Further studies of the hydration of MgO-hydromagnesite blends

Frank Winnefeld ^a, Eugenia Epifania ^{a,b}, Fabio Montagnaro ^b, Ellis M. Gartner ^{c,*}

^a Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for
 Concrete and Construction Chemistry, CH-8600 Dübendorf, Switzerland

^b Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso
 Universitario di Monte Sant'Angelo, 80126 Naples, Italy

^c Department of Civil and Environmental Engineering, Imperial College London,
 South Kensington Campus, London SW7 2AZ, United Kingdom

* Deceased as of February 13, 2018

ABSTRACT

The hydration of magnesium oxide in the presence of hydromagnesite
 ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) was investigated. The hydration products are a poorly-crystalline
 form of brucite ($\text{Mg}(\text{OH})_2$) and an unknown amorphous or poorly crystalline hydrate, which
 was evidenced by X-ray diffraction analyses and Raman spectroscopy. By thermogravimetry
 it was found that in the presence of hydromagnesite more water is bound in hydrate phases
 than can be explained by the formation of brucite only. The unknown hydrate is hypothesized
 to lead to cohesive binding in MgO-hydromagnesite blends. Due to thermodynamic
 predictions artinite ($\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) should be the stable hydrate in this system. The
 addition artinite crystal seeds, however, had no significant effect on hydration kinetics or
 nature of the reaction products. The hypothesis that the addition of sodium bicarbonate
 (NaHCO_3) could modify or accelerate the hydration reactions due to its high solubility and the
 supply of additional HCO_3^- ions was also not supported by the experiments.

Keywords: magnesium oxide, cement, hydration, hydromagnesite, artinite, dypingite, brucite

1. Introduction

Enormous volumes of concrete and other cement-based materials are used globally, essentially all based on hydraulic binders in which Portland Cement Clinker (PCC), comprising highly basic calcium silicates and aluminates, is the primary active component. Because even mildly basic calcium silicates and aluminates do not occur in significant quantities at the surface of the Earth, the manufacture of PCC requires calcium carbonate, readily available globally as limestone, as the calcium source and main raw material. As the limestone is decarbonated in the process, manufacture of PCC has a high carbon footprint, more than 50% of which represents “fossil” CO₂ released from the limestone raw material. The decarbonation of limestone is also strongly endothermic and thus requires significant thermal energy, generally derived by the combustion of carbon-rich fuels, which accounts for most of the rest of the manufacturing CO₂ emissions. It is estimated that specific CO₂ emissions for manufacture of PCC globally average 866 kg/t [1]. In practice, PCC is usually diluted to a significant extent with other ingredients (calcium sulfates, fillers, and “supplementary cementitious materials”) which generally have much lower specific carbon footprints, leading to a global average specific CO₂ footprint of 660 kg/t for all PCC-based hydraulic binders [1]. Because of this, and the fact that such hydraulic binders are currently used in vast quantities (4.6 Gt in 2015) [2], cement manufacture may now represent as much as 8% of global anthropogenic CO₂ emissions [3, 4]. The average CO₂ footprint of PCC-based cements can still be reduced further than this by additional clinker dilution, but seems unlikely to ever fall much below about 500 kg/t assuming a realistic target of the clinker factor of approximately 60% [5].

Because of this, the search continues for practical alternative active binder components, which we refer to as “alternative clinkers,” that can potentially replace PCC with a product of much lower carbon footprint in a significant fraction of its applications [6-10]. But most of the alternative clinkers that have been proposed are still based on calcium silicates and aluminates, which greatly limit the extent of the CO₂ reductions that can be achieved in theory, because the main calcium source is always limestone, even though the amounts required may be somewhat less than for PCC.

It is easy to make hydraulic binders from basic calcium silicates and aluminates because of their inherently high hydraulic reactivity. But the possibility also exists of making hydraulic binders from basic magnesium compounds, and in this case the potential raw materials are very different. Generally reactive MgO is used as raw material, which is mostly produced by the calcination of magnesite (MgCO₃) at significantly lower temperatures compared to Portland cement clinker [11]. The production of MgO from magnesite, however, releases approximately 1100 kg CO₂ per kg MgO [10, 12], which is significantly higher than for Portland cement. MgO can be used to make a variety of hydraulic binders as well as binders that harden by carbonation [11, 13]. Good progress has been made in recent years in understanding MgO-based binders that harden by carbonation, which are able to sequester a reasonable amount of CO₂, thus greatly improving the CO₂ balance of such binders [14-25]. Magnesium sources are at the Earth’s surface not only available as carbonates, but also in the form of highly basic silicate rocks which contain very little, if any, fossil CO₂ [26]. The two main mineral types of interest are (i) olivines close in composition to forsterite (Mg₂SiO₄), which are anhydrous minerals of igneous origin and have the highest MgO content of any common mineral, and (ii) serpentines (Mg₃Si₂O₅(OH)₄), which are more abundant and produced by partial hydration of olivines near the Earth’s surface. Basic magnesium silicate minerals react only very slowly with water and CO₂ at the Earth’s surface, which is why they

are readily available. Therefore, the challenge is to find energy-efficient ways to activate them such that they can be used to make hydraulic binders that hydrate at high enough rates for use in construction applications [8, 10]. Small amounts of brucite ($\text{Mg}(\text{OH})_2$) can also sometimes be found associated with serpentine, but not in sufficient quantity for the uses considered here, so in this sense brucite cannot be considered to be a “common” mineral.

