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Hydration of cementitious binders based on magnesium oxide / hydromagnesite blends

F. Winnefeld[1*], A. German[1,2], P. Lura[1,2] , D. Rentsch[3] and B. Lothenbach[1,4]

[1] *Empa, Laboratory for Concrete and Asphalt, Dübendorf, Switzerland*
Email: frank.winnefeld@empa.ch, alexander.german@empa.ch, pietro.lura@empa.ch,
barbara.lothenbach@empa.ch
[2] *ETH Zürich, Institute for Building Materials, Zürich, Switzerland*
[3] *Empa, Laboratory for Functional Polymers, Dübendorf, Switzerland*
Email: daniel.rentsch@empa.ch
[4] *NTNU, Department of Structural Engineering, Trondheim, Norway*

ABSTRACT

Cementitious binders based on MgO exhibit a low CO_2 footprint or can even be CO_2-negative, if the MgO is generated from carbonate-free raw materials. One class of such binders are blends of MgO with hydromagnesite. In this study, the hydration products formed in this system were investigated at temperatures between 7 and 60°C. A poorly-crystalline brucite containing some carbonate is the main hydration product. Furthermore, a kind of "gel-water" is observed, which is lost at temperatures above 40-60°C.

KEYWORDS: *Low-CO_2 cement, hydrated magnesium carbonate, magnesium oxide, hydromagnesite, brucite*

1. Introduction

MgO can be used to make a variety of hydraulic binders as well as binders that harden by carbonation (Gartner and Hirao (2018)). Potential raw materials for MgO production are magnesium silicates or Mg-containing brines, which can be carbonated and subsequently partially calcined. The mixture of MgO and basic magnesium carbonates obtained by this process is able to set and harden when mixed with water (Vlasopoulos and Cheseman (2009)). Similar compressive strengths values as for systems based on Portland cement can be reached. If the MgO source originates from carbonate-free raw materials, such cements exhibit a low carbon footprint or could even be carbon-negative.
Recent investigations on the hydration mechanisms of binders based on blends of magnesium oxide and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) revealed the presence of an unknown magnesium carbonate hydrate phase, while artinite ($Mg_2(CO_3)(OH)_2 \cdot 3H_2O$) is predicted by thermodynamic calculations, but not identified in the experiments (Kuenzel et al. (2018), Winnefeld et al. (2019)). The current study, see German et al. (2023) and German (2023) for more details, aims at a detailed investigation of the hydrates formed at temperatures between 7 and 60°C in such binders.

2. Materials and methods

Blends of 70 mass-% MgO (calcined from reagent-grade brucite at 900°C for 6 h) and 30 mass-% reagent-grade hydromagnesite (HY) were used to prepare suspensions with ultrapure water and a water-to-solid ratio of 20. The samples were cured in sealed vessels for 12 months at 7, 20, 40, and 60°C. At the age of testing, the samples were filtered. The further reaction of the solid residue was stopped by solvent exchange (Snellings et al. (2018)). The material was then ground by hand using an agate mortar to a particle size below 63 μm and investigated by X-ray diffraction analyses (XRD), thermogravimetry

coupled with infrared spectroscopy (TGA-IR), Raman spectroscopy and solid state ^{13}C nuclear magnetic resonance spectroscopy (^{13}C CP-MAS NMR). The liquid phase was analysed using a pH meter, ion chromatography and a TOC/TC analyser to determine pH, ion concentrations and inorganic carbon. Further details of the experimental procedures are given in German et al. (2023) and German (2023). Thermodynamic calculations were performed using GEMS (Wagner et al. (2012), Kulik et al. (2013)) coupled with the Nagra/PSI thermodynamic database (Hummel et al. (2002)) and additional data related to magnesium carbonates (Winnefeld et al. (2019), Bernard et al. (2022)).

3. Results

XRD (Fig. 1a) shows that MgO is almost consumed after 12 months, while HY is still present. A low-crystalline brucite forms, which shows broadened and shifted reflections compared to the reagent-grade brucite, which serves as reference. This refers especially to the (001) reflection, which is shifted to higher 2Θ-values. A small hump occurs at 16.1-16.8° 2Θ CuKα for the sample cured at 20°C, which had previously been tentatively assigned to an unknown phase (Kuenzel et al. (2018), Winnefeld et al. (2019)). The hump shifts to higher 2Θ-values for the 40°C sample and vanishes for the 60°C sample. Temperature influences as well the position of the (001) reflection of brucite. At 40°C it is shifted to lower 2Θ values compared to the sample cured at 20°C, and at 60°C the reflection is at the same position as for the brucite reference.

