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Formation and stability of magnesium silicate hydrate and hydromagnesite

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ABSTRACT

The effect of carbonate on the magnesium silicate hydrate (M-S-H) formation was studied at high Mg/Si molar ratio of 1.5. M-S-H pastes were synthesized from silica fume and MgO or MgO plus hydromagnesite in a Na_2CO_3 containing solution. X-ray diffraction data and thermogravimetric analysis indicated that brucite is destabilized and M-S-H phases formed much faster in the presence of carbonates. Additionally, in the system containing hydromagnesite, the hydromagnesite reacted to form M-S-H. In a third experiment, the carbonation of M-S-H with Mg/Si=1.5 in a suspension was investigated. While a reference suspension of M-S-H with Mg/Si=1.5 kept under inert atmosphere still contained brucite and a pH about 10.1, the forced carbonation of M-S-H decreased the pH to 7.3 and destabilized the brucite. No evidence of the formation of crystalline or amorphous hydrated magnesium (hydroxy)carbonate phases was observed.

KEYWORDS: *Magnesium silicate hydrate; hydrated magnesium carbonates; low-CO_2 cement, thermodynamic modelling*

1. Introduction

Binders based on Mg chemistries are one option to substitute Portland cement, because they can have a low or even negative carbon footprint when the MgO source comes from non-carbonate Mg-based minerals. The hydration of MgO in the presence of carbonates results in brucite potentially together with hydrated magnesium carbonate (HMC) phases, which provide relatively good mechanical properties (20 MPa to 50 MPa after 28 days). The hydration of reactive MgO-SiO_2 cements in the absence of carbonates results in precipitation of a magnesium silicate hydrate phase (M-S-H) as the primary reaction product, which can generate high compressive strength up to 50-80 MPa after 28 days. Thus, the combination of HMC and M-S-H in the hydrate assemblage seems promising to obtain a binder with both very low carbon footprint and optimized performance. However, the stability of M-S-H versus the stability of HMC is not yet understood. In this study three different experiments to tackle this issue are presented: i) the potential co-precipitation of M-S-H and HMC, ii) the formation of M-S-H in the presence of hydromagnesite and, iii) the carbonation of M-S-H.

2. Materials and methods

The co-precipitation of M-S-H and HMC was carried out using reactive SiO_2, MgO, and Na_2CO_3 as the source of carbonate as reported in Bernard et al (2022). The amount of MgO was chosen corresponding to an atomic ratio Mg/Si of 1.5. In literature generally M-S-H with a lower Mg/Si (1.2 to 1.3) has been

reported in Bernard et al (2017) such that hydration of the remaining MgO should therefore result in brucite (Mg(OH)$_2$), and the added carbonate could lead to the additional formation of HMC.

In a similar second experiment, half of the MgO was replaced by reactive as hydromagnesite has been proven to help in the formation of a poorly crystalline amorphous hydrate or other HMC phases (details can be found in Winnefeld et al (2019) and Dung et al (2017)).

In a third experiment, 100% CO$_2$ (flow of 100 cm^3/min) was bubbled through a suspension of an 8-year-old M-S-H with Mg/Si = 1.5 prepared as in Bernard et al (2017)for 2 days.

After the experiments, the samples were analysed by X-ray diffraction (XRD) and thermogravimetry (TGA), after 28 days for the co-precipitation samples of the first two experiments, and after 2 days for the carbonation of the M-S-H suspension. pH values of the samples were either measured when in suspension as in Bernard et al (2017) or measured by a leaching experiment. For the latter, more details can be found in Bernard et al (2022).

XRD data were collected using a PANalytical X'Pert Pro MPD diffractometer operating at 45 mV and 40 mA applying CuKα radiation (λ=1.54 Å), and equipped with a rotating sample stage, a fixed divergence slit and an anti-scattering slit on the incident beam side of 0.5° and 1°, respectively. The samples were scanned between 10° and 75° 2Θ with an X'Celerator detector. TGA measurements were carried out using a Netzsch STA 449 F3 Jupiter TGA apparatus coupled with a Bruker Fourier-transform infrared (FT-IR) spectrometer for the analysis of the exhaust gases. Approximately 40 mg of each sample was heated from 30 to 980 °C with a heating rate of 10 or 20 K/min in 150 µL alumina crucibles.