The theoretical enthalpy requirement for decomposing forsterite into MgO (periclase) and SiO_2 (quartz) is only about 0.86 kJ per gram of MgO [10]. This compares very favourably with the enthalpy requirement of 2.90 kJ per gram of MgO for the conventional industrial manufacturing process of MgO by thermally decomposing natural magnesite (MgCO_3) into MgO plus gaseous CO_2 [10]. Additionally, the use of forsterite as the raw material releases no fossil CO_2 , whereas the use of magnesite releases 1.1 g of fossil CO_2 for each g of MgO produced [10]. It would therefore be very advantageous if MgO could be manufactured efficiently by decomposition of forsterite-rich olivines. Unfortunately, no energy-efficient industrial process for this currently exists as high temperatures and high partial pressures of CO_2 are required [27-32]; but it is possible that such processes will be developed if they were made the subject of intensive research. Some recent progress in this area was made by one of the authors [33]. The use of serpentinite as a raw material is also possible [34], although less favourable because of its significant bound water content. The heat of formation of serpentine (assumed $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) from the oxides in their standard states is in the range of -150...-180 kJ/mol depending on the type of serpentine [35]. Taking the pessimistic value of -180 kJ/mol, 60 kJ/mol MgO result. If the enthalpy of evaporation of $\frac{2}{3}$ mole of water per mole of MgO is added, i.e. $44 \text{ kJ} \cdot \frac{2}{3} \approx 30 \text{ kJ}$, this gives 90 kJ/mol MgO or 2.25 kJ/g MgO. This is still less than making MgO from magnesite. However, if this water must be evaporated, the energy cost will be high, but if the MgO could be extracted by a leaching process without water evaporation, more acceptable extraction energies may be feasible. Furthermore, Mg-containing brines might be potential sources of MgO [36-39].

Carbonation hardening is of potential interest for factory-made products, and has the added advantage that it consumes large amounts of CO₂ in the hardening process. But the potential value of a hydraulic binder based on magnesium oxides and carbonates would be significantly greater than a binder that can only be hardened by carbonation. There is a wider range of potential applications for hydraulic binders because they do not need a concentrated source of gaseous CO₂, which is difficult to provide in many locations. In both cases, if the final composition of the hardened binder were sufficiently rich in carbonate such that the CO₂ sequestered by it could fully compensate for the CO₂ emitted by the production of the energy needed to drive the manufacturing process, we could talk of a truly carbon-neutral binder. We could even envisage carbon-negative binders, for which there was net consumption of CO₂ during manufacture and use. This was the original concept behind the “Novacem” start-up venture [40], which was built on the discovery that reactive MgO, when hydrated together with certain magnesium carbonates, such as hydromagnesite, (HY, Mg₅(CO₃)₄(OH)₂·4H₂O), gave a relatively strong hydraulic binder, compared to MgO hydrated alone, which had almost no binding capacity [41-46]. It was also observed that the brucite (Mg(OH)₂) formed in the presence of hydromagnesite gave very broad X-ray diffraction reflections compared to that formed from hydration of pure MgO, and it was assumed that the strength of the hydration products in these systems was related in some way to the form of the brucite precipitated.

A recent detailed study of the mechanisms involved in the hydration of this type of binder [46] forms the starting point for the work reported in this paper. It was found that the addition of hydromagnesite accelerates the hydration of reactive periclase and leads to a significant development of compressive strength, while the brucite formed by the hydration of pure periclase gives only very weak pastes. By thermodynamic calculations, artinite was predicted to occur as stable phase in MgO-hydromagnesite blends. However, the authors did not clearly identify any new phase in the MgO-hydromagnesite blends besides the formation of a poorly

crystalline brucite, and suggested that artinite formation is kinetically hindered. They hypothesized the formation of an amorphous phase intermediate between hydromagnesite and brucite, which could explain the strength development in MgO-hydromagnesite blends.

The current study was aimed at increasing the initial carbonate content of such binders in order to enhance their effectiveness as a means of reducing global CO₂ emissions as less MgO, whose production is associated with CO₂ emissions, especially when it is produced from the calcination of magnesite, is used in the blend. It was also aimed at testing the concept that a new hydrate phase may be responsible for the strong hydraulic binding obtained by the addition of hydromagnesite to reactive MgO pastes. Two approaches were applied in this study:

1. Finely ground crystalline (natural) artinite was added as seed crystals to MgO-HY mixtures to determine whether the crystallization of artinite could be promoted, as would be expected if it were the thermodynamically favoured product phase. If this approach were successful, the initial hydromagnesite contents of the binders could in theory be increased to about 80% based on the theoretical hydration reaction given in Eq. (1):

2. Sodium bicarbonate (NaHCO₃) was added to the mixing water to determine if it would modify or accelerate the hydration reactions. This salt was chosen because it is highly soluble and provides one ion (HCO₃⁻) in common with magnesium carbonates in the mildly basic pH range, and it is observed that salt-based hydration accelerators often share a common ion with the hydrating phases [47]. However, it was observed by [48, 49] that NaHCO₃ slightly reduced the dissolution kinetics of MgO without and with the addition of hydromagnesite seeds. The authors attributed this effect to the increase of the pH value in the presence of NaHCO₃. In addition, NaHCO₃ has been shown to aid in the carbonation of basic magnesium compounds [33, 48, 49].

