



HAL
open science

Magnesium and calcium silicate hydrates, Part I: Investigation of the possible magnesium incorporation in calcium silicate hydrate (C-S-H) and of the calcium in magnesium silicate hydrate (M-S-H)

Ellina Bernard, Barbara Lothenbach, Céline Cau-Dit-Coumes, Christophe Chlique, Alexandre Dauzeres, Isabelle Pochard

► To cite this version:

Ellina Bernard, Barbara Lothenbach, Céline Cau-Dit-Coumes, Christophe Chlique, Alexandre Dauzeres, et al.. Magnesium and calcium silicate hydrates, Part I: Investigation of the possible magnesium incorporation in calcium silicate hydrate (C-S-H) and of the calcium in magnesium silicate hydrate (M-S-H). *Applied Geochemistry*, 2018, 89, pp.229-242. 10.1016/j.apgeochem.2017.12.005 . hal-02021043

HAL Id: hal-02021043

<https://hal.science/hal-02021043>

Submitted on 19 Mar 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Accepted Manuscript



Magnesium and calcium silicate hydrates, part I: Investigation of the possible magnesium incorporation in calcium silicate hydrate (C-S-H) and of the calcium in magnesium silicate hydrate (M-S-H)

Ellina Bernard, Barbara Lothenbach, Céline Cau-Dit-Coumes, Christophe Chlique, Alexandre Dauzères, Isabelle Pochard

PII: S0883-2927(17)30369-4

DOI: [10.1016/j.apgeochem.2017.12.005](https://doi.org/10.1016/j.apgeochem.2017.12.005)

Reference: AG 4000

To appear in: *Applied Geochemistry*

Received Date: 20 July 2017

Revised Date: 4 December 2017

Accepted Date: 5 December 2017

Please cite this article as: Bernard, E., Lothenbach, B., Cau-Dit-Coumes, Cé., Chlique, C., Dauzères, A., Pochard, I., Magnesium and calcium silicate hydrates, part I: Investigation of the possible magnesium incorporation in calcium silicate hydrate (C-S-H) and of the calcium in magnesium silicate hydrate (M-S-H), *Applied Geochemistry* (2018), doi: 10.1016/j.apgeochem.2017.12.005.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

This document is the accepted manuscript version of the following article:
Bernard, E., Lothenbach, B., Cau-Dit-Coumes, C., Chlique, C., Dauzères, A., & Pochard, I. (2018). Magnesium and calcium silicate hydrates, part I: investigation of the possible magnesium incorporation in calcium silicate hydrate (C-S-H) and of the calcium in magnesium silicate hydrate (M-S-H). *Applied Geochemistry*, 89, 229-242. <http://doi.org/10.1016/j.apgeochem.2017.12.005>

This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

1 **Magnesium and calcium silicate hydrates, Part I: Investigation of the possible**
2 **magnesium incorporation in calcium silicate hydrate (C-S-H) and of the**
3 **calcium in magnesium silicate hydrate (M-S-H)**

4 Ellina Bernard^{1)*}, Barbara Lothenbach¹⁾, Céline Cau-Dit-Coumes²⁾, Christophe Chlique²⁾, Alexandre
5 Dautères³⁾, Isabelle Pochard⁴⁾

6 ¹⁾ Empa, Laboratory for Concrete & Construction Chemistry, 8600 Dübendorf, Switzerland

7 ²⁾ CEA, DEN, DE2D, SEAD, F-30207 Bagnols-sur-Cèze cedex, France

8 ³⁾ IRSN, Institute of Radiation Protection and Nuclear Safety, PSE/SEDRE/LETIS, BP 17, 92262
9 Fontenay aux Roses, France

10 ⁴⁾ Université Bourgogne-Franche-Comté, 21078 Dijon, France

11 *Corresponding author: Bernard E., email: ellina.bernard@empa.ch

12 **Abstract**

13 Calcium silicate hydrate (C-S-H) and magnesium silicate hydrate (M-S-H) have been described as two
14 separate phases. This work investigates their stability domains and the possible uptake of small amounts
15 of magnesium by C-S-H or, reversely, the uptake of small amounts of calcium by M-S-H. The phases,
16 synthesized by co-precipitation, are characterized using a large panel of techniques (thermogravimetry
17 analysis, X-ray diffraction, X-ray pair distribution function analysis, ²⁹Si MAS-NMR spectroscopy,
18 measurement of zeta potential and cation exchange capacity) while the compositions of the solutions at
19 equilibrium are determined by ion chromatography and pH measurements. Syntheses of C-S-H samples
20 in the presence of magnesium ((Ca+Mg)/Si = 0.8 and Mg/Si = 0.05 or 0.10) yield two separate phases:
21 C-S-H and M-S-H. There is no experimental evidence of any uptake of magnesium by C-S-H. On the
22 contrary, when M-S-H samples are synthesized in the presence of calcium ((Ca+Mg)/Si = 0.8 and Ca/Si

23 = 0.05 or 0.10), the low pH of the suspension (9-10) prevents the formation of C-S-H but favors the
24 precipitation of M-S-H with small amounts of calcium. This latter may be sorbed onto the surface of M-
25 S-H to outbalance its negative charges and/or incorporated into the interlayer, as suggested by small
26 structural changes.

27 **Keywords**

28 Low-pH cement, calcium silicate hydrate (C-S-H), magnesium silicate hydrate (M-S-H), surface
29 properties, thermodynamic modelling

30 **1. Introduction**

31 The formation of magnesium silicates hydrate (M-S-H), has been observed at the interfacial zone of
32 cement-based materials in contact with clays (Dauzères et al., 2016; Garcia Calvo et al., 2010; Jenni et
33 al., 2014; Lerouge et al., 2017; Mäder et al., 2017) and/or as secondary products from the degradation of
34 cementitious materials by groundwater or seawater (Bonen and Cohen, 1992; Jakobsen et al., 2016;
35 Santhanam et al., 2002). The combination of leaching and carbonation induces a pH decrease at the
36 surface of the cement sample, resulting in the decalcification of calcium silicate hydrate (C-S-H) and the
37 formation of amorphous silica which then reacts with magnesium to yield a Mg-enriched phase referred
38 as magnesium silicate hydrate (M-S-H) (Bonen and Cohen, 1992; Dauzères et al., 2016; De Weerd and
39 Justnes, 2015; Jakobsen et al., 2016; Jenni et al., 2014; Lerouge et al., 2017; Mäder et al., 2017;
40 Santhanam et al., 2002).

41 M-S-H phases have been synthesized in the laboratory (Brew and Glasser, 2005; d'Espinose de
42 Lacaillerie et al., 1995; Nied et al., 2016; Roosz et al., 2015; Walling et al., 2015); its structure has also
43 been investigated by molecular modelling (Pedone et al., 2017). Both C-S-H and M-S-H phases exhibit
44 a rather high water content, water being both present in the interlayer or sorbed at the surface, and

45 integrated in the structure (as H₂O and hydroxyl group (Jin and Al-Tabbaa, 2013; L'Hôpital et al.,
46 2016a; Lothenbach et al., 2016; Nied et al., 2016)). C-S-H consists of calcium oxide layers sandwiched
47 on both side by silicate chains with the typical dreierketten structure (Richardson, 2008). At low Ca/Si
48 ratio, the tetrahedral silicate sites in C-S-H are usually bound to two neighbors (= Q², leading to almost
49 infinite chains). In contrast, M-S-H has a layered structure (Brew and Glasser, 2005; Nied et al., 2016;
50 Roosz et al., 2015; Walling et al., 2015) similar to clay minerals and the tetrahedral silicate sites are
51 mainly bound to two or three neighbors (Q² and Q³). As for clays, M-S-H is stable at lower pH values
52 than C-S-H, i.e. at pH between 7.5 (Bernard et al., 2017a) and 10.5 (Bernard et al., 2017b; Nied et al.,
53 2016; Zhang et al., 2011) or even up to 11.5 (Bernard et al., 2017a). Given the different structures and
54 stability domains, most studies (Bernard et al., 2017a; Brew and Glasser, 2005; Chiang et al., 2014;
55 Lothenbach et al., 2015) have reported the precipitation of two distinct phases and not of a mixed
56 magnesium calcium silicate hydrate phase.

57 The structure of synthetic M-S-H has been related to very poorly crystalline tri-octahedral 2:1 (or 1:1)
58 phyllosilicate. It has also been observed that M-S-H has variable basal spacing (Roosz et al., 2015)
59 similar to clay minerals. In addition, TEM observations indicate the possible uptake of aluminum, iron
60 and calcium in its structure (Lerouge et al., 2017).

61 This paper is the first part of a study on the stability and the uptake of the magnesium and calcium
62 silicate hydrates and focuses on the possible incorporation of magnesium in C-S-H and of calcium in M-
63 S-H.

64 Replacement of magnesium oxide by calcium oxide in octahedral sheets of magnesium silicate minerals
65 is not reported in the literature. Mixed magnesium calcium minerals exist as dolomite (CaMg(CO₃)₂),
66 which has an alternating structural arrangement of calcium and magnesium ions. In this case, calcium or

67 magnesium oxides are not mixed in octahedral layers, but in alternate octahedral sites of calcium or
68 magnesium as the crystallographic radius of calcium (0.99Å (Conway, 1981)) in the octahedral layer is
69 significantly higher than that of magnesium (0.65Å (Conway, 1981)). The uptake of calcium in
70 magnesium silicate clay as e.g. saponite occurs at the negatively charged surface and in its interlayer to
71 compensate the charge. Similarly, in the amphibole group, the uptake of calcium can occur as charge
72 balancing Ca^{2+} in the *M4 sites* (i.e. in sites with 6 to 8-fold coordination between two T:O:T¹ blocks).

73 Even if the formation of a magnesium calcium silicate hydrate phase does not seem very likely, the
74 possible uptake of small amounts of magnesium by C-S-H (Bernard et al., 2017a; Lothenbach et al.,
75 2015) may be envisaged. The uptake of alkalis, sulfate, or aluminum in C-S-H has indeed already been
76 observed (Bach et al., 2013; L'Hôpital et al., 2016b; L'Hôpital et al., 2015; Lothenbach and Nonat,
77 2015; Plusquellec and Nonat, 2016; Renaudin et al., 2009; Richardson, 2008; Richardson et al., 1993;
78 Skibsted et al., 1993). Alkali and sulfate uptakes occur mainly by sorption onto the surface or in the
79 interlayer, while aluminum is taken up both in the interlayer and in the silicate chains. A high calcium
80 concentration and/or a low pH decrease the alkali uptake (L'Hôpital et al., 2016b). The uptake of ions by
81 C-S-H also decreases with the ions concentration in solution. Magnesium is, as calcium, a double
82 charged cation, with a similar ionic radius in its hydrated state (4.3 Å for Mg^{2+} , 4.1 Å for Ca^{2+})
83 (Conway, 1981). However in the presence of M-S-H and C-S-H at pH 10-11 (Bernard et al., 2017a;
84 Lothenbach et al., 2015), the aqueous magnesium concentrations are much lower (0.0001-0.1 mmol/L)
85 than those of calcium (0.1-1.5 mmol/L). Hence, the uptake of magnesium(II) by C-S-H is expected to be
86 smaller than the uptake of calcium(II).

87 This paper investigates the possible uptake of calcium by M-S-H and of magnesium by C-S-H. M-S-H is
88 synthesized in batch experiments in the presence of calcium. Similarly, C-S-H is synthesized in the

¹T= tetrahedral layer; O= octahedral layer

89 presence of magnesium. The surface charge of the particles in suspension is investigated by zeta
 90 potential measurements and their cation exchange capacity (CEC) is determined. The composition of the
 91 solutions at equilibrium is analysed by pH measurements and ion chromatography. The solid phases are
 92 characterized by thermogravimetry analysis (TGA), powder X-ray diffraction (XRD), and ^{29}Si solid-
 93 state MAS NMR.

94 2. Materials and methods

95 2.1. Synthesis

96 All the syntheses were performed in a glovebox under nitrogen atmosphere to minimize CO_2
 97 contamination. MgO (Merck, pro analysis, containing 0.18 ± 0.02 wt% Na_2O), CaO (obtained by
 98 burning calcium carbonate (CaCO_3 , Merck, pro analysis) for 12 h at 1000 °C) and SiO_2 (SiO_2 , Aerosil
 99 200, 0.9 wt% HCl) were directly mixed with ultrapure water as detailed in (Lothenbach et al., 2015) to
 100 obtain M-S-H or C-S-H with small amounts of calcium or magnesium. The synthesized products are
 101 summarized in Table 1. The syntheses were carried out to obtain ~ 5 g of solid and the water-to-solid
 102 (W/S) ratio was set to 45.

103 *Table 1: Labelling and initial composition of mixes of the plain M-S-H and C-S-H samples and of the co-precipitated*
 104 *samples. Bold co-precipitated samples correspond to the fully analyzed samples while the Co-0.40 and the Co-0.50*
 105 *samples are presented in the paper to supplement the analytical data of the aqueous phase.*

Samples	M-S-H 0.8	Co-0.05	Co-0.10	Co-0.40	Co-0.50	Co-0.70	Co-0.75	C-S-H 0.8
Total Mg/Si	0.8	0.75	0.70	0.40	0.30	0.10	0.05	
Total Ca/Si		0.05	0.10	0.40	0.50	0.70	0.75	0.80
Total (Mg+Ca)/Si	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80

106

107 These suspensions were equilibrated at different temperatures (20°C and 50°C) and for different times
108 (from 6 months up to 2 years) to determine the solubility; these long equilibration times and the
109 increased temperature aimed to provide samples at/or very close to equilibrium (Bernard et al., 2017b).

110 The solid and liquid phases were separated by filtration under pressure (4-5 bars N₂) using nylon filters
111 (0.45 µm).

112 Following the filtration, the solids were washed with a 50/50 (volume) water-ethanol mix and then with
113 ethanol (94 wt% alcohol) to remove dissolved ions and to prevent the precipitation of salts during drying
114 (L'Hôpital et al., 2015). The samples were freeze-dried with liquid nitrogen (for approximately 20 min
115 at -195°C) and kept at -40°C under vacuum (pressure of 0.28 mbar) for 7 days. The solid phases were
116 analyzed after further equilibration in N₂-filled desiccators at a relative humidity of ~30% (saturated
117 CaCl₂ solution) for a period of 14 days or longer. After drying, the samples were gently ground by hand.

118 Pure C-S-H (Bernard et al., 2017a) and pure M-S-H (Bernard et al., 2017b) were analyzed for
119 comparison. In addition, powdered reference mixtures labelled Mix-0.05, Mix-0.10, Mix-0.70 and Mix-
120 0.75 were prepared by mechanical mixing in a grinder, pure C-S-H and pure M-S-H (prepared
121 separately) to obtain the same molar ratios as the co-precipitated samples. In those mixes, the formation
122 of any magnesium calcium silicate hydrate phase (M-C-S-H) could be excluded due to the absence of
123 water.

124

125 **2.2. Analytical techniques**

126 The composition of the liquid phase was analysed by ion chromatography (IC) immediately after
127 filtration. The dissolved concentrations of Mg, Ca, Si, Na, Cl, K, SO₄ in undiluted solutions or in
128 solutions diluted by a factor 10, 100 or 1000 were quantified using a Dionex DP series ICS-3000 ion

129 chromatography system with a measurement error $\leq 10\%$. All concentrations were determined as
130 duplicates and the mean value is given in this paper. Na, Cl, K, SO_4 concentrations were also measured
131 as traces were present in the starting materials. The composition of the aqueous phase of M-S-H did not
132 change significantly during the 30 minutes necessary to cool down the solutions from 50°C to ambient
133 temperature (Bernard et al., 2017b). The pH values (± 0.1) were measured at ambient temperature
134 ($23 \pm 2^\circ\text{C}$) in an aliquot of the unfiltered suspension and the results were corrected to 20 or 50°C as
135 described in (Bernard et al., 2017b).

