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The mechanism of hydration of MgO-hydromagnesite blends

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ABSTRACT

The hydration of reactive periclase (MgO) in the presence of hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) was investigated by a variety of physical and chemical techniques. Hydration of pure MgO-water mixtures gave very weak pastes of brucite ($\text{Mg}(\text{OH})_2$), but hydration of MgO-hydromagnesite blends gave pastes which set quickly and gave compressive strengths of potential interest for construction applications. The strengths of the blends increased with hydration time at least up to 28 days, and were not significantly decreased by increasing the hydromagnesite content up to 30%. Raman spectroscopy suggests that an amorphous phase, of composition between that of brucite, hydromagnesite and water, may form. Small amounts of calcite also form due to CaO in the MgO source. Thermodynamic calculations imply that the crystalline phase artinite ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) should be the stable product in this system, but it is not observed by either XRD or FTIR techniques, which suggests that its growth may be kinetically hindered.

Keywords: MgO, cement, hydration, hydromagnesite, artinite, brucite,

1. Introduction

MgO (periclase) reacts with water to give brucite ($\text{Mg}(\text{OH})_2$) under conditions relevant to normal construction materials. The rate of reaction increases as the crystallinity of the periclase decreases (i.e. smaller mean crystallite size). Periclase is usually manufactured by calcination (decarbonation) of magnesite (MgCO_3) that is obtained from natural mineral deposits. The lower the decarbonation temperature, the lower the degree of crystallinity of the resulting periclase. Lightly-burned magnesite is of particular interest for use in hydraulic cements because it reacts very rapidly with water [1].

The hydration of MgO has been extensively studied [2-6]. Water molecules, even from the vapour phase, react rapidly with the anhydrous MgO surface to form a surface layer of $\text{Mg}(\text{OH})_2$, but with a structure probably significantly different from that of brucite due to interactions with the underlying oxide. This surface hydrate displays an apparent solubility somewhat higher than pure brucite. Thus, at high relative

39 humidity, when significant amounts of physically adsorbed water, or excess liquid water, is present, this
40 hydrated surface layer can dissolve in the mobile water layer and reprecipitate as brucite crystallites
41 further away from the surface. The hydrated surface layer on the oxide is continually reformed by further
42 reaction of the underlying oxide with water. The hydration rate of MgO is effectively limited by the rate
43 at which the $\text{Mg}(\text{OH})_2$ layer on the surface of the MgO dissolves in the water layer. This in turn is
44 influenced by the rate at which dissolved Mg^{++} and OH^- ions are removed from the water layer by, for
45 example, precipitation.

46

47 Periclase can also react with CO_2 in the presence of water (liquid or vapour) to give hydrated carbonates
48 or hydroxy-carbonates such as nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4$
49 $(\text{OH})_2 \cdot 4\text{H}_2\text{O}$). It is reported that nesquehonite forms readily from aqueous solutions at ambient
50 temperature [9,10]. Table 1 lists the known phases in the MgO- CO_2 - H_2O system under conditions of
51 interest, and gives standard free energies of formation from the elements at 25°C [7, 8]. From this data
52 it can be shown that under ambient atmospheric conditions, all hydrated magnesium (hydroxy-)
53 carbonates should convert to magnesite. However, the kinetics of magnesite growth is very slow,
54 especially below 100°C , and so the hydrated carbonates and hydroxy-carbonates, which have much
55 higher growth rates, usually form and do not convert substantially to magnesite over decades under
56 typical exposure conditions for construction materials [11].

57

58 Sealed samples of pure pastes of reactive MgO and water do not gain any significant compressive
59 strength, despite the formation of brucite. Moreover, if such pastes are left in the open air, they only
60 carbonate very slowly and do not harden (unlike pastes made of lime, which harden rapidly by
61 atmospheric carbonation - the basis of the lime mortar technology used for many millennia). For this
62 reason, MgO has not until recently been considered of value in simple binders except when significant
63 amounts of other inorganic chemicals are added (e.g. chlorides, sulfates, or phosphates: to make
64 magnesium oxy-chloride, magnesium oxy-sulfate or magnesium phosphate cements, respectively).
65 However, over the last decade or so, there has been increasing interest in using MgO in silicate-based
66 binder system, or in carbonated binders. Blends of MgO with Portland cement, granulated blast furnace
67 slag (GBFS) or coal fly ash (FA) have been studied to produce low-carbon hydraulic binders [1-5,9].
68 However, there is little evidence for significant contribution of MgO hydration to the strength
69 development of such cements. MgO hydration is also known to cause harmful expansion in Portland
70 cement concretes [10] under certain conditions. Moreover, the fact that conventional MgO production
71 methods are very energy and CO_2 intensive makes it difficult to justify the use of MgO in low-carbon
72 hydraulic cements [12]. A more promising approach for CO_2 emissions reduction is to use MgO in
73 cements that hardens by carbonation, [6-8], but even then, only a fraction of the CO_2 released during
74 manufacture is recaptured. The most desirable approach would be to use MgO derived from natural
75 magnesium silicate raw materials by a new low-energy route, as first proposed by Vlasopoulos [13], but

76 no practical low-energy production process for achieving this goal yet exists [12]. However, developing
77 such a process remains an important long-term research goal.

78
79 A significant advance in developing low-carbon hydraulic cements based on MgO was made in 2009,
80 when the addition of hydrated magnesium carbonates was found to significantly change the hydration
81 of MgO, resulting in pastes that rapidly set and developed significant strength [14-16]. These findings
82 were unexpected and novel [19]. The results have been confirmed for mixtures containing
83 hydromagnesite (HY) as the additive at up to 50% MgO replacement levels [14-16]. The fact that
84 cements made from such mixtures contain significant levels of carbonate is the key to reducing the
85 carbon footprint [12]. The addition of HY reportedly results in more rapid and extensive dissolution of
86 MgO and the precipitation of Mg(OH)₂ in the form of very small interlocking crystallites with different
87 morphology from that formed when just MgO is hydrated[16]. However, the reason for this change in
88 morphology, and how it leads to strength development, is still unclear. An improved understanding of
89 the hydration reaction mechanism is essential if these magnesium hydroxy-carbonate cements are to be
90 further developed and optimised. This paper reports on a systematic investigation into the hydration
91 reactions of MgO in the presence of hydromagnesite in order to improve understanding of the hydration
92 mechanism and strength development.