3. Results

Figure 1 displays the XRD and the TGA data of the pastes and suspensions. M-S-H is the main product in all samples. While the MS paste contains still a large amount of brucite after 28 days, the MS paste synthesised with Na$_2$CO$_3$ shows only traces of brucite (< 1 mass-%). M-S-H forms faster when sodium carbonate is present as Mg and carbonate ions form complexes which destabilizes brucite as detailed in Bernard et al (2022). However, the formation of crystalline or amorphous hydrated magnesium phases is not observed by XRD and TGA.
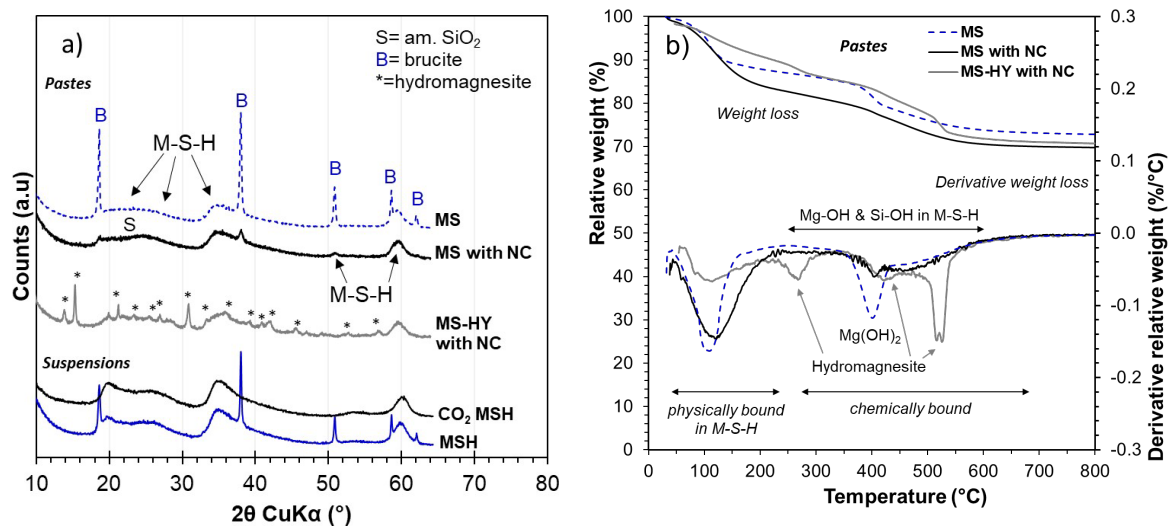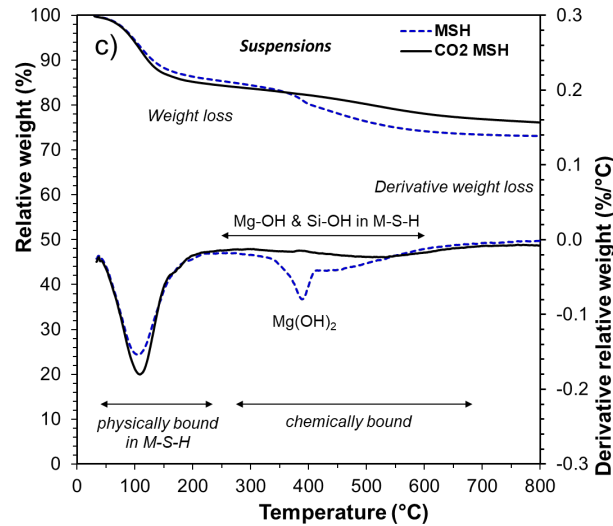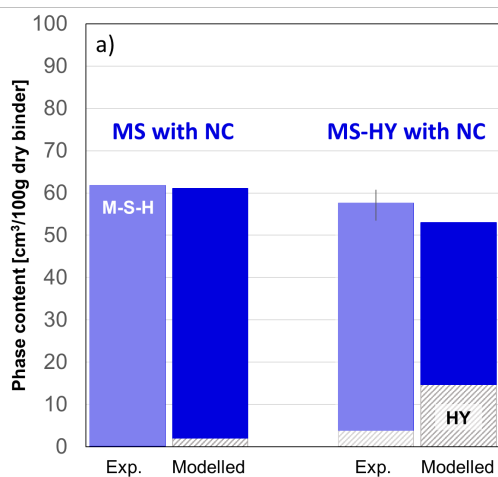
Figure 1: a) XRD data of magnesium silicate pastes without (MS) and with Na₂CO₃ (MS with NC), magnesium silicate paste with hydromagnesite and Na₂CO₃ (MS-HY with NC) after 28 days, and M-S-H suspension before (MSH) and after 2 days of interaction with 100% CO₂ (CO₂ MSH); TGA data of b) of MS, MS with Na₂CO₃, MS-HY with Na₂CO₃ pastes after 28 days, and of c) MSH and CO₂ MSH suspensions.