136 Thermogravimetric analyses (TGA) were carried out on ground powder (~ 30 mg) with a Mettler Toledo
137 TGA/SDTA 8513 instrument using a heating rate of $20^\circ\text{C}/\text{min}$ from 30 to 980°C . The amount of
138 $\text{Mg}(\text{OH})_2$ (brucite) was quantified from the water weight loss at around $400\text{--}420^\circ\text{C}$ using the tangential
139 method (Lothenbach et al., 2016) and calculated according to the equation (1):

$$141 \text{ wt. \% brucite}_{\text{dry}} = \frac{\text{water loss (brucite)}}{100 - \text{water loss}_{(30-550^\circ\text{C})}} \times \frac{M_{\text{brucite}}}{M_{\text{H}_2\text{O}}} \times 100 \quad (1)$$

142 where wt. % brucite_{dry} corresponds to the wt.% of brucite for 100g of dry mass, the water loss is
143 expressed in wt. %, the M_{brucite} is taken equal to 58.32 g/mol, while the $M_{\text{H}_2\text{O}}$ is taken equal to 18.02
144 g/mol. The relative error on the brucite content is $\pm 5\text{--}10\%$ (Deschner et al., 2012; Lothenbach et al.,
145 2016).

146 XRD data were collected using a PANalytical X'Pert Pro MPD diffractometer equipped with a rotating
147 sample stage in a $\Theta\text{--}2\Theta$ configuration applying $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at 45mV voltage and 40mA
148 intensity with a fixed divergence slit size and an anti-scattering slit on the incident beam of 0.5° and 1° .
149 The samples were scanned between 5° and $75^\circ 2\Theta$ with a X'Celerator detector.

150 In addition to typical XRD measurements, X-ray Pair Distribution Function (PDF) analyses were
151 performed. This analysis focusses on the entire signals including Bragg peaks and diffuse scattering.
152 PDF represents the distribution of interatomic distances in a compound, regardless of its crystalline
153 state, determined experimentally by a Fourier transform of the powder pattern. PDF is thus an efficient
154 technique for studying of short coherence lengths materials such as cement (Meral et al., 2011) or
155 geopolymers (White et al., 2013). The reduced PDF, $G(r)$, was obtained by taking a sine Fourier
156 transform of the measured total scattering function $S(Q)$, as shown in equation (2), where Q is the
157 momentum transfer given in equation (3) with θ as the scattering angle and λ as the wavelength of the
158 incident radiation (Egami and Billinge, 2003; White et al., 2013).

$$159 \quad G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (2)$$

$$160 \quad Q = \frac{4\pi \sin\theta}{\lambda} \quad (3)$$

161 It is important to obtain diffraction data with a high momentum transfer (Q) in order to maximize the
162 resolution after the Fourier transform. We, therefore, used an X'Celerator Panalytical diffractometer
163 equipped with a Mo source ($\lambda_{K\alpha} = 0.70926\text{\AA}$). The powder diffraction pattern was scanned over the
164 $6.004\text{-}153.932^\circ$ angular range with a step size of 0.0083° . The total acquisition was the average of 2 runs
165 recorded over 24 hours. The PDF and standard corrections (Egami and Billinge, 2003) were calculated
166 with PDFGetX2 (Qiu et al., 2004). The density number of atoms ρ_0 used to calculate the PDF was 0.10
167 atoms \AA^{-3} . The use of a finite value of Q (17\AA^{-1}) for the PDF analysis led to the addition of spurious
168 oscillations to $G(r)$ depending on the distance r . These oscillations were smoothed by the use of a Lorch
169 (1969) function.

170 The ^{29}Si MAS NMR experiments were recorded on a Bruker Avance III NMR spectrometer using a 7
 171 mm CP/MAS probe at 79.5 MHz applying the following parameters: 4500 Hz sample rotation rate,
 172 minimum of 3072 scans or more, 90° ^1H pulse of 7.5 μs , 20 s relaxation delays, RF field strength of
 173 33.3 kHz during SPINAL64 proton decoupling. The ^{29}Si chemical shifts NMR spectra were referenced
 174 to the Aldrich external sample of tetramethylsilane (TMS) with a ^{29}Si chemical shift at -2.3 ppm. The
 175 observed ^{29}Si resonances were analysed using the Q^n classification, where a Si tetrahedron is connected
 176 to n Si tetrahedra with n varying from 0 to 4. The quantification was performed by non-linear least-
 177 square fits using the ‘‘DMFIT’’ software developed by Massiot et al. (Massiot et al., 2002). Amorphous
 178 silica was quantified taking into account the shift at -100.9 ppm (Q^3 from the surface of the amorphous
 179 silica (d’Espinoze de Lacaillerie et al., 1995; Nied et al., 2016)) and the Q^4 shift at -110 ppm. However,
 180 the T_1 relaxation time of amorphous silica can be very long and the amount of amorphous silica might
 181 be underestimated.

182 The deconvolutions of the C-S-H signals were performed following the procedure outlined in literature
 183 (Myers et al., 2015), with a constant Lorentzian/Gaussian ratio equal to 0.5 and by keeping the ratio
 184 between bridging and pairing silicate tetrahedra constant according to equation (3):

$$185 \quad \frac{Q_b^2 + Q_u^2}{Q_p^2} = 0.5 \quad (3)$$

186 where Q_b^2 is the bridging silicate tetrahedron with one calcium neighbor in the interlayer, Q_u^2 is the
 187 bridging tetrahedron with one H^+ neighbor in the interlayer and finally Q_p^2 is the pairing tetrahedron.

188 The mean chain length (MCL) of the silicate chains in C-S-H was calculated following equation (4):

$$189 \quad MCL = \frac{2(Q^1 + Q_b^2 + Q_u^2 + Q_p^2)}{Q^1} \quad (4)$$

190 The Q^1 and Q^2 environments in M-S-H were deconvoluted using mainly Lorentzian functions while the
191 Q^3 environment was deconvoluted with Gaussian functions following the procedure outlined by
192 (Bernard et al., 2017b). Based on the available M-S-H deconvolutions in literature (Bernard et al.,
193 2017b; Nied et al., 2016; Roosz et al., 2015; Walling et al., 2015), the Q^2/Q^3 ratio was kept between 0.4
194 and 1.

195 The TEM characterizations were carried out on a JEOL JEM 2100F microscope operating at 200 kV and
196 fitted out with a Bruker XFlash 5030 for EDS analysis. A few milligrams of powder was vigorously
197 mixed with a few milliliters of pure ethanol in a mortar with a pestle for less than one minute. A TEM
198 carbon-covered copper grid held with tweezers was then dipped just below the ethanol surface to collect
199 suspended particles on it. The grid was then inserted in the TEM chamber and the vacuum was
200 recovered after about 15 min.

201 The zeta potential measurements were carried out directly in suspension before filtration with 5 g of
202 solid per 225 mL. The samples were stirred in a beaker at 500 rpm during 10 minutes to reach a stable
203 value before the measurement. During the measurements, they were stirred at 400 rpm and each
204 measurement was repeated 10 times. Zeta potential data were recorded with a ZetaProbe from Colloidal
205 Dynamics Inc., which is based on the frequency-dependent electroacoustic effect. Shortly, an alternating
206 voltage is applied to the suspension which causes charged particles to move back and forth at a mobility
207 that depends on their zeta potential. The software calculates the zeta potential from the frequency-
208 dependent mobility using the O'Brien equation (James et al., 1992). Finally the values obtained were
209 background corrected with a measurement of the filtrated aqueous phase. The zeta potential ($-8.1 \text{ mV} \pm$
210 0.9 mV) measured for the C-S-H reference ($\text{Ca/Si} = 0.8$) is consistent with data from the literature (Haas
211 and Nonat, 2015; Labbez et al., 2007; Viallis-Terrisse et al., 2001).

212 Cation exchange capacity (CEC) in the samples was measured on 100 mg of powder. The cations on the
213 surface and/or from the interlayer were exchanged with cobalt hexamine trichloride during 30 min at
214 room temperature (Jenni et al., 2014) using a solution/solid mass ratio of 30. The suspensions were
215 filtered and the concentrations of Na^+ , K^+ , Ca^{2+} , Mg^{2+} in solution were determined by ion
216 chromatography (IC) as detailed above. The sum of measured cations was compared to the total CEC
217 which was obtained from the difference in the cobalt hexamine concentration from the original solution
218 and from the leachate. Such concentrations were determined by colorimetry (absorption band at 473 nm)
219 using a UNI-CAM UV visible spectrometer. The good agreement between the total CEC measured by
220 colorimetry and the CEC calculated from the measured cations showed that dissolution of M-S-H and C-
221 S-H was negligible. The $\text{Mg}_{\text{exch}}/\text{Si}$ and the $\text{Ca}_{\text{exch}}/\text{Si}$ ($\text{Cat}_{\text{exch}}/\text{Si}$) were calculated from the CEC
222 measurement following the equation (5):

$$223 \quad \frac{\text{Cat}_{\text{exch}}}{\text{Si}} = \frac{\text{Cation (CEC)}}{0.1/M} \quad (5)$$

224 where Cation (CEC) is the mol of cations (magnesium or calcium) obtain by the CEC (IC), the 0.1
225 corresponds to the 0.1 g of solid used in the CEC measurement and M is the molar mass in g/mol of the
226 phase corresponding ($\text{M}_{0.8}\text{SH}_{1.5}$ or $\text{M}_{0.75}\text{C}_{0.05}\text{SH}_{1.5}$ for example).

227 The solids were washed after the CEC and dissolved in 0.1 mol/L HCl to investigate whether any
228 calcium remained in the M-S-H after the exchange with the cobalt hexamine. The solutions were
229 analyzed by ICP-MS with Agilent triplequad MS (Agilent 8900 QQQ ICP-MS). Sodium and magnesium
230 concentrations have been measured in the “NoGas” mode while the calcium concentration has been
231 measured in the “Helium” mode. It might be that calcium was slightly overestimated due the presence of
232 residual calcium from the exchange. ICP-MS had been used as in IC it was not possible to detect small
233 calcium concentrations in the presence of high magnesium concentrations.

234 **2.3. Thermodynamic modelling**

235 Thermodynamic modelling of the experiments was carried out using the Gibbs free energy minimization
236 program GEMS (Kulik et al., 2013). GEMS is a broad-purpose geochemical modelling code which
237 computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk
238 elemental composition. The thermodynamic data for aqueous species as well as for brucite and
239 portlandite were taken from the PSI-GEMS thermodynamic database (Thoenen et al., 2014). The
240 amorphous SiO₂ data were from Bernard et al. (2017b).

241 The ion activity products (IAP) were calculated from the measured composition of the solutions for all
242 the samples with respect to M_{0.78}SH_{1.48} and C_{0.80}SH_{1.94} to observe whether any change occurred upon
243 variation of the pH and/or the concentration of other species.

244 The solubility of low-crystalline phases with variable composition such as C-S-H and M-S-H can be
245 described either by solid solutions, which allow a continuous change of composition of the solid, or by
246 defining solubility products for a range of possible compositions leading to a large number of different
247 solubility products (as has been done e.g. by Dauzères et al., 2016; Gaucher et al., 2004; Trapote-
248 Barreira et al., 2014). If single solubility products are used the resulting aqueous concentrations or solid
249 compositions are described by steps as shown in e.g. (Nied et al., 2016), while a solid solution approach,
250 which defines only the solubility products of end-members solids, allows describing gradual changes in
251 the C-S-H or the M-S-H composition and in the aqueous phases (for more detailed see (Bernard et al.,
252 2017b; Kulik, 2011; Nied et al., 2016)). The solid solution models used have been developed for C-S-H
253 with $0.67 < \text{Ca/Si} < 1.5$ by Kulik (2011) and M-S-H with $0.78 < \text{Mg/Si} < 1.3$ (Bernard et al., 2017b).

254 The thermodynamic data used of the solid solutions of M-S-H (defined by two end-members) and of C-
 255 S-H (defined by three end-members), and of brucite, portlandite, and amorphous silica are summarized
 256 in Table 2.

257 Based on the experimental observations (as presented below in Results and discussions), M-S-H phases
 258 containing small amounts of calcium were defined. The solubility products of two possible end-
 259 members, $M_{0.68}C_{0.1}SH_{1.48}$ and $M_{1.2}C_{0.1}SH_{1.80}$, were fitted using the measured concentrations and
 260 implemented in the solid solution model of M-S-H as detailed in Table 2. The formation of an ideal
 261 solid solution between the 4 endmembers ($M_{0.78}SH_{1.48}$, $M_{1.3}CSH_{1.80}$, $M_{0.68}C_{0.1}SH_{1.48}$ and $M_{1.2}C_{0.1}SH_{1.80}$)
 262 was assumed.

263

264 Table 2: Standard thermodynamic properties at 25 °C and $P = 1$ atm.

	*	$\text{Log}K_{s0}^a$	$\Delta_f G^\circ$ [kJ/mol]	V° [cm ³ /mol]	density [g/cm ³]	Ref.
Brucite	MH	-11.16	-832.23	24.6	2.37	(Thoenen et al., 2014)
Portlandite	CH	-5.2	-897.01	33.1	2.24	(Thoenen et al., 2014)
SiO _{2,am}	S	-2.9	-849.9	29	2.07	(Bernard et al., 2017b)
<i>M-S-H</i>						
Mg/Si = 0.78	$M_{0.78}SH_{1.48}$	-14.59	-1682.2	56	2 ^b	(Bernard et al., 2017b)
Mg/Si=1.30	$M_{1.30}SH_{1.80}$	-21.44	-2073.5	72	2 ^b	(Bernard et al., 2017b)
Mg/Si = 0.68 Ca/Si = 0.10	$M_{0.68}C_{0.1}SH_{1.48}$	-14.42^c	-1689.7	57	2 ^b	this
Mg/Si = 1.20 Ca/Si = 0.10	$M_{1.20}C_{0.1}SH_{1.80}$	-21.57^c	-2082.0	73	2 ^b	study
<i>C-S-H</i>						
Ca/Si = 0.67	$C_{0.67}SH_{1.67}$	-10.24	-1707.3	56.6	2.25	(Kulik, 2011)
Ca/Si = 1.0	$C_{1.00}SH_{2.00}$	-13.41	-2014.5	63.4	2.4	(Kulik, 2011)
Ca/Si = 1.5	$C_{1.5}SH_{2.50}$	-16.61	-2466	80.6	2.35	(Kulik, 2011)

265 *cement shorthand notations: C= CaO; H =H₂O; M = MgO; S = SiO₂

266 ^a all solubility products refer to the solubility with respect to the species Mg^{2+} , Ca^{2+} , SiO_2^0 , OH^- , or H_2O

267 ^b estimated from M-S-H volumes

268 ^c values at 20°C.