94 **2. Materials and Methods**

96 **2.1 Materials**

97 A commercial MgO powder prepared by calcining magnesite at 900°C (Baymag 30, Baymag Inc.,
98 Alberta, Canada) and technical grade hydromagnesite (Calmag CALMAGS GmbH, Germany) were
99 used in all experiments. The chemistry of the raw materials is given in Table 2. XRF results are presented
100 as total mass percentage of non-volatile elemental oxides in the material (i.e. on an ignited basis.) The
101 measured and expected loss on ignition (LoI) data are included to demonstrate the purity of each powder.
102 The particle size distribution of the as-received raw materials are given in Fig. 1.

104 **2.2 Preparation of samples**

105 MgO and HY were mixed at mass ratios of 9:1, 8:2 and 7:3. Water was added to form pastes using the
106 recommended mixing method for mortar and pastes [17]. A water/total solids mass ratio of 0.62 was
107 used in all samples. This was the minimum water content that allowed formation of a homogenous paste
108 in all cases, although increasing the hydromagnesite content always increased paste viscosity. Pastes
109 were cast into 50 x 10 x 10 mm rectangular moulds and vibrated for 5 minutes to remove air bubbles.
110 They were then covered with a glass plate to prevent moisture loss and limit reaction with atmospheric
111 CO₂, and allowed to hydrate for 24 hours at 22 ± 1°C. The samples were then de-moulded and stored in
112 deionised water at 22 ± 1°C for periods up to 56 days.

114 **2.3** *Physical/chemical properties*

115 The heat of hydration of trial mixes was monitored by isothermal conduction calorimetry (Wexham
116 Developments Ltd, UK). The bath temperature was set at $20.0 \pm 0.1^\circ\text{C}$ and 25g of paste samples with
117 0.62 w/s ratio were mixed by hand for 2 minutes before being placed in the calorimeter. The time
118 between the start of mixing and obtaining the first calorimetry data point was ~10 minutes.

119

120 Cured cast samples were removed from the water bath, cut in half to give 25 x 10 x 10 mm prisms and
121 immediately tested in uniaxial compression, parallel to the long axis at a constant loading rate of 0.08
122 kN/s (ADR Auto strength machine, ELE International, UK) to give compressive strength data.
123 Preliminary tests demonstrated that this non-standard test procedure gave highly reproducible results.

124

125 The pH of slurry samples made with a w/s ratio of 3 was determined using an Inlab Routine Pro
126 electrode, (Mettler Toledo, Switzerland). The slurry was continuously stirred while **exposed to the**
127 **atmosphere**, and the pH measured at various times throughout the hydration process at $22 \pm 1^\circ\text{C}$.

128

129 **2.4** *Microstructural and phase analysis*

130 Powder x-ray diffraction (XRD) using Cu K α radiation in the range of 5 to $65^\circ 2\theta$ was used to semi-
131 quantitatively compare the relative amounts of crystalline phases in paste samples (X-Pert PRO MPD,
132 PANalytical, Netherlands). Fourier transform infrared spectroscopy (FTIR) was used to detect
133 additional phases in the reaction products. Brucite control samples were prepared by hydrating MgO
134 (Baymag 30) in distilled water. Raman spectrometry (Renishaw inVia Raman Microscope, UK) was
135 used to characterise the different MgO/HY mixes. The microstructures of the as-received powder
136 materials and hydrated, fractured MgO/HY samples were analysed using scanning electron microscopy
137 (SEM, JEOL JSM 5610, Japan). SEM samples were gold coated using a current of 20 mA.

138

139 Prior to analysis the paste samples were ground with acetone in a mortar and pestle to inhibit further
140 hydration. This is an accepted way to inhibit hydration of calcium silicate-based cements as hydration
141 water is replaced by acetone [18]. The slurry formed was then filtered and rinsed with additional acetone
142 using vacuum filtration and the solid residue dried at 60°C to constant weight.

143

144 **3. Results**

145

146 **3.1** *Physical properties*

147 Isothermal conduction calorimetry power output and total heat evolution curves for pastes of pure MgO
148 and a 9:1 MgO: HY blend are shown in Fig. 2. The inclusion of 10% HY greatly accelerates the early
149 hydration compared to pure MgO paste. Hydration occurs prior to obtaining the first calorimetry data
150 point. Both samples show an acceleration period followed by a reducing rate of hydration, suggesting a
151 nucleation and growth process in which the added HY acts as growth sites for hydrates. The maximum

152 hydration rate occurs after about 10 hours for pure MgO and 2 hours for the sample with 10% HY. The
153 total heat curves may not be very accurate due to the loss of heat in the first few minutes, due to external
154 mixing, and the well-known problem of calibration and baseline drift in long-term isothermal
155 calorimetry experiments, but they appear to indicate that the pure MgO hydrates to a significantly greater
156 extent than the MgO in the 9:1 blend over the one week (168 hours) period shown. Thermodynamic data
157 bases give a heat of hydration of MgO of about 930 J/g [19], so the total heat evolution data suggests
158 that pure MgO is only about 50% hydrated after one week, and the blended MgO is even less hydrated.
159

160 Fig. 3 shows the variation in solution pH over 28 days for w/s = 3 slurries of pure MgO, pure HY and a
161 9:1 MgO: HY mixture. Slurries made with 8:2 and 7:3 MgO: HY mixtures gave similar results to the
162 9:1 mixture, so the data for these are not shown. The initial pH value for the pure MgO and the MgO:
163 HY mixtures was about 12.4 whereas for pure HY it was close to 10. The pure MgO slurry shows a slow
164 reduction in pH with time, reaching a value of about 11.2 after one week, whereas MgO: HY mixes all
165 showed a much more rapid decrease in pH, reaching values close to, or even slightly below, those of
166 pure HY after ~1 day.
167

