

New Insights on the Prehydration of Cement and its Mitigation

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Abstract

Ordinary portland cement (OPC) prehydrates during storage or handling in moist environments, forming hydration products on or near its particles' surfaces. Prehydration is known to reduce OPC reactivity, but the extent of prehydration has not yet been quantitatively linked to reaction rate and mechanical property changes. A series of experiments and simulations are performed to develop a better understanding of prehydration, by intentionally exposing an OPC powder to either water vapor or liquid water, to investigate the extent to which premature contact of OPC with water and other potential reactants in the liquid and/or vapor state(s) can induce differing surface modifications on the OPC grains. Original results obtained using isothermal calorimetry, thermogravimetric analysis and strength measurements are correlated to a prehydration index, which is defined for the first time. The addition of fine limestone to a mixture formed using prehydrated cement is shown to mitigate the detrimental effects of prehydration.

Keywords: physisorption, prehydration, nucleation, limestone

1. Introduction and Background

Ordinary portland cement (OPC) reacts on contact with water in the liquid or the vapor states. Therefore, unintentional exposure to moisture or to other known reactants such as CO₂ during the storage and handling of the OPC powder can result in premature hydration^{xii} or aging of its constituent phases. Any such unintentional reaction of the cement reduces the thermodynamic

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^{xii} The term "hydration" is used in cement chemistry to generically indicate any and all net reactions of cementitious mineral phases with water, and we will use the term in this broad sense here despite the fact that the same term may have a more restricted meaning in other fields of chemistry.

28 driving force for its subsequent reactions with liquid water, and the resultant loss of reactivity
29 typically manifests as undesirable reductions in the rate of hardening and strength gain of
30 concrete [1,2]. In this paper, we will use the term “prehydration” generically to refer to all the
31 processes that cause unintentional loss of reactivity prior to the usual mixing of cement with
32 water. To be specific, this includes physical adsorption of water on the cement particle surfaces,
33 as well as the chemical reactions between water and the anhydrous OPC minerals to form solid
34 hydration products such as calcium silicate hydrate (C-S-H^{xiii}), Ca(OH)₂, gypsum, and ettringite.
35 In addition, CO₂ in air or dissolved in water can react with several cement components, forming
36 magnesite (MgCO₃) from periclase (MgO), and forming CaCO₃ from free lime (CaO) or Ca(OH)₂,
37 the latter being present primarily because of prior reaction with water [3,4,5,6]. All of these
38 changes initiate at the exposed surfaces of OPC grains but penetrate deeper into the grains
39 with prolonged exposure.

40
41 To better understand these aspects, Dubina and coworkers studied the effects of prehydration
42 on the constituent phases present in OPC and in commercial OPC formulations [7,8,9,10]. They
43 quantified the prehydration sensitivity of the different phases in OPC, especially due to water
44 vapor exposure by: (1) identifying the RH at which a given OPC phase may become susceptible
45 to water adsorption or phase transformations, and (2) characterizing the influence of both RH
46 and exposure time on reactions and property development. These studies showed that the
47 calcium silicates, calcium aluminates, and calcium sulfates in OPC all undergo interactions with
48 water vapor that influence the reaction response of the OPC to water during normal hydration.
49 In particular, prehydration was observed to upset the balance between the soluble aluminate
50 and sulfate minerals that is intentionally built into OPC to regulate the otherwise rapid reaction
51 of C₃A with water, likely by capillary condensation [7,8,9,11].

52
53 This work expands on previous studies by quantitatively correlating the changes in reactivity
54 and strength evolution in OPC pastes to the duration (and magnitude) of exposure to either
55 liquid water or water vapor. The addition of fine limestone powder to prehydrated cement is
56 observed to partially restore some reactivity. Simulations performed using a phase boundary
57 nucleation and growth (BNG) model and with a kinetic cellular automaton model (KCA) are
58 used to gain insight into the factors controlling OPC prehydration and into the mechanisms by
59 which fine limestone can offset the detrimental effects of prehydration.

60
61 **2. Materials and Experimental Methods**
62 An ASTM C150 compliant Type I/II ordinary portland cement (OPC) was used herein. X-ray
63 fluorescence (XRF) was used to estimate the major oxide composition of the OPC on a mass

^{xiii} C-S-H (ACaO•SiO₂•BH₂O): is a poorly crystalline calcium silicate hydrate, of variable composition. In the case of cement hydrated in sufficient liquid water, A and B take values of 1.7 and 4.0 respectively, such that the Ca/Si molar ratio = 1.7 [18].

64 basis: 20.57 % SiO₂, 5.19 % Al₂O₃, 3.44 % Fe₂O₃, 65.99 % CaO, 1.37 % MgO, 2.63 % SO₃, 0.17 %
 65 Na₂O, 0.31 % K₂O, 0.26 % TiO₂ and 0.08 % P₂O₅. Quantitative X-ray diffraction (QXRD), using
 66 Rietveld refinement, was used to estimate the mineralogical composition of the OPC, on a mass
 67 basis [12]: 56.5 % MIII-Ca₃SiO₅, 16.0 % β-Ca₂SiO₄, 6.3 % Ca₃Al₂O₆ (i.e., a mixture of the cubic and
 68 orthorhombic forms [18]), 11.4 % Ca₄Al₂Fe₂O₁₀, 1.1 % CaSO₄·2H₂O, 0.5 % CaSO₄·0.5H₂O, 1.2 %
 69 CaSO₄, 1.2% Ca(OH)₂, 0.5% CaO and 4.6 % CaCO₃. To fully examine the efficacy of fine limestone
 70 powder additions to prehydrated OPC on restoring reactivity, a commercially available,
 71 nominally pure limestone powder (> 98 % CaCO₃) was used.^{xiv,xv} The particle size distributions
 72 (PSDs) of OPC and limestone were measured by static light scattering (SLS) using isopropanol
 73 and ultrasonication for dispersing the powders to primary particles, and are shown in Fig. 1. The
 74 largest variation in the light scattering measurements is about 6 % based on measurements
 75 performed on six replicates and assuming the density of the OPC and limestone to be 3150
 76 kg/m³ and 2700 kg/m³, respectively. Assuming that the particles are spherical, the measured
 77 PSDs of OPC and limestone correspond to specific surface areas (SSAs) of 520 m²/kg and 1353
 78 m²/kg. Accounting for the irregular shape of OPC particles often results in SSA estimates that
 79 are higher by a factor of 1.6-to-1.8 [13].

80

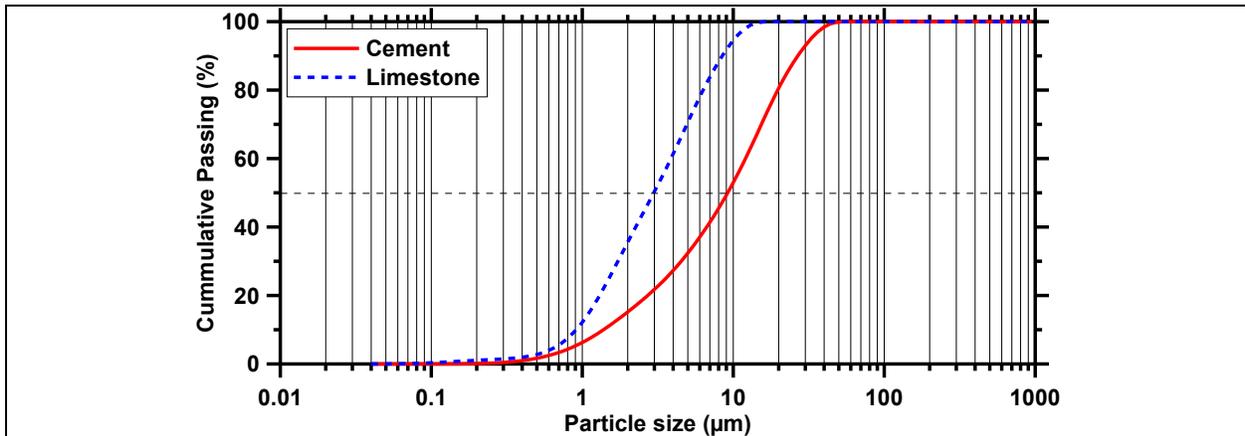


Figure 1: Particle size distributions for the OPC (as-received) and the limestone evaluated in this study. The largest variation in the light scattering measurements is around ±6 %.