269 **3. Results and discussions**

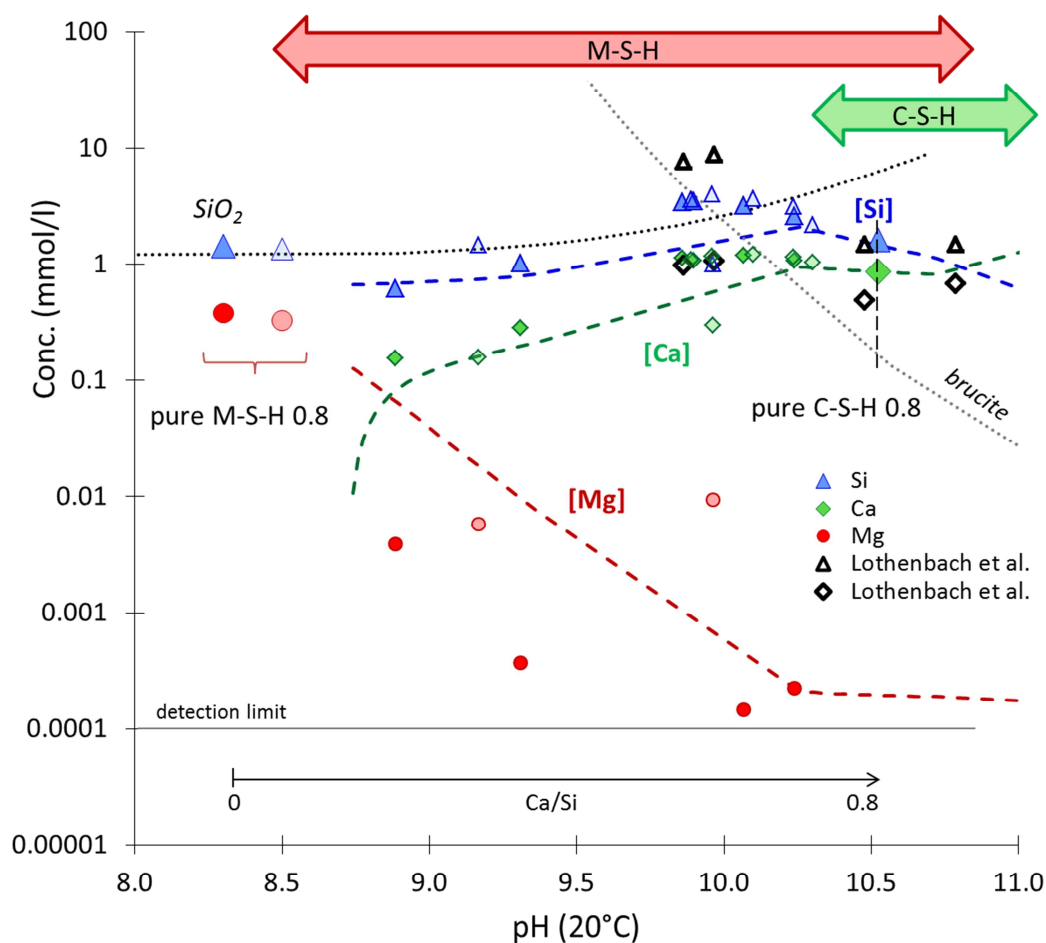
270 **3.1. Co-0.05 and Co-0.10 samples**

271 This section focusses on M-S-H syntheses labelled Co-0.05 and Co-0.10. The (Mg+Ca)/Si ratio was set
272 to 0.8 and a small fraction of MgO was substituted by CaO (Ca/Si=0.05 and 0.10).

273 **3.1.1. Aqueous phase composition**

274 The pH values and measured concentrations of the solutions equilibrated with the co-precipitated
275 samples are plotted in Figure 1 and compared to the data obtained for pure M-S-H and C-S-H.

276 In the solution at equilibrium with the pure M-S-H sample, a pH of 8.3 was measured, together with
277 magnesium and silicon concentrations of 0.38 mmol/L and 1.44 mmol/L respectively. The substitution
278 of magnesium by calcium at constant (Mg+Ca)/Si ratio of 0.8 increased the pH (Figure 1, Appendix A)
279 from 8.3 to 8.9 (sample Co-0.05) or 9.3 (sample Co-0.10). At the same time, the magnesium
280 concentration was lowered. A comparable decrease of magnesium has been observed for pure M-S-H at
281 higher pH values (Bernard et al., 2017b; Nied et al., 2016) and for M-S-H in the presence of some
282 calcium (Lothenbach et al., 2015). Little difference was observed in the concentrations and pH values
283 between 1 and 2 years confirming that the samples were very close to equilibrium.



284
 285 *Figure 1: Measured silicon (triangles), magnesium (circles), and calcium (diamonds) concentrations at 20°C at 1 year*
 286 *(lighter symbols) and 2 years (full symbols) as a function of pH. Empty symbols are from Lothenbach et al. (Lothenbach et*
 287 *al., 2015). The solubility of M-S-H, C-S-H (dashed lines), brucite and amorphous silica (dotted lines) were calculated from*
 288 *the thermodynamic data (solid solutions for M-S-H and C-S-H) detailed in Table 2 without considering the formation of*
 289 *mixed M-(C)-S-H phase.*

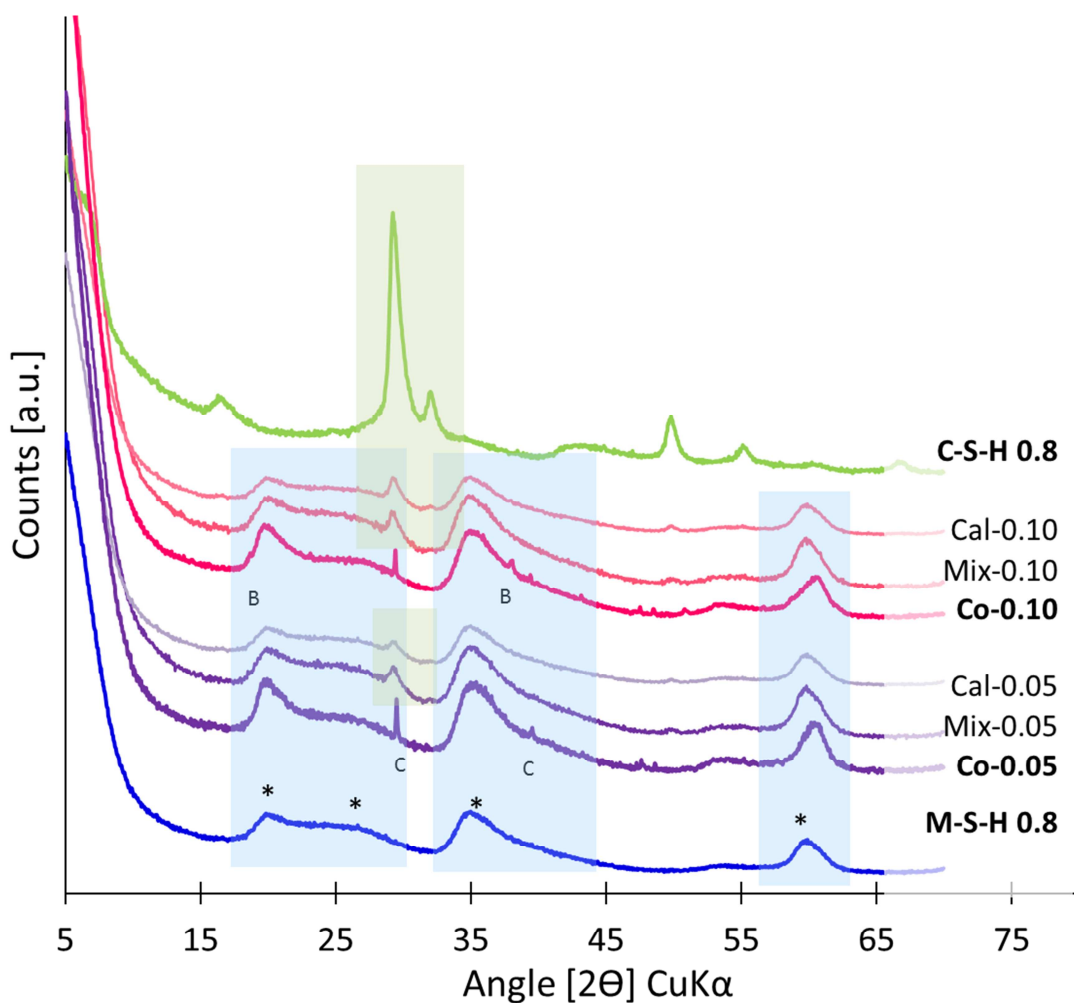
290

291 C-S-H phases are not stable at this range of pH (<9.5) (Bernard et al., 2017a; Leisinger et al., 2014;
 292 Peyronnard et al., 2009; Shi and Stegemann, 2000; Swanton et al., 2016). It can be noted however that
 293 the calcium concentrations were much lower (0.15 to 0.46 mmol/L, depending on the initial calcium
 294 content, temperature and time) than the total amount of calcium that could theoretically be present in
 295 solution (11.93 ± 1.50 and 23.66 ± 2.60 mmol/L), which suggests the uptake of calcium by the solid
 296 phases.

297 **3.1.2. Solid phase analysis**

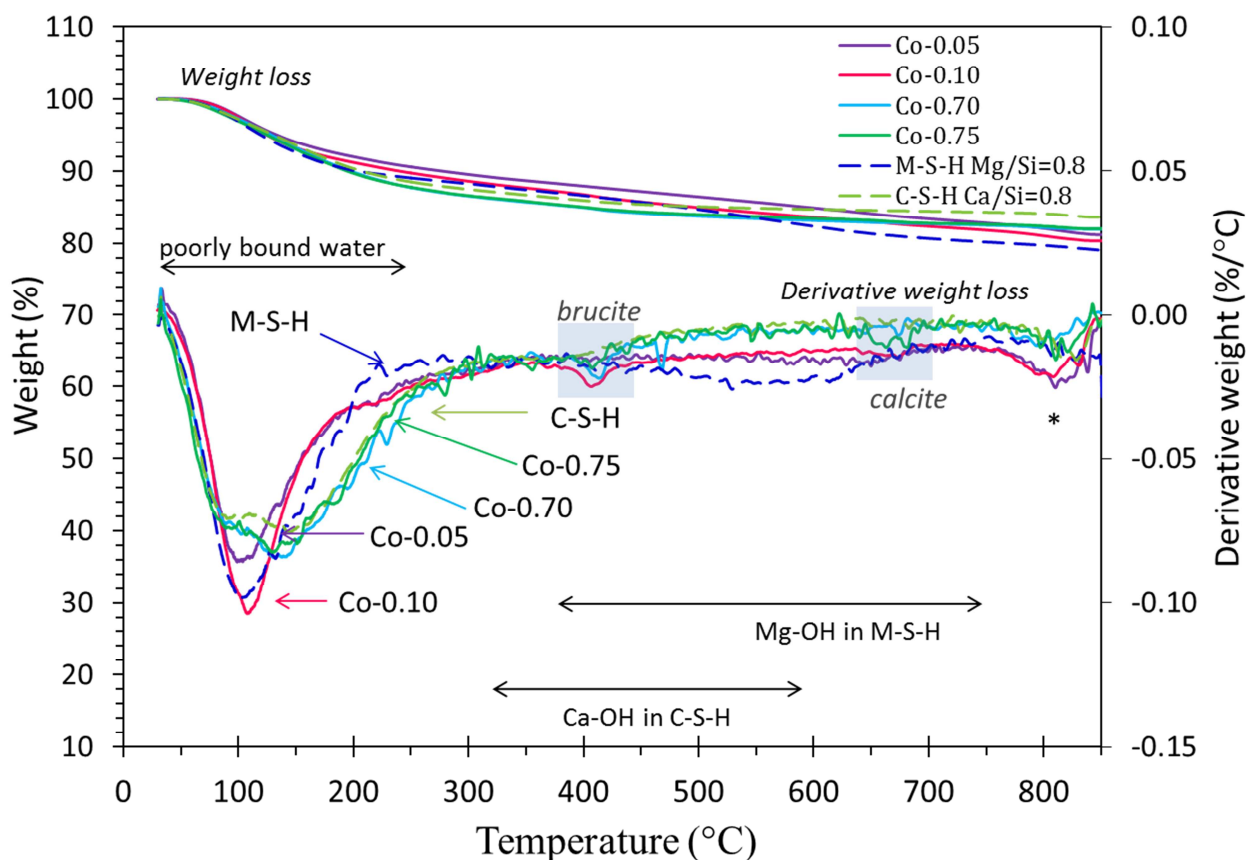
298 The solid analysis focused on the samples equilibrated for 1 year at 50°C. However, similar results were
299 obtained for the samples equilibrated for 2 years at 20°C indicating that the equilibrium was reached in
300 both conditions (see Appendix A).

301 The XRD patterns of the two co-precipitated (Co-0.05 and Co-0.10) samples are compared to those of
302 M-S-H and C-S-H in Figure 2. The broad peaks at 19.7, 26.7, 35.0, 60.3° 2 Θ (Nied et al., 2016) were
303 attributed to M-S-H, the main phase observed in the samples. In addition, traces of calcite (CaCO₃, PDF-
304 00-005-0586) and brucite (Mg(OH)₂, PDF-01-083-0114) were present. Their amount was less than 1%,
305 as assessed from TGA (Figure 3).



306

307 *Figure 2: XRD patterns of samples Co-0.05 and Co-0.10 after 1 year of curing at 50°C compared to XRD patterns of M-S-H*
 308 *0.8 (1 year at 50°C), C-S-H 0.8 (1 year at 50°C), mixed samples (0.10mix and 0.05mix), calculated reference patterns (Cal-*
 309 *0.05 and Cal-0.10) B=Mg(OH)₂ (brucite); C= CaCO₃ (calcite).*
 310



311
 312 *Figure 3: Thermogravimetric analysis of co-precipitated samples after 1 year of curing at 50°C compared to TGA of C-S-H*
 313 *0.8 and M-S-H 0.8 (1 year, 50°C), * indicates the formation of wollastonite from C-S-H (Martin et al., 2017) and enstatite*
 314 *from M-S-H (as observed from talc (MacKenzie and Meinhold, 1994)).*

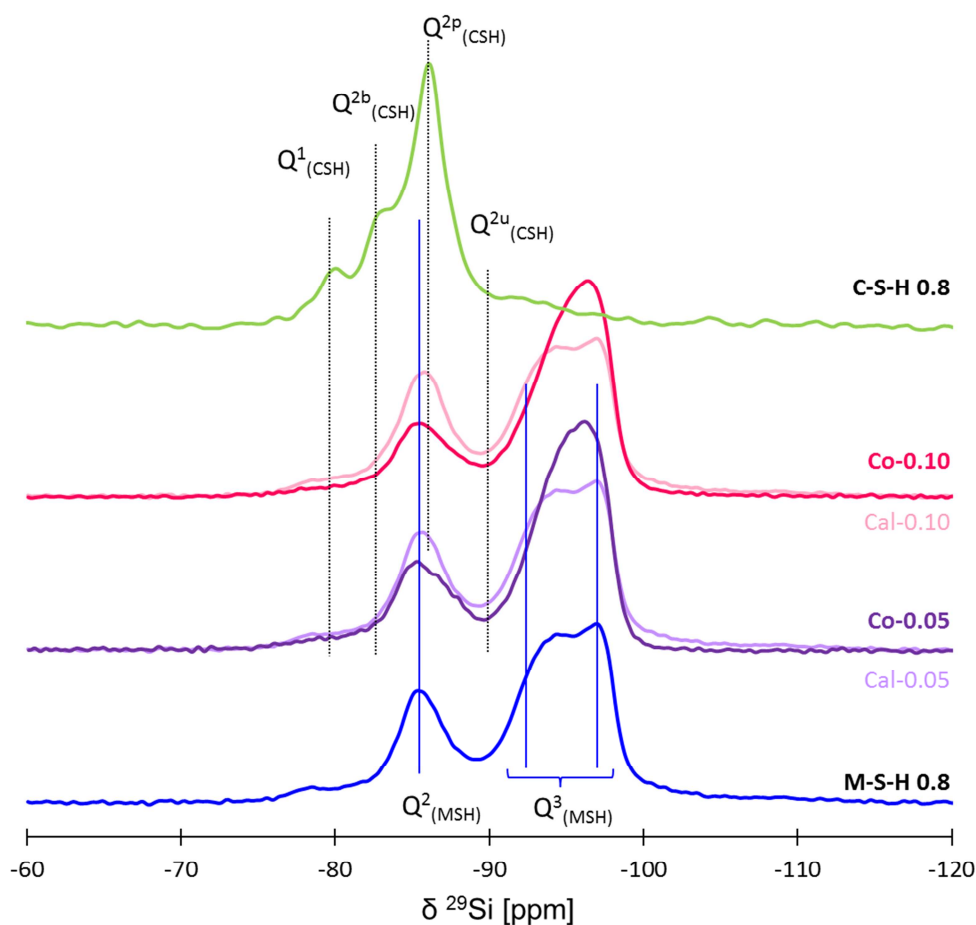
315

316 Complementary XRD patterns were measured and calculated for mixes of separately synthesized M-S-H
 317 and C-S-H phases. These mixes (Mix-0.05 and Mix-0.10) contained the same Mg/Si and Ca/Si ratios
 318 than samples Co-0.05 and Co-0.10, but the presence of any magnesium calcium silicate hydrate (M-C-S-
 319 H) could be excluded. The calculated XRD patterns (Cal-0.05, Cal-0.10) resulted from linear
 320 combinations of the patterns of plain M-S-H and C-S-H respecting the Mg/Si and Ca/Si ratios. Mix-
 321 0.05 and Mix-0.10 samples exhibited the same XRD patterns as the calculated ones (Figure 2), but slight
 322 differences were noticed for the co-precipitated samples. C-S-H, characterized by a main reflection peak

323 at $\sim 29.2^\circ 2\theta$, was present in the separately mixed samples but not in the co-precipitated ones. The sole
324 observation of M-S-H by XRD was in good agreement with the low pH of the solution which should
325 prevent the precipitation of C-S-H. The main part of the calcium initially added was thus neither present
326 in the solution nor in C-S-H (or only in very small quantities not observable by XRD).