2. Materials and Methods

2.1 Materials

Magnesium oxide (MgO) was prepared by igniting laboratory-grade brucite (Fisher Scientific, UK) in a furnace at 900°C for 6 h, which yields a light-burned, high reactive MgO [19].

Laboratory grade hydromagnesite (HY, Alfa Aesar, Germany) and sodium hydrogen carbonate (NaHCO₃, Honeywell, Germany) were used.

Artinite is not available from commercial suppliers of laboratory chemicals, and no synthesis procedure is described in open literature. Thus a natural mineral originating from San Benito County, California, USA (Fig. 1a), was purchased from Siber+Siber AG, Aathal, Switzerland. From the sample, approximately 20 g artinite crystals were separated and gently ground by hand in an agate mortar to a particle size below 63 µm.

Table 1 gives the chemical composition of the Mg-based raw materials as determined by X-ray fluorescence analysis. The reactivity of the magnesium oxide was tested using the citric acid method, where the time needed for 2.00 g of MgO to neutralize 100 mL of a 0.4 M citric acid solution is measured [50]. The sample showed a neutralization time of 145 s and thus proved to be of medium reactivity (neutralization time between 180 and 300 s).

The composition of the artinite sample is close to the theoretical composition of the pure phase. Its XRD pattern (Fig. 1b) is similar to the ones contained in the ICSD database; however some differences occur between all patterns, which might be related to different sample preparation and XRD measuring techniques as well as to possible differences in the composition of the various natural artinite samples.

180 Table 1: Chemical composition and density of the used binder components.

Oxide (mass-%)	MgO	Hydromagnesite	Artinite
CaO	0.14	0.27	0.06
SiO ₂	< 0.05	< 0.05	0.80
Al ₂ O ₃	0.06	< 0.04	< 0.04
Fe ₂ O ₃	< 0.024	0.03	0.08
MgO	99.27	42.56	42.01
K ₂ O	< 0.02	< 0.02	< 0.02
Na ₂ O	< 0.04	< 0.04	< 0.04
TiO ₂	< 0.007	< 0.007	< 0.007
P ₂ O ₅	0.006	0.026	0.006
Cr ₂ O ₃	0.004	< 0.002	0.003
MnO	0.004	0.006	0.003
SO ₃	0.21	0.20	0.07
L.O.I. ^a	0.32	56.91	56.93
Total	100.00	100.00	99.96
CO ₂ (mass-%) ^b	0.70	38.50	22.32
Density (g/cm ³) ^c	3.45	2.14	n.d.

181 ^a loss on ignition determined according to EN 196-2

182 ^b combustion analysis

183 ^c according to EN 196-6 (pycnometric method)

184 n.d.: not determined

185

186

Fig. 1: (a) Artinite mineral used in the experiments. The diameter of the sample is approximately 4 cm. (b) Comparison of the XRD pattern of the artinite sample with reference patterns ICSD 1320 [51], ICSD 16831 [52] and ICSD 24637 [53].

The particle size distributions of the raw materials were analyzed using a laser particle analyzer Malvern Mastersizer X. The powders were dispersed in isopropanol by ultrasound. Fig. 2 shows the results. The laboratory chemicals (MgO, HY) show a finer particle size distribution than the ground artinite. The particle size of NaHCO_3 was not analyzed as it was dissolved in the mixing water prior to use. Table 2 shows the paste mix designs used in this study. A high water/solid ratio of 1.2 was necessary to achieve workable pastes.

Fig. 2: Particle size distribution of the binder constituents. (a) differential particle size distribution, (b) cumulative particle size distribution.

Table 2: Mix designs of the pastes used in this study referring to 100 g solid.

MgO	Hydromagnesite (HY)	Artinite (Art)	NaHCO ₃	Water
g	g	g	g	g
100	-	-	-	120
70	30	-	-	120
70	28	2	-	120
70	28	-	2	120
50	50	-	-	120

2.2 Methods

2.2.1 Thermodynamic modelling

Thermodynamic modelling was used to calculate the thermodynamically stable phases in the system MgO-CO₂-H₂O at ambient temperature and pressure. The geochemical GEMS-PSI software [54, 55] was applied together with the Nagra/PSI database [56], the SLOP98 [57, 58] database and additional data for lansfordite [59, 60] and nesquehonite [61]. Recently, the solubility product of dypingite, Mg₅(CO₃)₄(OH)₂·5H₂O, was determined as $\log K^\circ = -34.94$ at

23°C [62], which is several log units higher than for hydromagnesite, see [63] and references cited therein, indicating that dypingite is expected to be less stable than hydromagnesite. The $\log K^\circ$ value was used together with values for S° and C_p° estimated according to [57] to calculate $\Delta_f G^\circ$ and $\Delta_f H^\circ$ of dypingite using the Nagra/PSI thermodynamic data base [56]. Table 3 displays the thermodynamic data of the solid phases used in the calculations. The theoretical phase assemblage of mixtures of MgO and hydromagnesite was calculated. The formation of magnesite, which is predicted to form as the thermodynamically stable phase, was suppressed as it is generally not identified in such systems [46, 63].