81

82 Prehydration of the as-received OPC was simulated by exposing it to either liquid water or
 83 humid air. For water vapor exposure, the OPC powder was placed for either one month or three
 84 months in a room maintained at 55 % ± 10 % RH and 25 °C ± 3 °C, during which time the
 85 powders were mixed on a weekly basis to encourage uniform exposure to water vapor. These
 86 specific conditions were chosen to understand the impacts of prehydration in locations such as
 87 Southern California (Los Angeles), when the ambient RH is low and temperatures are modest.

^{xiv} OMYA A.G., Cincinnati, OH.

^{xv} Certain commercial materials and equipment are identified to adequately specify experimental procedures. In no case does such identification imply recommendation or endorsement by the University of California, Los Angeles, the National Institute of Standards and Technology, or Arizona State University, nor does it imply that the items identified are necessarily the best available for the purpose.

88

89 For exposure to (deionized, DI) liquid water, several hundred grams of the OPC powder were
90 spread in a thin layer and then misted in two equal cycles, separated by 30 minutes, with a
91 uniform mass of water corresponding to a moisture dosage of 2.5 % (Sprayed-1) or 5.0 %
92 (Sprayed-2) by mass of powder. The OPC powder was homogenized in a planetary mixer after
93 each cycle. After the second mixing, the powders were sealed in airtight containers to limit
94 drying and maintained in an environmental chamber at 25 °C. After one week, the OPC
95 powders were homogenized once again and placed in airtight containers for another week to
96 ensure consistent prehydration.

97

98 Paste mixtures of either the as-received or prehydrated OPC powder were prepared with a
99 (deionized) water-to-solids mass ratio of $w/s = 0.45$ as described in ASTM C 305 [14]. To explore
100 the influences of limestone on the reaction response of systems prehydrated with water vapor,
101 small amounts of the as-received limestone powder were introduced either by adding to the
102 cement powder (increasing the total solid mass) or by partially replacing the cement powder at
103 constant total solid mass. By either means, the limestone dosages were 2.5 %, 5 % or 10 % by
104 mass of OPC. When the limestone was dosed by addition, the amount of water in the mixture
105 was 0.45 g H₂O per gram of OPC. In contrast, when limestone was dosed by partial replacement
106 of OPC, the mixture had a constant water content of 0.45 g H₂O per gram of total solids.

107

108 **2.1. Characterizing the extent of cement prehydration**

109 As already described, the term “prehydration” is used to capture a range of premature reaction
110 phenomena that result from exposure not only to water (i.e., liquid or vapor) but also to other
111 reactants that OPC is likely to encounter during storage. The primary substance, besides water,
112 that can react with cementitious minerals is CO₂, which is present in air and in liquid water at
113 typical concentrations of about 390 ppm and 50 ppm, respectively. Therefore, our attempt to
114 quantify prehydration, as defined here, must be careful to account for the effects both of water
115 and of CO₂, especially because no special efforts were made to exclude CO₂ either from the air
116 or from the liquid water used in the prehydration step. Most OPCs contain some CaCO₃ which is
117 added intentionally (to reduce the cement clinker content), but which is difficult to distinguish
118 from CaCO₃ that forms by the direct carbonation of the free lime (CaO) present in the OPC, or
119 by the carbonation of Ca(OH)₂ formed by the hydration of CaO, or from reactions of the silicate
120 phases with liquid water during storage and/or handling. Separating these different potential
121 sources of CaCO₃ is especially difficult because OPC often begins prehydrating (or carbonating)
122 immediately after it is manufactured, long before it is acquired for analysis or use. Therefore, it
123 is reasonable to only characterize prehydration of a cement powder relative to its as-received
124 state, that is, as the *incremental prehydration* that is induced by the liquid or vapor treatments
125 described in the previous section.

126
127 With these considerations in mind, the most direct way to characterize prehydration is to
128 record the quantities of physisorbed water by desorption experiments and to measure the
129 changes in the amounts of solid hydrates and carbonates before and after a given prehydration
130 step using quantitative X-ray diffraction [7,8,9,11]. However, the total volume of each of the
131 solid hydrates and carbonates formed by prehydration is small, often below the detection limit,
132 $\approx 1\%$ by mass, of lab-scale X-ray diffraction (XRD) analyses. Further, numerous OPC hydrates are
133 poorly ordered and thus difficult to quantify accurately by XRD. Because of these difficulties, we
134 choose to apply thermogravimetry to characterize prehydration by measuring the mass loss
135 upon heating to 975 °C, a temperature above which no additional mass loss is observed even by
136 fully hydrated OPC. The mass lost by an anhydrous OPC when heated from room temperature
137 to 975 °C in N₂ comes from several sources. Between room temperature and ≈ 110 °C, liquid
138 water condensed in the porosity evaporates, and the calcium alumino/sulfate hydrate phases
139 begin to dehydrate. The continued dehydration of the calcium alumino/sulfate phases, together
140 with volatilization of the grinding aids added during OPC manufacture and decomposition of
141 minor hydrated phases such as syngenite, continues between 110 °C and 400 °C. In the next
142 step, the decomposition of calcium hydroxide, magnesium carbonate, and calcium alumino-
143 sulfate-hydrates occurs between 425 °C and 550 °C. Above 550 °C, the main contributions to
144 the mass loss are decomposition of calcium carbonate and the final dehydration of the calcium
145 silicate hydrate (C-S-H) phases.

146
147 The mass loss of the as-received OPC powder from 35 °C to 975 °C provides a baseline, from
148 which the incremental prehydration of that powder can be *defined* as the additional mass loss
149 in the same temperature range of that powder at a later time. Therefore, if we normalize the
150 powder masses by the mass of the ignited OPC, we can define the dimensionless *incremental*
151 *prehydration index* (PI, %) as:

$$PI = \left[\left(\frac{\Delta m}{m_i} \right) - \left(\frac{\Delta m}{m_i} \right)_0 \right] \times 100 \quad (1)$$

153
154 where Δm is the mass loss between 35 °C and 975 °C, m_i is the ignited mass—taken here to be
155 the mass after heating to 975 °C—and the subscript “0” refers to the baseline measurement
156 made on the as-received powder. As defined, this prehydration index accounts for all additional
157 aging of the as-received powder, whether due to (pre)hydration or carbonation.

158
159 The prehydration index could have been defined in alternative ways that attempt to neglect the
160 contribution of carbonation by omitting the portion of the mass loss that is associated with the
161 decomposition of CaCO₃. However, we choose to include all mass loss in our definition because

162 carbonation can be both a direct effect of aging and a secondary effect of reaction with water.
163 It should be noted that CaCO₃ formed very early during carbonation, as may be the case during
164 prehydration, may start to decompose at lower temperatures (<600 °C) compared to bulk CaCO₃
165 [15]. As such, adjustments were made in determinations of CaCO₃ decarbonation (i.e., via the
166 DTG patterns) to incorporate mass losses occurring at both lower (< 600 °C) and typical values of
167 CaCO₃ decarbonation temperatures.

