca/Si=0.8	3			0.114	0.96	---	2.36	0.09	9.5
					12			0.025	1.23	---	4.61	0.01	9.0
M-S-H		Mg/Si=0.8	3		✓	0.0028	---	0.22	2.81	0.02	8.3		
			12		✓	0.0014	---	0.10	2.57	0.03	8.1		
20°C	C-S-H+MgCl ₂	0.05	3		<i>n.d.</i>	0.076	8.23	0.037	0.90	18.61	10.0		
			12		✓	0.084	8.48	0.002	0.84	19.28	10.0		
		0.11	3		<i>n.d.</i>	0.059	16.38	0.078	0.82	37.77	9.9		
			12		<i>n.d.</i>	0.066	17.12	0.001	0.64	38.91	9.9		
		0.15	3		<i>n.d.</i>	0.051	21.09	0.092	0.77	48.80	9.8		
			12		<i>n.d.</i>	0.060	22.94	0.003	0.59	52.65	9.9		
		0.26	3		<i>n.d.</i>	0.039	38.53	0.064	0.61	91.72	9.6		
			12		✓	0.051	40.36	0.006	0.52	96.62	9.8		
		0.87	3		<i>n.d.</i>	0.0019	120.83	10.00	0.26	319.00	8.3		
			12		✓	0.0014	117.72	9.44	0.29	305.34	8.2		
		1.34	3		<i>n.d.</i>	0.0006	125.32	73.98	0.29	482.65	7.8		
			12		<i>n.d.</i>	0.0005	128.31	76.32	0.30	535.93	7.7		
		50°C	C-S-H+MgCl ₂	0.03	3		<i>n.d.</i>	0.073	8.76	0.002	0.72	17.34	9.4
					12		<i>n.d.</i>	0.058	8.83	0.001	0.79	15.24	9.3
				0.11	3		<i>n.d.</i>	0.061	18.21	0.001	0.68	35.39	9.3
					12		<i>n.d.</i>	0.051	17.24	0.001	0.68	32.27	9.2
0.15				3		<i>n.d.</i>	0.055	22.78	0.001	0.63	45.54	9.2	
				12		<i>n.d.</i>	0.047	23.51	0.001	0.70	44.48	9.2	
0.26				3		<i>n.d.</i>	0.044	41.88	0.002	0.63	86.65	9.2	
				12		<i>n.d.</i>	0.038	45.46	0.001	0.70	84.20	9.1	

		0.87	3		<i>n.d.</i>	0.0009	125.40	7.03	0.61	288.18	7.8
			12		<i>n.d.</i>	0.0007	135.72	10.67	0.68	328.61	7.7
		1.34	3		<i>n.d.</i>	0.0003	134.32	77.00	0.66	433.25	7.4
			12		<i>n.d.</i>	0.0003	145.38	84.57	0.64	466.22	7.4
20°C	C-S-H+MgO	0.04	3	✓	<i>n.d.</i>	0.324	0.79	0.0005	1.31	0.17	10.7
			12	✓		0.243	0.84	0.0001	1.47	0.01	10.5
		0.23	3	✓	<i>n.d.</i>	2.176	1.54	0.0002	0.17	0.1	11.5
			12	✓	✓	1.066	0.97	0.0001	0.44	0.01	11.2
		0.59	3	✓	<i>n.d.</i>	4.427	2.85	0.0001	0.07	0.09	11.8
			12	✓		3.614	2.30	0.0001	0.09	0.01	11.7
		0.86	3	✓	<i>n.d.</i>	3.780	2.21	0.0002	0.08	0.01	11.7
			12	✓	<i>n.d.</i>	3.790	2.31	0.0001	0.07	0.01	11.7
		0.04	3	✓	<i>n.d.</i>	0.298	0.79	0.0002	1.15	0.16	9.9
			12	✓	<i>n.d.</i>	0.276	0.84	0.0001	1.05	0.01	9.8
		0.23	3	✓	<i>n.d.</i>	2.587	1.84	0.0002	0.11	0.46	10.6
			12	✓	<i>n.d.</i>	1.619	1.43	0.0001	0.14	0.01	10.4
50°C		0.59	3	✓	<i>n.d.</i>	4.763	3.17	0.0002	0.07	0.14	10.8
			12	✓	<i>n.d.</i>	4.127	2.96	0.0001	0.06	0.01	10.8
		0.86	3	✓	<i>n.d.</i>	5.844	3.68	0.0001	0.06	0.49	10.9
			12	✓	<i>n.d.</i>	5.217	3.48	0.0001	0.05	0.01	10.8