168 Table 3 shows that all three MgO-HY paste samples give very similar compressive strength
169 development, achieving about 18 MPa after 7 days, and increasing to about 24 MPa at 28 days. Pure
170 MgO pastes did not give sufficient strength for sample demoulding and so cannot be compared directly
171 in the table.
172

173 **3.2 Microstructural and phase analyses**

174 The XRD scans shown in Fig. 4 are only semi-quantitative, as there were no internal standard. However,
175 given that the sample preparation and analysis techniques were quite repeatable, comparisons of peak
176 intensities seem justifiable as a way of examining changes in the relative amounts of the main crystalline
177 phases present. In the pure system, (Fig. 4b) periclase disappears (dissolves) with time while brucite
178 forms (precipitates). Even after 28 days of hydration, the periclase peak in the pure system has not
179 completely disappeared. A weak peak in Fig. 4a also indicates the formation of some calcite (CaCO₃).
180 CaO is an impurity in the MgO that carbonates by reaction with atmospheric CO₂.
181

182 The reactions of MgO: HY blends show similar trends as a function of hydration time, with the
183 disappearance of periclase and formation of brucite, but at different rates, as clearly shown in Fig 4c for
184 pure MgO and 9:1 MgO: HY pastes hydrated for 28 days. Significantly more MgO appears to have
185 hydrated and more Mg(OH)₂ has formed in the pure paste than in the 9:1 blend. In addition, the Mg(OH)₂
186 peak in the 9:1 blend is significantly broader than in the pure system, suggesting a smaller mean
187 crystallite size [20]. This is in agreement with calorimetry data, where MgO does not fully hydrate to
188 brucite.
189

190 In the XRD data for MgO: HY blends, HY peaks were observed mainly for samples with MgO: HY
191 ratios of 8:2 and 7:3 but hardly at all for the 9:1 samples due to the low concentration of HY and the
192 corresponding weak diffraction peaks. Mg(OH)₂ and MgO were always present, as expected, and the
193 Mg(OH)₂ peak always shows significant broadening compared to those found in the pure system. No
194 additional peaks are observed, so any other phases which might be present must be effectively x-ray
195 amorphous.

196

197 The FTIR spectra of samples produced by hydrating MgO, HY and the MgO: HY 70:30 mix for 28 days
198 are shown in Fig. 5. The MgO: HY mixes with ratios of 90:10 and 80:20 are not shown because HY is
199 only present in small quantities and the corresponding bands are too weak to observe [21]. Several bands
200 can be detected which have been characterised in previous studies, as shown in Table 4. All the bands
201 identified are seen in the spectra for the three samples containing HY, except for that due to O-H bonds
202 in Mg(OH)₂ at 3700 cm⁻¹ which are, as expected, not observed in the pure HY sample. Small amounts
203 of carbonate are observed in hydrated MgO. This is consistent with the XRD data and confirms that the
204 MgO reacts with atmospheric CO₂ over time, although the carbonate ions detected in this case are
205 probably mainly present as CaCO₃. The presence of carbonate impurities in brucite (Mg(OH)₂) has
206 previously been reported in FTIR studies [22]. Previous research has shown that for pure magnesite,
207 (MgCO₃), a single asymmetric stretching band is observed between 1478 and 1450 cm⁻¹. The presence
208 of two bands in the 1420-1480 cm⁻¹ region, as in HY, indicates the presence of two different carbonate
209 ion environments [21, 23, 24]. The HY signal at ~600cm⁻¹ is unassigned, although this band has been
210 observed by other researchers [25]. Studies on the dehydration and rehydration of HY have also
211 identified a band at ~2350cm⁻¹ which has been assigned either to a CO₂ inclusion or a terminal CO₂,
212 corresponding to the ν₃ fundamental of CO₂ [25, 26]. However, this band cannot be measured in our
213 study, probably due to the background noise level.

214

215 Raman spectroscopy was used to search for other phases not ‘visible’ using FTIR. Fig. 6 shows the
216 Raman spectra of pure HY, hydrated MgO, hydrated MgO: HY samples with ratios of 9:1 and 7:3. All
217 samples had been cured for 28 days. Three main peaks at 280 cm⁻¹, 440 cm⁻¹ and 1100 cm⁻¹ can be
218 identified. The peaks at 280 cm⁻¹ and 440 cm⁻¹ observed in the hydrated MgO sample also appear in the
219 other spectra except for the spectrum of HY. These two peaks are related to Mg(OH)₂ [27]. The peak at
220 ~1120cm⁻¹ is due to symmetrical stretching of the CO₃²⁻ ion, [28, 29], which is why it is much stronger
221 in Raman spectra. However, of more interest is the formation of a broad weak peak or series of small
222 peaks between 1050 and 1120 cm⁻¹ for MgO: HY mixes. These peaks are not seen for pure MgO and
223 HY and are probably due to symmetrical stretching of CO₃²⁻ in other magnesium carbonate phases,
224 which could be very poorly crystalline. Table 5 lists a number of possible phases with peaks in this
225 range.

226

227 Fig. 7 shows SEM images of hydrated MgO and HY and fracture surfaces of pastes cured for 7 and 28
228 days. Fig. 7 (c, d, e and f) show that over time well-developed crystalline morphologies (plates) are
229 formed. These are not observed either in hydrated pure MgO or in pure HY samples.

