

# 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 are performed to develop a better understanding of prehydration by intentionally exposing an OPC powder to either water vapor or

liquid water. The experiments aim 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. Experimental results are used to evaluate hypotheses of mechanisms which control the process. The addition of fine limestone particles to a mixture formed using prehydrated cement is shown to mitigate the detrimental effects of cement prehydration.

**Keywords:** physisorption, prehydration, nucleation, limestone

## 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  $\text{CO}_2$  during the storage and handling of the OPC powder can result in premature hydration<sup>i</sup> or aging of its constituent phases. Any such unintentional reaction of the cement reduces the thermodynamic driving force for its subsequent reactions with water, and the resultant loss of reactivity is typically manifested as undesirable reductions in the rate of hardening and strength gain of concrete [1,2]. In this paper, we will use the term “prehydration” generically to refer to all the processes that cause unintentional loss of reactivity prior to the usual mixing of cement with water. To be specific, this includes physical adsorption of water on the cement particle surfaces, as well as the chemical reactions between water and the anhydrous OPC minerals to form solid hydration products such as calcium silicate hydrate (C-S-H<sup>ii</sup>),  $\text{Ca}(\text{OH})_2$ , gypsum, and ettringite. In addition,  $\text{CO}_2$  in air or dissolved in water can react with several cement components, forming magnesite ( $\text{MgCO}_3$ ) from periclase ( $\text{MgO}$ ), and forming  $\text{CaCO}_3$  from free lime ( $\text{CaO}$ ) or  $\text{Ca}(\text{OH})_2$ , the latter being present primarily because of prior reaction with water [3,4,5,6]. All of these changes initiate at the exposed surfaces of OPC grains but penetrate deeper into the grains with prolonged exposure.

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

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<sup>i</sup> 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.

<sup>ii</sup> C-S-H ( $\text{ACaO} \cdot \text{SiO}_2 \cdot \text{B} \cdot \text{H}_2\text{O}$ ): 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 [16].

This work expands on previous studies by quantitatively correlating the changes in reactivity and strength evolution in OPC pastes to the duration (and magnitude) of exposure to either liquid water or water vapor. The addition of fine limestone powder to prehydrated cement is observed to partially restore some reactivity. Likely mechanisms by which fine limestone can offset the detrimental effects of prehydration are briefly discussed.

## MATERIALS AND EXPERIMENTAL METHODS

An ASTM C150 compliant Type I/II ordinary portland cement (OPC) was used herein. X-ray fluorescence (XRF) was used to estimate the major oxide composition of the OPC on a mass basis: 20.57 %  $\text{SiO}_2$ , 5.19 %  $\text{Al}_2\text{O}_3$ , 3.44 %  $\text{Fe}_2\text{O}_3$ , 65.99 %  $\text{CaO}$ , 1.37 %  $\text{MgO}$ , 2.63 %  $\text{SO}_3$ , 0.17 %  $\text{Na}_2\text{O}$ , 0.31 %  $\text{K}_2\text{O}$ , 0.26 %  $\text{TiO}_2$  and 0.08 %  $\text{P}_2\text{O}_5$ . Quantitative X-ray diffraction (QXRD), using Rietveld refinement, was used to estimate the mineralogical composition of the OPC, on a mass basis [11]: 57.46 %  $\text{MIII-Ca}_3\text{SiO}_5$ , 23.81 %  $\beta\text{-Ca}_2\text{SiO}_4$ , 2.24 %  $\text{Ca}_3\text{Al}_2\text{O}_6$  (i.e., a mixture of cubic and orthorhombic forms [16]), 9.75 %  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ , 1.72 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 2.09 %  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and 2.91 %  $\text{CaCO}_3$ . To examine the efficacy of fine limestone powder additions to prehydrated OPC on restoring reactivity, a commercially available, nominally pure limestone powder (> 98 %  $\text{CaCO}_3$ ) was used.<sup>iii,iv</sup> The particle size distributions (PSDs) of the OPC and the limestone were measured by static light scattering (SLS) using isopropanol and ultrasonication for dispersing the powders to primary particles, and are shown in Fig. 1. The largest variation in the light scattering measurements is about 6 % based on measurements performed on six replicates and assuming the density of the OPC and limestone to be  $3150 \text{ kg/m}^3$  and  $2700 \text{ kg/m}^3$ , respectively. Assuming that the particles are spherical, the measured PSDs of OPC and limestone correspond to specific surface areas (SSAs) of  $520 \text{ m}^2/\text{kg}$  and  $1353 \text{ m}^2/\text{kg}$ . Accounting for the irregular shape of OPC particles often results in SSA estimates that are higher by a factor of 1.6-to-1.8 [12].