327 The reflection at approx. $60.3^\circ 2\theta$ in pure M-S-H is shifted to 60.4 and $60.5^\circ 2\theta$ in the Co-0.05 and Co-
328 0.10 samples, respectively. The reflection at higher angles is usually rather characteristic for talc
329 structure, i.e. for a low Mg/Si (0.75) phyllosilicate.

330 ^{29}Si MAS NMR spectra of the co-precipitated samples are presented together with the calculated spectra
331 of the linear combination of pure M-S-H and C-S-H in Figure 4. Pure M-S-H 0.8 usually contains a
332 small amount of amorphous silica (3-5% of SiO_2) (Bernard et al., 2017b; Nied et al., 2016) with a
333 resonance at -110 ppm (Q^4) and a resonance at -100.9 ppm $\text{Q}^3(-\text{OH})$ (d'Espinose de Lacaillerie et al.,
334 1995; Nied et al., 2016). The comparison of the calculated spectra with those of samples Co-0.05 and
335 Co-0.10 shows the absence of amorphous silica in the co-precipitated samples.



336

337 *Figure 4: ^{29}Si MAS NMR spectra of Co-0.05 and Co-0.10 samples (1 year at 50°C) compared to spectra of C-S-H 0.8, M-S-H*
 338 *0.8 and calculated reference samples Cal-0.05 and Cal-0.10.*

339

340 The ^{29}Si MAS NMR spectra of Co-0.05 and Co-0.10 samples were similar to that of M-S-H 0.8 (Figure
 341 4) with the presence of Q^2 tetrahedral silicate (chemical shifts at approx. -85.6 ppm) and Q^3 tetrahedral
 342 silicate (chemical shift between -92 and -97 ppm (Brew and Glasser, 2005; d'Espinoose de Lacaille et
 343 al., 1995; Nied et al., 2016; Roosz et al., 2015; Walling et al., 2015)). No C-S-H could be detected. The
 344 comparison with the calculated spectra in Figure 4 points out a lower intensity of the Q^2 signal, but a
 345 higher content of Q^3 species. The Q^2 signal was broader and the Q^3 signal was less symmetrical and
 346 shifted to slightly more negative chemical shifts. This would be consistent with the presence of calcium

347 in the vicinity of silicon since calcium shields silicon stronger than magnesium (Lothenbach et al., 2015;
348 Mägi et al., 1984).

349 The associated deconvolutions are detailed in Table 3. The spectra were deconvoluted based on the
350 deconvolution of pure M-S-H (Bernard et al., 2017b; Brew and Glasser, 2005; Nied et al., 2016). The
351 fraction of Q^3 silicate sites in M-S-H 0.8 ($61\% \pm 7\%$) increased to $73\% (\pm 8\%)$ in Co-0.05 and Co-0.10
352 samples. The Q^2/Q^3 ratio calculated in the co-precipitated samples of ~ 0.4 (Table 3) was lower than the
353 0.6 usually found in pure M-S-H 0.8 (Bernard et al., 2017b). As the Q^2/Q^3 in M-S-H decreases with the
354 decrease of Mg/Si (Bernard et al., 2017b), this low Q^2/Q^3 ratio suggests that the co-precipitated samples
355 might have a Mg/Si lower than 0.8 (approx. to 0.7-0.75). The higher polymerization of the silicate
356 network in the co-precipitated sample, together with the shift observed by XRD at high angles, seems to
357 indicate a lower content of magnesium rather than the presence of calcium in the octahedral layers and
358 thus that calcium might rather be adsorbed than incorporated in the octahedral layers. This is further
359 investigated by complementary analyses.

360 *Table 3: Relative peak area of the different silicon chemical shifts obtained from the deconvolution of the ^{29}Si MAS NMR*
361 *spectra for the co-precipitated samples after 1 year of curing at 50°C (C-S-H (1 year at 20°C) and M-S-H (1 year at 50°C)*
362 *shown as references).*

	C-S-H		MCL				M-S-H					App. Q^2/Q^3	% of Si in		
	Q^1	Q^2_b	Q^2_p	Q^2_u	$Q^3(?)$	Q^1	Q^2	Q^3_a	Q^3_b	Q^3_c	$Q^3(\text{SiO}_2)$		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	-100.9				
M-S-H 0.8	-	-	-	-	-	1	35	24	10	28	0.6	3	-	97	
Co-0.05	-	-	-	-	-	1	27	18	25	29	0.4	-	-	100	
Co-0.10	-	-	-	-	-	1	27	17	28	28	0.4	-	-	100	
Co-0.70	6	17	42	3	23	3	0	9	8	5	7	0	69	28	
Co-0.75	7	19	47	5	22	3	0	5	5	3	5	1	78	18	
C-S-H 0.8	8	22	59	7	25	4	-	-	-	-	-	-	96	-	

363 *Error = $\pm 8\%$ of absolute amounts of (%Si) + 2.5%.*

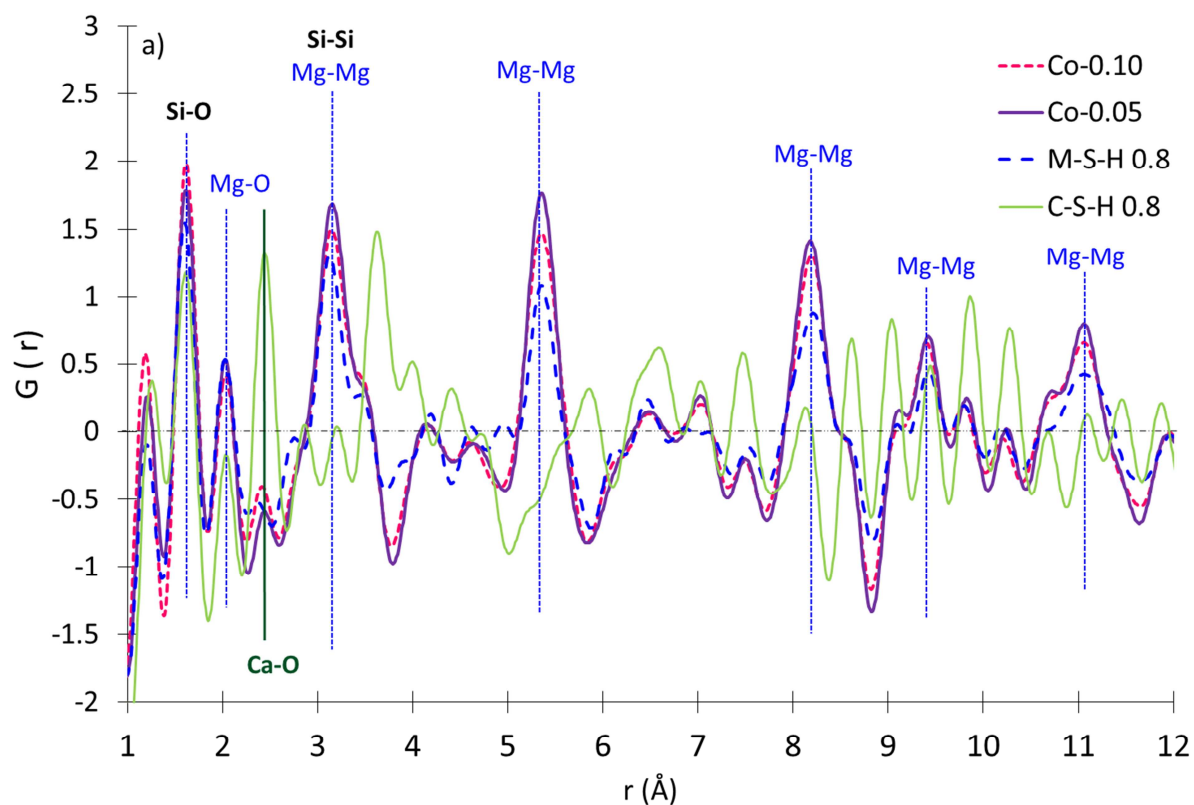
364

365 The decrease in the fraction of Q^2 sites (resonance at -85.6 ppm) from $35\pm 5\%$ in M-S-H 0.8 to $27\pm 4\%$
366 for the co-precipitated samples (Co-0.05 and Co-0.10) also confirmed the absence of any significant

367 amount of C-S-H (comparison between Co-0.05 and Co-0.10 and the calculated spectra in Figure 4),
368 which was consistent with their characterization by XRD and with the low pH of their solution, outside
369 the stability domain of C-S-H. ^{29}Si MAS NMR thus confirmed that the fraction of calcium in the solid
370 phase was not precipitated as C-S-H.

371 Additional characterizations of M-S-H 0.8, C-S-H 0.8, Co-0.05 and Co-0.10 solid fractions were
372 performed using X-ray pair distribution function (PDF) analysis (Figure 5a). The X-ray PDF analysis of
373 pure M-S-H 0.8 indicated a structure where magnesium was bound to silicon and hydroxide.

374 The X-ray PDF analysis of M-S-H 0.8, Co-0.05 and Co-0.10 samples were very similar, and
375 significantly different from that of C-S-H (Figure 5a), which confirmed again that the products formed
376 using the co-precipitation method had a M-S-H structure. The structural correlation peaks could be
377 tentatively assigned using the structure of talc as a reference (Gruner, 1934): they mainly corresponded
378 to Mg-Mg distances ($r = 3.13 \text{ \AA}$, 5.36 \AA , 8.21 \AA , 9.42 \AA , 11.06 \AA) and Mg-O (2.03 \AA) within a same
379 layer as well as Si-Si (3.20 \AA) and Si-O distances in silicate tetrahedra ($r = 1.61 \text{ \AA}$). Two additional
380 peaks at $r = 2.41 \text{ \AA}$ and 7.06 \AA might be observed in the presence of calcium. The first distance is related
381 Ca-O distances in the solid (detailed below). The peak at 2.4 \AA would indicate the presence of CaO_7
382 polyhedra (Skinner et al., 2010) as also present in C-S-H or in other octahedral layer minerals such as
383 e.g. dolomite or tobermorite, indicating either the presence of small quantities of C-S-H or the
384 incorporation of some calcium in the octahedral layers of M-S-H.



385

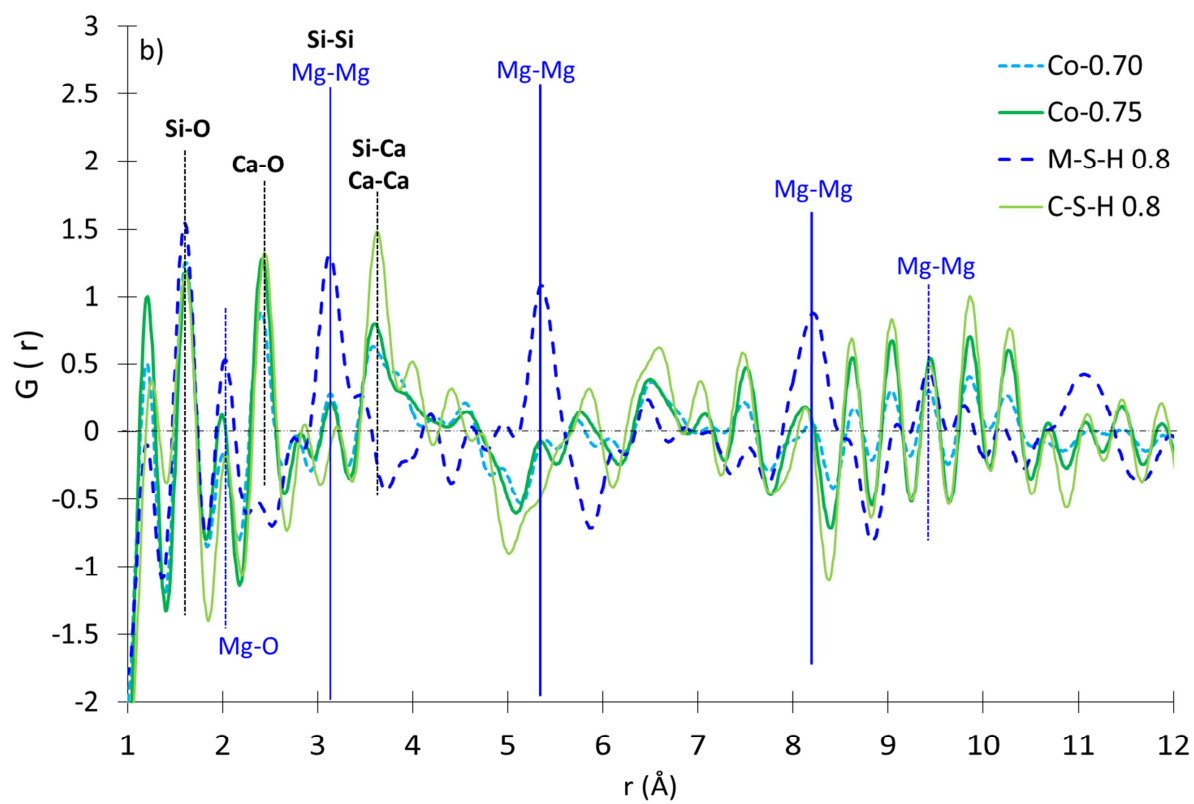
386
387
388

Figure 5: Reduced pair distribution function of M-S-H, C-S-H compared to a) co-precipitated Co-0.05 and Co-0.10 samples and to b) co-precipitated Co-0.70 and Co-0.75 samples.