230

231 4. Discussion

232

233 The initial rate of hydration of MgO is strongly increased by HY, which suggests that HY additions
234 provide additional growth sites for the hydrates (Mg(OH)₂ and probably other x-ray amorphous hydrate
235 phases) promoting further MgO hydration [13]. It was expected that pure MgO would fully hydrate to
236 Mg(OH)₂, but this was not shown by calorimetry or XRD. This incomplete hydration is probably due to
237 a brucite layer forming on the MgO particle surface that inhibits water reaching unreacted MgO by
238 acting as a passivation layer. However, it is expected that eventually pure MgO will fully hydrate to
239 Mg(OH)₂. Of particular interest is the high initial pH of 12.4 for MgO and MgO: HY systems when
240 mixed with water, because a pH of ~10 had been expected. The measured pH is actually close to that of
241 a saturated portlandite (Ca(OH)₂) solution, leading to the conclusion that CaO impurities in the MgO
242 and HY cause the high initial pH. The pH of the pure MgO slurry then falls slowly with time due to
243 atmospheric carbonation to produce calcite, consistent with XRD observations of calcite in the system.
244 When MgO is mixed with HY, the pH falls much more rapidly, which can be explained by HY
245 containing readily soluble carbonate ions which are capable of neutralizing Ca(OH)₂ much more rapidly
246 than CO₂ from the atmosphere. Rapid precipitation of calcite at early ages due to reaction with HY could
247 provide another source of nucleation sites for hydration products of MgO and **the formation of CaCO₃**
248 **may also contribute to rapid setting and compressive strength development.**

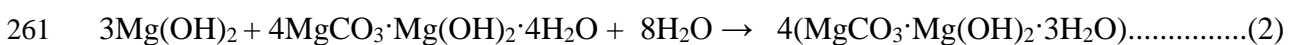
249

250 After the first peak in the calorimetry data, the rate of heat evolution is significantly lower for the MgO:
251 HY blends, and the XRD data confirm that the amount of unreacted MgO is higher in these blends at
252 later ages than in the pure system, despite the fact that blends give far higher compressive strengths.
253 This suggests that additional hydrates produced in the blends have a retarding effect on the later
254 hydration of MgO. The effect might be due to surface blocking or to the formation of diffusion barriers.
255 These additional hydrates are also presumed to be responsible for strength development.

256

257 Table 1 gives the free energies of the known crystalline phases of interest in this system. Artinite
258 {MgCO₃·Mg(OH)₂·3H₂O} is intermediate in composition between Mg(OH)₂ and HY and can, in
259 principle, be formed from these two phases and water by the following reaction:

260



262

263 A calculation using the thermodynamic data from Table 1 gives the free energy change of the reaction
264 as -6.42 kJ/mol, which implies that the equilibrium should lie on the right-hand side at 25°C. Thus,

265 artinite should form in MgO: HY blends. However, it is not detected in the XRD data. This could be
266 due to weak XRD peaks or it could be due to a very low degree of crystallinity. Artinite has a carbonate
267 symmetric stretching peak at 1092 cm^{-1} (Table 5) which should be observable in both IR and Raman
268 spectra. No such peak is visible in the FTIR spectra of MgO: HY blends (Fig. 5) but it could be too weak
269 to detect. The Raman spectra of hydrated MgO: HY blends (Fig. 6) show a very broad peak between
270 about 1040 and 1120 cm^{-1} which suggests a disordered hydroxy-carbonate phase that might not be too
271 far from artinite in composition. It thus seems possible that some kind of amorphous hydroxy-carbonate,
272 intermediate in composition between HY and brucite, may form in MgO: HY pastes and be responsible
273 for high compressive strengths relative to pure MgO pastes.

274

275 The SEM images in Fig. 7 neither confirm nor deny the hypothesis of a new phase in MgO: HY pastes.
276 It is notable that quite large ($\sim 5\mu\text{m}$) platy crystals are formed after 28 days in the 9:1 MgO: HY paste.
277 These could be $\text{Mg}(\text{OH})_2$, but they are much larger than the crystals observed in pure MgO. Moreover,
278 the XRD peak broadening of brucite observed in the MgO: HY blends would tend to suggest smaller,
279 rather than larger, crystals. It is therefore possible that these crystals are the new phase, in which case
280 the poor x-ray crystallinity is due to either being very thin in the direction perpendicular to the basal
281 plane, or possibly to some other kind of internal disorder.

282

283 5. Conclusions

284

285 Addition of hydromagnesite, (HY, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), significantly accelerates the hydration of
286 reactive periclase (MgO) in pastes. The hydration of pure MgO gives very weak pastes despite fairly
287 rapid formation of brucite ($\text{Mg}(\text{OH})_2$), but the addition of HY at MgO at replacement dosages of 10-
288 30% results in pastes that give significant compressive strengths, despite the absence of significant
289 increases in the apparent degree of hydration of the MgO. Evidence from pH measurements also
290 suggests that carbonate ions from HY can combine rapidly in solution with calcium ions released by
291 CaO, (an impurity in the MgO source,) to precipitate small amounts of calcite at early ages. This might
292 also contribute to an acceleration of the hardening reactions, perhaps by acting as nucleation sites.

293

294 Analyses of the hydrated pastes by XRD and FTIR techniques do not clearly show any new MgO-based
295 phases, but there is a broad but weak Raman peak at 1120 - 1040 cm^{-1} that could represent a new
296 amorphous phase. It is thus concluded that if any new cohesive phase forms in this system, it is probably
297 X-ray amorphous with a composition roughly intermediate between that of HY and brucite. A
298 thermodynamic calculation suggests that artinite ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) should form-be a stable
299 product phase during the hydration of MgO:-HY blends, but the fact that it is not observed by XRD or
300 FTIR suggests that its formation may be kinetically hindered.

301

302 The formation of an amorphous phase intermediate in composition between ~~HY₂~~ and Mg(OH)₂ and
303 water is a possible explanation for the surprisingly high strengths produced by hydrating MgO: HY
304 blends, compared to the very low strengths produced by hydration of pure MgO. Such a phase must
305 have a high degree of cohesion.

306
307 These results hold promise for the development of improved binders in the magnesium-hydroxy-
308 carbonate system. Such binders have the potential to reduce carbon emissions from manufacturing
309 construction materials, provided that MgO can be obtained from magnesium silicates by an energy-
310 efficient process. However, there are currently many aspects of hydration and strength development in
311 this system that remain unclear.