^afrom TGA,

^bfrom ²⁹Si MAS NMR,

^cHydroxide concentrations calculated from the measured pH values

Magnesium's detection limit: 0.00001mM

To investigate whether any calcium remained in the M-S-H, three of the samples have been dissolved in 0.1 M HCl. The results in Table 5 show a Ca/Mg ratio in the M-S-H of only 0.006 ± 0.01 for the sample with Mg/Si = 0.87, thus confirming the complete destabilization of C-S-H and pointing towards no or a very low uptake of calcium within the M-S-H structure.

The magnesium measurements summarized in Table 5 agree well with the total amounts present as given in Table 1, which indicates a good accuracy of the measured aqueous concentrations. The measured calcium content in the solid together with the liquid phase is with 13.1 ± 1.5 to 14.5 ± 1.6 mmol somewhat lower than the 15.2 mmol of calcium initially used, which indicates either an underestimation of the measured calcium concentrations, the presence of less calcium in the C-S-H than expected or the removal of calcium ions loosely associated in the diffusive layer

of M-S-H and C-S-H during washing with isopropanol and water. The slight decrease of the amount of measured total calcium in the samples with very high dissolved calcium (sample 0.87MgCl₂), could point towards a removal of calcium during the washing process and thus to the presence of some calcium at the surface of M-S-H even if effect of errors during the preparation of the samples, filtration and IC measurements cannot be excluded.

The Mg/Si and Ca/Si in M-S-H and C-S-H have been calculated from the measured Ca and Mg in the solid part taking into account only the amount of silicate associated with M-S-H or C-S-H from the ²⁹Si MAS NMR analysis. For the 0.26MgCl₂ sample Ca/Si (0.5±0.3) and Mg/Si (0.6 ± 0.2) ratios have been determined. These ratios are in agreement with the 0.67 usually reported for C-S-H and the 0.67-0.8 [10-13, 15] for M-S-H.

Table 5: Composition of the solids from dissolution, of the aqueous phase from filtration, the total experimentally determined and the experimentally determined ratios Mg/Si in M-S-H and Ca/Si in C-S-H from mass balance and ²⁹Si MAS NMR deconvolutions.

Initial Mg/Si	In the solid (from diss.)		+	In the liquid (IC)			=	total _{experimental} (mass balance) ^a		% Si ^b in M-S-H	Mg/Si	Ca/Si
	mmol			mmol				mmol				
	Ca	Mg		Ca	Mg	Si		Ca	Mg	(NMR)		
0.05	13.6±1.5	0.9±0.2		0.9±0.1	~0 ^c	0.1±0.01		14.5±1.6	0.9±0.2	7	0.7±0.5	0.8±0.2
0.26	9.6±0.9	5.3±0.5		4.4±0.5	~0 ^c	0.1±0.01		14.0±1.4	5.3±0.5	44	0.6±0.2	0.5±0.3
0.87	0.1±0.1	15.4±1.9		13.0±1.4	1.0±0.1	~0 ^c		13.1 ±1.5	16.4±2.0	98	0.8±0.2	0.005

^a solid part + liquid part

^b error detailed in the text

^c detected by IC (cf. Table 4) but below 0.01mmol and neglected in the calculations

In summary, the different techniques indicate the destabilization of C-S-H and the formation of M-S-H upon the addition of MgCl₂ even if only little MgCl₂ (0.05MgCl₂) is added. C-S-H was observed to be unstable at pH values lower than 9.5 and M-S-H is expected to be destabilized at pH lower than 7.5.