Table 3: Selected standard thermodynamic properties of the solid phases at 25°C and 1 bar used in the calculations.

Phase ¹⁾	$\log K^\circ$ ²⁾	$\Delta_f G^\circ$ kJ/mol	$\Delta_f H^\circ$ kJ/mol	S° J/(mol·K)	C_p° J/(mol·K)	V_m cm ³ /mol	Ref.
Periclase, MgO		-569.38	-601.66	26.95	37.8	11.25	[57, 58]
Brucite, Mg(OH) ₂	-11.16	-832.23	-923.27	63.14	77.28	24.63	[56]
Magnesite, MgCO ₃	-8.29	-1029.3	-1112.9	65.69	75.85	28.02	[56]
Nesquehonite, MgCO ₃ ·3H ₂ O	-5.34	-1724.0	-1977.3	195.6	237.8 ³⁾	74.8	[57, 58, 61]
Lansfordite, MgCO ₃ ·5H ₂ O	-5.24	-2197.8	-2574.3	249.5	317.9 ⁴⁾	103.19	[59, 60]
Hydromagnesite, Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	-38.47	-5864.7	-6504.1	541.3	571.3	208.8	[57, 58]
Dypingite ⁵⁾ , Mg ₅ (CO ₃) ₄ (OH) ₂ ·5H ₂ O	-34.94	-6081.7	-6777.4	585.9	611.3	225.9	[62, 64]
Artinite, Mg ₂ (CO ₃)(OH) ₂ ·3H ₂ O	-18.67	-2568.6	-2920.6	232.9	296.1	96.9	[57, 58]

¹⁾ Several other phases exist in the system MgO-CO₂-H₂O, namely barringtonite (MgCO₃·2H₂O), pokrovskite (Mg₂(CO₃)(OH)₂), giorgiosite (Mg₅(CO₃)₄(OH)₂·5H₂O), an unnamed dypingite-like phase (Mg₅(CO₃)₄(OH)₂·8H₂O), protohydromagnesite (Mg₅(CO₃)₄(OH)₂·11H₂O) and shelkovite (Mg₇(CO₃)₅(OH)₄·24H₂O) [65-68], where no thermodynamic data are available in open literature.

²⁾ $\log K^\circ$ values refer to reactions formulated with Mg²⁺, CO₃²⁻, OH⁻ and H₂O. They were calculated using the Nagra/PSI thermodynamic data base [56] except for dypingite, where the value taken from [62] is given.

³⁾ The Slop98 database [57, 58] integrated in GEMS gives for nesquehonite a negative value of C_p° . The original value taken from [61] was used instead.

⁴⁾ For lansfordite, [59] gives a C_p° of 386 J/(mol·K), which deviates strongly from the value of S° and thus does not seem to be trustworthy. Therefore C_p° was estimated according to Helgeson et al. [57] using C_p° of nesquehonite and of structural water (40.04 J/(mol·K)).

⁵⁾ S° and C_p° were estimated according to [57] from the respective values of hydromagnesite and structural water ($S^\circ = 40.17$ J/(mol·K), $C_p^\circ = 40.04$ J/(mol·K)). From these values and $\log K^\circ$, $\Delta_f G^\circ$ and $\Delta_f H^\circ$ were calculated using the Nagra/PSI thermodynamic data base [56]. The density was taken from Raade [64].

2.2.2 Sample preparation for hydration experiments

For isothermal calorimetry and for phase analyses at each hydration step (6 h, 1, 3, 7, 28 d) an appropriate amount of paste (10 g except for mixes with artinite, where 5 g were used) was mixed by hand for 2 minutes using a spatula. The powders were premixed by hand, with the exception of NaHCO_3 , which was dissolved in the mixing water prior to use.

The samples for phase analysis were stored in a sealed PE container at 20°C until testing. For hydration stoppage, the samples were gently crushed and stored in isopropanol during 15 minutes. Subsequently, the material was filtered, washed with isopropanol and rinsed with diethyl ether to remove the isopropanol. Then the samples were dried during 8-10 minutes at 40°C, and if necessary stored in a desiccator under nitrogen atmosphere to minimize carbonation prior to analysis. This sample stoppage method is generally recommended for hydrated cementitious systems [69-72] and is gentler than the one used in the previous study [46], where the hydration was stopped using acetone followed by drying at 60°C until constant weight.

Before further analysis, the samples were freshly ground by hand below a particle size of 63 μm using an agate mortar.

2.2.3 Isothermal calorimetry

Isothermal conduction calorimetry was performed using a Thermometric TAM Air instrument at 20°C. Approximately 5-6 g of freshly mixed paste were transferred into a glass vial, which was then capped and placed into the calorimeter. Due to the external mixing, the initial heat peak could not be captured. The heat flow was recorded for 72 hours. Cumulative heat was determined by integration of the heat flow data, omitting the first 30 min after mixing.