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- 390

1
2 Table 1: Gibbs free energies of formation from the elements in their standard states at 298K for
3 phases of interest to this work. [7, 8]

4

Phase	chemical composition	ΔG_f^0 [kJ mol ⁻¹]
Periclase	MgO	-566
Carbon dioxide (gas)	CO ₂	-394
Water (liquid)	H ₂ O	-237
Brucite	Mg(OH) ₂	-835
Magnesite	MgCO ₃	-1028
Nesquehonite	MgCO ₃ ·3H ₂ O	-1724
Lansfordite	MgCO ₃ ·5H ₂ O	-2200
Artinite	MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O	-2569
Hydromagnesite	(MgCO ₃) ₄ ·Mg(OH) ₂ ·4H ₂ O	-5865
Calcite	CaCO ₃	-1129
Aragonite	CaCO ₃	-1128

5
6
7 Table 2: Chemical composition of MgO and hydromagnesite (HY) used in this study analysed
8 by XRF using powder samples. The non-volatile elements (i.e. excluding CO₂ and H₂O) are
9 assumed to be present as oxides, totalling 100% on an ignited basis. Measured and expected
10 1000°C ignition loss values are also given for the actual materials as used.

11

element	sample	
	HY	MgO
MgO	95.55	92.55
CaO	3.33	1.74
SiO ₂	0.47	2.72
Na ₂ O	0.28	0.76
NiO	0.19	nd
Fe ₂ O ₃	0.11	0.77
Al ₂ O ₃	nd	1.02
SO ₃	0.07	0.44
LoI measured	55.60	2.0
LoI expected	56.90	0
BET surface area [m ² /g]	n.a	30

nd = not detected

12
13
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15
 16 Table 3: Compressive strengths of paste samples at 7 and 28 days. Means and standard
 17 deviations are calculated from 6 replicate measurements.

18

Time [days]	7		28	
MgO:HY ratio	strength	SD	strength	SD
	[MPa]		[MPa]	
9:1	17.3	0.8	24.6	0.6
8:2	17.1	0.9	23.8	0.7
7:3	17.3	1.0	24.5	0.4

19
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22 Table 4: Summary of the bands detected and their origins, for the FTIR spectra in Fig.5.

23

Band position (cm⁻¹)	origin	movement	reference
~ 600	Unknown	Unknown	[25, 26]
800 - 880	CO ₃ ²⁻ from HY	Bending vibrations	[23, 30]
1120	CO ₃ ²⁻ from HY	V ₁ symmetric stretching vibration	[23, 30]
1420 - 1480	CO ₃ ²⁻ / HCO ₃ ⁻ from HY	V ₃ asymmetric stretching vibration	[23, 24, 30]
1650 (shoulder)	H ₂ O	Bending vibration	[31, 32]
3450, 3510	HY water of crystallisation		[23, 30]
3650	Mg(OH) ₂ from HY	Free O-H vibration	[23, 33]
3700	Mg(OH) ₂	Anti-symmetrical O-H stretching vibration of lattice hydroxide	[22, 23]

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29 Table 5: Bands summary of different hydrated magnesium carbonates as well as selected
30 calcium carbonates in the region of 1200 - 1000 cm^{-1} [28, 34, 35].

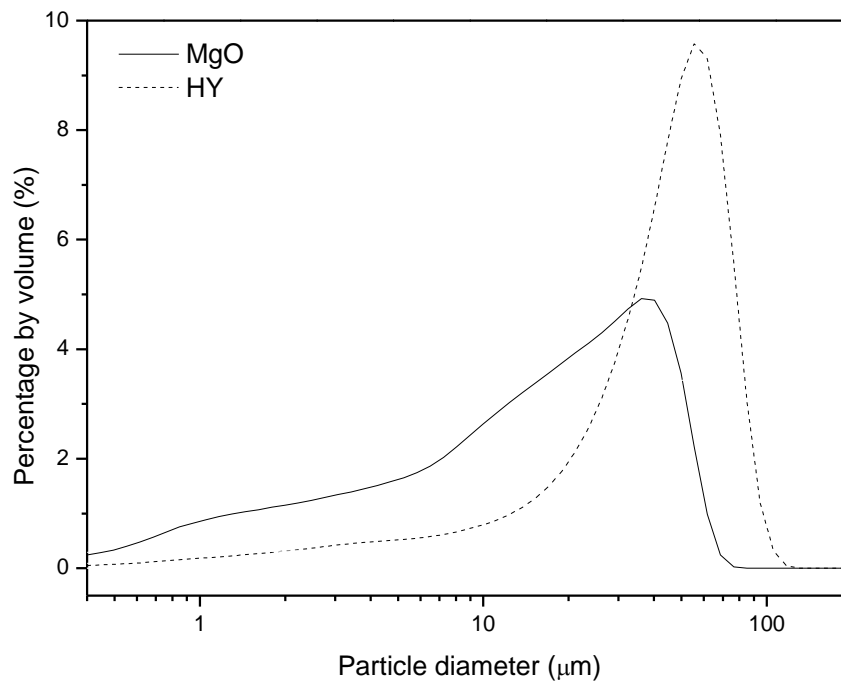
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Mineral name	chemical formula	Wavenumber [cm^{-1}]
Artinite	$\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$	1092
Dypingite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	1120
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	1098
Huntite	$\text{Mg}_3\text{Ca}(\text{CO}_3)_4$	1123
Hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	1119
Magnesite	MgCO_3	1094
Nesquehonite	$\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2(\text{H}_2\text{O})$	1100
Calcite	CaCO_3	1084
Aragonite	CaCO_3	1084
Vaterite	CaCO_3	1089
-	HCO_3^-	1017
-	CO_3^{2-}	1065