3.1. C-S-H + MgO

The addition of MgO to C-S-H increases the pH values, in contrast to the MgCl_2 additions. The XRD patterns and the TGA curves of the C-S-H samples with the different additions, 0.04MgO, 0.23MgO and 0.59MgO (cf. Table 1), are shown in Figure 7 and Figure 8 respectively. Independently of the MgO additions, C-S-H is clearly observed by XRD and TGA in all the samples while no clear XRD reflections of M-S-H can be observed in contrast to the samples where MgCl_2 had been added, as discussed previously. TGA data could indicate the formation of small quantities of M-S-H as visible by the minor water loss between 400-700°C.

Figure 7: XRD patterns of C-S-H samples where MgO has been added: 0.04MgO, 0.23MgO and 0.59MgO after 1 year of curing at 20°C, patterns of M-S-H 0.8 and C-S-H 0.8 shown as references (B=brucite ($\text{Mg}(\text{OH})_2$), +=C-S-H, *= M-S-H).

Figure 8: Thermogravimetric analysis of C-S-H samples where MgO has been added: 0.04MgO, 0.23MgO and 0.59MgO after 1 year of curing at 20°C, patterns of M-S-H 0.8 and C-S-H 0.8 shown as references. B=brucite ($Mg(OH)_2$).

^{29}Si MAS NMR spectra are shown in Figure 9 and the deconvolution following the procedure outlined in [11, 15, 17] is given in Table 6. The presence of MgO and the increase of pH (see below) results in shorter silicate chains in the C-S-H as visible in the higher amount of the Q^1 tetrahedra site attributed to C-S-H at -79.6 ppm. This is in accordance with [17], where a shortening of the silicate chains of pure C-S-H has been observed when the pH is increasing. The increase of the Q^1 signal points towards an increase of Ca/Si in C-S-H [20, 36], which agrees with the calculated Ca/Si in C-S-H in Table 6.

In contrast to the XRD and TGA data, the ^{29}Si MAS NMR data indicate clearly the formation of a small amount of M-S-H with the chemical shift between -92 and -97 ppm, characteristic of M-S-H's Q^3 tetrahedral sites, in addition of the signals characteristic of C-S-H. The quantifications based on the deconvolutions of the Q^3 bands give $9 \pm 3 \%$, $14 \pm 3.5 \%$ and $19 \pm 4 \%$ of the silica (Table 6) attributed to M-S-H in the 3 samples.

The total intensity of the sites attributed to C-S-H decreases slightly but remains high: 80 % of the silica is attributed to C-S-H even for the highest addition. The formation of some M-S-H is consistent with the observed increase of the Ca/Si in the remaining C-S-H as some silica is used to form M-S-H.

The FTIR and Raman spectra (Figure 10 and Figure 11) of all samples confirm the ^{29}Si MAS NMR results; the samples are mainly composed of C-S-H as the spectra are similar to the pure C-S-H spectra. The FTIR band (Figure 10) at $\sim 970 \text{ cm}^{-1}$, characteristic of C-S-H, develops a small shoulder at 1045 cm^{-1} if MgO is added confirming the precipitation of a small amount of M-S-H as does the additional presence of a band at 870 cm^{-1} in the Raman spectra, characteristic of Si-O symmetrical stretching of Q^2 tetrahedra site in M-S-H.

Figure 9: ^{29}Si MAS NMR spectra of C-S-H samples where MgO has been added: 0.04MgO, 0.23MgO and 0.59MgO after 1 year of curing at 20 °C, (C-S-H and M-S-H shown as references).

Table 6: Relative intensities (% $\pm$ 2.5 %) of different silicon shifts obtained from the deconvolution of the ^{29}Si MAS NMR spectra for the samples 0.04MgO, 0.23MgO and 0.59MgO after 1 year of curing at 20 °C (C-S-H and M-S-H shown as references) ($\delta^{29}\text{Si}$ in ppm $\pm$ 0.3 ppm).