2.2.4 X-ray diffraction

X-ray diffraction analyses (XRD) were performed with a Panalytical X'Pert Pro in a Θ - Θ configuration using $\text{CoK}\alpha$ -radiation and the X'Celerator detector. The samples were scanned between 5° and $115^\circ 2\theta$ for 45 minutes. The consumption of MgO in the hydrated samples was assessed semi-quantitatively by fitting peak areas using CaF_2 as an external standard for the intensity correction. After quantification, the results were recalculated according to [70] to 100 g unhydrated binder using the weight losses of the unhydrated binder and the hydrated pastes as determined by thermogravimetry (Eq. 2):

$$MgO_B = MgO_H \cdot \frac{W_H}{W_B} \quad (2)$$

with MgO_B = MgO content in g per 100 g of unhydrated binder, MgO_H = MgO content in g per 100 g of the hydrated sample, W_B = ignited weight (980°C) of the unhydrated binder, W_H = ignited weight (980°C) of the hydrated paste.

2.2.5 Thermogravimetry

Thermogravimetric analyses (TGA) were performed using a Mettler Toledo TGA/SDTA 851e instrument under nitrogen atmosphere. Weight changes were measured while heating about 50 mg samples from 30 - 980°C with a heating rate of 20°C per minute in $150\ \mu\text{L}$ alumina crucibles. Chemically bound water referred to 100 g unhydrated binder can be calculated according to [70] using Eq. (3), subtracting the bound water already present in the unhydrated binder originating from the hydromagnesite. Furthermore, it was assumed that no further carbonation occurred during hydration, sample preparation and TGA measurement.

$$bw = \frac{WL_H}{W_H} \cdot W_B - WL_B = \frac{100-W_H}{W_H} \cdot W_B - (100 - W_B) \quad (3)$$

with bw = bound water weight in g per 100 g unhydrated binder, W_B = ignited weight (980°C) of the unhydrated binder, $WL_B = 100 - W_B$ = weight loss (980°C) of the unhydrated binder, W_H = ignited weight (980°C) of the hydrated paste, $WL_H = 100 - W_H$ = weight loss (980°C) of the hydrated paste.

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For selected samples, 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. The same temperature range and heating rate were chosen as for the other TGA instrument. The infrared absorbances of H_2O and CO_2 were integrated in the ranges of 3400-4000 cm^{-1} (O-H stretching vibration) and 2200-2450 cm^{-1} (C=O stretching vibration), respectively, and used as relative measures of H_2O and CO_2 contents in the exhaust gases.

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302 **2.2.6 Raman spectroscopy**

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

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307 **3 Results**

308 **3.1 Thermodynamic modelling**

Thermodynamic modelling reveals that artinite, $Mg_2(CO_3)(OH)_2 \cdot 3H_2O$, should be the thermodynamic stable hydrate phase in MgO-hydromagnesite blends (Fig. 2) as suggested previously [46], but it seems to form experimentally only below 15°C [63]. Based on artinite formation, a ratio of 80% hydromagnesite and 20% MgO would be the optimum to incorporate as much CO_2 in the mix as possible. However, other hydrates, whose

compositions and thermodynamic properties are not known and thus cannot be predicted by thermodynamic modelling, might be present as well. The pH of the paste containing only brucite formed by the hydration of pure MgO is calculated to be 10.6. When hydromagnesite is added up to 80 mass-%, and artinite is present in the calculated hydrate assemblage, pH drops to 10.4. Beyond 80 mass-% of hydromagnesite, no brucite, but excess hydromagnesite is present, and pH drops to 9.5. Suspensions of technical MgO and hydromagnesite show similar behaviour [46, 48, 49], however their pH values are higher due to the presence of minor elements.

Fig. 2: Thermodynamic modelling of the stable hydrate assemblage in MgO-hydromagnesite blends hydrated at 20°C using a water/solid ratio of 1.20.

3.2 Isothermal calorimetry

The replacement of 30 or 50% of the MgO with hydromagnesite accelerates the hydration of the pure MgO at early ages (i.e. for about the first half day) as shown in Fig. 3a. The replacement of 2% of hydromagnesite with artinite seeds does not show any significant additional beneficial effect regarding acceleration of the hydration reactions. The replacement of 2% of hydromagnesite by NaHCO_3 leads to a slight retardation (Fig. 3b). This is in agreement with the results for pure MgO and MgO blended with hydromagnesite seeds published by other authors [48, 49]. With the addition of NaHCO_3 the induction period ends after approximately 2 h (MgO/HY 70/30: 40 min), and the main hydration peak reaches its maximum after approximately 5.5 h (MgO/HY 70/30: 40 min).

The heat of hydration of MgO to brucite is estimated to be about 930 J/g MgO [73]. On this basis, all samples were about 70-75% hydrated when the measurements stopped after three days (Fig. 3c and 3d). Qualitatively, the early acceleration of MgO hydration shown here seems to occur on a very similar time scale to that observed by [46] despite the fact that, in their work, a much higher MgO/HY ratio was used (90/10, as opposed to 70/30 and 50/50 here). It thus seems that the acceleratory effect may not be very strongly dependent on the HY/MgO ratio. Furthermore it seems that the MgO used in this study is of higher reactivity compared to the one used in the previous study [46], where the authors found a degree of hydration of approximately 50% after 7 days.

Fig. 3: Isothermal heat flow calorimetry of MgO hydrated in the presence of different additions using a water/binder ratio of 1.20; a), b) heat flow, and c), d) cumulative heat.