389 **3.1.3. Surface properties**

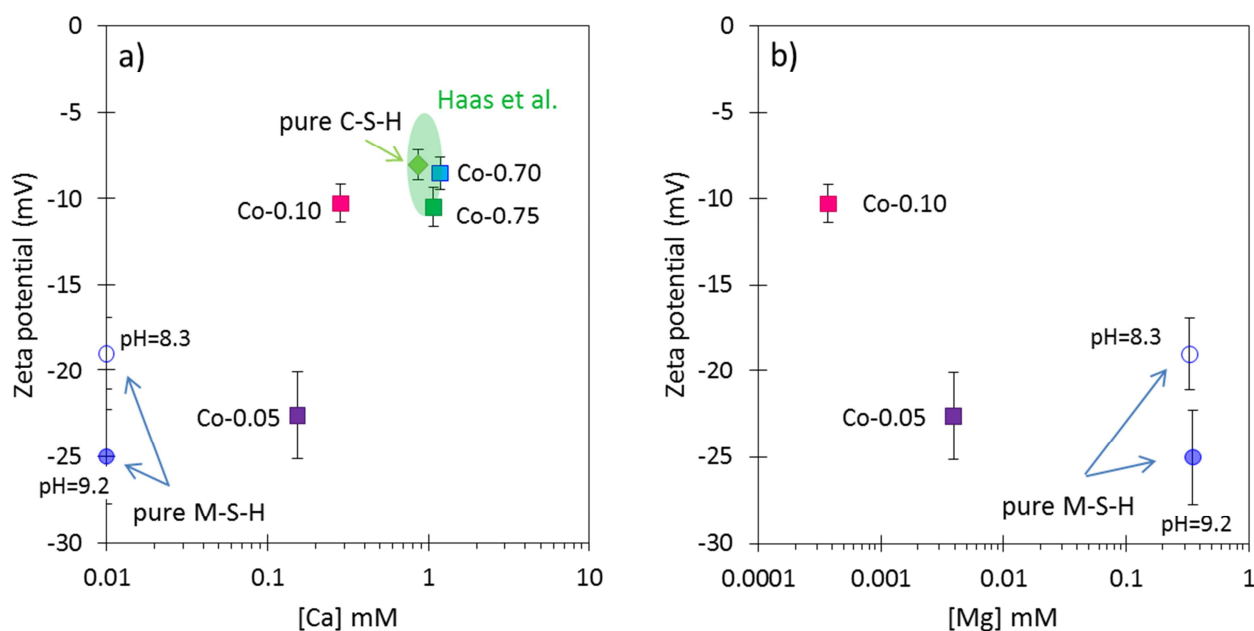
390 The zeta potential of M-S-H 0.8, M-S-H 1.0 and of the co-precipitated samples (cured during 2 years at
391 20°C) are plotted versus the calcium concentrations in solution in Figure 6a and versus the magnesium
392 concentrations in solution in Figure 6b. After 2 years, the less than 2 wt. % of brucite is present (see
393 Appendix A **Error! Reference source not found.**); such a low amount would not affect the zeta
394 potential measured. The effective surface charge of M-S-H was negative with zeta potential values
395 between -19 ± 3 mV and -25 ± 3 mV depending on the pH of the solution (within the pH range 8.3 -
396 9.2).

397 The substitution of MgO by CaO increased the pH from 8.3 to 8.9 and 9.3 for Co-0.05 and Co-0.10
398 samples respectively. This pH increase will thus lead to more negatively charge silanol groups of the Q¹
399 & Q² silicon species at the surface and edge sites of M-S-H, and should result in an increase of the
400 negative surface charge density.

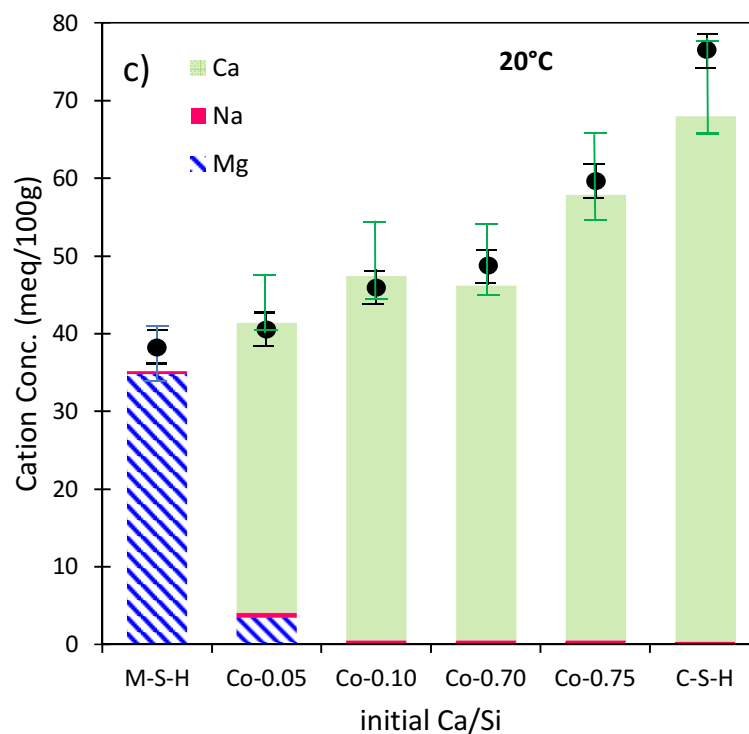
401 At the same time, the calcium concentration in solution increased from 0 to 0.15 and 0.29 mmol/L
402 respectively and the magnesium concentration in solution dropped from 0.38 to 0.004 and below the
403 detection limit of 0.001 mmol/L respectively. The Co-0.05 sample exhibited almost the same zeta
404 potential as pure M-S-H with -22 ± 3 mV at pH 8.9, which is an intermediate value between the two
405 points of pure M-S-H (in zeta potential as well as in pH) whereas the zeta potential of the Co-0.10
406 sample was significantly less negative (-10 ± 1 mV). The surface charge of M-S-H thus depended on the
407 calcium concentration as shown in Figure 6a. As in the case of C-S-H (Haas and Nonat, 2015; Labbez et
408 al., 2007; Labbez et al., 2011; Plusquellec and Nonat, 2016; Viallis-Terrisse et al., 2001), the zeta
409 potential became less negative at higher concentration of dissolved calcium, indicating a sorption of
410 calcium at the surface. One may postulate that, in the case of Co-0.05 sample, calcium substituted a
411 similar amount of magnesium at the surface, resulting in little change of the zeta potential. The strong

412 increase in the zeta potential of the second sample (Co-0.10) would indicate that calcium was more
 413 effectively adsorbed at the surface of M-S-H than magnesium, thus partially compensating the negative
 414 charge of the silicate sites.

415 The magnesium concentration in solution did not seem to influence the zeta potential of M-S-H as
 416 strongly as the calcium concentration, as shown in Figure 6b. In this Figure, we can see no influence of
 417 the magnesium concentration on the effective negative surface of M-S-H. Calcium has been observed to
 418 sorb stronger than magnesium on quartz (Conway, 1981; Dove and Nix, 1997) probably due its slight
 419 smaller hydrated size. Such a preferential sorption of calcium could explain the strong increase in zeta
 420 potential when the calcium concentration increased.



421



422

423 *Figure 6: Zeta potential of M-S-H, co-precipitated sample particles a) versus calcium concentration in suspension (range*
 424 *of values for C-S-H from Haas et al. (Haas and Nonat, 2015) added for comparison) and b) versus magnesium*
 425 *concentration; c) Concentrations of the cations sorbed on co-precipitated samples compared to M-S-H 0.8 and C-S-H 0.8*
 426 *measured by the cobalt hexamine method as a function of the initial Ca/Si. CEC measurements by colorimetry (black*
 427 *circles) have been added for comparison.*

428

429 The measurement of the cation exchange capacity of M-S-H showed a positive CEC of 35 meq/100g
 430 (Figure 6c), which indicated a negative surface charge of the M-S-H particle. This is in agreement with
 431 the effective negative surface charge obtained by zeta potential measurement. The exchangeable
 432 magnesium in pure M-S-H 0.8 was calculated following the equation (5) and was equal to 0.02 per
 433 silicon. The CEC of the Co-0.05 and Co-0.10 samples was slightly higher in the presence of calcium. It
 434 increased from 35 meq/100g to 47 meq/100g for Co-0.10 sample. This sample, thus, contained slightly
 435 more exchangeable calcium, about 0.03 per silicon. In the Co-0.05 sample, most of the magnesium at
 436 the surface was replaced by calcium (Figure 6c and Table 4) and all of it in the Co-0.10, in agreement

437 with the much higher calcium concentration than magnesium one in solution. The general CEC increase
 438 from the pure M-S-H to the Co-0.05 and Co-0.10 indicates a more negative surface charge.

439 *Table 4: Exchangeable magnesium and calcium per silicon in co-precipitated samples compared to M-S-H 0.8 and C-S-H*
 440 *0.8 calculated from CEC*

sample	exchangeable Mg ²⁺ per Si	exchangeable Ca ²⁺ per Si	total
M-S-H	0.021	--	0.021
Co-0.05	0.002	0.022	0.024
Co-0.10	<0.001	0.028	0.028
Co-0.70	<0.001	0.032	0.032
Co-0.75	<0.001	0.040	0.040
C-S-H	<0.001	0.048	0.048

441

442 The uptake of 0.022 and 0.028 Ca_{exch}/Si (CEC in Table 4) at exchangeable sites compared to the total
 443 calcium uptake of 0.05 and 0.10 Ca/Si (if all the initially added calcium would be on CEC sites in the
 444 solid) showed that only a part of calcium was found adsorbed at the surface of M-S-H.

445 To confirm that, CEC was also measured at room temperature on the samples synthesized at 50°C.
 446 Similar results were obtained with Ca_{exch}/Si ratios of 0.03 and 0.04 at CEC sites in the Co-0.05 and Co-
 447 0.10 samples (**Error! Reference source not found. & Error! Reference source not found.**).

448 The remaining calcium may substitute some magnesium in the octahedral layer. Although substitution of
 449 magnesium by calcium (with a bigger size) is unusual, it might occur during co-precipitation within the
 450 poorly ordered M-S-H.

451 Alternatively, a part of calcium might have been washed during the filtration process. To check whether
 452 calcium was still present in the solid phase (i.e. in the octahedral layers) after the CEC and to account
 453 for the missing calcium, the co-precipitated samples after cation exchange by cobalt hexamine
 454 trichloride were dissolved in 0.1 mol/L HCl, to differentiate between surface-sorbed calcium
 455 (determined by CEC measurement) and calcium in the structure. As the CEC measurement should

456 remove the surface-sorbed calcium, any calcium still found is present as non-exchangeable. $Ca_{\text{not exch}}/Si$
 457 ratios of 0.02 and 0.05 were measured in the solids after dissolution (Table 5), confirming the presence
 458 of calcium in the solid part and the total Ca/Si found by the addition of the Ca_{exch}/Si and $Ca_{\text{not exch}}/Si$ was
 459 approximately equal to the initial Ca/Si added to the suspensions.

460 *Table 5: Ca/Si and Mg/Si in the solids synthesized at 50°C from mass balance and dissolution, before and after the CEC.*

	Mass balance		Dissolution		Not exchangeable cation* Ca/Si*
	Ca/Mg	Mg/Si	Before CEC Ca/Mg	After CEC Ca/Mg	
Co-0.05	0.06±0.02	0.76±0.02	0.07±0.02	0.03±0.01	0.02±0.02
Co-0.10	0.14±0.02	0.71±0.02	0.13±0.02	0.08±0.02	0.05±0.02

461 * $Ca/Si = Ca/Mg$ (after CEC) \times Mg/Si (Mass balance).

462 In summary, the different analyses indicated an adsorption of calcium on the surface of M-S-H; a small
 463 calcium uptake in the M-S-H main layers might occurred; alternatively a small amount of C-S-H could
 464 be present although this seemed unlikely due to the low pH value and based on different solid analyses.
 465 Thus, M-(C)-S-H corresponds to a M-S-H phase containing small quantities of adsorbed and/or
 466 incorporated calcium. The exact nature of calcium incorporation, however, still remains unclear.

467 **3.2. Co-0.75 and Co-0.70 samples**

468 This second section investigates the effect of small amounts of MgO ($Mg/Si=0.05$ and 0.10) added
 469 during the synthesis of C-S-H. The $(Ca+Mg)/Si$ ratio was set to 0.8, and the resulting samples were
 470 labelled Co-0.75 and Co-0.70.

471 **3.2.1. Aqueous phase composition**

472 The aqueous phase equilibrated with pure C-S-H (Ca/Si ratio of 0.8) exhibited a pH of 10.5 and
 473 dissolved calcium and silicon concentrations of 0.86 mmol/L and 1.62 mmol/L respectively (Figure 1,
 474 Appendix A). These results are in good agreement with previously reported data (Lothenbach and
 475 Nonat, 2015). At the later age (2 years at 20°C where only traces of brucite were present, see Appendix

476 A), the partial replacement of CaO by MgO in Co-0.75 and Co-0.70 samples caused a decrease in pH to
477 10.2 and 10.1 respectively, and an increase in the calcium and silicon concentrations.

478 The higher pH values resulted in very low concentrations of magnesium in solution (Figure 1, Appendix
479 A), as also observed when only M-S-H is formed at pH 10 (Bernard et al., 2017b; Zhang et al., 2011).
480 The high pH and the very low concentration of magnesium tentatively indicated the presence of both M-
481 S-H and C-S-H.

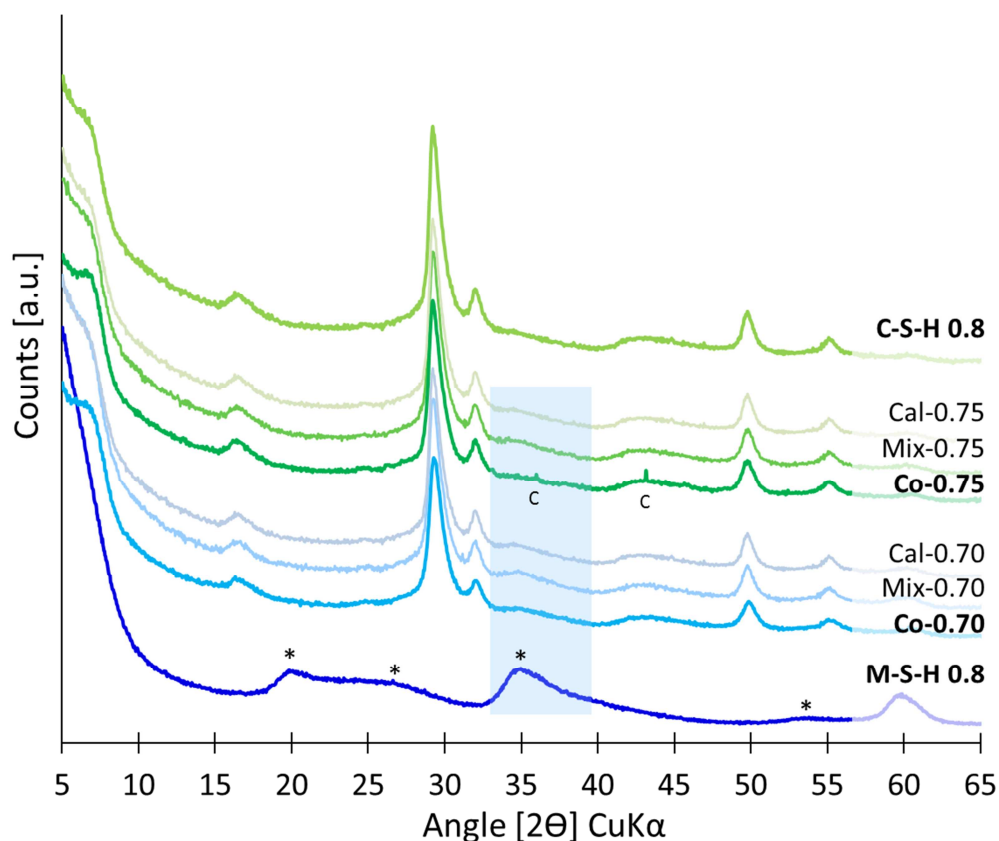
482 **3.2.2. Solid analysis**

483 The solid analysis focused on the samples synthesized 1 year at 50°C; similar analyses were done on the
484 samples synthesized 2 years at 20°C and only traces of brucite were present in both cases.