$\delta^{29}\text{Si}$ (C-S-H)							$\delta^{29}\text{Si}$ (M-S-H)							Am. silica	Total	
Q ¹	Q ² b	Q ² p	Q ² u	MCL	Ca/Si	Q ³	Q ¹	Q ²	Q ³ a	Q ³ b	Q ³ c		Q ³ (SiO ₂)	C-S-H	M-S-H	
-79.6	-82.8	-85.8	-88.2			-93.5	-78.3	-85.5	-92.7	-94.7	-96.7	Q ² /Q ³	-100.9	% of silica		
C-S-H 0.8	8	22	59	7	25	4	-	-	-	-	-	-	-	96	-	
0.04 MgO	14	20	51	5	13	0.85	3	-	4	3	0	2	0.9	89	9	
0.23 MgO	18	18	43	5	9	0.90	2	-	6	2	2	3	0.9	83	14	
0.59 MgO	26	18	36	0	6	1.00	1	-	9	5	2	2	0.9	80	19	
M-S-H 0.8	-	-	-	-	-	-	2	34	23	8	27	0.6	6	-	94	
M-S-H 1.2	-	-	-	-	-	-	6	47	14	12	21	1.0	-	-	100	

In addition, the presence of brucite ($\text{Mg}(\text{OH})_2$) is observed by XRD and TGA with the characteristic reflection peaks at 18.6, 32.7, 38.0° 2theta (Figure 7) and the water loss located at ~ 400°C in the TGA curves (Figure 8). Brucite is also visible by FTIR with a band at 3692 cm^{-1} [15, 66] in all the samples (data not shown). The amount of brucite quantified from TGA is compiled in Table 7. This amount is lower than the theoretical maximum brucite content and corresponds to 31, 41 and 74 % $\pm$ 20 % of the total magnesium content in the different samples, confirming the presence of magnesium bound in M-S-H. Table 7 also shows the quantification of brucite by TGA in the samples cured at 50 °C. In all cases, less brucite is present and more magnesium is found bound in M-S-H at 50°C than at 20 °C. This difference is related to the very slow reaction kinetics of brucite dissolution and M-S-H formation at 20 °C, while the reaction kinetics are faster at higher temperature, as discussed in more detail in [11].

Table 7: Theoretical maximum amount of brucite calculated from total amount of magnesium added, experimental measured brucite content, and magnesium distribution between brucite and M-S-H.

Temperature	20°C			50°C		
Mg/Si	0.04	0.23	0.59	0.04	0.23	0.59
Theo. max $\text{Mg}(\text{OH})_2^a$ (g/100 g)	3.9	17.1	30.3	2.9	14	33
Exp. $\text{Mg}(\text{OH})_2^b$ (g/100 g)	1.2	7	22.5	0.8	3.5	19.2
% of Mg in brucite	31	41	74	28	25	58
% of Mg in M-S-H	69	59	26	72	75	42
Mg in M-S-H (mmol)	0.5	2.7	2.9	0.4	2.9	5.6

^a Theo. max % of $\text{Mg}(\text{OH})_2$ is the amount of brucite formed based on the initial amount of MgO added considering the total mass of solid, the initial MgO is obtained by dissolution

^b calculated from TGA

The presence of only a small quantity of M-S-H is observed by FTIR, Raman and ^{29}Si MAS NMR for C-S-H if MgO is added, while 30 to 70 % of magnesium is present as brucite.

Figure 10: FTIR spectra of C-S-H samples where MgO has been added: C-S-H +0.04MgO, C-S-H +0.23MgO and C-S-H +0.59MgO after 1 year of curing at 20°C, spectra of M-S-H 0.8 and C-S-H 0.8 shown as references (the vertical line indicates the shoulder due to the Q³ silicate sites in M-S-H).