3.3 X-ray diffraction analyses

XRD data allowed the degree of MgO consumption to be followed over much longer periods of time than could be followed by calorimetry. The results shown in Fig. 4 are reasonably consistent with the calorimetry data in the sense that most of the acceleratory effect of HY addition occurs in the first day. The most important additional conclusion is that, by one week, the MgO in all samples is over 90% consumed. The XRD data appear to show a positive effect of artinite seeding at one day of hydration, but given that this XRD method is far less quantitative than calorimetry at least during the first day of hydration, these data cannot be considered to be proof of such a beneficial effect, which is not seen in the

calorimetry data. In agreement to calorimetry, the addition of NaHCO_3 seems to retard the reaction of MgO .

Fig. 4: Reaction degree of MgO as determined by XRD. The sample MgO/HY 50/50 was omitted in the graph as its reaction degrees of MgO were very similar (slightly higher) than for MgO/HY 70/30.

X-ray diffraction patterns for the hydration of pure MgO pastes from 6 hours to 28 days are shown in Fig. 5a. From 1 day to 28 days the disappearance of periclase and the appearance of a crystalline brucite with sharp diffraction peaks are observed.

The XRD patterns of the sample MgO/HY 70/30 are displayed in Fig. 5b. In this case the scans are far more complex due to the presence of hydromagnesite reflections, but those peaks do not appear to change significantly during the hydration. As expected, periclase disappears and brucite appears in its place, but the brucite reflections are extremely broad, as has been observed before whenever a reactive magnesium carbonate is present [46]. Furthermore, the

378 maxima of the brucite reflections are also shifted compared to the ones in the sample with
 379 MgO only, i.e. from 21.6° 2Θ CoK α ($d = 4.77$ Å) to 22.6° 2Θ CoK α ($d = 4.57$ Å), and from
 380 44.4° 2Θ CoK α ($d = 2.37$ Å) to 44.2° 2Θ CoK α ($d = 2.38$ Å).
 381 But also two additional broad reflections that were not reported before by [46] can be
 382 recognized. One occurs at a very low angle (about 5.5° 2Θ CoK α , $d = 18.6$ Å) which we
 383 tentatively refer to as “dypingite-like” since it is not far away from the low angle peak
 384 reported for dypingite (6.7° 2Θ CoK α , $d = 15.2$ Å) [64]. Another broad peak occurs at
 385 approximately 16.5 – 19.5° 2Θ CoK α ($d = 6.2$ – 5.3 Å), which develops with time and well
 386 separated from expected brucite peaks. The assignment of this reflection remains unclear, but
 387 it might be due to the presence of an unknown amorphous magnesium carbonate. De Vito et
 388 al. synthesized amorphous magnesium carbonate by precipitation from magnesium chloride
 389 solutions using gaseous CO₂ [74]. Their product was mainly X-ray amorphous, but showed a
 390 tiny reflection centred at a d -value of approximately 6.1 Å, which is similar to the d -value of
 391 the broad reflection at approximately 16.5 – 19.5° 2Θ CoK α shown in Fig. 5b. The same
 392 research group investigated the CO₂ sequestration by magnesium containing wastewater [75].
 393 When using high Mg concentrations and high CO₂ fluxes amorphous magnesium carbonates
 394 were formed, and the authors could identify dypingite in samples stored for five months. Also
 395 in those samples an unidentified reflection with a d -value centred at approximately 6.1 Å can
 396 be recognized.
 397 When 2 mass-% artinite seed crystals are added, giving the MgO/HY/artinite 70/28/2 blend,
 398 the artinite reflections are very sharp and clearly visible both in the unhydrated and hydrated
 399 pastes (Fig. 5c). They do not disappear with time, but neither can it be said unequivocally that
 400 they increase with hydration time. There seem to be random variations in their intensities, but
 401 they clearly do not lead to a significant diminution of the HY peaks, so there is no qualitative
 402 evidence for formation of artinite at the expense of hydromagnesite. Meanwhile, the two
 403 previously discussed reflections observed in the artinite-free MgO/HY 70/30 blend are formed

in essentially the same way as in the absence of artinite seed crystals. Similar results as for the MgO/HY 70/30 blend are obtained with the addition of NaHCO_3 , and with the MgO/HY 50/50 blend (not shown). Thus, from semi-quantitative XRD scans, there is no evidence that the addition of either artinite seed crystals or NaHCO_3 significantly changes the nature of the hydration products.

Fig. 5: XRD patterns after different hydration times of a) MgO, b) MgO/HY 70/30, c) MgO/HY/Artinite 70/28/2. A = artinite, B = brucite, H = hydromagnesite, P = periclase, * = reflections which cannot be assigned unambiguously. Note that the scale of the y-axis differs between a) and b), c), respectively.

3.4 Thermogravimetric analyses

Fig. 6a shows the TGA analyses of hydrated MgO pastes. As expected, increasing amounts of brucite are formed with increasing hydration times.

TGA analyses of hydrated pastes of MgO/HY 70/30 shows one particularly interesting and apparently novel feature: the appearance of a dehydration peak centred at about 100°C, as seen in Fig. 6b. This peak is not present in pure hydromagnesite, nor in the initial blend of MgO and hydromagnesite that was hydrated in this experiment, and nor does it appear when pure periclase is hydrated on its own. It has formed already by the first stopped hydration measurement at 6 hours, and does not change significantly after that. In total amplitude it represents about a 5% mass loss by mass of the hydrated paste. Dypingite loses one mole of

429 H₂O at around 100°C [64, 65, 76], and it could be speculated that the TGA water loss at
430 around 100°C attributes to the “dypingite-like” phase identified by XRD and/or to the poorly
431 crystalline brucite, which might be able to bind additional water.