TGA-IR (Fig. 1b) of the sample cured at 20°C shows mass losses, which can be mainly assigned to brucite and HY. Mass balance calculations obtained from TGA-IR and verified by ^{13}C CP-MAS NMR revealed that about 50-75% of the HY has reacted, rather independently from the curing temperature. At the decomposition temperature of brucite, not only H_2O, but also CO_2 is released between 300 and 480°C. This CO_2 release cannot be solely explained by the decomposition of HY, suggesting that either an unknown carbonate phase is decomposed, or that the brucite contains carbonate. In addition, at 30-160°C a mass loss is observed for the 20°C sample, which cannot be assigned to brucite or any known magnesium carbonate and indicates the presence of loosely bound water. For the samples cured at 60°C, this mass loss is not clearly evident.

At least three Raman bands of unknown origin occur in the region of 1025-1080 cm^{-1} regardless of curing temperature (Fig. 2a). The position of the bands is typical for hydrated magnesium carbonates (Edwards et al. (2005)).

^{13}C CP-MAS NMR (Fig. 2b) of the 20°C sample shows two signals for HY (163.4 ppm and 165.6 ppm) and a signal at 167-168 ppm, which was tentatively assigned to sorbed HCO_3^- (Bernard et al. (2022)). Two further resonances at 159.4-160.0 ppm and at 173 ppm could not be assigned to any known magnesium carbonate phase so far. The signals of the 60°C sample are very similar to those at 20°C.

Mg and inorganic carbon concentrations of the liquid phase increase with curing temperature, while the pH decreases (Figure 3a).

Effective saturation indices (SI) for brucite and hydrated magnesium carbonates were calculated by GEMS (Figure 3b). Magnesite is highly oversaturated at all investigated temperatures, but it does not form at the temperatures studied due to kinetic reasons. Artinite, brucite and hydromagnesite are oversaturated as well, and dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) is near saturation. Despite being (over)saturated with respect to the pore solution, neither artinite nor dypingite can be identified, in agreement with Kuenzel et al. (2018) and Winnefeld et al. (2019), indicating a kinetic hindrance in formation. Lansfordite ($MgCO_3 \cdot 5H_2O$) and nesquehonite ($MgCO_3 \cdot 3H_2O$) are undersaturated and are not identified as well. Based on the solution chemistry, the ion activity products of various hypothetical hydrated magnesium carbonates, whose compositions were derived from mass balance calculations, were calculated using GEMS. However, the calculations revealed that these hypothetical phases were unstable compared to a mix of brucite and HY of the same bulk composition.
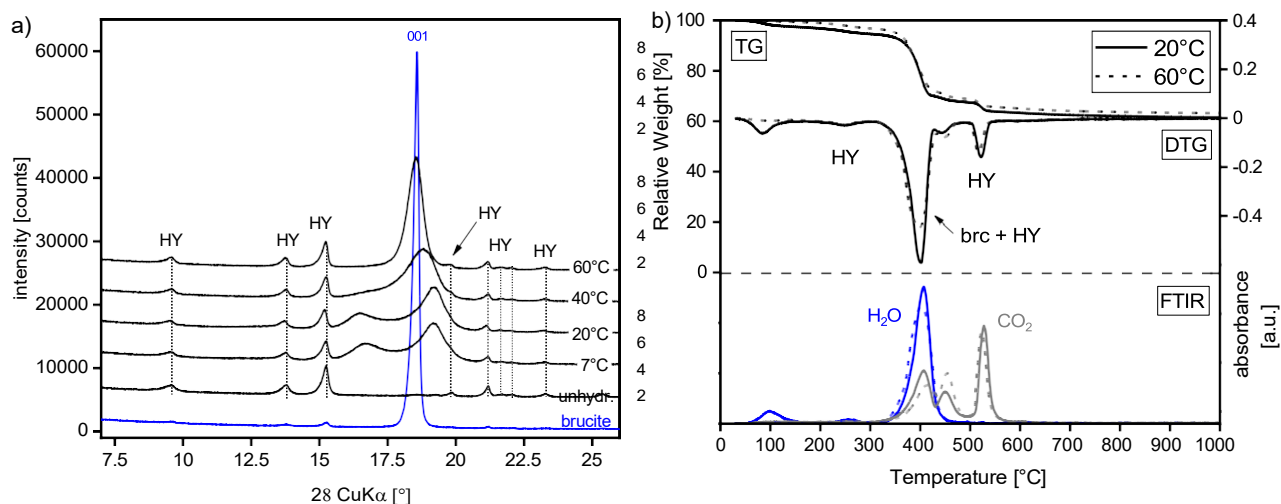
Fig. 1: a) XRD patterns of MgO/hydromagnesite 70/30 blends hydrated at 7, 20, 40 and 60°C for 12 months. The unhydrated sample and the brucite reference are shown for comparison, and b) TGA-IR of MgO/HY 70/30 blends hydrated at 20 and 60°C for 12 months.
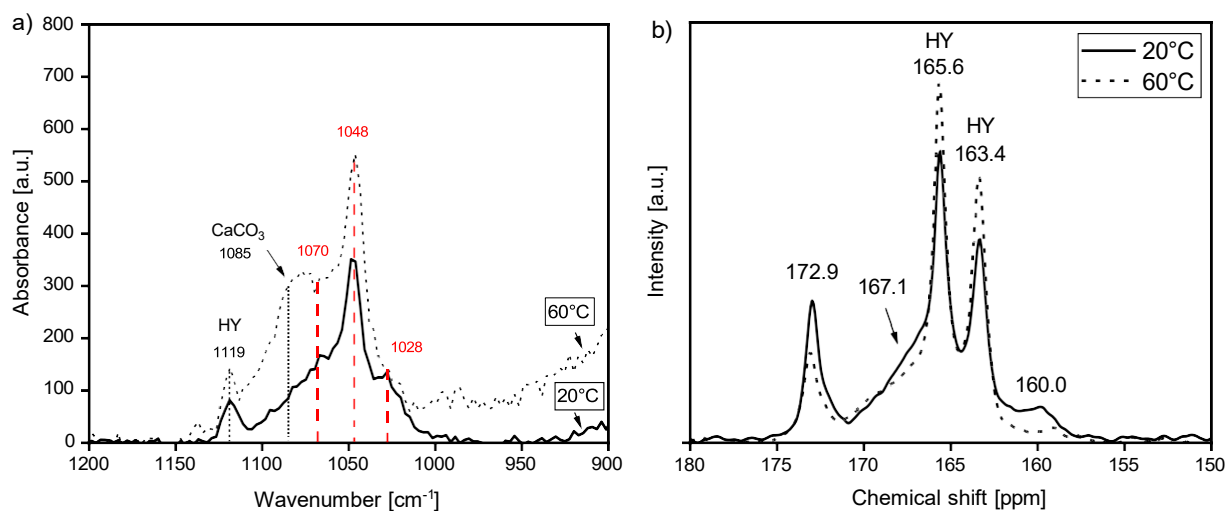