Figure 11: Raman spectra of C-S-H samples where MgO has been added: C-S-H +0.04MgO, C-S-H +0.23MgO and C-S-H +0.59MgO after 1 year of curing at 20°C, (C-S-H and M-S-H shown as references), B=brucite ($\text{Mg}(\text{OH})_2$).

The experimentally determined Mg/Si and Ca/Si in M-S-H and C-S-H have been calculated from the quantification of the brucite by TGA (Table 7), the quantification of the silica attributed to C-S-H or M-S-H (^{29}Si MAS NMR, Table 6) and taking into account the dissolved ions in solution and are summarized in Table 8. The increase of Ca/Si in the C-S-H corresponds to the experimental observations with the decrease of MCL in C-S-H. A Mg/Si of ≈ 0.9 is observed. However, the data derived from mass balance calculations are associated with a high experimental error.

Table 8: Initial composition of the samples C-S-H +0.04MgO, C-S-H +0.23MgO and C-S-H +0.59MgO in mmol, amount of Ca, Si and Mg attributed to the solution at equilibrium, % of silica attributed to M-S-H and C-S-H, experimental % of magnesium attributed to M-S-H, and experimentally determined Mg/Si and Ca/Si in M-S-H and C-S-H.

initial Mg/Si	initial ^a mmol			liquid part (from IC) mmol			% Si (NMR) in		% Mg (TGA) in	Mg/Si	Ca/Si
	Ca ^a	Si ^a	Mg ^a	Ca	Si	Mg	M-S-H	C-S-H	M-S-H		
0.04	15.2	19.1	0.7	0.1	0.2	~0 ^b	9	89	69	-	0.9 ± 0.1
0.23	15.2	19.1	4.5	0.1	0.1	~0 ^b	15	84	59	0.9 ± 0.5	1.0 ± 0.1
0.59	15.2	19.1	11.2	0.3	~0 ^b	~0 ^b	19	77	26	0.8 ± 0.5	1.0 ± 0.1

^a from Table 1,

^b detected by IC (cf. Table 4) but ≤ 0.01 mmol and not taking account in the calculations

The addition of MgO to pure water leads to the formation of brucite and a pH value of 10.5. Interestingly, the addition of MgO to C-S-H increases the pH well above the pH 10.5 observed for pure C-S-H (Ca/Si = 0.8) (Table 4) and the solutions are clearly undersaturated with respect to brucite (Figure 6). This increase in pH and hydroxide concentrations is related to the release of calcium from C-S-H at higher Ca/Si as visible in the increased calcium concentrations (Table 4 and Figure 6). While the calcium and hydroxide concentrations increase, the silicon concentrations are lowered (Figure 6) in agreement with the changes expected for pure C-S-H phase if the Ca/Si of C-S-H is increased from 0.8 to 1.0 [17, 20, 22]. This confirms that the addition of MgO to C-S-H leads to the formation of C-S-H with a higher Ca/Si as indicated in Table 8 in agreement with the higher fraction of Q¹ silicate tetrahedra which has been observed by ²⁹Si MAS NMR. The magnesium concentrations remain clearly below the solubility of brucite as shown in Figure 6, although brucite is still present. This is due to the very slow dissolution of brucite when silicon and M-S-H are present, as discussed in details in [11].

Comparable calcium and silicon concentrations have been measured after 3 months and 1 year, while the magnesium concentrations decrease with time. At 50°C, similar concentrations were measured as at 20°C as detailed in Table 4, in agreement with the observations in pure M-S-H

[11] and in pure C-S-H [67, 68]. However, less brucite is present at 50°C where the dissolution of brucite, even in the presence of silicon, proceeds faster than at 20°C as in pure M-S-H [11].