168
169 A simultaneous thermal analyzer^{xvi} was used to measure the thermogravimetric (TG) and the
170 differential thermogravimetric (DTG) signals of the cementitious samples, as raw powders, and
171 after 1 d, 3 d, 7 d, and 28 d of hydration in liquid water. The temperature and mass sensitivity
172 of the analyzer were 0.25 °C and 0.1 µg, respectively. Hydration was arrested at desired times
173 by crushing the paste mass to granules (i.e., < 5 mm diameter) and then submerging them in
174 isopropanol (IPA) for 6 d, with IPA being replaced every 2 d [16]. Following solvent exchange,
175 which was applied only to OPC samples hydrated in sufficient water, i.e., not the prehydrated
176 OPC powders, the cementitious samples were placed under vacuum in a desiccator for 3 d and
177 then crushed to a very fine powder. The powders were all heated under a (99.999 % purity) N₂
178 purge at a flow rate of 20 mL/min and a heating rate of 10 °C/min in pure aluminum oxide
179 crucibles from 35 °C to 975 °C.

180
181 The TG data were used to calculate the prehydration index (PI), and to approximate both the
182 evaporable and non-evaporable water contents, the amount of Ca(OH)₂ and CaCO₃ present in
183 the system—inferred from the mass loss between 425 °C and 550 °C and between about 550 °C
184 and 800 °C, respectively. The degree of OPC reaction, α , for normal hydration in sufficient liquid
185 water can then be estimated by assuming that the mass of non-evaporable water, $m_n(t)$ varies
186 linearly from zero to a terminal value of $m_{n,\infty}$ at complete reaction,

$$\alpha = \frac{m_n(t)}{m_{n,\infty}} \quad (2)$$

187
188
189 While the non-evaporable water mass can be estimated from TG data, volatilization of CO₂ also
190 contributes to the mass loss and therefore can make the non-evaporable water mass difficult to
191 isolate. However, errors made in incorrectly assigning different portions of the TG data to non-
192 evaporable water will largely cancel in Eq. (2) if the same procedure is used to calculate both
193 $m_n(t)$ and $m_{n,\infty}$. Therefore, we arbitrarily choose a formulation that also has been applied in
194 some previous studies [17,18]:

$$m_n(t) = m(t, 145) - m(t, 975) - [m(t, \approx 550) - m(t, 800)] \quad (3)$$

^{xvi} STA 6000, Perkin Elmer, Waltham, MA.

196
197 where $m(t, 145)$, for example, is the mass of a specimen after t days of reaction when heated
198 to 145 °C, and is the mass after loss of evaporable water [17,18]. The term in square brackets in
199 Eq. (3) is intended to account for the mass loss due to CaCO_3 decomposition; in this study we
200 use the DTG signal to determine the onset temperature accurately for each paste specimen.
201 The terminal value of the non-evaporable water mass at complete reaction can be determined
202 experimentally by a long-term bottle hydration experiment to ensure complete reaction. We
203 estimate this for this specific OPC, based on its mineral composition and using a procedure
204 described previously [18], that $m_{n,\infty} \approx 0.23$ g per gram of ignited, as-received OPC.

205
206 **2.2. Characterizing mixture reactivity and its impacts on mechanical properties**
207 An isothermal calorimeter^{xvii} was used to measure the heat evolved during normal hydration of
208 as-received and prehydrated OPC pastes at constant temperature (25 °C ± 0.1 °C). The thermal
209 power and the energy measured were used to assess the influence of prehydration and of
210 limestone dosage on reaction kinetics and total heat release of the cementitious samples.

211
212 The progress of reactions, and their impacts on mixture properties were characterized by
213 measuring the compressive strength of OPC paste specimens (50 mm cubes) cured at 25 °C ± 1
214 °C for 1 d, 3d, 7 d, and 28 d, as described in ASTM C109 [14]. Each strength measurement was
215 repeated on three replicates to obtain an average value at each time (i.e., age), with a highest
216 variation of 7 % being noted for samples formed from the same mixing batch.

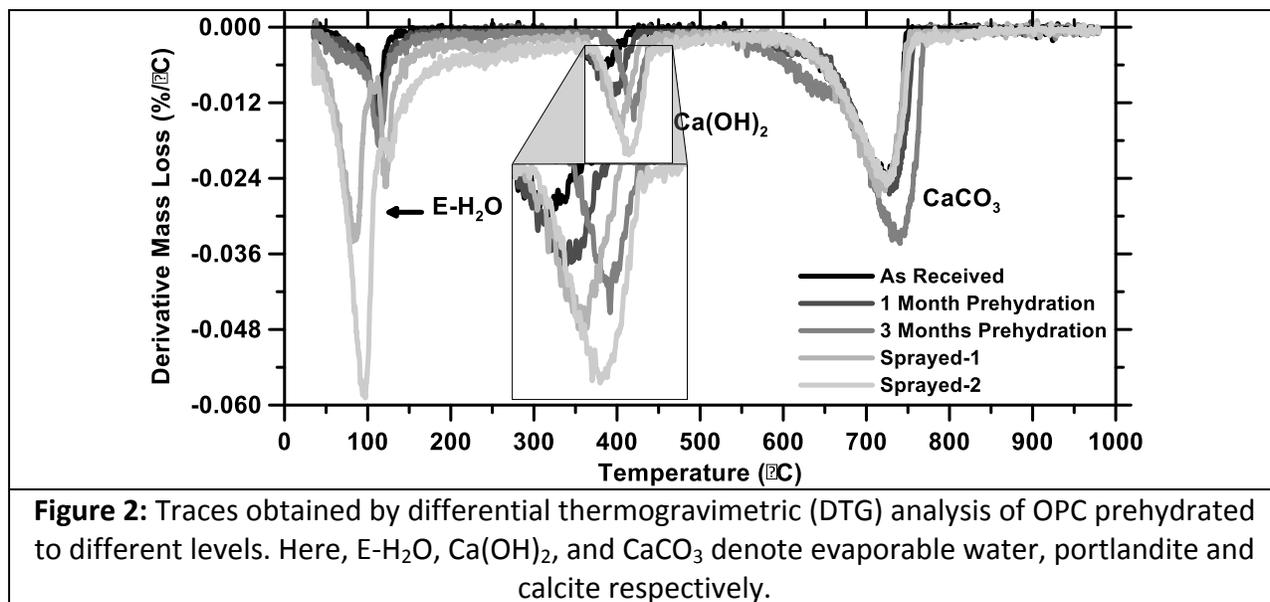
217
218 **3. Results and Discussion**

219
220 **3.1. Plain OPC pastes**
221 The loss on ignition (LoI) upon heating the as-received OPC powder to 975 °C was 2.99 %, using
222 the unignited powder as the reference. Based on the DTG data shown in Fig. 2, if we assume
223 that all the mass loss in the range 600 °C-to-800 °C is CO_2 gas released by CaCO_3 decomposition,
224 then the LoI can be partitioned with ≈ 2.04 % due to CO_2 from CaCO_3 and 0.95 % due to other
225 sources. This indicates an intrinsic CaCO_3 content of ≈ 4.64 % (by mass) in the as-received OPC.