485 Since the formation of M-S-H is very slow at 20°C, especially at high pH (Lothenbach et al., 2015), the
486 presence of brucite ($\text{Mg}(\text{OH})_2$) was observed up to 1 year (Appendix A). After 2 years however, only
487 traces of brucite were detected. The samples cured at 50°C reacted faster and equilibrium was reached
488 after 1 year.

489 The XRD patterns of Co-0.75 and Co-0.70 samples are compared to pure C-S-H pattern in Figure 7. C-
490 S-H was the main phase present in these samples. However, a small amount of M-S-H (10-20wt.%) is
491 difficult to detect by XRD in the presence of C-S-H (Bernard et al., 2017a). As for the magnesium co-
492 precipitated samples (see 3.1.), complementary XRD patterns were measured and calculated to make the
493 comparison easier. Some reference samples (Mix-0.75 and Mix-0.70) were prepared by mixing pure M-
494 S-H and C-S-H phases with total $(\text{Mg}+\text{Ca})/\text{Si}$ ratios corresponding to those of experiments Co-0.75 and
495 Co-0.70. Their diffraction patterns were recorded and calculated by linear combination of the patterns of
496 plain M-S-H and C-S-H (Cal-0.75 and Cal-0.70). The calculated and separately mixed samples showed
497 the same reflections. Similarly, all the patterns exhibited almost the same diffraction patterns and M-S-H

498 phases were very difficult to observe. The co-precipitated samples could thus contained small amounts
 499 of M-S-H, but other characterizations were needed to ascertain the presence of this phase.



500

501 *Figure 7: XRD patterns of Co-0.70 and Co-0.75 samples (1 year at 50°C) compared to XRD patterns of C-S-H 0.8, M-S-H 0.8*
 502 *and calculated and mechanically mixed samples. C=calcite, *=M-S-H.*

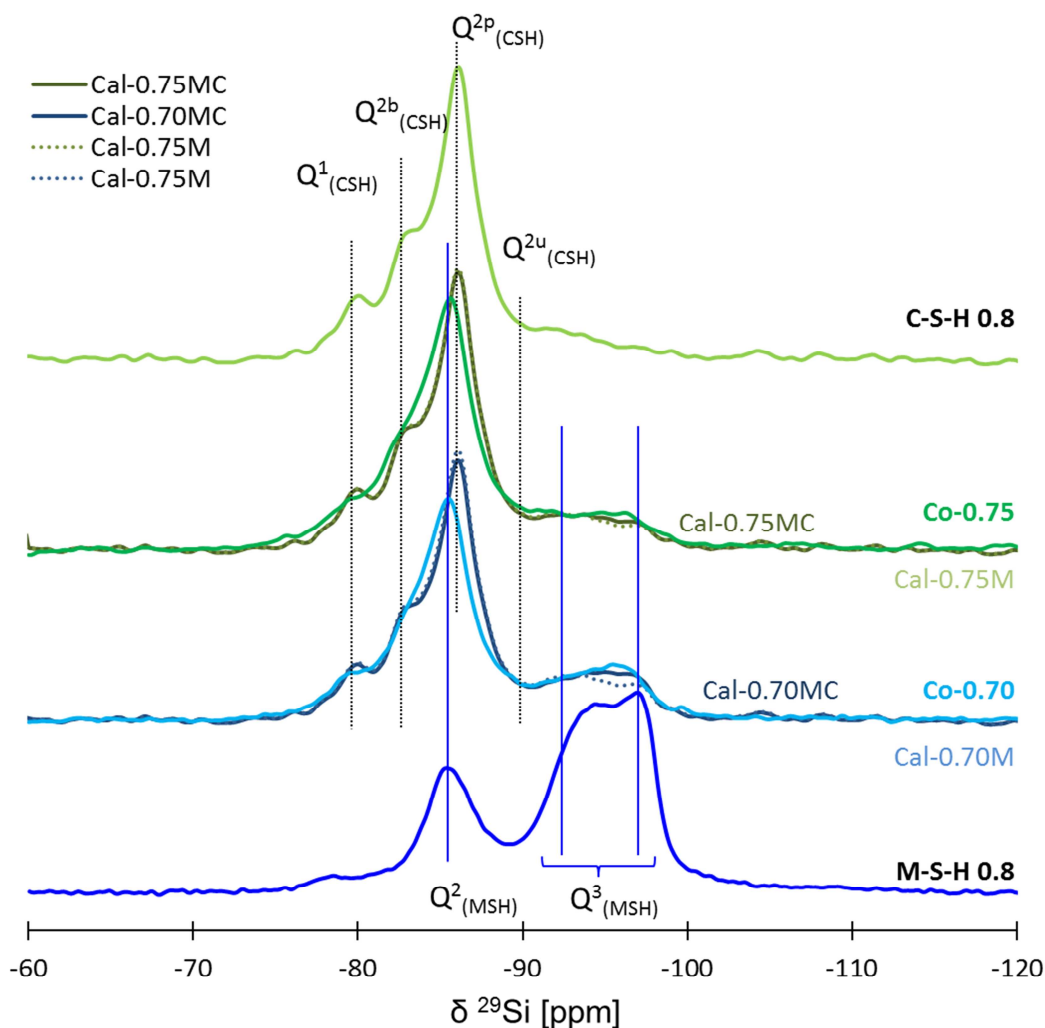
503

504 The X-ray PDF of Co-0.70 and Co-0.75 and C-S-H (Figure 5b) bore strong resemblance. According to
 505 the literature (Grangeon et al., 2013; Lequeux et al., 1999; Meral et al., 2011; Skinner et al., 2010;
 506 White, 2016; White et al., 2015), the correlations peaks might correspond to Si-O distances ($r = 1.61 \text{ \AA}$
 507 and 3.63 \AA), Ca-O distances ($r = 2.44 \text{ \AA}$), Ca-Ca distances ($r = 3.80 \text{ \AA}$ and 6.63 \AA) Si-Ca distances ($r =$
 508 3.20 \AA and 3.63 \AA) and possibly Si-Si distances ($r = 3.20 \text{ \AA}$). Small differences were however noticed
 509 between the pure C-S-H and the co-precipitated samples: the correlation peaks observed at $r = 3.14 \text{ \AA}$

510 and 5.38 Å in the co-precipitated samples were characteristic of Mg-Mg distances observed in M-S-H.
511 The intensity of the correlation peaks assigned to Ca-Ca distances was also lower. These results might
512 suggest the presence of small amounts of M-S-H in the co-precipitated samples, but this again needed to
513 be confirmed by other techniques.

514 The ^{29}Si MAS NMR spectra of the co-precipitated samples (Co-0.75 and Co-0.70) are shown in Figure
515 8. ^{29}Si MAS NMR data confirmed the presence of C-S-H with typical chemical shifts (Andersen et al.,
516 2003; Bell et al., 1990; Chen et al., 2004; Klur et al., 1998; L'Hôpital et al., 2015; Richardson et al.,
517 2010) at approx. -79.7, -82.9, -85.8 and -88.4 ppm corresponding to Q^1 (end of chains), Q^2_b (bridging
518 position), Q^2_p (pairing position) and Q^2_u (bridging position with binding to H^+ (L'Hôpital et al., 2015; Le
519 Saout et al., 2006; Sato and Grutzeck, 1991)) of the silicate tetrahedra in C-S-H, as shown in Figure 8.
520 The pure C-S-H sample with a Ca/Si ratio of 0.8 contained mainly Q^2 species, and only very small
521 amounts of Q^3 species (broad signal at -93.5 ppm which accounted for $\approx 4\%$ of the total silicate), in
522 agreement with previous studies of C-S-H with low Ca/Si ratio (Le Saout et al., 2006; Myers et al.,
523 2015). The presence of M-S-H in the samples was evidenced by the presence of the resonance peaks
524 between -92 and -97 ppm corresponding to Q^3 tetrahedral sites of M-S-H (Brew and Glasser, 2005;
525 d'Espinose de Lacaillerie et al., 1995; Nied et al., 2016; Roosz et al., 2015; Walling et al., 2015).

526



527

528 *Figure 8: ^{29}Si MAS NMR spectra of Co-0.70 and Co-0.75 samples (1 year at 50°C) compared to spectra of C-S-H 0.8, M-S-H*
 529 *0.8 and the calculated reference samples with M-S-H 0.8 (Cal-0.70M, Cal-0.75M) and with Co-0.05 (Cal-0.70MC, Cal-*
 530 *0.75MC).*

531 Deconvolution of the ^{29}Si MAS NMR spectra was carried out following the procedure outlined in
 532 literature (Bernard et al., 2017a; Bernard et al., 2017b; L'Hôpital et al., 2016a; Nied et al., 2016) and the
 533 results are detailed in Table 3. Because of the formation of M-S-H, the content of silicate in C-S-H
 534 decreased from 96 ($\pm 5\%$) in pure C-S-H to 69 ($\pm 8\%$) in the Co-0.70 sample. The content of Q^1 and Q^2
 535 sites attributed to C-S-H decreased with the replacement by magnesium. The calculated MCL remained
 536 above 20, which is typical for C-S-H with a low Ca/Si ratio.

537 The content of Q³ tetrahedral sites between -92 and -97 ppm increased from 0 to 28% ($\pm 5\%$) (see Table
538 3) with the magnesium addition, confirming the presence of M-S-H. The amount of silicate attributed to
539 M-S-H was higher than expected in Co-0.75 and Co-0.70 samples. The Mg/Si=0.8 in M-S-H and
540 Ca/Si=0.8 in C-S-H should distribute the tetrahedral silicate to 6% in M-S-H and 94% in C-S-H and in
541 13% in M-S-H and 87% in C-S-H, respectively, for the two co-precipitated samples. ²⁹Si MAS NMR
542 indicated the presence of significantly more tetrahedral silicate attributed to M-S-H (18% instead of 6%
543 and 28% instead of 13%), indicating that the content of M-S-H is higher than expected (as detailed in
544 Table 3).

545 The recorded ²⁹Si MAS NMR data were compared to calculated reference spectra (Cal-0.70MC and Cal-
546 0.75MC) using a linear combination of the spectra of C-S-H 0.8 and Co-0.05 samples. This latter was
547 preferred to pure M-S-H (Cal-0.70M and Cal-0.75M) since it provided a better fit of the experimental
548 spectra, as shown in Figure 8.

549 This better agreement together with the high fraction of silicate attributed to pure M-S-H could be
550 explained by some uptake of calcium in M-S-H also at higher pH. However, it remained unclear whether
551 calcium was sorbed on the surface and edge sites of M-S-H only or whether it could be present in the
552 octahedral layer as well.

553 Given the large amount of silicate associated with the M-(C)-S-H phase (28 and 18 % respectively,
554 Table 3), all the magnesium in the solid fraction of the samples Co-0.70 and Co-0.75 seemed to be in M-
555 (C)-S-H. This, together with the low magnesium concentration in solution, suggested no or very little
556 incorporation of magnesium in C-S-H. The uptake of magnesium at the exchangeable sites of C-S-H
557 could also be excluded as the CEC measurements showed the presence of mainly calcium (Table 4).

558 The TEM observations of Co-0.70 sample (**Error! Reference source not found.**) and the corresponding
559 EDS measurements (**Error! Reference source not found.**) showed two different types of products in
560 the sample. The first one contained mainly calcium and silicon and thus corresponded to C-S-H. The
561 second one, in smaller amount, contained significant amounts of magnesium and silicon, which
562 confirmed the presence of M-S-H. The M-S-H particles exhibited a layered texture which agreed well
563 with the sheet-like morphology already observed for pure M-S-H or mixed samples containing calcium
564 (Lothenbach et al., 2015; Roosz et al., 2015). The (Mg+Ca)/Si ratio remained lower than 0.8 regardless
565 the type of product. The mean Ca/Si and Mg/Si ratios were 0.65 ± 0.15 and 0.05 ± 0.05 respectively for
566 the C-S-H particles, and 0.15 ± 0.05 and 0.65 ± 0.15 for the M-S-H particles (**Error! Reference source**
567 **not found.**). This confirms the uptake of no or only very small amounts of magnesium in C-S-H, in
568 agreement with the ^{29}Si MAS NMR and PDF observations and indicates the possibility of a more
569 substantial uptake of calcium by M-S-H. However, as the EDS measurements were performed on areas
570 with a typical diameter of 100-150 nm, some intermixing of C-S-H and M-S-H phases can be expected,
571 such as for the data at Ca/Si ratios of 0.5 and 0.6 and Mg/Si ratios 0.3 to 0.6 which are based on
572 intermixing of C-S-H and M-S-H.

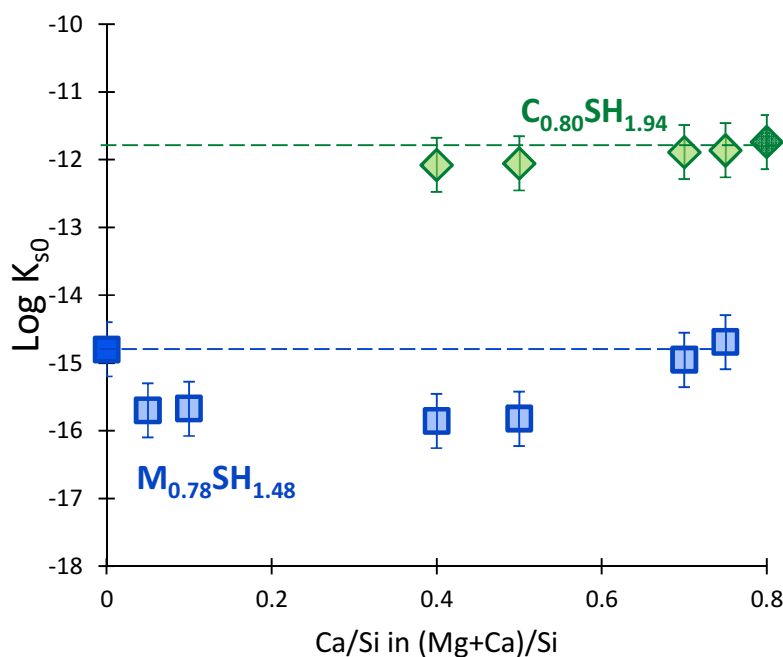
573
574 In summary, separate M-S-H (henceforward, M-(C)-S-H) and C-S-H phases were observed in the Co-
575 0.70 and Co-0.75 samples by TEM/EDS observations, ^{29}Si MAS NMR spectra, XRD and X-ray PDF
576 analysis. Traces of brucite were observed at 20°C after 2 years, due to the slow kinetic of brucite
577 dissolution in batch experiments (Bernard et al., 2017b; Szczerba et al., 2013). The data seemed to
578 indicate that a significant uptake of calcium in M-S-H occurred also at high pH. In C-S-H, however, no
579 or very limited uptake of magnesium seemed to occur. This result could be explained by the very low
580 magnesium concentrations in solution which resulted in a negligible fraction of charge balancing

581 magnesium at the C-S-H surface. The very low concentration of magnesium could also prevent its
582 incorporation in C-S-H during the precipitation process.