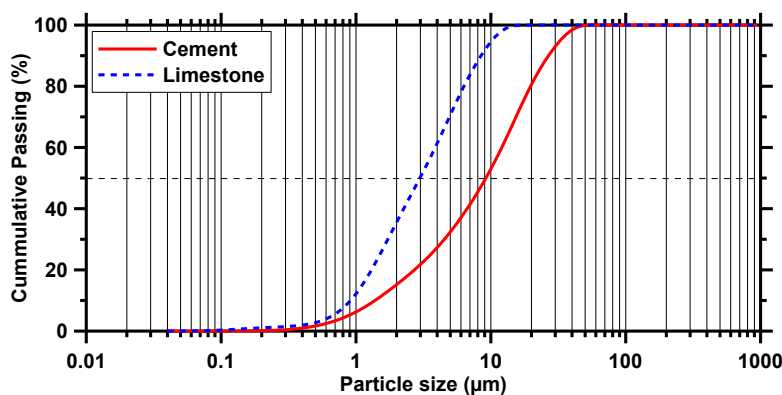


Figure 1 – Particle size distributions for the OPC (as-received) and the limestone evaluated in this study. The largest variation in the light scattering measurements is around  $\pm 6\%$ .

Prehydration of the as-received OPC was simulated by exposing it to either liquid water or humid air. For water vapor exposure, the OPC powder was placed for either one month or three

<sup>iii</sup> OMYA A.G., Cincinnati, OH.

<sup>iv</sup> 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.

months in a room maintained at  $55 \% \pm 10 \%$  RH and  $25\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ , during which time the powders were mixed on a weekly basis to encourage uniform exposure to water vapor. For exposure to liquid water (deionized), several hundred grams of the OPC powder were spread in a thin layer and then misted in two equal cycles, separated by 30 minutes, with a uniform mass of water corresponding to a moisture dosage of 2.5 % (Sprayed-1) or 5.0 % (Sprayed-2) by mass of powder. The OPC powder was homogenized in a planetary mixer after each cycle. After the second mixing, the powders were sealed in airtight containers to limit drying and maintained in an environmental chamber at  $25\text{ }^{\circ}\text{C}$ . After one week, the OPC powders were homogenized once again and placed in airtight containers for another week to ensure consistent prehydration.

Paste mixtures of either the as-received or prehydrated OPC powder were prepared with a (deionized) water-to-solids mass ratio of  $w/s = 0.45$  as described in ASTM C 305 [13]. To explore the influences of limestone on the reaction response of systems prehydrated with water vapor, small amounts of the as-received limestone powder were introduced either by adding to the cement powder (increasing the total solid mass) or by partially replacing the cement powder at constant total solid mass. By either means, the limestone dosages were 2.5 %, 5 % or 10 % by mass of OPC. When the limestone was dosed by addition, the amount of water in the mixture was 0.45 g  $\text{H}_2\text{O}$  per gram of OPC. In contrast, when limestone was dosed by partial replacement of OPC, the mixture had a constant water content of 0.45 g  $\text{H}_2\text{O}$  per gram of total solids.

## Characterizing the Extent of Cement Prehydration

As already described, the term “prehydration” is used to capture a range of premature reaction phenomena that result from exposure not only to water (liquid or vapor) but also to other reactants that OPC is likely to encounter during storage. The primary substance, besides water, that can react with cementitious minerals is  $\text{CO}_2$ , which is present in air and in liquid water at typical concentrations of about 390 ppm and 50 ppm, respectively. Therefore, our attempt to quantify prehydration, as defined here, must be careful to account for the effects both of water and of  $\text{CO}_2$ , especially because no special efforts were made to exclude  $\text{CO}_2$  either from the air or from the liquid water used in the prehydration step. Most OPCs contain some  $\text{CaCO}_3$  which is added intentionally (to reduce the cement clinker content), but which is difficult to distinguish from  $\text{CaCO}_3$  that forms by the direct carbonation of the free lime ( $\text{CaO}$ ) present in the OPC, or by the carbonation of  $\text{Ca}(\text{OH})_2$  formed by the hydration of  $\text{CaO}$ , or from reactions of the silicate phases with liquid water during storage and/or handling. Separating these different potential sources of  $\text{CaCO}_3$  is especially difficult because OPC often begins prehydrating (or carbonating) immediately after it is manufactured, long before it is acquired for analysis or use. Therefore, it is reasonable to only characterize prehydration of a cement powder relative to its as-received state, that is, as the *incremental* prehydration that is induced by the liquid or vapor treatments described in the previous section.