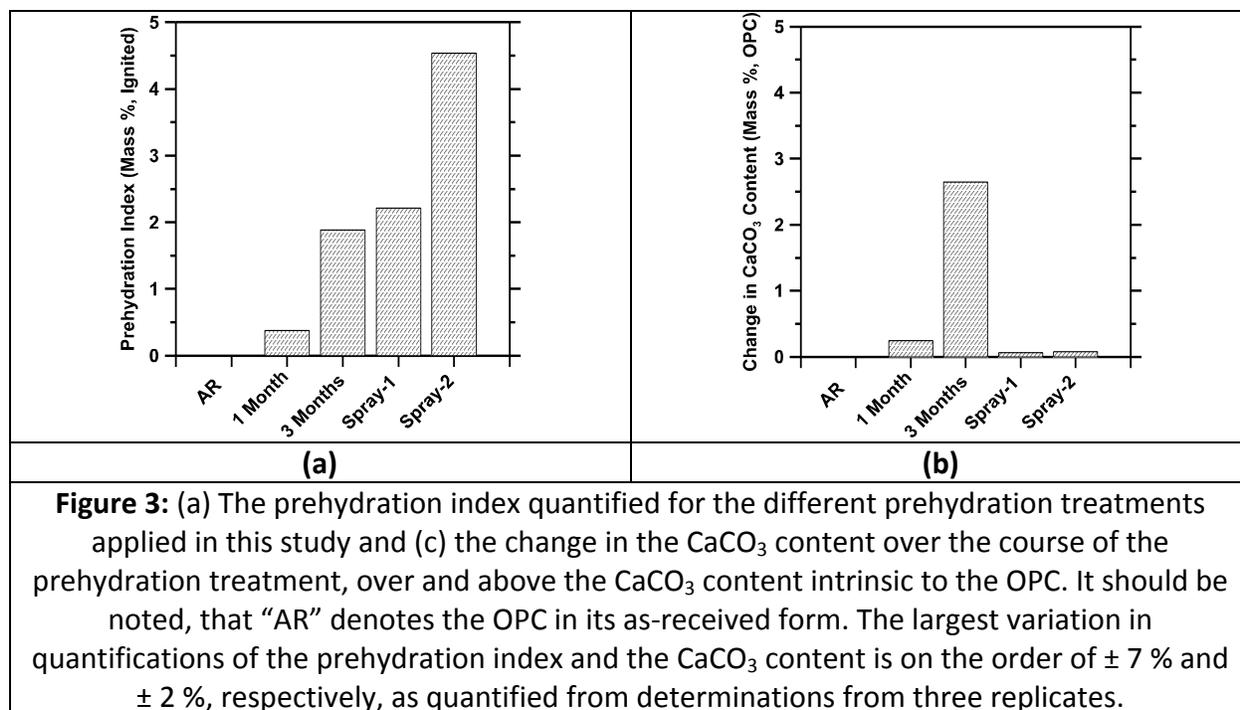
226
227 Fig. 2 shows DTG measurements for the as-received cement and for the cement prehydrated
228 due to water vapor or liquid water exposure. Even the as-received OPC has some evaporable
229 water and $\text{Ca}(\text{OH})_2$, mainly due to hydration of CaO , which reacts even at very low RHs (relative
230 humidities). Therefore, this OPC has experienced some prehydration prior to being used in this
231 study, as is common among many OPCs. Increasing water dosages (i.e., 55 % RH or by spraying)
232 increase the prehydration index, as shown in Fig. 2. A similar effect is noted with increasing

^{xvii} TamAir, TA Instruments, Newcastle, DE.

233 times of exposure, from one month to three months, at 55 % RH. Unsurprisingly, the extent of
234 CaCO_3 detected increases with the exposure time.
235



236
237 The increases in the CaCO_3 content are caused by the carbonation of CaO or Ca(OH)_2 present in
238 the OPC, or formed over the course of the prehydration treatment [8]. The DTG data in Figs. 2-3
239 indicates that incremental carbonation leads to $\leq 0.25\%$ increase in the CaCO_3 content of the
240 OPC for all prehydration treatments except for the 3-month exposure to water vapor. The 3-
241 month exposure, however, caused an increase in the CaCO_3 content of $\approx 2.65\%$ by initial mass
242 of OPC powder. These increases in the CaCO_3 content correspond to contributions to the PI of
243 $\approx 1.2\%$ for the 3-month exposure but only around $\approx 0.1\%$ for all other prehydration treatments.
244 Carbonation of Ca(OH)_2 is known to occur more slowly in water, with about 50 ppm CO_2 , than in
245 humid air with about 390 ppm CO_2 [19]. Therefore, the enhanced CaCO_3 content in the OPC
246 sample exposed to moist air for 3 months is likely due to both the duration and the type of
247 exposure [20,21,22]. Therefore, the effects of OPC prehydration can be primarily ascribed to
248 moisture exposure at shorter times, with the relative contribution of CO_2 exposure increasing
249 with: (i) increasing duration, (ii) the (increasing) concentration of CO_2 , or (iii) under ambient
250 conditions which favor direct carbonation processes [20,21,22].



251
 252 Fig. 2 shows that all prehydration treatments lead to increases in the mass loss between 350 °C
 253 and 450 °C, which we attribute to increases in Ca(OH)₂. The increase in Ca(OH)₂ is far greater for
 254 systems prehydrated with liquid water than water vapor. Such elevated Ca(OH)₂ contents are
 255 produced by the reactions of the silicate phases, principally alite (Ca₃SiO₅) and to a lesser extent
 256 belite (Ca₂SiO₄), and by the hydration of CaO. Judging from the CaO content measured by QXRD
 257 in the anhydrous OPC, Ca(OH)₂ formation in the vapor prehydrated systems is broadly due to
 258 CaO hydration, which suggests that for 55% RH exposure, very slight silicate phase *prehydration*
 259 (but not surface reconstruction, see below) occurs. This is in support of RH thresholds defined
 260 by Dubina [8]. Furthermore, the sprayed systems also contain more water in the evaporable
 261 range (i.e., ≤ 145 °C [17,18]) than do the water vapor hydrated systems. These differences are
 262 related to differences in the prehydration route, for example by the adsorption of water vapor
 263 and induced surface modifications or by means of dissolution-precipitation reactions mediated
 264 through liquid water.

265
 266 It should be noted that the vapor-phase RH used in this study is lower than the threshold noted
 267 by Dubina et al. [8], especially for alite and belite. This may suggest negligible reaction, between
 268 water vapor, and the silicate phases, in the vapor prehydration case. In the absence of reaction,
 269 however, water can still sorb on silicate surfaces and induce surface relaxation/reconstruction,
 270 although no attempt is made to distinguish such surface phenomena from the generic term
 271 “prehydration”. Such physisorption could lead to the formation of C-S-H, though likely not of
 272 the form that is observed during hydration with liquid water. Such C-S-H formation, or surface

273 reconstruction could dramatically alter the reactivity of the silicate phases, and OPC in liquid
 274 water. Evidence for such an effect is provided by Dubina et al. who note that C_3S hydration is
 275 retarded, by enhancing the exposure duration of C_3S ; even for a *subcritical RH* (for C_3S) of 60%
 276 [23]. The DTG traces show that quantities of evaporable water, and $Ca(OH)_2$ present, increase
 277 with exposure time (see Figure 2) – in spite of the latter having a higher potential to carbonate,
 278 and form $CaCO_3$. This indicates such surface-specific phenomena (e.g., surface reconstruction of
 279 the silicate phases) and that, in addition to the C_3A , the C_3S and C_2S may also undergo some
 280 prehydration type process. It should be noted that the variability in imposed environmental
 281 conditions ($55 \pm 10\%$ RH) leaves open the possibility that at times the RH was high enough for
 282 water vapor to condense onto the surface of cement particles (i.e., in proximity to each other
 283 where a captive meniscus could form between the necks of particles) causing prehydration of
 284 both the silicate, and aluminate phases.
 285