32

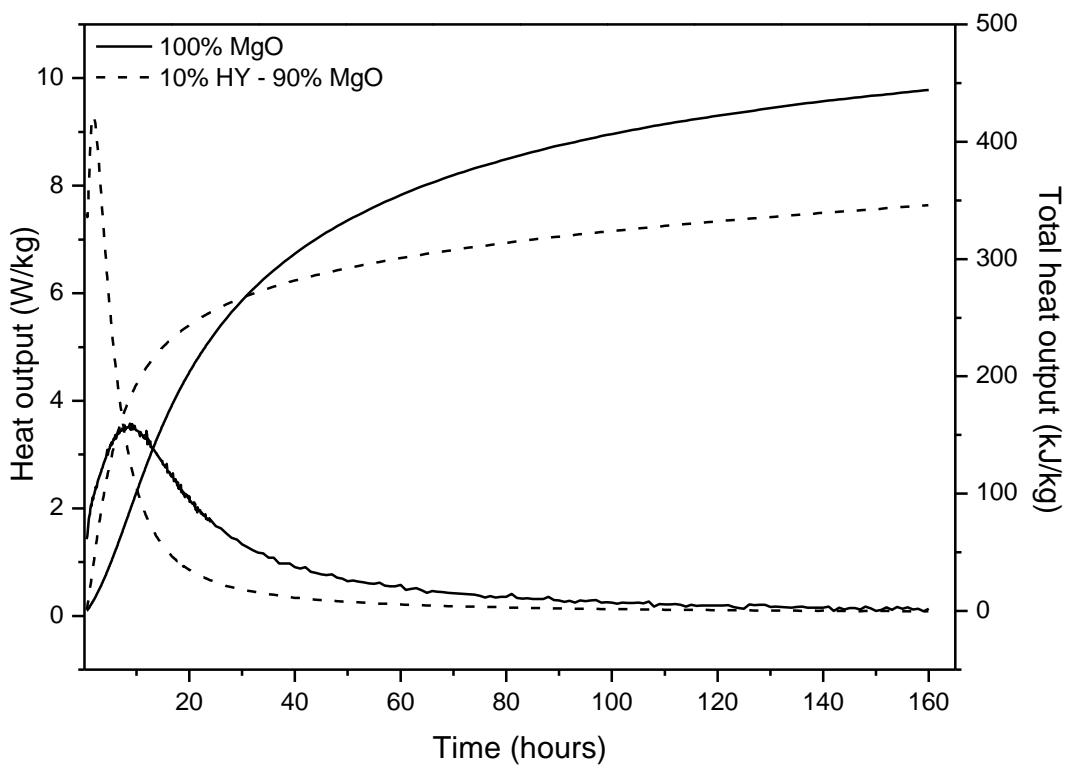
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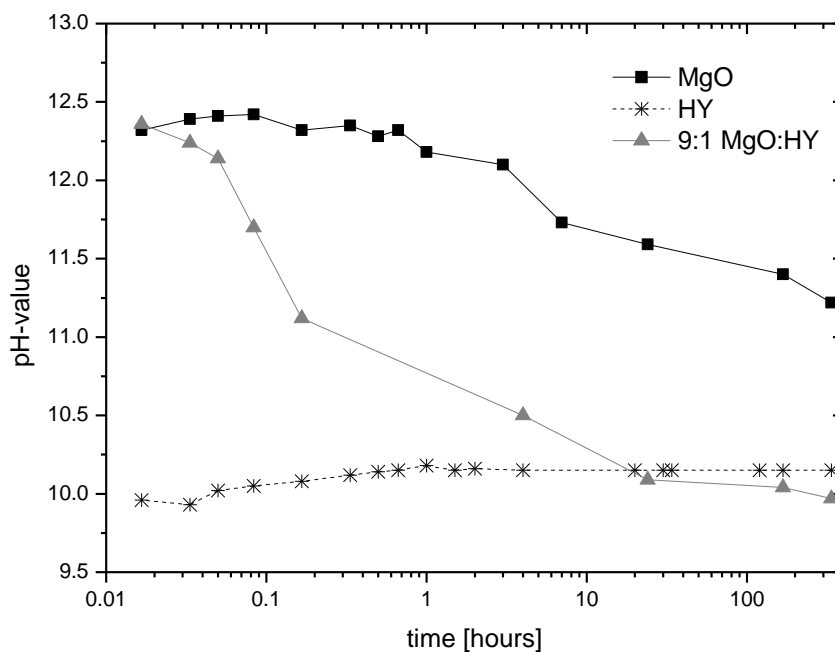
36 **Fig. 1.** Particle size distributions of the MgO and hydromagnesite (HY) used in this research.



37

38 **Fig. 2.** Isothermal conduction calorimetry data for the pure MgO and 9:1 MgO: HY pastes.

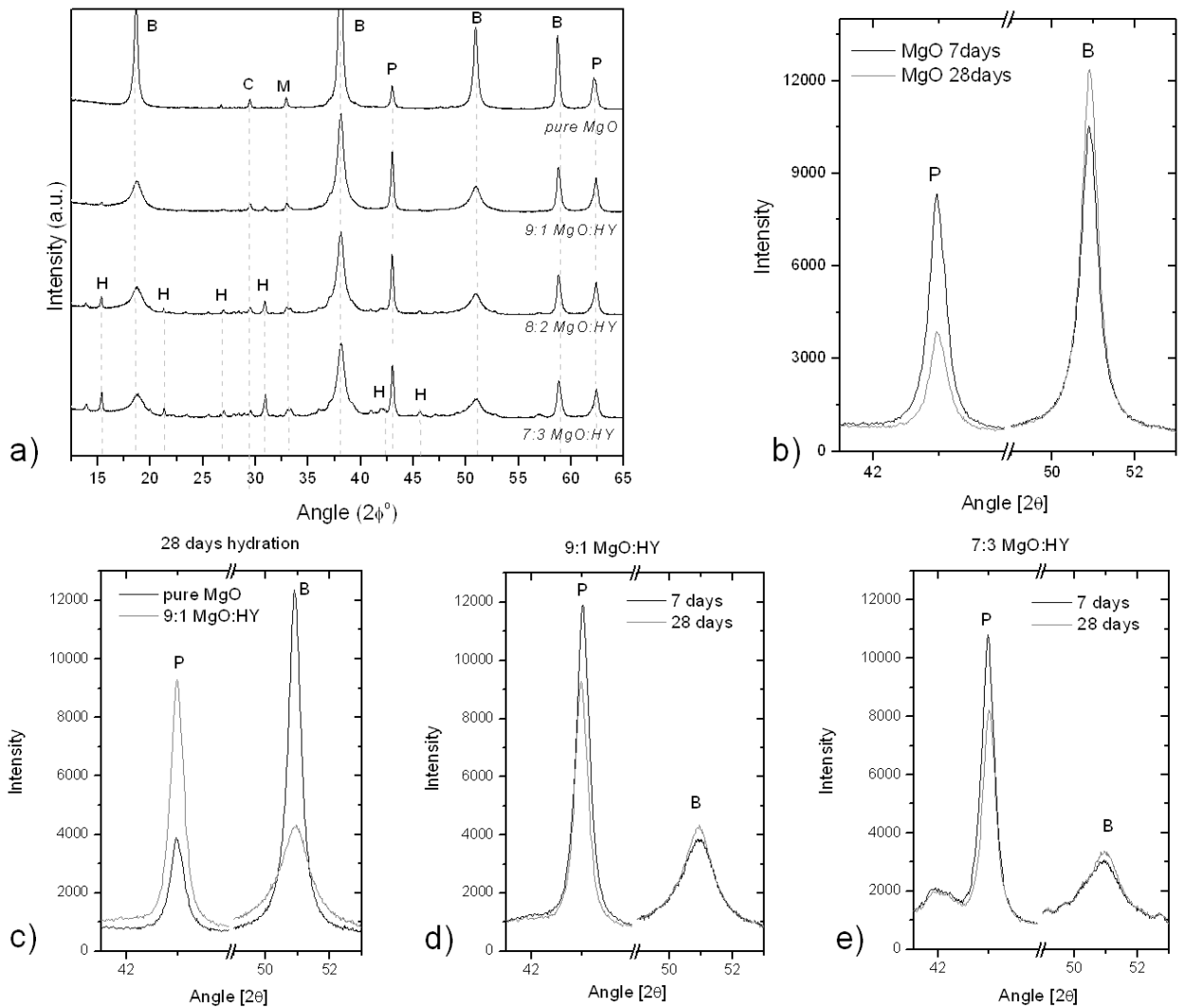
39 Heat output is per kg of total sample mass.