With these considerations in mind, the most direct way to characterize prehydration is to record the quantities of physisorbed water by desorption experiments and to measure the changes in the amounts of solid hydrates and carbonates before and after a given prehydration step using quantitative X-ray diffraction [7,8,9]. However, the total volume of each of the solid hydrates and carbonates formed by prehydration is small, typically below the detection limit,  $\approx 1\text{ }%$  by

mass, of lab-scale X-ray diffraction (XRD) analyses. Further, numerous OPC hydrates are poorly ordered and thus difficult to quantify accurately by XRD. Because of these difficulties, we choose to apply thermogravimetry to characterize prehydration by measuring the mass loss upon heating to 975 °C, a temperature above which no additional mass loss is observed even by fully hydrated OPC. The mass lost by an anhydrous OPC when heated from room temperature to 975 °C in N<sub>2</sub> comes from several sources. Between room temperature and ≈110 °C, liquid water condensed in the porosity evaporates, and the calcium alumino/sulfate hydrate phases begin to dehydrate. The continued dehydration of the calcium alumino/sulfate phases, together with volatilization of the grinding aids added during manufacture and decomposition of minor hydrated phases such as syngenite, continues between 110 °C and 400 °C. The decomposition of the calcium hydroxide, magnesium carbonate, and calcium alumino/sulfate-hydrates occurs between about 425 °C and 550 °C. Above 550 °C, the main contributions to the mass loss are decomposition of calcium carbonate and the final dehydration of the calcium silicate hydrate (C-S-H) phases.

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

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

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

The prehydration index could have been defined in alternative ways that attempt to neglect the contribution of carbonation by omitting the portion of the mass loss that is associated with the decomposition of CaCO<sub>3</sub>. However, we choose to include all mass loss in our definition because carbonation can be both a direct effect of aging and a secondary effect of reaction with water.

A simultaneous thermal analyzer<sup>v</sup> was used to measure the thermogravimetric (TG) and the differential thermogravimetric (DTG) signals of the cementitious samples, as raw powders, and after 1 d, 3 d, 7 d, and 28 d of hydration in liquid water. The temperature and mass sensitivity of the analyzer were 0.25 °C and 0.1 µg, respectively. Hydration was arrested at each desired time by crushing the paste mass to granules (< 5 mm diameter) and then submerging them in isopropanol (IPA) for 6 d, with IPA being replaced every 2 d [14]. Following solvent exchange, the samples were placed under vacuum in a desiccator for 3 d and then crushed to a very fine powder. The powders were heated under a (99.999 % purity) N<sub>2</sub> purge at a flow rate of 20 mL/min and a heating rate of 10 °C/min in pure aluminum oxide crucibles from 35 °C to 975 °C.

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<sup>v</sup> STA 6000, Perkin Elmer, Waltham, MA.

The TG data were used to calculate the prehydration index (PI), and to approximate both the evaporable and non-evaporable water contents, the amount of  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  present in the system—inferred from the mass loss between 425 °C and 550 °C and between about 550 °C and 800 °C, respectively. The degree of OPC reaction,  $\alpha$ , for normal hydration in sufficient liquid water can then be estimated by assuming that the mass of non-evaporable water,  $m_n(t)$  varies linearly from zero to a terminal value of  $m_{n,\infty}$  at complete reaction,

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

While the non-evaporable water mass can be estimated from TG data, volatilization of  $\text{CO}_2$  also contributes to the mass loss and therefore can make the non-evaporable water mass difficult to isolate. However, errors made in incorrectly assigning different portions of the TG data to non-evaporable water will largely cancel in Eq. (2) if the same procedure is used to calculate both  $m_n(t)$  and  $m_{n,\infty}$ . Therefore, we arbitrarily choose a formulation that also has been applied in some previous studies [15,16]:

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

where  $m(t, 145)$ , for example, is the mass of a specimen after  $t$  days of reaction when heated to 145 °C, and is the mass after loss of evaporable water [15,16]. The term in square brackets in Eq. (3) is intended to account for the mass loss due to  $\text{CaCO}_3$  decomposition, the onset of which usually begins at about 550 °C, although for this study we use the DTG signal to determine the onset temperature more accurately for each paste specimen. The terminal value of the non-evaporable water mass at complete reaction could be determined experimentally by a long-term bottle hydration experiment to ensure complete reaction. However, we estimate for this OPC powder, based on its mineral composition and using a procedure described previously [16], that  $m_{n,\infty} \approx 0.23$  g per gram of ignited, as-received OPC.

### Characterizing Mixture Reactivity and its Impacts on Mechanical Properties

An isothermal calorimeter<sup>vi</sup> was used to measure the heat evolved during normal hydration of as-received and prehydrated OPC pastes at constant temperature (25 °C ± 0.1 °C). The thermal power and the energy measured were used to assess the influence of prehydration and of limestone dosage on reaction kinetics and total heat release of the cementitious samples. The progress of reactions, and their impacts on mixture properties were characterized by measuring the compressive strength of OPC paste specimens (50 mm cubes) cured at 25 °C ± 1 °C for 1 d, 3d, 7 d, and 28 d, as described in ASTM C109 [13]. Each compressive strength measurement was repeated on three replicates to obtain an average value at each time (age), with a highest variation of 7 % being noted for samples formed from the same mixing batch.

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<sup>vi</sup> TamAir, TA Instruments, Newcastle, DE.

## EXPERIMENTAL RESULTS AND THEIR DISCUSSION

### Plain OPC Pastes

The loss on ignition (LoI) upon heating the as-received OPC powder to 975 °C was 2.99 %, using the unignited powder as the reference. Based on the DTG data shown in Fig. 2(a), if we assume that all the mass loss in the range 600 °C-to-800 °C is CO<sub>2</sub> gas released by CaCO<sub>3</sub> decomposition, then the LoI can be partitioned with 2.04 % due to CO<sub>2</sub> from CaCO<sub>3</sub> and 0.95 % due to other sources. This indicates an intrinsic CaCO<sub>3</sub> content of ≈ 4.45 % (by mass) in the as-received OPC.