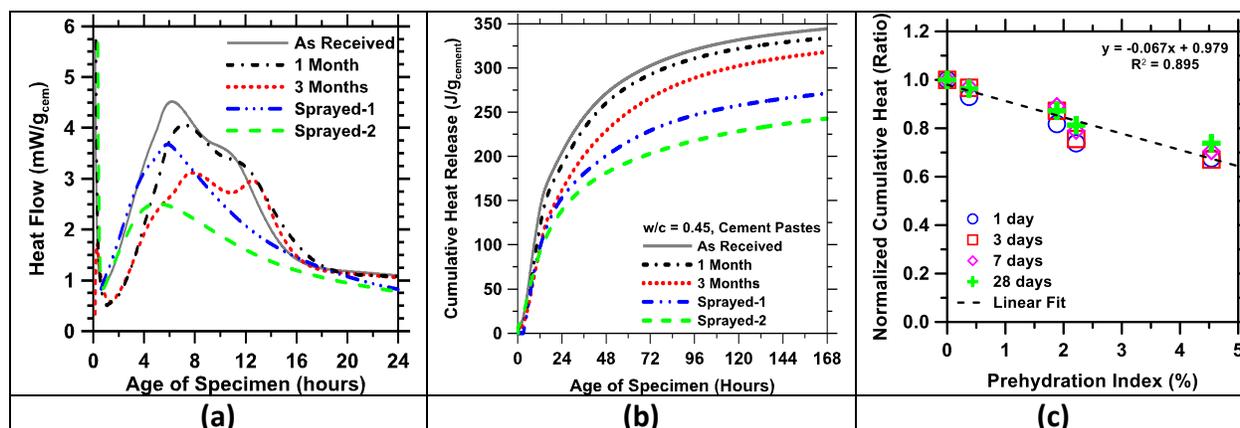


Figure 4: The influence of prehydration on the rates of reactions as measured using isothermal calorimetry for: (a) heat flow and (b) cumulative heat release and (c) cumulative heat released at 1 d, 3 d, 7 d, and 28 d for all cement paste mixtures normalized by the heat released by the as-received paste mixture. The largest variation in the measured heat flow of any mixture is $\pm 2\%$ based on the heat flow measured on six replicate paste specimens.

286
 287 Fig. 4(a) shows the effects of prehydration on the rates of OPC reaction during subsequent
 288 hydration in sufficient liquid water as measured using isothermal calorimetry. This figure
 289 confirms that prehydration reduces the intensity of reactions. In particular, the extents of OPC
 290 reaction decrease with increasing (water) exposure time and water availability: as-received > 1
 291 month > 3 months > Sprayed-1 > Sprayed-2. Interestingly, the two different methods of water
 292 delivery have qualitatively very different effects on the reaction curve. Prehydration by water
 293 vapor causes a fixed delay in the onset of the main silicate reaction peak by about two hours,
 294 regardless of the exposure time, and reduces the height of the main silicate reaction peak
 295 relative to the secondary aluminate reaction peak that occurs at a later time. In contrast,
 296 prehydration by sprayed liquid water causes no delay in, or even very slightly accelerates the

297 onset of the main silicate peak and also diminishes the relative strength of the subsequent
298 aluminate peak. The differences produced in the aluminate reaction peak allude to alteration of
299 the aluminate phases to form aluminate hydrates (e.g., AFt, AFm, C_xAH_y) following prehydration
300 – a response also noted via DTG patterns which show significant mass loss at temperatures
301 lower than 145°C [24]. As shown in Figs. 4(b) and 4(c), the prehydrated systems are unable to
302 reach the same extent of reaction as the as-received system. Furthermore, Fig. 4(c) indicates
303 that the severity of the depression in the total amount of OPC reactions, as measured by
304 cumulative heat released, is a linear function of the incremental PI, across all ages, independent
305 of the prehydration exposure type or duration (see also Figure 7a).

306
307 One might suppose that this decrease in heat evolution is similar to the heat released over the
308 course of prehydration. However, in the absence of direct heat evolution measurements during
309 the prehydration exposure, the validity of that supposition cannot be evaluated without making
310 an assumption about how heat release is related to degree of reaction, α , during prehydration.
311 For normal hydration in liquid water, the non-evaporable water at complete reaction, $m_{n,\infty}$, is
312 known to be about 0.23 g per gram of OPC reacted [17,18]. Therefore, $m_{n,\infty}$ is a linear function
313 of α with a slope of 0.23 (Eq. 2). However, the reaction products formed during prehydration
314 may have different non-evaporable water contents because the water activity is far different
315 than during normal hydration. Furthermore, it is expected that during prehydration, C_3A and
316 C_3S phases would be affected differently (e.g., [8]), and as such the linear relationship between
317 non-evaporable water and degree of hydration would either not be valid or would have a slope
318 different from 0.23. Even if it were to be assumed that a linear relationship between $m_{n,\infty}$ and
319 α still prevails during prehydration, our uncertainty about its slope make it difficult to infer the
320 degree of reaction during prehydration from TGA data. If it is to be assumed, $m_{n,\infty} = 0.23 \text{ g/g}_{\text{OPC}}$
321 for hydrates formed during prehydration, the calculated heat release, Q , during prehydration
322 would be $\alpha \cdot \Delta H$, where ΔH is the enthalpy of complete OPC hydration; $\Delta H \approx 458 \text{ J/g}$ for this OPC.
323 Equating all the heat reduction observed at 168 h of hydration in Fig. 4(b) to the heat released
324 during prehydration would therefore require a high degree of reaction, ≈ 0.21 , for the Sprayed-2
325 case; which is unlikely over the course of prehydration.

326
327 It seems unusual that systems prehydrated by liquid water are less retarded during hydration at
328 early times than systems prehydrated by water vapor at similar or greater values of the PI. This
329 indicates that the nature of the products of prehydration are important, rather than just the
330 absolute level of prehydration. For example, at 55% RH, prehydration is expected to result in
331 some reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ to form a calcium aluminohydrate [18], some reaction of CaO to form
332 Ca(OH)_2 , and the partial hydration of CaSO_4 to form bassanite and/or gypsum [11]. Under the
333 same conditions, the silicate reactions are likely limited to a hydroxylation or similar change in a
334 thin surface layer [26]. Such formations of surface layers on the silicate phases, however, have

335 been previously hypothesized to reduce dissolution rates of these minerals [25], and may even
336 be capable of altering their apparent solubility [26]. On the other hand, prehydration in liquid
337 water likely results in the formation of C-S-H nuclei on silicate surfaces [26], in addition to the
338 aluminate and sulfate reactions.

339
340 Therefore, the differences observed between prehydration in liquid water and water vapor are
341 likely related to the degree and type of reactions at silicate surfaces. C-S-H exhibits enhanced
342 growth rates in the presence of silicate hydrate seeds that offer preferred nucleation sites and
343 thus accelerate reactions in Ca_3SiO_5 systems [27,28,29,30]. A similar mechanism *may operate* in
344 the liquid-phase prehydrated systems, wherein silicate surface reactions result in the formation
345 of a type of C-S-H that provides sites for preferential nucleation of *typical C-S-H* during normal
346 hydration. This would also explain why liquid-phase prehydrated systems reach their maximum
347 hydration rate at times that are similar to those of the as-received OPC, despite having a higher
348 prehydration index than systems exposed to water vapor. However, the degree of reaction at
349 later times is lowest in systems prehydrated with liquid water, which is contrary to a seeding
350 effect [27,29]. The lower extent of reaction at later times may be related to the enhanced initial
351 surface coverage of OPC grains by C-S-H, which can have the following effects:

- 352 • Reduce the exposed surface area of the anhydrous phases available for dissolution, and,
- 353 • Then cause an earlier transition to a diffusion-controlled mechanism when a continuous C-
354 S-H layer on the OPC grains has grown thick enough to limit the transport of dissolved ions
355 to-and-from the bulk solution.

356 In contrast, silicate phase surface modifications caused by OPC prehydration in water vapor are
357 gradually etched away upon normal hydration in liquid water, because their hydration rates
358 approach that of the as-received system after about 12 h (see Fig. 4a). The plausibility of these
359 hypotheses of silicate surface modifications is examined in more detail in Section 4.