583 3.3. Effect on solubility

584 The solubility products of $C_{0.80}SH_{1.94}$ and $M_{0.78}SH_{1.48}$ were calculated using the measured concentrations
585 in solution at equilibrium (Figure 9 and Appendix A). The solubility product of $C_{0.80}SH_{1.94}$ remained
586 approximatively constant at ≈ -12 regardless of the presence or absence of magnesium. This indicates
587 that the uptake of magnesium by C-S-H and the formation of a solid-solution are rather unlikely. In
588 contrast, the decrease in the calculated solubility product of pure $M_{0.78}SH_{1.48}$ in the presence of calcium
589 by up to 1 log unit at the maximum showed a stabilization of M-S-H in the presence of calcium (Figure
590 9). This supported the formation of a solid-solution with an incorporation of calcium in M-S-H, in
591 agreement with the experimental observations.

592 The expected concentrations of calcium, magnesium and silicon were calculated using separate C-S-H
593 (Kulik, 2011) and M-S-H (Bernard et al., 2017b) phases, i.e. M-S-H without calcium and compared with
594 the measured data in Figure 1. The thermodynamic modelling pointed out that C-S-H was stable only at
595 pH higher than 10, in agreement with the experimental results. However, the calculated pH (10.4) in the
596 presence of magnesium (Co-0.05 and Co-0.10) was notably higher than the pH experimentally observed
597 (8.9 and 9.3 respectively) while the calculated silicon concentrations were lower than the experimental
598 ones (Appendix A). Such deviations between experiments and calculations may have resulted from the
599 occurrence of calcium in M-S-H which was neglected in this calculation. The uptake of calcium by M-
600 S-H would, indeed, reduce the pH values.



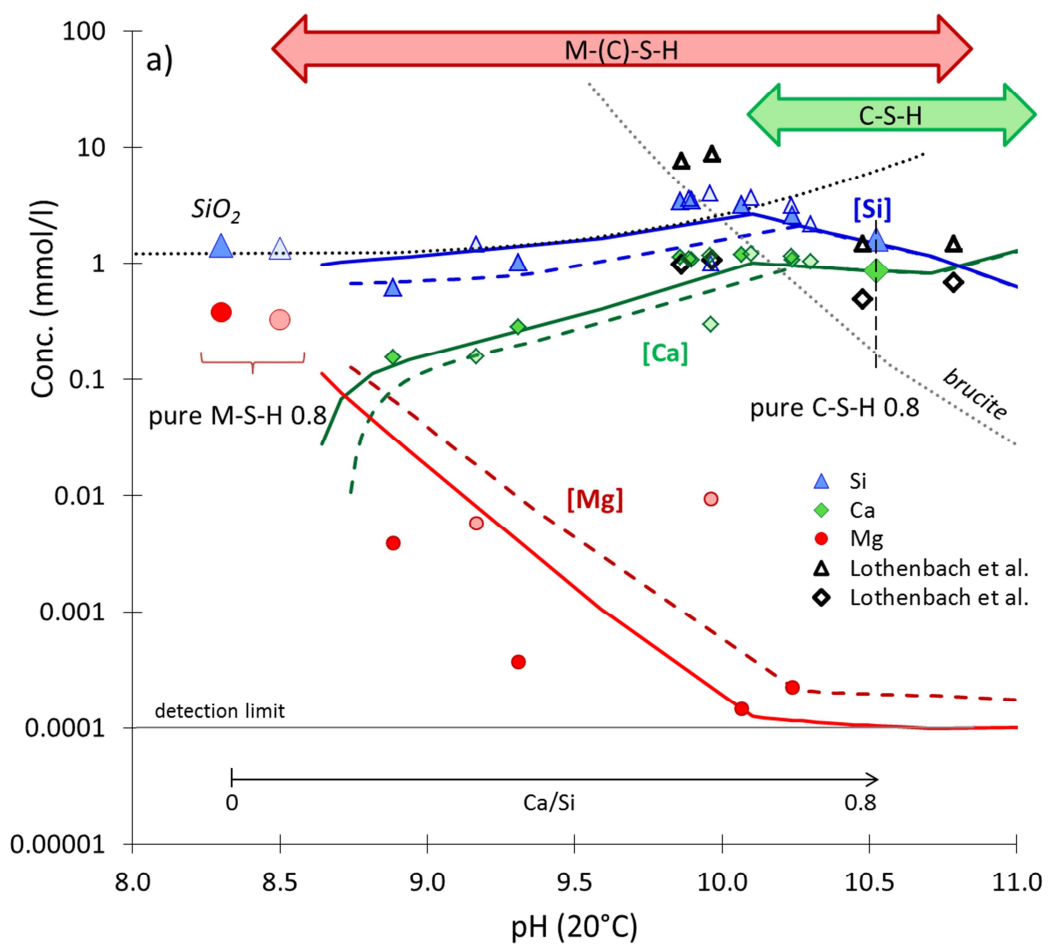
601

602 Figure 9: Solubility products of $M_{0.78}SH_{1.48}$ (squares) and solubility products of $C_{0.80}SH_{1.94}$ (diamonds) calculated for the
 603 co-precipitated samples at 20°C after 2 years. The M-S-H calculation is based on the end-members from Bernard et al.
 604 (Bernard et al., 2017b), the C-S-H calculation is derived from (Kulik, 2011).

605

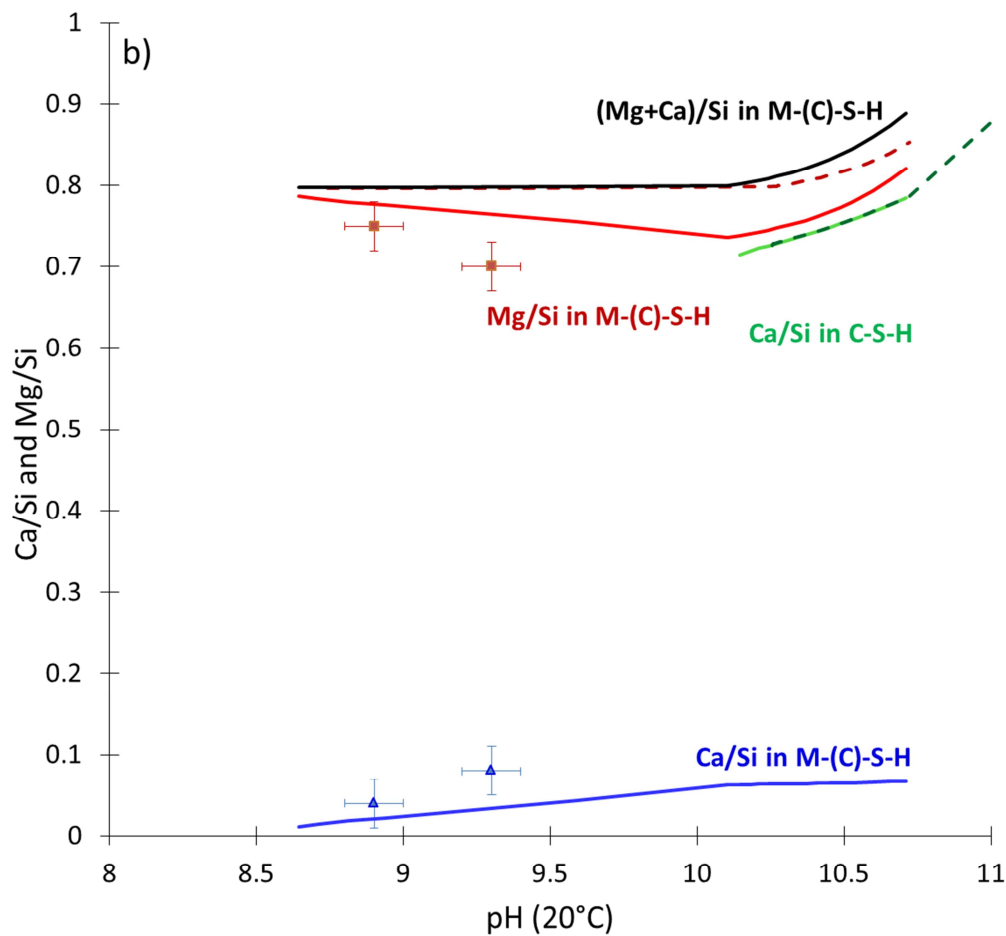
606 To check this assumption, two additional end-members with a Ca/Si ratio of 0.1 were introduced in the
 607 M-S-H solid solution model developed previously (Bernard et al., 2017b). The total of cation to silica
 608 ratios of 0.78 and 1.30 were kept constant, leading to the following stoichiometries: $M_{0.68}C_{0.1}SH_{1.48}$ and
 609 $M_{1.2}C_{0.1}SH_{1.80}$ as detailed in Table 2.

610 The calculated concentrations and atomic ratios in C-S-H and M-S-H (solid lines) are compared to the
 611 results obtained by the model containing only M-S-H and C-S-H (dashed lines) and with the
 612 experimental data (dots) in Figure 10. The experimentally observed calcium and silicon concentrations
 613 and pH measured experimentally were better described by the model taking into account the possible
 614 incorporation of calcium in M-S-H. The model was also able to predict the presence of calcium (Ca/Si
 615 up to 0.07) in M-S-H, in agreement with the experimental observations.



616

617



618

619 Figure 10: a) Calculated solubility curves (solid lines) associated to the co-precipitated samples using the M-(C)-S-H
 620 solution and C-S-H solid-solution models compared to the calculated solubility curves (dashed lines) using the M-S-H
 621 (Bernard et al., 2017b) and C-S-H solid-solution models. Solubilities of brucite and amorphous SiO₂ are shown in dotted
 622 lines. Empty symbols are from Lothenbach et al. (Lothenbach et al., 2015). b) Evolution of atomic ratios calculated by
 623 GEMS using the M-(C)-S-H solution and C-S-H solid-solution models compared to the M-S-H (Bernard et al., 2017b) and C-
 624 S-H solid-solution models and compared to the experimental results from mass balance.

625

626 4. Conclusions

627

628 This work aimed at investigating the relative stabilities of M-S-H and C-S-H and the possibility to
 629 incorporate small amounts of calcium into M-S-H, or small amounts of magnesium into C-S-H. The
 630 main conclusions can be summarized as follows.

- 631 1. C-S-H is unstable at pH values below 10.
- 632 2. When small amounts of calcium were added during the synthesis of M-S-H ($(\text{Mg}+\text{Ca})/\text{Si} = 0.8$, Ca/Si
633 $= 0.05$ or 0.10), the uptake of calcium by M-S-H is evidenced. CEC measurements showed that calcium
634 is present as an exchangeable cation on the surface of M-S-H and is responsible for the less negative
635 surface charge density of M-S-H particles measured by zeta potential. Nevertheless, a small fraction of
636 the calcium incorporated into M-S-H may be non-exchangeable. Thermodynamic calculations confirm
637 that an incorporation of calcium into M-S-H is likely since the presence of calcium stabilizes the M-S-H
638 formed. A solid solution may thus occur between pure M-S-H and a M-C-S-H phase containing small
639 amounts of calcium. The site of incorporation is not yet fully elucidated, nor the maximal uptake.
640 However, the two additional end-members ($\text{M}_{0.68}\text{C}_{0.1}\text{SH}_{1.48}$ and $\text{M}_{1.2}\text{C}_{0.1}\text{SH}_{1.80}$) make it possible to
641 describe the aqueous concentrations and solid compositions observed experimentally.
- 642 3. At pH values above 10, both M-S-H and C-S-H phases are stable and coexist. A similar uptake of
643 calcium by M-S-H as at lower pH values is suggested. The simultaneous presence of C-S-H and M-S-H
644 makes it difficult to evidence a possible uptake of magnesium by C-S-H. However, if such uptake
645 occurs, it is not in the cation exchangeable sites and the incorporation of magnesium in the structure
646 should be strongly limited by the very low concentration of magnesium in solution controlled by M-S-H.
647
- 648 The new solid solution model developed in this study to describe the uptake of calcium by M-S-H may
649 offer new prospects to simulate the deterioration of calcium silicate cement-based materials in the
650 presence of magnesium (provided by clayey minerals, ground- or seawater) or to optimize the design of
651 novel binders containing calcium, magnesium and silicates.

652 **Acknowledgements**

653 The authors would like to thank Daniel Rentsch and Catherine Lerouge for helpful discussions, Remi
654 Chassagnon for the TEM analyses, Numa Pfenninger for the ICP measurements, Luigi Brunetti and
655 Fabien Le Goff for the support in the preparation of the samples and analysis. The NMR hardware was
656 partially granted by the Swiss National Science Foundation (SNSF, grant no. 206021_150638/1).

657

658

659

660

661

662

663

664

665

666

667

668

669

670 **References**

- 671 Andersen, M.D., Jakobsen, H.J., Skibsted, J., 2003. Incorporation of aluminum in the
672 calcium silicate hydrate (CSH) of hydrated Portland cements: a high-field ^{27}Al and
673 ^{29}Si MAS NMR investigation. *Inorganic Chemistry* 42, 2280-2287.
- 674 Bach, T., Chabas, E., Pochard, I., Cau Dit Coumes, C., Haas, J., Frizon, F., Nonat, A.,
675 2013. Retention of alkali ions by hydrated low-pH cements: Mechanism and Na^+/K^+
676 selectivity. *Cement and Concrete Research* 51, 14-21.
- 677 Bell, G., Bensted, J., Glasser, F., Lachowski, E., Roberts, D., Taylor, M., 1990. Study of
678 calcium silicate hydrates by solid state high resolution ^{29}Si nuclear magnetic
679 resonance. *Advances in Cement Research* 3, 23-27.
- 680 Bernard, E., Lothenbach, B., Le Goff, F., Pochard, I., Dauzères, A., 2017a. Effect of
681 magnesium on calcium silicate hydrate (C-S-H). *Cement and Concrete Research* 97,
682 61-72.
- 683 Bernard, E., Lothenbach, B., Rentsch, D., Pochard, I., Dauzères, A., 2017b. Formation
684 of magnesium silicate hydrates (M-S-H). *Physics and Chemistry of the Earth, Parts*
685 *A/B/C* 99, 142-157.
- 686 Bonen, D., Cohen, M.D., 1992. Magnesium sulfate attack on portland cement paste—
687 II. Chemical and mineralogical analyses. *Cement and Concrete Research* 22, 707-
688 718.
- 689 Brew, D.R.M., Glasser, F.P., 2005. Synthesis and characterisation of magnesium
690 silicate hydrate gels. *Cement and Concrete Research* 35, 85-98.
- 691 Chen, J.J., Thomas, J.J., Taylor, H.F., Jennings, H.M., 2004. Solubility and structure of
692 calcium silicate hydrate. *Cement and Concrete Research* 34, 1499-1519.
- 693 Chiang, W.-S., Ferraro, G., Fratini, E., Ridi, F., Yeh, Y.-Q., Jeng, U., Chen, S.-H., Baglioni,
694 P., 2014. Multiscale structure of calcium-and magnesium-silicate-hydrate gels.
695 *Journal of Materials Chemistry A* 2, 12991-12998.
- 696 Conway, B., 1981. Ion hydration co-sphere interactions in the double-layer and ionic
697 solutions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*
698 123, 81-94.
- 699 d'Espinose de Lacaillerie, J.-B., Kermarec, M., Clause, O., 1995. ^{29}Si NMR observation
700 of an amorphous magnesium silicate formed during impregnation of silica with
701 $\text{Mg}(\text{II})$ in aqueous solution. *The Journal of Physical Chemistry* 99(47), 17273-17281.
- 702 Dauzères, A., Achiedo, G., Nied, D., Bernard, E., Alahrache, S., Lothenbach, B., 2016.
703 Magnesium perturbation in low-pH concretes placed in clayey environment - solid
704 characterizations and modeling. *Cement and Concrete Research* 79, 137-150.
- 705 De Weerd, K., Justnes, H., 2015. The effect of sea water on the phase assemblage of
706 hydrated cement paste. *Cement and Concrete Composites* 55, 215-222.