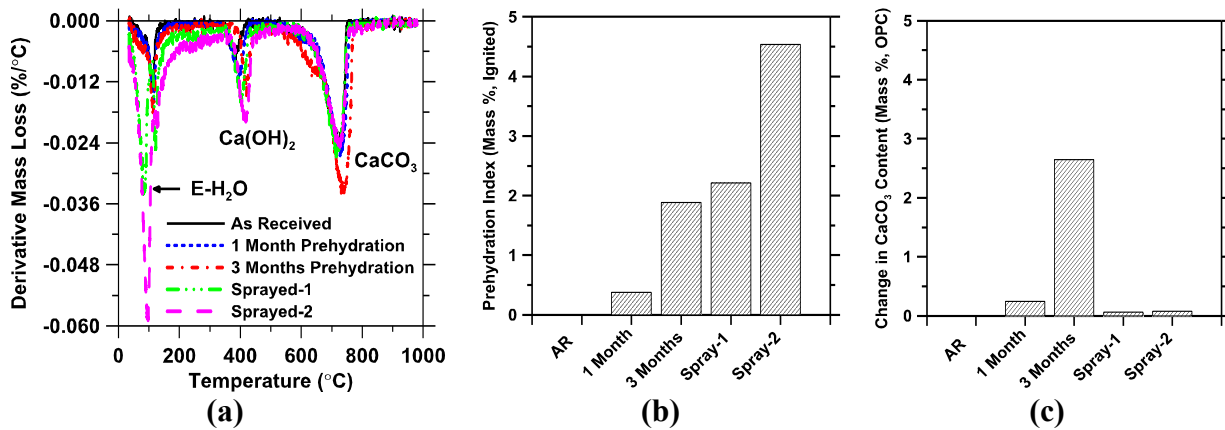


Figure 2 – (a) Traces obtained by differential thermogravimetric (DTG) analysis for cement prehydrated to different levels. Here, E-H<sub>2</sub>O, Ca(OH)<sub>2</sub>, and CaCO<sub>3</sub> denote evaporable water, portlandite and calcite respectively. (b) The prehydration index quantified for the different prehydration treatments applied in this study and (c) the change in the CaCO<sub>3</sub> content over the course of the prehydration treatment, over and above the CaCO<sub>3</sub> content intrinsic to the OPC. It should be noted, that “AR” denotes the OPC in its as-received form. The largest variation in quantifications of the prehydration index and the CaCO<sub>3</sub> content is on the order of ± 7 % and ± 2 %, respectively, as quantified from determinations from three replicates.

Fig. 2(a) shows DTG measurements for the as-received cement and for the cement prehydrated due to water vapor or liquid water exposure. Even the as-received OPC has some evaporable water and Ca(OH)<sub>2</sub>. Therefore, this cement experienced some prehydration prior to being used in this study. Increasing water dosages (*i.e.*, 55 % RH or by spraying) increase the prehydration index, as shown in Fig. 2(b). A similar effect is noted with increasing times of exposure, from one month to three months, at 55 % RH. Unsurprisingly, the extent of CaCO<sub>3</sub> detected increases with the exposure time. The increases in the CaCO<sub>3</sub> content are caused by the carbonation of CaO or Ca(OH)<sub>2</sub> present in the OPC, or formed over the course of the prehydration treatment [8]. The DTG data in Fig. 2(a) indicate that incremental carbonation leads to ≤ 0.25 % increase in the CaCO<sub>3</sub> content of the OPC for all prehydration treatments except for the 3-month exposure to water vapor. The 3-month exposure, however, caused an increase in the CaCO<sub>3</sub> content of ≈ 2.65 % by initial mass of OPC powder. These increases in the CaCO<sub>3</sub> content correspond to contributions to the PI of ≈ 1.2 % for the 3-month exposure but only around ≈ 0.1 % for all other prehydration treatments. Carbonation of Ca(OH)<sub>2</sub> is known to occur more slowly in water, with

about 50 ppm CO<sub>2</sub>, than in humid air with about 390 ppm CO<sub>2</sub> [17]. Therefore, the enhanced CaCO<sub>3</sub> content in the OPC sample exposed to moist air for 3 months is likely due to both the duration and the type of exposure [18,19,20]. Therefore, the effects of prehydration can be primarily ascribed to moisture exposure at shorter times, with the relative contribution of CO<sub>2</sub> exposure increasing with increasing duration, the concentration of CO<sub>2</sub>, or under ambient conditions which favor direct carbonation processes [18,19,20].

Fig. 2(a) shows that all prehydration treatments lead to increases in the mass loss between 350 °C and 450 °C, which we attribute largely to increases in Ca(OH)<sub>2</sub>. The increase in Ca(OH)<sub>2</sub> is greater for systems prehydrated with liquid water than water vapor. Elevated Ca(OH)<sub>2</sub> contents are produced by the reactions of the silicate phases, principally alite (Ca<sub>3</sub>SiO<sub>5</sub>) and to a lesser extent belite (Ca<sub>2</sub>SiO<sub>4</sub>), and by the hydration of CaO. Furthermore, the sprayed systems also contain more water in the evaporable range (i.e., ≤ 145 °C [15,16]) than do the water vapor hydrated systems. These differences are related to differences in the prehydration route, for example by the adsorption of water vapor and induced surface modifications or by means of dissolution-precipitation reactions mediated through liquid water.