360

361 **3.2. Influence of fine limestone**

362 Recently, additions of fine limestone have been demonstrated as a novel means of enhancing
363 and/or controlling OPC reaction rates [31,32,36]. In light of these observations and especially
364 that limestone is amongst the best *catalysts* for OPC hydration, several mixtures were prepared
365 with different dosages of limestone, as described in Section 2, to determine if it can mitigate
366 the effects of prehydration^{xviii}. Fig. 5 shows that fine limestone can indeed partially or even fully
367 offset prehydration effects, and that its efficacy increases with limestone dosage. Therefore,
368 while complete restoration of normal hydration is easily achieved at low levels of prehydration
369 (*e.g.*, at one month), only partial mitigation is possible when prehydration is more severe (*e.g.*,
370 after three months). This is because the extent to which limestone restores normal hydration,

^{xviii} External dosage of fine limestone should be distinguished from limestone formation (carbonation) during prehydration. The “external” limestone provides additional surface area for reactions and hastens them [21,36]. On the other hand, carbonation during prehydration likely results in the formation of a mass transport barrier which would impede the dissolution of the cement grains.

371 falls short of the retardation caused by aggressive prehydration. As vapor phase prehydration
 372 causes relatively minor retardation effects, the provision of limestone is able to successfully
 373 restore normal hydration. For the dosages considered herein, both limestone replacement and
 374 addition are similarly effective. Limestone's ability to restore the hydraulic reactivity of OPC is
 375 linked to at least three effects. First, the large surface area provided by fine limestone catalyzes
 376 the silicate hydration reactions by providing increased surface area and a lower energy barrier
 377 for nucleation of hydration products; i.e., by serving as a heterogeneous catalyst.

378

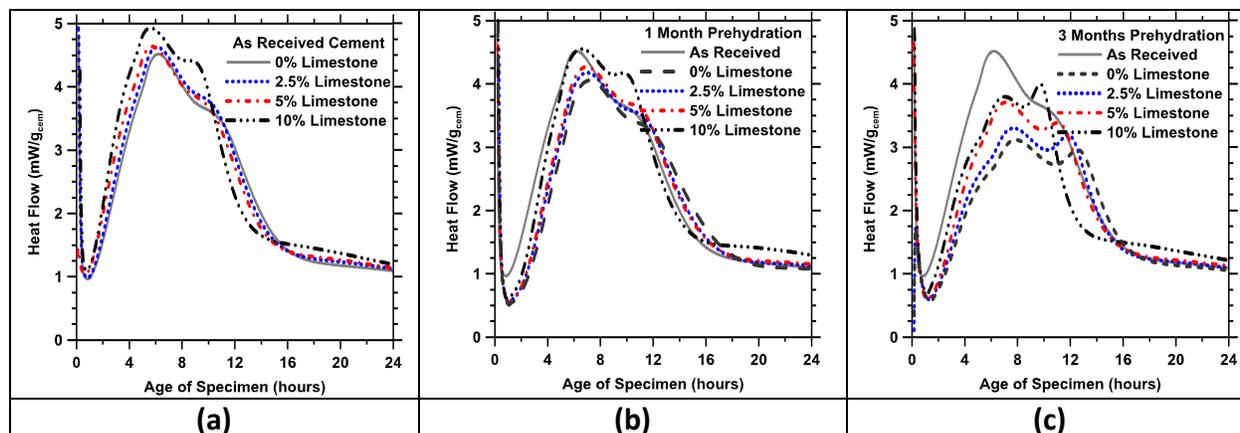


Figure 5: Representative graphs showing the influence of limestone on mitigating the influences of vapor-phase prehydration for: (a) as received cement, (b) 1 month of vapor phase prehydration (c) 3 months of vapor phase prehydration. In each case, limestone dosages are noted as percent replacement by mass of OPC. The effects are noted to be similar even when limestone is dosed by addition. The term “as received” in (b) and (c) refers to an OPC that has not been exposed to any (intentional) prehydration action and contains no limestone. The largest variation in the measured heat flow of any mixture is $\pm 2\%$ based on the heat flow measured on six replicate paste specimens.

379

380 Second, the dissolution of CaCO_3 in water provides carbonate anions to the solution, some of
 381 which could be incorporated within the C-S-H through an ion-exchange reaction that releases
 382 OH^- ions from the C-S-H to preserve charge neutrality. We have no direct evidence to support
 383 this assumption about carbonate uptake by C-S-H, but an analogous ion exchange reaction for
 384 sulfate uptake by C-S-H explains the observed increase of pH in Ca_3SiO_5 systems when soluble
 385 calcium sulfate is available during OPC hydration [33,34]. When limited CO_3^{2-} incorporation is
 386 allowed by this kind of reaction, the accelerating effect of limestone is virtually unchanged at
 387 the beginning because it still offers the same preferential nucleation sites for C-S-H. However,
 388 progressively more ion exchange occurs as more C-S-H is formed by ongoing hydration. This is
 389 significant because OH^- released by ion-exchange increases the driving force for C-S-H growth
 390 [35,36] relative to the driving force without CO_3^{2-} ion-sorption. The result is a higher degree of
 391 reaction at later times [36]. Finally, the availability of CO_3^{2-} stabilizes a carboaluminate phase

392 (CO₃-AFm) at the expense of the sulfoaluminate hydrate that would form otherwise [37,38]. Of
 393 course, the CaCO₃ formed during prehydration could trigger either of the last two effects, but
 394 that source is quite small for all prehydration treatments other than the 3-month duration.

395
 396 The trends in the reaction rates are more clearly revealed in Fig. 6 by plotting the parameters
 397 extracted from the calorimetric measurements as a function of the prehydration index, such as
 398 the slope during the acceleration period (Fig. 6a), the heat flow value at main heat peak (Fig.
 399 6b), and the inverse of the time of the main heat peak (Fig. 6c). These calorimetric parameters
 400 all decrease with increasing prehydration, but the rate of decrease in the OPC's reactivity with
 401 prehydration is less severe for liquid exposure (PI ≥ 2 %) than water vapor exposure (PI ≤ 2%).
 402 This indicates that the effects of liquid, and vapor phase prehydration are very distinct. It is also
 403 noted that limestone is able to effectively mitigate the effects of prehydration, by enhancing
 404 the calorimetric parameters; increasing values of which indicate higher reaction rates. It should
 405 be noted, however, that while, in limestone is able to mitigate the effects of prehydration even
 406 at higher levels of prehydration - at low levels of prehydration, it is far easier to recreate the
 407 reaction rate of a pristine OPC (i.e., eliminate the effects of prehydration) by simply adding or
 408 replacing limestone to the OPC; an effect which cannot be achieved at higher prehydration
 409 levels. This highlights the ability of *externally provisioned* limestone to offset any prehydration
 410 effects, with increasing success at lower PI.

411

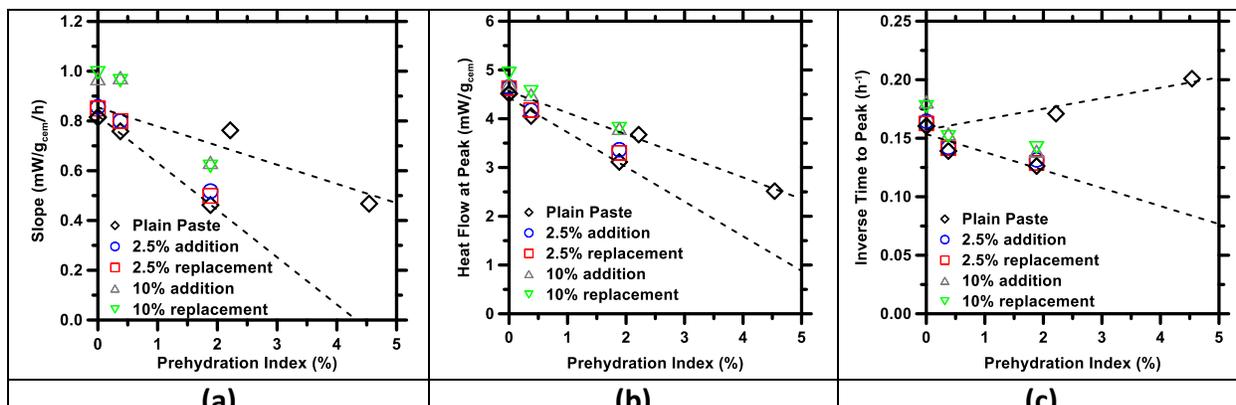


Figure 6: Calorimetric parameters and best fits (dotted lines) as a function of the prehydration index for: (a) slope during the acceleration period, (b) heat flow value at the main heat peak and (c) inverse time required to achieve the main heat peak. The lower and upper dashed lines show linear fits to the data points associated with the plain OPC pastes (i.e., not including any limestone) prehydrated with water vapor or liquid, respectively.