41

42 **Fig. 3.** Change in solution pH over time of w/s = 3 slurries containing 100% MgO, 100% HY
43 and 10% HY - 90% MgO mixes. Each point represents the average of two measurements.

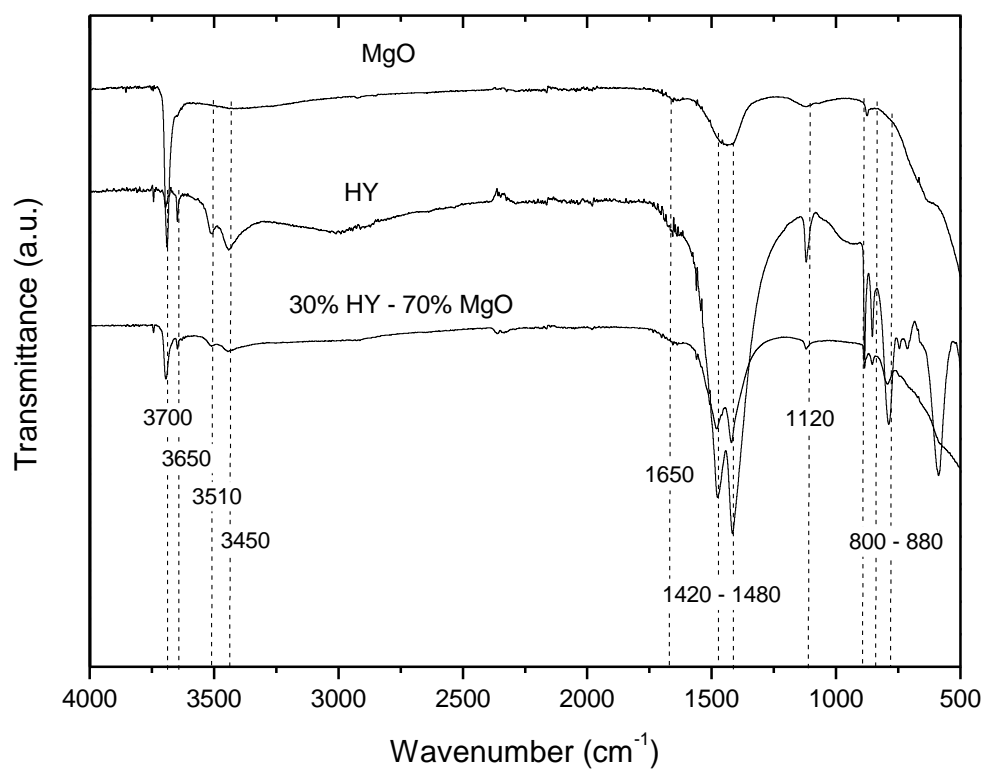
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46 **Fig. 4.** Powder XRD scans of hydrated MgO and MgO-HY pastes made at 0.62 initial w/s
 47 ratio. a) full scans of all four samples after 28 days curing; b) comparison of main periclase
 48 and brucite peaks for pure MgO pastes at 7 and 28 days; c) Comparison of the main periclase
 49 and brucite peaks for pure MgO and 9:1 MgO: HY mixture after 28 days; d) Comparison of
 50 the main periclase and brucite peaks for the 9:1 MgO: HY mixture after 7 and 28 days; e)
 51 Comparison of the main periclase and brucite peaks for the 7:3 MgO: HY mixture after 7 and
 52 28 days. Key: B = brucite $[\text{Mg}(\text{OH})_2]$, C = calcite $[\text{CaCO}_3]$, H = hydromagnesite
 53 $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$, M = magnesite $[\text{MgCO}_3]$ and P = periclase $[\text{MgO}]$.