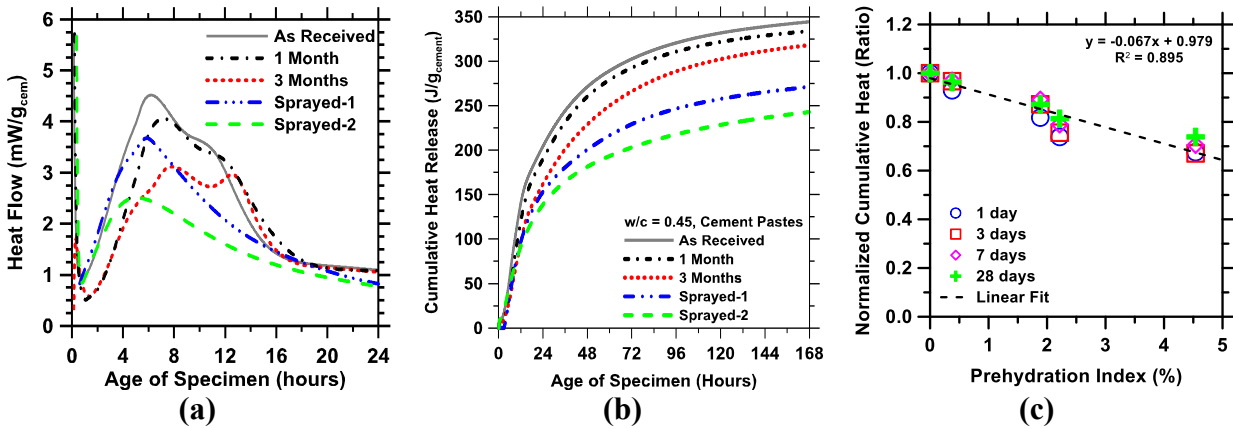


Figure 3 – The influence of prehydration on the rates of reactions as measured using isothermal calorimetry for: (a) heat flow and (b) cumulative heat release and (c) cumulative heat released at 1 d, 3 d, 7 d, and 28 d for all cement paste mixtures normalized by the heat released by the as-received paste 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.

Fig. 3(a) shows the effects of prehydration on the rates of OPC reaction during subsequent hydration in sufficient liquid water as measured using isothermal calorimetry. This figure confirms that prehydration reduces the intensity of reactions. In particular, the extents of reaction decrease with increasing (water) exposure time and water availability: as-received > 1 month > 3 months > Sprayed-1 > Sprayed-2. Interestingly, the two different methods of moisture delivery have qualitatively very different effects on the reaction curve. Prehydration by water vapor causes a fixed delay in the onset of the main silicate reaction peak by about two hours, regardless of the exposure time, and then reduces the height of the main silicate reaction peak relative to the secondary aluminate reaction peak that occurs later. In contrast, prehydration by sprayed liquid water causes no delay in, or even very slightly accelerates the onset of the main silicate peak and also diminishes the relative strength of the subsequent aluminate peak. As shown in Figs. 3(b) and 3(c), the prehydrated systems are unable to reach the same extent of reaction as the as-



received system. Furthermore, Fig. 3(c) indicates that the severity of the depression in the total amount of OPC reactions, as measured by cumulative heat released, is a linear function of the incremental PI, independent of prehydration exposure type or duration (see also Figure 6a).

One might suppose that this decrease in heat evolution is similar to the heat released over the course of prehydration. However, in the absence of direct heat evolution measurements during the prehydration exposure, the validity of that supposition cannot be evaluated without making an assumption about how heat release is related to degree of reaction,  $\alpha$ , during prehydration. For normal hydration in liquid water, the non-evaporable water at complete reaction,  $m_{n,\infty}$ , is known to be about 0.23 g per gram of OPC reacted [15,16]. Therefore,  $m_{n,\infty}$  is a linear function of  $\alpha$  with a slope of 0.23 (Eq. 2). However, the reaction products formed during prehydration may have different non-evaporable water contents because the water activity is far different than during normal hydration. Therefore, a linear relationship between  $m_{n,\infty}$  and  $\alpha$  may still prevail during prehydration, but our uncertainty about its slope make it difficult to infer the degree of reaction during prehydration from TG data. Even if it is to be assumed,  $m_{n,\infty} = 0.23 \text{ g/g}_{\text{OPC}}$  for reaction products formed during prehydration, the calculated heat release,  $Q$ , during prehydration would be  $\alpha \cdot \Delta H$ , where  $\Delta H$  is the enthalpy of complete OPC hydration and  $\Delta H \approx 458 \text{ J/g}$  for this OPC. Equating all the heat reduction observed at 168 h of hydration in Fig. 3(b) to the heat released during prehydration would therefore require a high degree of reaction, about 0.21, for the Sprayed-2 case; which is unlikely over the course of prehydration.