412
 413 Confirming the mechanisms hypothesized in these two sections, regarding both the influence of
 414 duration and type of water exposure and the influence of fine limestone in restoring hydration
 415 rates, is not possible based solely on these experimental data. The extraordinary complexity of
 416 the phase chemistries, possible surface reactions or rearrangement, and other microstructural

417 variables are not directly observable with the methods at hand. However, simulations that
418 account statistically for microstructure evolution, based on boundary nucleation and growth
419 (BNG) methods [39,40,41,42,43,44,45,46,47,48], or that explicitly account for 3D
420 microstructure and chemistry (*e.g.*, HydratiCA) [49,50,51,52], could be used to test the
421 plausibility that these mechanisms can control hydration kinetics of prehydrated powders in the
422 ways discussed here. Even to do this, however, a large number of simplifying assumptions must
423 be made about the phase distributions, their relative stability, dissolution and growth
424 mechanisms, and the corresponding dependence on solution composition. A detailed
425 description of these assumptions is outside the scope of this paper, but here we simply mention
426 that both BNG models and HydratiCA have been used as a check on the plausibility of the
427 mechanisms already proposed. Taken together, the simulations suggest (i) that retardation of
428 anhydrous cement phase dissolution by overgrowth of prehydrated layers, the compositions
429 and stabilities of which may depend on the type of exposure, is a mechanism that can be made
430 qualitatively consistent with the observed hydration kinetics; and (ii) nucleation and
431 subsequent growth of C-S-H gel on the surface of fine limestone particles can explain the partial
432 restoration of hydraulic activity of prehydrated cements.

433

434 **3.3. Effects on compressive strength**

435 Fig. 7(a) and Fig. 7(b) show the degree of hydration and the evolution of compressive strength
436 in cement pastes made from as-received and prehydrated OPC's respectively. It is noted that
437 while the degree of reaction-PI curves show consistency (*i.e.*, similar slopes) for ages greater
438 than 3 days, the 1 day relationship is different. It is (reasonably) anticipated that this is because
439 prehydration most significantly influences the progress of reactions of phases that react within
440 the first day (*e.g.*, C₃S, C₃A). After one day, as the rate of reaction has decreased, and these
441 phases substantially reacted, prehydration has lesser impact on the evolution of reactions. This
442 is likely the cause of different slopes, from 1 day to later ages.

443

444 It is noted that the compressive strength decreases linearly with prehydration index, as shown
445 in Fig. 7(c). Expectedly, the strength is also linearly correlated with the degree of reaction of the
446 OPC and with the cumulative heat release when normalized by the quantity of water in the
447 system, as indicated by the strength-heat master curves (SHMC) shown in Figs. 8(a-b) for both
448 as-received and prehydrated materials [31,32,53]. For the latter, the normalization is based on
449 the water mass in the mixture because this indicates the space that needs to be filled by the
450 hydration products to achieve higher strengths [54]. These results are significant because they
451 indicate that predicting the decrease in strength due to prehydration is straightforward if the
452 PI, degree of hydration or heat release behavior of an OPC is known. This ability to forecast
453 strength is especially important for binders containing substantial levels of OPC replacement by

454 other materials because these binders have both reduced ultimate strength and slower rates of
 455 strength gain at early ages [31,32].
 456

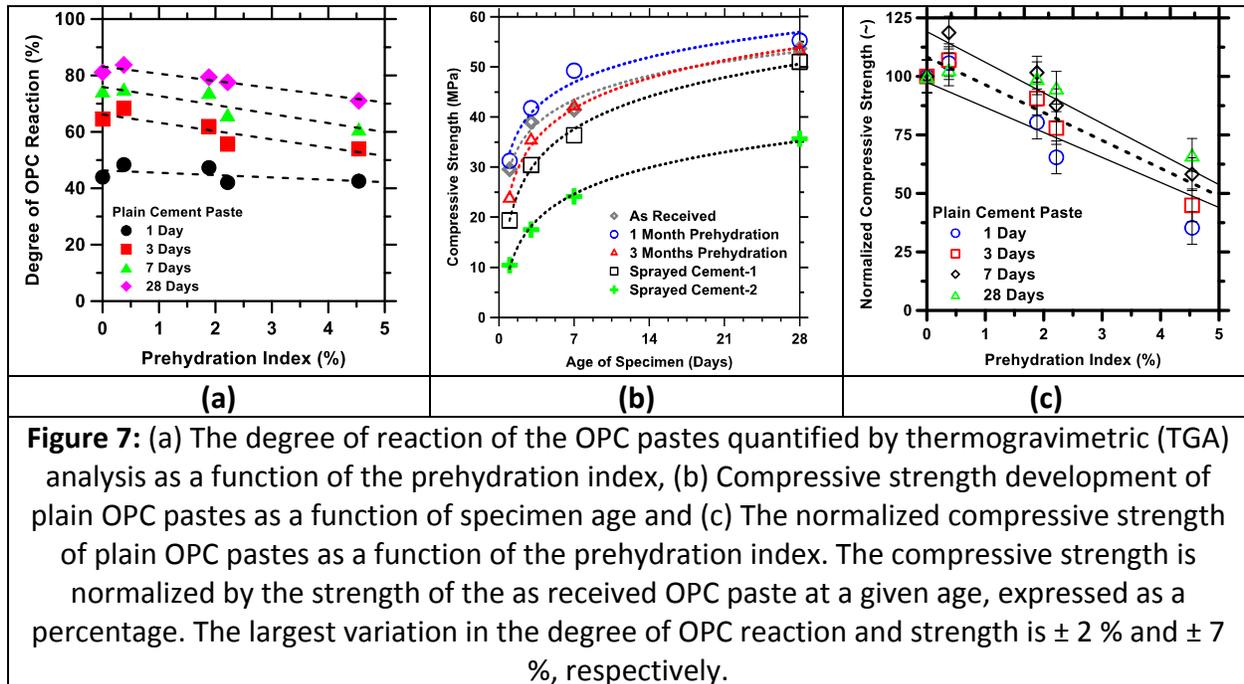
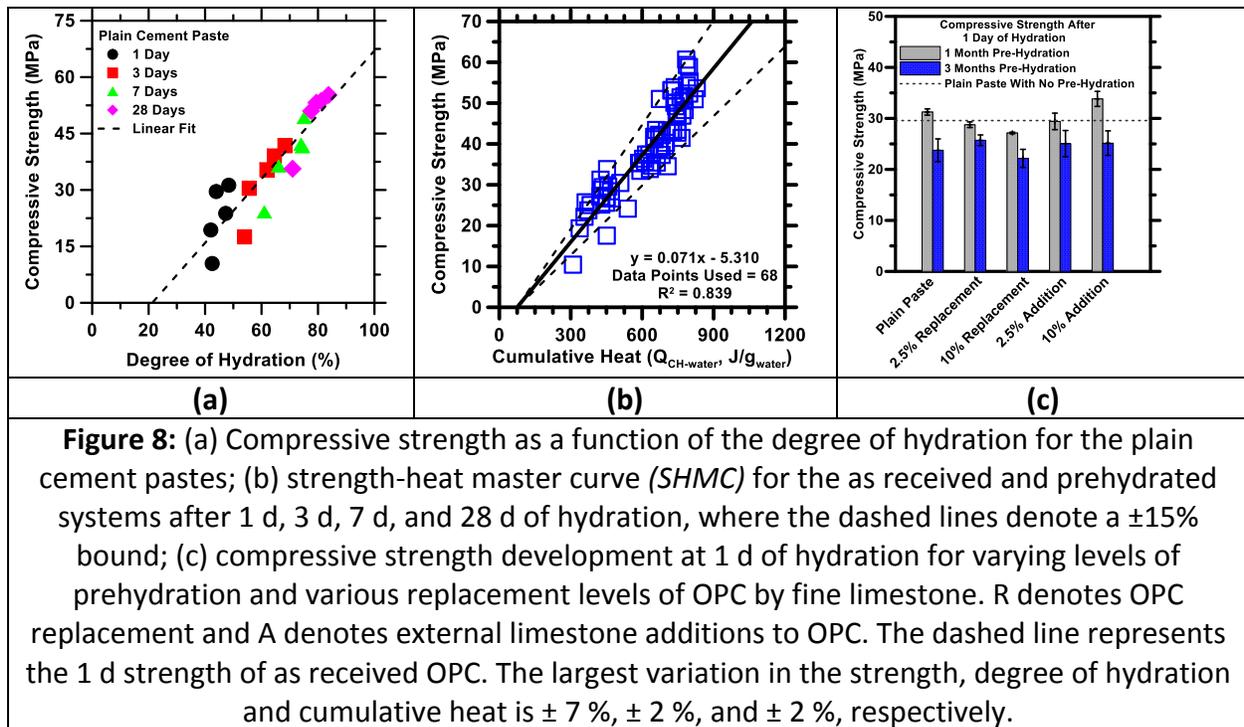