- 707 Deschner, F., Winnefeld, F., Lothenbach, B., Seufert, S., Schwesig, P., Dittrich, S.,
708 Goetz-Neunhoeffler, F., Neubauer, J., 2012. Hydration of Portland cement with high
709 replacement by siliceous fly ash. *Cement and Concrete Research* 42, 1389-1400.
- 710 Dove, P.M., Nix, C.J., 1997. The influence of the alkaline earth cations, magnesium,
711 calcium, and barium on the dissolution kinetics of quartz. *Geochimica et*
712 *Cosmochimica Acta* 61, 3329-3340.
- 713 Egami, T., Billinge, S.J.L., 2003. Chapter 3. The method of total scattering and atomic
714 pair distribution function analysis. Pergamon Materials Series.
- 715 Garcia Calvo, J.L., Hidalgo, A., Alonso, C., Fernández Luco, L., 2010. Development of
716 low-pH cementitious materials for HLRW repositories: Resistance against ground
717 waters aggression. *Cement and Concrete Research* 40, 1290-1297.
- 718 Grangeon, S., Claret, F., Lerouge, C., Warmont, F., Sato, T., Anraku, S., Numako, C.,
719 Linard, Y., Lanson, B., 2013. On the nature of structural disorder in calcium silicate
720 hydrates with a calcium/silicon ratio similar to tobermorite. *Cement and Concrete*
721 *Research* 52, 31-37.
- 722 Gruner, J.W., 1934. The crystal structures of talc and pyrophyllite. *Zeitschrift für*
723 *Kristallographie-Crystalline Materials* 88, 412-419.
- 724 Haas, J., Nonat, A., 2015. From C-S-H to C-A-S-H: Experimental study and
725 thermodynamic modelling. *Cement and Concrete Research* 68, 124-138.
- 726 Jakobsen, U.H., De Weerd, K., Geiker, M.R., 2016. Elemental zonation in marine
727 concrete. *Cement and Concrete Research* 85, 12-27.
- 728 James, M., Hunter, R.J., O'Brien, R.W., 1992. Effect of particle size distribution and
729 aggregation on electroacoustic measurements of zeta potential. *Langmuir* 8, 420-
730 423.
- 731 Jenni, A., Mäder, U., Lerouge, C., Gaboreau, S., Schwyn, B., 2014. In situ interaction
732 between different concretes and Opalinus clay. *Physics and Chemistry of the Earth,*
733 *Parts A/B/C* 70, 71-83.
- 734 Jin, F., Al-Tabbaa, A., 2013. Thermogravimetric study on the hydration of reactive
735 magnesia and silica mixture at room temperature. *Thermochimica Acta* 566, 162-
736 168.
- 737 Klur, I., Pollet, B., Virlet, J., Nonat, A., 1998. CSH structure evolution with calcium
738 content by multinuclear NMR, Nuclear magnetic resonance spectroscopy of cement-
739 based materials. Springer, pp. 119-141.
- 740 Kulik, D., Wagner, T., Dmytrieva, S.V., Kosakowski, G., Hingerl, F., Chudnenko, K.V.,
741 Berner, U., 2013. GEM-Selektor geochemical modeling package: revised algorithm
742 and GEMS3K numerical kernel for coupled simulation codes. *Computational*
743 *Geochemistry* 17, 1-24.
- 744 Kulik, D.A., 2011. Improving the structural consistency of CSH solid solution
745 thermodynamic models. *Cement and Concrete Research* 41, 477-495.

- 746 L'Hôpital, E., Lothenbach, B., Kulik, D., Scrivener, K., 2016a. Influence of calcium to
747 silica ratio on aluminium uptake in calcium silicate hydrate. *Cement and Concrete*
748 *Research* 85, 111-121.
- 749 L'Hôpital, E., Lothenbach, B., Scrivener, K., Kulik, D., 2016b. Alkali uptake in calcium
750 alumina silicate hydrate (CASH). *Cement and Concrete Research* 85, 122-136.
- 751 L'Hôpital, E., Lothenbach, B., Le Saout, G., Kulik, D., Scrivener, K., 2015. Incorporation
752 of aluminium in calcium-silicate-hydrates. *Cement and Concrete Research* 75, 91-
753 103.
- 754 Labbez, C., Nonat, A., Pochard, I., Jönsson, B., 2007. Experimental and theoretical
755 evidence of overcharging of calcium silicate hydrate. *Journal of Colloid and Interface*
756 *Science* 309, 303-307.
- 757 Labbez, C., Pochard, I., Jönsson, B., Nonat, A., 2011. CSH/solution interface:
758 Experimental and Monte Carlo studies. *Cement and Concrete Research* 41, 161-168.
- 759 Le Saout, G., Lécolier, E., Rivereau, A., Zanni, H., 2006. Chemical structure of cement
760 aged at normal and elevated temperatures and pressures: Part I. Class G oilwell
761 cement. *Cement and Concrete Research* 36, 71-78.
- 762 Leisinger, S.M., Bhatnagar, A., Lothenbach, B., Johnson, C.A., 2014. Solubility of
763 chromate in a hydrated OPC. *Applied Geochemistry* 48, 132-140.
- 764 Lequeux, N., Morau, A., Philippot, S., Boch, P., 1999. Extended X-ray Absorption Fine
765 Structure Investigation of Calcium Silicate Hydrates. *Journal of the American*
766 *Ceramic Society* 82, 1299-1306.
- 767 Lerouge, C., Gaboreau, S., Grangeon, S., Claret, F., Warmont, F., Jenni, A., Cloet, V.,
768 Mäder, U., 2017. In situ interactions between Opalinus Clay and Low Alkali Concrete.
769 *Physics and Chemistry of the Earth, Parts A/B/C* 99, 3-21.
- 770 Lothenbach, B., Durdzinski, P., DeWeerd, K., 2016. Thermogravimetric analysis, in:
771 Scrivener, K., Snellings, R., Lothenbach, B. (Eds.), *A Practical Guide to*
772 *Microstructural Analysis of Cementitious Materials*. CRC Press, Oxford, UK, pp. 177-
773 212.
- 774 Lothenbach, B., Nied, D., L'Hôpital, E., Achiedo, G., Dauzères, A., 2015. Magnesium
775 and calcium silicate hydrates. *Cement and Concrete Research* 77, 60-68.
- 776 Lothenbach, B., Nonat, A., 2015. Calcium silicate hydrates: Solid and liquid phase
777 composition. *Cement and Concrete Research* 78, 57-70.
- 778 MacKenzie, K., Meinhold, R., 1994. The thermal reactions of talc studied by ^{29}Si and
779 ^{25}Mg MAS NMR. *Thermochimica Acta* 244, 195-203.
- 780 Mäder, U., Jenni, A., Lerouge, C., Gaboreau, S., Miyoshi, S., Kimura, Y., Cloet, V.,
781 Fukaya, M., Claret, F., Otake, T., Shibata, M., Lothenbach, B., 2017. 5-year chemico-
782 physical evolution of concrete-claystone interfaces. *Swiss Journal of Geosciences*
783 110, 307-327.

- 784 Mägi, M., Lippmann, E., Samoson, A., Engelhardt, G., Grimmer, A.R., 1984. Solid-state
785 high-resolution silicon-29 chemical shifts in silicates. *The Journal of Physical*
786 *Chemistry* 88, 1518-1522.
- 787 Martin, L.H., Winnefeld, F., Tschopp, E., Müller, C.J., Lothenbach, B., 2017. Influence of
788 fly ash on the hydration of calcium sulfoaluminate cement. *Cement and Concrete*
789 *Research* 95, 152-163.
- 790 Massiot, D., Fayon, F., Capron, M., King, I., Le Calvé, S., Alonso, B., Durand, J.O., Bujoli,
791 B., Gan, Z., Hoatson, G., 2002. Modelling one- and two-dimensional solid-state NMR
792 spectra. *Magnetic Resonance in Chemistry* 40, 70-76.
- 793 Meral, C., Benmore, C., Monteiro, P.J., 2011. The study of disorder and
794 nanocrystallinity in C-S-H, supplementary cementitious materials and geopolymers
795 using pair distribution function analysis. *Cement and Concrete Research* 41, 696-
796 710.
- 797 Myers, R.J., L'Hôpital, E., Provis, J.L., Lothenbach, B., 2015. Effect of temperature and
798 aluminium on calcium (alumino)silicate hydrate chemistry under equilibrium
799 conditions. *Cement and Concrete Research* 68, 83-93.
- 800 Nied, D., Enemark-Rasmussen, K., L'Hôpital, E., Skibsted, J., Lothenbach, B., 2016.
801 Properties of magnesium silicate hydrates (MSH). *Cement and Concrete Research*
802 79, 323-332.
- 803 Pedone, A., Palazzetti, F., Barone, V., 2017. Models of Aged Magnesium-Silicate-
804 Hydrate Cements Based on the Lizardite and Talc Crystals: A Periodic DFT-GIPAW
805 Investigation. *The Journal of Physical Chemistry C*.
- 806 Peyronnard, O., Benzaazoua, M., Blanc, D., Moszkowicz, P., 2009. Study of mineralogy
807 and leaching behavior of stabilized/solidified sludge using differential acid
808 neutralization analysis: Part I: Experimental study. *Cement and Concrete Research*
809 39, 600-609.
- 810 Plusquellec, G., Nonat, A., 2016. Interactions between calcium silicate hydrate (CSH)
811 and calcium chloride, bromide and nitrate. *Cement and Concrete Research* 90, 89-
812 96.
- 813 Qiu, X., Thompson, J.W., Billinge, S.J., 2004. PDFgetX2: a GUI-driven program to
814 obtain the pair distribution function from X-ray powder diffraction data. *Journal of*
815 *Applied Crystallography* 37, 678-678.
- 816 Renaudin, G., Russias, J., Leroux, F., Cau-dit-Coumes, C., Frizon, F., 2009. Structural
817 characterization of C-S-H and C-A-S-H samples—Part II: Local environment
818 investigated by spectroscopic analyses. *Journal of Solid State Chemistry* 182, 3320-
819 3329.
- 820 Richardson, I.G., 2008. The calcium silicate hydrates. *Cement and Concrete Research*
821 38, 137-158.

- 822 Richardson, I.G., Brough, A.R., Brydson, R., Groves, G.W., Dobson, C.M., 1993.
823 Location of aluminum in substituted calcium silicate hydrate (C-S-H) gels as
824 determined by ^{29}Si and ^{27}Al NMR and EELS. *Journal of the American Ceramic Society*
825 *76*, 2285-2288.
- 826 Richardson, I.G., Skibsted, J., Black, L., Kirkpatrick, R.J., 2010. Characterisation of
827 cement hydrate phases by TEM, NMR and Raman spectroscopy. *Advanced Cement*
828 *Based Materials* *22*, 233-248.
- 829 Roosz, C., Grangeon, S., Blanc, P., Montouillout, V., Lothenbach, B., Henocq, P., Giffaut,
830 E., Vieillard, P., Gaboreau, S., 2015. Crystal structure of magnesium silicate hydrates
831 (MSH): The relation with 2: 1 Mg-Si phyllosilicates. *Cement and Concrete Research*
832 *73*, 228-237.
- 833 Santhanam, M., Cohen, M.D., Olek, J., 2002. Mechanism of sulfate attack: a fresh look:
834 part 1: summary of experimental results. *Cement and concrete research* *32*, 915-
835 921.
- 836 Sato, H., Grutzeck, M., 1991. Effect of starting materials on the synthesis of
837 tobermorite, *MRS Proceedings*, 245. Cambridge Univ Press, pp. 235-240.
- 838 Shi, C., Stegemann, J., 2000. Acid corrosion resistance of different cementing
839 materials. *Cement and Concrete Research* *30*, 803-808.
- 840 Skibsted, J., Henderson, E., Jakobsen, H.J., 1993. Characterization of calcium
841 aluminate phases in cements by aluminum- ^{27}MAS NMR spectroscopy. *Inorganic*
842 *chemistry* *32*, 1013-1027.
- 843 Skinner, L., Chae, S., Benmore, C., Wenk, H., Monteiro, P., 2010. Nanostructure of
844 calcium silicate hydrates in cements. *Physical review letters* *104*, 195502.
- 845 Swanton, S., Heath, T., Clacher, A., 2016. Leaching behaviour of low Ca: Si ratio CaO-
846 SiO₂-H₂O systems. *Cement and Concrete Research* *88*, 82-95.
- 847 Szczerba, J., Prorok, R., Śnieżek, E., Madej, D., Maślona, K., 2013. Influence of time and
848 temperature on ageing and phases synthesis in the MgO-SiO₂-H₂O system.
849 *Thermochimica Acta* *567*, 57-64.
- 850 Thoenen, T., Hummel, W., Berner, U., Curti, E., 2014. The PSI/Nagra Chemical
851 Thermodynamic Database 12/07. PSI report 14-04, Villigen PSI, Switzerland.
- 852 Viallis-Terrisse, H., Nonat, A., Petit, J.-C., 2001. Zeta-potential study of calcium
853 silicate hydrates interacting with alkaline cations. *Journal of colloid and interface*
854 *science* *244*, 58-65.
- 855 Walling, S.A., Kinoshita, H., Bernal, S.A., Collier, N.C., Provis, J.L., 2015. Structure and
856 properties of binder gels formed in the system Mg(OH)₂-SiO₂-H₂O for
857 immobilisation of Magnox sludge. *Dalton Transactions* *44*, 8126-8137.
- 858 White, C.E., 2016. Effects of temperature on the atomic structure of synthetic
859 calcium-silicate-deuterate gels: A neutron pair distribution function investigation.
860 *Cement and Concrete Research* *79*, 93-100.

- 861 White, C.E., Daemen, L.L., Hartl, M., Page, K., 2015. Intrinsic differences in atomic
862 ordering of calcium (alumino) silicate hydrates in conventional and alkali-activated
863 cements. *Cement and Concrete Research* 67, 66-73.
- 864 White, C.E., Provis, J.L., Bloomer, B., Henson, N.J., Page, K., 2013. In situ X-ray pair
865 distribution function analysis of geopolymer gel nanostructure formation kinetics.
866 *Physical Chemistry Chemical Physics* 15, 8573-8582.
- 867 Zhang, T., Cheeseman, C., Vandeperre, L., 2011. Development of low pH cement
868 systems forming magnesium silicate hydrate (MSH). *Cement and Concrete Research*
869 41, 439-442.
- 870

Highlights:

- C-S-H is unstable at pH values below 10
- At pH values between 10 and 10.5, M-S-H and C-S-H phases are stable and coexist
- A calcium uptake occurs in M-S-H, at the cation exchange sites, potentially at other sites
- A solid solution model can be used to describe the calcium uptake in M-S-H: M-(C)-S-H