Fig. 2: a) Raman and b) ^{13}C CP-MAS NMR spectra of MgO/hydromagnesite 70/30 blends hydrated at 20 and 60°C for 12 months.
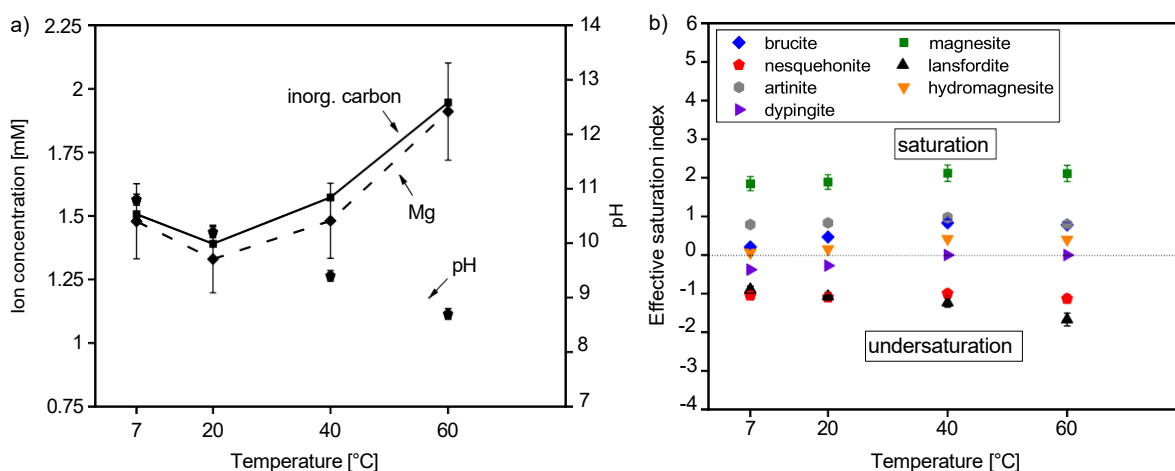

Fig. 3: a) Mg, inorganic carbon and pH of the liquid phase (lines for eye-guide only), and b) effective saturation indices of relevant hydrate phases in MgO/hydromagnesite 70/30 blends after 12 months depending on temperature.

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4. Conclusions

The hydration products of blends of MgO and hydromagnesite were investigated at temperatures between 7 and 60°C. The main hydration product is brucite with a low crystallinity. The dissolution of a part of the hydromagnesite during hydration provides carbonate ions; however, no known hydrated magnesium carbonate phase could be identified. Thermodynamic properties of hypothetical hydrated magnesium carbonate phases were estimated, but all phases proved to be thermodynamically unstable. Based on these results, it is therefore suggested that the brucite formed in such systems contains some carbonate. Furthermore, thermogravimetric data shows a significant mass loss in the region of approximately 30-160°C, which is associated with the loss of loosely bound water. Tentatively this water is assigned as a kind of "gel-water" within the low-crystalline brucite. This "gel-water" cannot be identified at 60°C, while the carbonate associated with brucite is still present.

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