Figure 7: (a) The degree of reaction of the OPC pastes quantified by thermogravimetric (TGA) analysis as a function of the prehydration index, (b) Compressive strength development of plain OPC pastes as a function of specimen age and (c) The normalized compressive strength of plain OPC pastes as a function of the prehydration index. The compressive strength is normalized by the strength of the as received OPC paste at a given age, expressed as a percentage. The largest variation in the degree of OPC reaction and strength is $\pm 2\%$ and $\pm 7\%$, respectively.

457
 458 Compressive strengths of the prehydrated systems remain inferior to those of pastes made
 459 from the as-received powder even at 28 d, as shown in Fig. 7(b). This suggests that the effects
 460 of prehydration are evident not only at early times, but also longer times where they continue
 461 to prevent an equivalence in properties. It is not yet clear if these depressive effects are only a
 462 function of reaction progress or if aspects of the microstructure of prehydrated systems (*e.g.*,
 463 changes in pore size distributions, or phase compositions as caused by elevated temperature
 464 curing [55]) may be different. However, it is clear that externally provisioned limestone offsets
 465 the detrimental effects of prehydration on strength evolution especially at early times (see Fig.
 466 8c) in spite of the fact that limestone replacement for OPC increases the ratio of the water filled
 467 pore volume to cementing material (since limestone contributes very slightly to binding product
 468 formation); this is a dilution effect which normally would decrease strength. In summary, when
 469 limestone is dosed by OPC replacement, two competing effects are noted: (a) dilution, which
 470 would result in a decrease in strength and (b) an increase in the rate of reaction, which would
 471 improve early age strengths. In light of these effects, it may be expected that an increase in the
 472 limestone replacement level would not necessarily result in strength improvement as compared
 473 to the pristine OPC. However, at lower levels of limestone replacement (*e.g.*, 2.5 %) while gains
 474 in strength are admittedly small, the acceleration of OPC reactions is sufficient to ensure that in
 475 spite of water vapor exposure, cements can be dosed with limestone to compensate for the
 476 deleterious effects of prehydration, especially so for low values of the PI.



478

479 A significant point to be noted from the strength data (Figure 7b, 7c and 8c) is that it appears as though the OPC when exposed to water vapor for one-month seems to show slightly superior
 480 strength development as compared to the as-received OPC. While this difference is not large
 481 enough to unequivocally state a benefit (i.e., due to the measurement uncertainty in strength
 482 measurements) it is likely that rather than a monotonic reduction in properties with increasing
 483 prehydration, small extents of prehydration are indeed beneficial. While the reasons for this are
 484 not fully clear, it is speculated that it has to do with the available CaO content of the OPC, which
 485 diminishes with increasing prehydration; optimum values of which will favor faster reaction of
 486 the C_3S , especially at early reaction times (e.g., see Figure 5b). As such, it appears reasonable to
 487 conclude that at modest levels, prehydration does not alter reaction/property behavior, until
 488 some threshold – beyond which a monotonic reduction in properties and reaction evolution is
 489 noted. While it is indeed likely that the prehydration levels noted herein may take very long
 490 durations to occur in OPCs stored in sealed containers, water vapor transfer through paper bag
 491 products (e.g., as used in the U.S.), or water vapor contact with cement stored in silos may be
 492 more substantial, due to issues of air-leakage and -exchange.
 493

494

495

496 4. Summary and Conclusions

497 Experiments and simulations have been described that fully investigate the nature of cement
 498 prehydration. Exposure to either water vapor or liquid water causes a loss in the subsequent

499 hydraulic reactivity. The extent of prehydration relative to an as-received OPC powder can be
500 quantified, using thermogravimetric measurements, by a prehydration index (PI) that is defined
501 here for the first time. Carbonation during prehydration is minimal in all cases except extended
502 exposure to water vapor for three months. Therefore, we attribute the loss of reactivity after
503 prehydration to the formation of a layer of hydrated (i.e., water inclusive) solids on the cement
504 particles. The hypothesized prehydration layer acts as a mass transport barrier that impedes
505 the progress of chemical reactions when the cement is subsequently introduced into the mixing
506 water. The severity of suppression of the OPC reaction scales with the duration of exposure to
507 either water vapor or liquid water. In both cases, the activity (RH) of water is sufficient to cause
508 reactions with the aluminate components in the OPC to form aluminosulfate hydrates.

509
510 The reduced availability and chemical activity of water during vapor phase OPC prehydration
511 probably inhibits the formation of the *typical C-S-H* phase formed during normal hydration,
512 although a precursor silicate hydrate does form on the surface of the anhydrous silicate phases.
513 In contrast, liquid water prehydration likely enables formation of a product that is somewhat
514 similar to typical C-S-H formed during normal OPC hydration, and that is certainly less effective
515 at inhibiting the dissolution of the cement grains – as compared to the phase that forms on
516 particle surfaces during water vapor contact. Consequently the hydration progress of a liquid
517 prehydrated OPC is similar to an as-received OPC. These broad inferences are supported by
518 experiments and simulations designed to test the influences of the two types of barrier layers
519 thought to be formed during prehydration by water vapor or liquid water. The results shed light
520 on the nature and mechanisms of prehydration as well as its influences on the OPC hydration
521 kinetics, and other materials that are sensitive to moisture exposure.

522
523 The effects of prehydration are evident not only in early stages of normal hydration, but also
524 propagate to much later times by reducing the overall amount of reaction and the compressive
525 strength relative to materials made from the as-received powders. The magnitude of these
526 effects is highly correlated with the prehydration index. Dosages of fine limestone powder are
527 able to mitigate the effects of OPC prehydration. Such mitigation actions are probably both
528 catalytic and chemical in nature: availability of preferable surfaces for nucleation catalyzes the
529 precipitation of C-S-H, and increases in pH resulting from sorption of dissolved carbonate ions
530 by the C-S-H enhance the driving force for C-S-H growth. When the extent of prehydration is
531 modest, fine limestone can restore reaction rates and properties in prehydrated OPCs to nearly
532 the same levels as for the as-received OPC powder(s). This has important implications on the
533 addition of fine limestone to OPC, not only to reduce cement (i.e., clinker) contents, but also to
534 build in a *safety-valve* which can help overcome the detrimental effects of OPC prehydration,
535 which are often experienced in field applications.

536

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548

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