432 With the help of TGA measurements of pure hydromagnesite, see also [67, 77], and the
433 MgO/HY 70/30 sample hydrated for 28 days, subsequent TGA mass loss peaks can be
434 simplistically attributed to:

- 435 (a) loss of the hydrate water from hydromagnesite at about 270°C;
436 (b) dehydration of OH groups in both hydromagnesite and brucite at about 400°C;
437 (c) decarbonation of the carbonate groups remaining from hydromagnesite at about 520°C.

438 However, TGA-FTIR analysis of pure hydromagnesite (Fig. 7a) and of the MgO/HY 70/30
439 sample hydrated for 28 days (Fig. 7b) shows that there is actually a considerable amount of
440 carbonate lost also under the peak at 400°C, and some water lost under the 520°C peak.

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445 Fig. 6: Thermogravimetric analyses after different hydration times of a) MgO, b) MgO/HY
 446 70/30. The samples after 3 and 7 days of hydration are omitted. “*” marks the dehydration
 447 peak centred at about 100°C.

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449

Fig. 7: Thermogravimetric analysis coupled with FT-IR of a) pure hydromagnesite and b) MgO/HY 70/30 hydrated for 28 days.

Fig. 8a shows the amount of bound water referred to 100 g unhydrated binder for MgO and the two MgO/HY blends (70/30 and 50/50). In agreement with calorimetry and XRD results, an acceleration of the hydration reactions can be observed when hydromagnesite is added to MgO, while the amount of bound water after 28 days is in the same order for all three mixtures. However, when normalizing the amount of bound water to the amount of MgO in the binder (Fig. 8b), a significant increase of the bound water content with increasing amount of hydromagnesite in the blend can be observed. When the amount of bound water is recalculated as mol H₂O per mol MgO reacted, values of 1.0 (MgO, referring to the formation of brucite), 2.0 (MgO/HY 70/30) and 3.3 (MgO/HY 50/50) mol H₂O per mol MgO are derived. Thus it can be concluded that in the presence of hydromagnesite more water is bound in hydrate phases than can be explained by the hydration of MgO to brucite, as also suggested by the presence of the TGA water loss peak centred at around 100°C.

Fig. 8: Influence of the MgO/hydromagnesite ratio on the amount of water bound in the hydration reactions, normalized to (a) unhydrated binder and (b) unhydrated MgO.

3.5 Raman spectroscopy

Raman spectroscopy of the MgO/HY 70/30 blend hydrated for 28 d shows in the region below 1200 cm^{-1} the presence of brucite as identified by two main peaks at 445 cm^{-1} and 280 cm^{-1} , and a broad peak centred at around 730 cm^{-1} (Fig. 9a) in agreement to [78]. The peak at 1120 cm^{-1} in the hydrated MgO/HY 70/30 blend refers to the symmetrical stretching vibration of the CO_3^{2-} ion in hydromagnesite [46]. An additional weak peak at 1050 cm^{-1} (Fig. 9b) formed in the MgO/HY 70/30 blend (and in all other hydrated blends of pure MgO with hydromagnesite), but this peak does not correspond to a major peak of artinite, dypingite [79] or any other known magnesium carbonate and so remains unassigned. The main Raman peak of artinite, at about 1095 cm^{-1} (symmetrical stretching vibration of the CO_3^{2-} ion [79]), was not observed when no artinite seed crystals were added, although a weak broad peak close to it is present and could indicate another amorphous phase related to artinite. But overall the Raman evidence supports the conclusion that no significant amounts of an artinite-like phase form in this system.

Fig. 9: Raman spectrum of MgO/HY 70/30 after 28 d of hydration in the range of a) 1200-55 cm^{-1} and b) 1200-1000 cm^{-1} . Raman spectra of brucite, hydromagnesite and artinite are shown for comparison. * = unassigned.

4. Discussion and conclusions

In agreement with a previous study [46] it was found that hydromagnesite accelerates the reaction of MgO. Blends of MgO with hydromagnesite were shown to provide strength properties, which would be suitable to manufacture construction materials, but still significantly below the performance of Portland cement, while MgO alone does not provide any strength [43, 44, 46]. This was confirmed within this study using mortars based on a technical MgO blended with hydromagnesite, see Appendix.

However, the results obtained in this work point towards negative conclusions on both of our initial hypotheses.

The hypothesis that artinite is the stable hydrate in a mixture of brucite and hydromagnesite (HY), based on a thermodynamic calculation, is not supported by our observation as the

503 seeding of the hydrating MgO-HY blends with finely ground natural artinite had no
504 significant effect on the rate of hydration or on the final product assemblage. However, the
505 hydration was followed up to 28 days only, and the samples might not have reached
506 equilibrium.

507 The hypothesis that addition of a soluble salt with a common ion, sodium bicarbonate, could
508 accelerate the hydration of MgO blends is also not supported by our data. It appears to have
509 no significant effect on the rate of hydration (a slight retardation of MgO dissolution is
510 observed) or on the products of the hydration reactions.