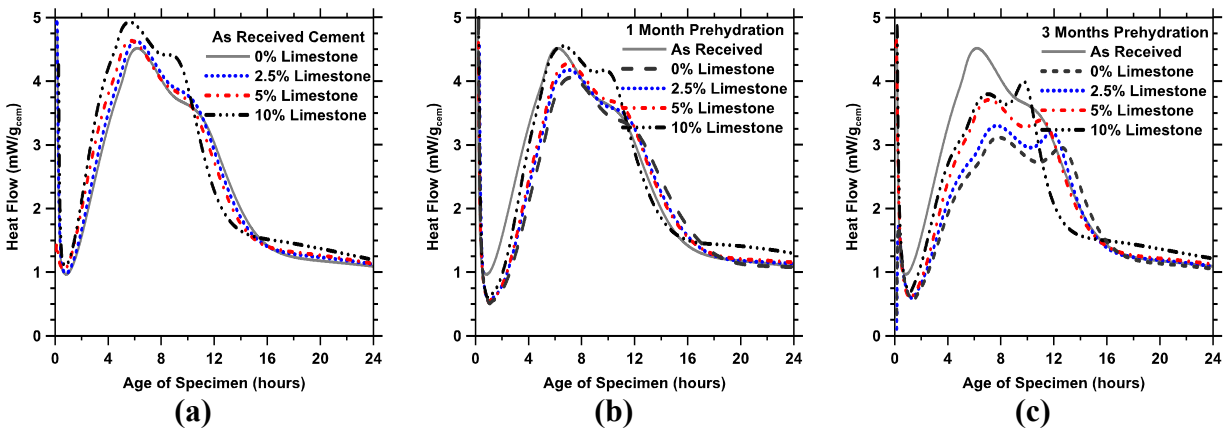


Figure 4 – Representative graphs showing the influence of limestone on mitigating the influences of vapor-phase prehydration for: (a) as received cement, (b) 1 month of vapor phase prehydration (c) 3 months of vapor phase prehydration. In each case, limestone dosages are noted as percent replacement 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.

It seems unusual that systems prehydrated by liquid water are less retarded during hydration at early times than systems prehydrated by water vapor at similar or greater values of the PI. This indicates that the nature of the products of prehydration are important, rather than just the absolute level of prehydration. For example, at 55% RH, prehydration is expected to result in

some reaction of  $\text{Ca}_3\text{Al}_2\text{O}_6$  to form a calcium aluminohydrate [16], some reaction of  $\text{CaO}$  to form  $\text{Ca}(\text{OH})_2$ , and the partial hydration of  $\text{CaSO}_4$  to form bassanite and/or gypsum. Under the same conditions, the silicate reactions are likely limited to a hydroxylation or similar change in a thin surface layer [22]. Such formations of surface layers on the silicate phases, however, have been previously hypothesized to reduce dissolution rates of these minerals [21], and may even be capable of altering their apparent solubility [22]. On the other hand, prehydration in liquid water likely results in the formation of C-S-H nuclei on silicate surfaces [22], in addition to the aluminate and sulfate reactions. Therefore, the differences observed between prehydration in liquid water and water vapor are likely related to the degree and type of reactions at silicate surfaces. C-S-H exhibits enhanced growth rates in the presence of silicate hydrate seeds that offer preferred nucleation sites and thus accelerate reactions in  $\text{Ca}_3\text{SiO}_5$  systems [23,24,25,26]. A similar mechanism likely operates in the liquid-phase prehydrated systems, wherein silicate surface reactions result in the formation of a type of C-S-H that provides sites for preferential nucleation of *typical C-S-H* during normal hydration. This would also explain why liquid-phase prehydrated systems reach their maximum hydration rate at times that are similar to those of the as-received OPC, despite having a higher prehydration index than systems exposed to water vapor. However, the degree of reaction at later times is lowest in systems prehydrated with liquid water, which is contrary to a seeding effect. The lower extent of reaction at later times may be related to enhanced initial surface coverage of the OPC grains by C-S-H, which can have the following effects: (1) reduce the exposed surface area of the anhydrous phases available for dissolution and (2) then cause an earlier transition to a diffusion-controlled mechanism when a continuous C-S-H layer on the OPC grains has grown thick enough to limit transport of dissolved ions to/from the bulk solution. In contrast, silicate phase surface modifications caused by prehydration in water vapor are gradually etched away upon normal hydration in liquid water, because their hydration approaches that of as-received systems after about 12 h (see Fig. 3a).