XRD and TGA data of the MS-HY paste synthesised with Na_2CO_3 indicates the presence of unreacted hydromagnesite in addition to M-S-H. Figure 2a shows the phase contents observed in the experiments after 6 months and the thermodynamically predicted phase assemblage, consisting simply of M-S-H and unreacted hydromagnesite. However, experimentally the amount of hydromagnesite strongly decreased as detailed Bernard et al (2022), indicating an apparent contradiction between thermodynamic prediction and experiments as detailed in Bernard et al (2022), pointing either towards an incomplete thermodynamic dataset and/or the presence of an additional not identified solid phase.

Figure 2: a) Phase assemblages estimated from the experimental results and thermodynamic modelling for the MS with Na₂CO₃, MS-HY with Na₂CO₃ pastes, adapted from Bernard et al (2022) and b) pH of the different samples measured at room temperature.

The suspension of M-S-H with Mg/Si=1.5 kept in inert atmosphere still contains brucite after 8 years (XRD and TGA data in Figure 1). The pH value has slightly decreased from 10.4 after 2 years (Bernard et al. 2017) to 10.1 after 8 years (Figure 2b), probably due to carbonation of the solution over time by CO_2 from the atmosphere. While the formation of M-S-H with Mg/Si=1.5 in the presence of carbonates was

fast (brucite had completely reacted within 1 month as shown in Figure 1), the presence of silicate seems to kinetically hinder the dissolution of the brucite in the absence of carbonates.

The forced carbonation of a M-S-H suspension, aged for 8 years, significantly decreases the pH from 10.1 to 7.3 (Figure 2b) and destabilizes the brucite (XRD and TGA data in Figure 1). Carbonation, however, does not decrease the amount of M-S-H present, indicating in agreement with the studies above, a high resistance of M-S-H towards carbonation. The magnesium originally presence in brucite seems to be in solution and/or used to form additional M-S-H, as there is no clear evidence for the formation of crystalline or amorphous hydrated magnesium (hydroxy)carbonate phases.

4. Conclusions

Na_2CO_3 accelerates the formation of M-S-H with a Mg/Si = 1.5 as the presence of carbonates destabilizes the brucite initially formed. However, the presence of crystalline or amorphous Mg-carbonate phases could not be confirmed. The hydration of a blend of $MgO-SiO_2$ and hydromagnesite (one of the HMC phases) results mainly in M-S-H, as also the hydromagnesite partially reacts to M-S-H. The bubbling of 100% CO_2 through a suspension of an 8-year-old M-S-H with Mg/Si= 1.5, presenting a pH value of 10.1, leads to a lower pH and the release Mg ions from brucite. Even under these harsh carbonation conditions, no Mg-carbonate phases could be observed, indicating that the formation of HMC from the carbonation of M-S-H is unlikely. In the three investigated cases, i.e. i) the co-precipitation of M-S-H and HMC, ii) the formation of M-S-H in presence of hydromagnesite and iii) the carbonation of M-S-H, M-S-H seems to be more stable than hydromagnesite, while crystalline HMC did not form or even were destabilized to form M-S-H. These observations are in contradiction with thermodynamic modeling results using the most recent data for Mg-phases, which predict the precipitation of HMC phases in addition to M-S-H, when dissolved CO_3^{2-}/HCO_3^- is present in concentrations of above 80 mmol/L. This discrepancy between experiments and thermodynamic modelling needs further investigations. Nevertheless, the high stability of the strength-forming M-S-H phase in the presence of CO_2/carbonates seems promising regarding the future application of such cements.

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