511 However, there were important new observations in the TGA and XRD analyses. Because of
512 the careful preparation procedure used to stop the hydration of the pastes prior to analyses, we
513 were able to show that in the presence of hydromagnesite more water is bound in hydrate
514 phases than can be explained by the formation of brucite only. The MgO-HY blends always
515 produced a significant amount of an unknown hydrate with a thermal decomposition peak
516 centred on about 100°C. This hydrate formed quickly – it was already present after 6 hours of
517 hydration and did not increase significantly after that. We hypothesise that this peak
518 represents an amorphous or very poorly-crystalline phase that leads to cohesive binding in
519 these blends.

520 XRD analyses revealed that in MgO-HY blends two reflections are present, one at $5.5^\circ 2\theta$
521 $\text{CoK}\alpha$ ($d = 18.6 \text{ \AA}$), and a second broad reflection at about $16.5\text{-}19.5^\circ 2\theta$ $\text{CoK}\alpha$ ($d = 6.2\text{-}5.3$
522 $\text{\AA}$), which belong neither to hydromagnesite nor to brucite. It can be speculated that those
523 reflections belong to an amorphous or very poorly crystalline phase containing the additional
524 water observed by TGA.

525 Another difference between the hydrated MgO-HY pastes and the pure MgO paste is the
526 observation of very broad diffraction peaks for brucite whenever hydromagnesite is present. It
527 is tempting to speculate that the low-temperature TGA peak might be associated with water

weakly bound to this very poorly crystalline form of brucite and/or to the amorphous or poorly crystalline phase identified by XRD.

Further investigations to unravel the nature of hydrate phases in the MgO-hydromagnesite system and their role regarding strength formation will be necessary.

5. Acknowledgements

Boris Ingold, Luigi Brunetti and Daniel Käppeli are acknowledged for their assistance in the lab, Andreas Leemann for taking the photograph of the artinite mineral, and Ellina Bernard, Andrea Mancini and Alessio di Giacomo for assistance with Raman and TG-FT-IR. Barbara Lothenbach is acknowledged for fruitful discussions and critical review of the manuscript.

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Appendix

For measurement of flexural and compressive strength of MgO blended with hydromagnesite (70/30 by mass) a technical magnesium oxide (MgO-t) was used instead of the pure one calcined from brucite. The technical product is a reactive MgO calcined at low temperatures and contains approximately 83 mass-% of MgO as determined by X-ray diffraction. Its reactivity measured according to [50] is somewhat lower than for the pure MgO (neutralization time of 200 s compared to 145 s for the pure MgO), but still in the range of medium reactivity. Fig. A1 shows that the particle size distribution of the technical MgO is significantly coarser than the one of the pure MgO.

Fig. A1: Particle size distribution of pure MgO and technical MgO (MgO-t). (a) differential particle size distribution, (b) cumulative particle size distribution.

Mortars of MgO-t blended with hydromagnesite (70/30 by mass) were prepared according to EN 196-1, except that higher water/binder ratios and smaller prisms (25 mm × 25 mm × 100 mm, 9-fold mould) were produced. Table A1 gives the mix designs. Three different water/binder (w/b) ratios of 1.20, 0.95 and 0.70 were used. Workability of mixtures with w/b ratios of 0.95 and 0.70 was adjusted by adding a commercial superplasticizer based on polycarboxylate ether.

776

777 Table A1: Mix designs of the mortars used in this study referring to 100 g binder.

MgO-t	HY	Water	Super- plasticizer ¹⁾	Sand ²⁾ 0-0.5 mm	Sand ²⁾ 0.5-1 mm	Sand ²⁾ 1-2 mm
g	g	g	g	g	g	g
70	30	120	-	100	100	100
70	30	95	1.5	100	100	100
70	30	70	3.0	100	100	100

778 ¹⁾ A commercial superplasticizer based on polycarboxylate ether (solid content 40 mass-%)
779 was used. The dosage refers to the product as delivered.

780 ²⁾ Obtained by sieving EN 196-1 standard sand.
781

782

783 Flexural and compressive strength were tested after 1, 3, 7 and 28 days on 2 prisms each.

784 Flexural strength was measured using a span of 75 mm and a load rate of 0.02 kN/s, while for

785 compressive strength a load rate of 0.3125 kN/s was used.

786 Fig. A2 shows the results for flexural and compressive strength. As expected, flexural

787 strength and compressive strength increase with decreasing w/b. For w/b = 0.70 a quite

788 acceptable compressive strength of 21 MPa after 28 days is reached, which could be further

789 optimized by lowering the w/b ratio to 0.5-0.6.

790 The results also suggest that the used superplasticizer does not lead to strong retardation

791 despite the high dosage used, which is confirmed by isothermal calorimetry (Fig. A3). This

792 behavior towards superplasticizers is quite different to the one of Portland cement, where such

793 high dosages would cause a strong retardation [80-82].

794

Fig. A2: a) Flexural and b) compressive strength of mortars with binder MgO-t/HY 70/30 using different water/binder ratios and superplasticizer (SP) amounts. Maximum standard deviations are 12.5% for flexural strength and 6.6% for compressive strength.

Fig. A3: Isothermal heat flow calorimetry of MgO-t/HY 70/30 hydrated using different water/binder ratios and superplasticizer (SP) amounts; a) heat flow, and b) cumulative heat.