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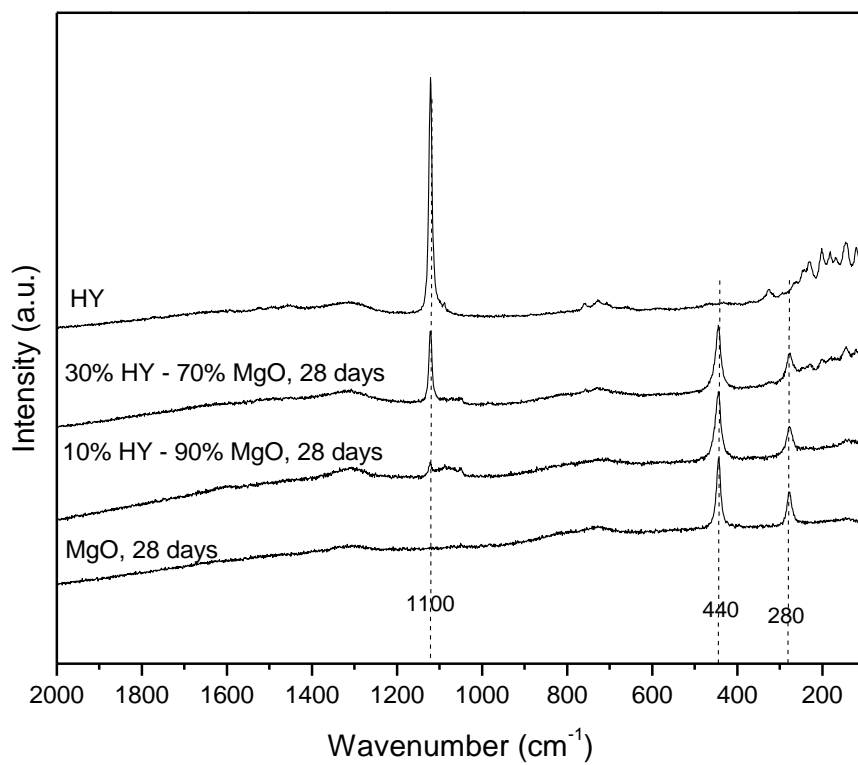


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57 **Fig. 5.** FTIR spectra of pure MgO and 3:7 HY: MgO paste hydrated for 28 days, and HY as
58 used. The peaks of interest are indicated with dotted lines and their wave number labelled.

59



60

61 **Fig. 6.** Raman spectra of the HY sample as used; plus the pastes of 3:7 and 9:1 HY: MgO
 62 blends, and pure MgO, hydrated for 28 days.

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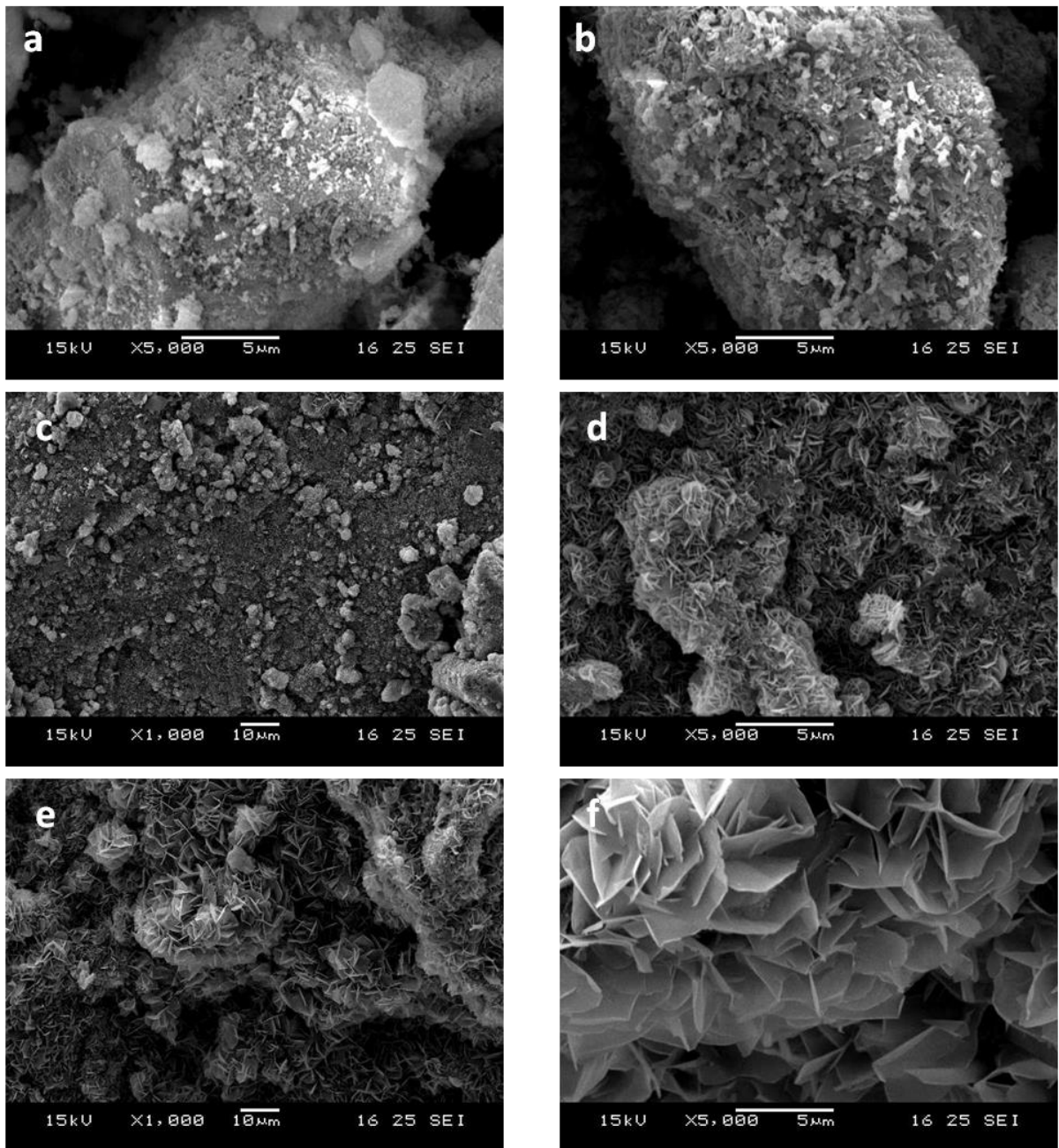
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79 **Fig. 7.** SEM images of a) **as-received** MgO; b) **as-received** HY sample; c and d) 9:1 MgO:
 80 HY pastes after 7 days hydration; e and f) 9:1 MgO: HY pastes after 28 days hydration.