4. Comparison with thermodynamic modelling

The measured calcium, magnesium and silicon concentrations and the solubility curves calculated by GEMS [41] at 20°C are plotted as a function of pH in Figure 6. The results of thermodynamic modelling, using the thermodynamic data for C-S-H and M-S-H as detailed in Table 2, show in general a good agreement with the changes observed. The modelling predicts the formation of C-S-H and M-S-H for pH values between 9.6 and 12. At lower pH values (7.8 to 9.6) only M-S-H is predicted. Figure 12 shows that the calculated Mg/Si and Ca/Si decrease if MgCl_2 is added to the C-S-H and increase if MgO is added to C-S-H. The trends compare well with the experimentally determined Mg/Si and Ca/Si from mass balance (Table 6 & Table 9) except the Mg/Si at pH values above 10.5. The Ca/Si in C-S-H estimated from the MCL (Table 3 & Table 6) shows in all cases comparable trends.

The MgCl_2 additions lower the pH values from above 10 to 8 as the magnesium precipitates as M-S-H while the chloride ions remain in solution. The addition of low quantities of MgCl_2 led to formation of M-S-H while the Ca/Si in C-S-H is lowered. Higher additions lowered the pH below 9.5 which resulted in the destabilization of C-S-H as shown in Figure 12. The modelled decrease of both Ca/Si and Mg/Si in the C-S-H and M-S-H is in the same range as the experimentally determined atomic ratios (Table 5, Figure 12).

Also the modelled effect of MgO addition to C-S-H (Figure 6 and Figure 12) fits well to the measured calcium and silicon concentrations and to the increase of the Ca/Si (Table 8 and Figure 12) in C-S-H. The formation of M-S-H is predicted, which agrees with the very low magnesium

concentrations. No brucite formation is predicted up to pH 12, although brucite has been observed experimentally. The strong under saturation of the solution with respect to brucite visible in Figure 6 indicates a kinetic hindrance of brucite dissolution in the presence of dissolved silicon, which has been observed also in M-S-H systems if brucite is present [9, 10, 12], which can be explained by the partial reaction of brucite. It can be expected that, after longer reaction times or higher temperature, higher Mg/Si would be reached as indicated by the presence of less brucite at 50 °C.

Figure 12: Evolution of atomic ratios calculated by GEMS and comparison with the ratios obtained experimentally (from MCL (^{29}Si MAS NMR, Table 3 & Table 7), and from MB, mass balance (Table 5 & Table 8)).

5. Conclusions

It has been observed experimentally that low Ca/Si C-S-H is stable in the pH range 9.6 to 11.5. Lowering the pH due to the addition of low quantities of MgCl_2 leads to a decrease of the Ca/Si in C-S-H and to the formation of M-S-H. At pH values below 9.6, C-S-H is destabilized while M-S-H remains stable down to pH values ~ 7.5 . The M-S-H formed from the dissolution of C-S-H and MgCl_2 is comparable to M-S-H prepared from MgO and SiO_2 [10, 11, 13, 15].

Increasing the pH values from 10 to 11.5 by the addition of MgO leads to an increase of the Ca/Si ratio in C-S-H, i.e. to shorter silicate chains, higher calcium concentrations and lower silicon concentrations. M-S-H formation is observed up to a pH of 11.5. Experimentally, the persistence of some brucite is observed as the dissolution of brucite is very slow in the presence of silicon while modelling predicts only the presence of M-S-H which is thermodynamically more stable. It is shown that M-S-H is stable in the pH range 7.5 to 12. A small incorporation of calcium in M-S-H seems possible, although it could not be proven and further investigations are needed.

The present paper has demonstrated that C-S-H can be destabilized in the presence of magnesium in the pH range 7.5 to 12. The destabilization is fast at pH values below 10 and proceeds very slowly at pH values above 10. This fast kinetic at lower pH values might explain why M-S-H has been observed clearly after 2 and 5 years at the interface between clays and “low pH cements”, where pH values ranges from 10 to 12 [4-6], but not at the interface between clays and Portland cements [1-3], where pH values above 13 are present [69]. In the long-term, however, M-S-H could be expected to form also at the interface with Portland cement, as M-S-H has been observed in both Portland cement and in blended concretes exposed for long times to seawater, which also contains significant quantities of magnesium [70].

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