## Influence of Fine Limestone

Recently, additions of fine limestone have been demonstrated as a novel means of enhancing and/or controlling OPC reaction rates [27,28,32]. In light of these observations, several mixtures were prepared with different dosages of limestone, as described in Section 2, to determine if it can mitigate the effects of prehydration<sup>vii</sup>. Fig. 4 shows that fine limestone can indeed partially or fully offset prehydration effects, and that its efficacy increases with the limestone dosage. Therefore, while complete restoration of normal hydration is easily achieved at low levels of prehydration (*e.g.*, at one month), only partial mitigation is possible when prehydration is more severe (*e.g.*, after three months). For the dosages considered, both limestone replacement and addition are similarly effective. Limestone's ability to restore the hydraulic reactivity of OPC is linked to at least three effects. First, the surface area provided by fine limestone catalyzes the silicate hydration reactions by providing increased surface area and a low(er) energy barrier for heterogeneous nucleation of hydration products. Second, the dissolution of  $\text{CaCO}_3$  in water provides carbonate anions to the solution, some of which could be incorporated within the C-S-H through an ion-exchange reaction that releases  $\text{OH}^-$  ions from the C-S-H to preserve charge neutrality. We have no direct experimental confirmation to support this assumption about

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<sup>vii</sup> 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 [21,32]. On the other hand, carbonation during prehydration results in the formation of a mass transport barrier which would impede the dissolution of the cement grains.

carbonate uptake by C-S-H, but an analogous ion exchange reaction for sulfate uptake by C-S-H does explain the observed increase of pH in  $\text{Ca}_3\text{SiO}_5$  systems when soluble calcium sulfate is available during hydration [29,30]. When limited  $\text{CO}_3^{2-}$  incorporation is allowed by this kind of reaction, the accelerating effect of the limestone is virtually unchanged at the beginning because it still offers the same preferential nucleation sites. However, progressively more ion exchange can occur as more C-S-H is formed by ongoing hydration. This is significant because  $\text{OH}^-$  released by ion exchange increases the driving force for C-S-H growth [31,32] relative to the driving force without  $\text{CO}_3^{2-}$  sorption. The result is a higher degree of reaction at later times [32]. Finally, the availability of  $\text{CO}_3^{2-}$  ions stabilizes a carboaluminate product at the expense of the sulfoaluminate hydrate that would form otherwise [33,34]. Of course, the  $\text{CaCO}_3$  formed during prehydration could trigger either of the last two effects, but that source is quite small for all prehydration treatments other than the 3-month duration.

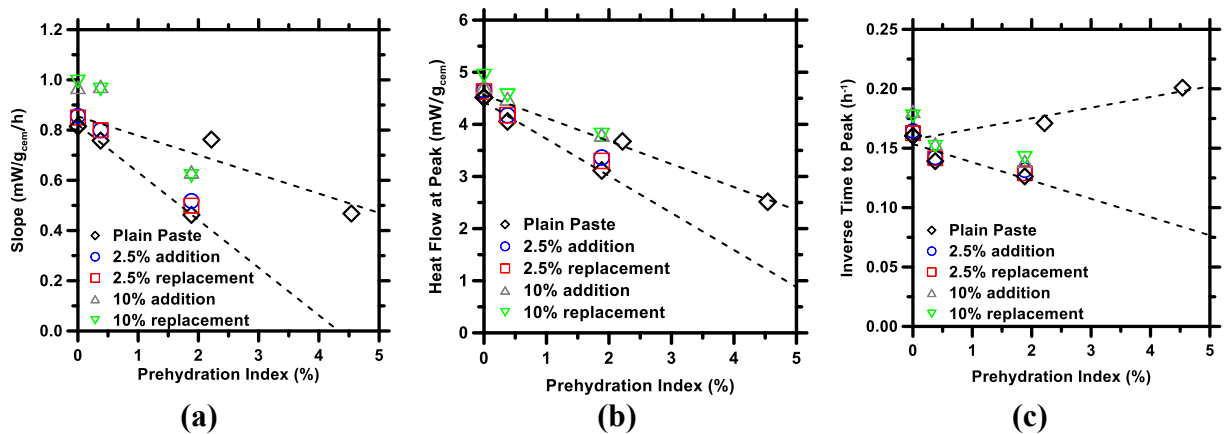


Figure 5 – Calorimetric parameters and best fits (dotted lines) as a function of the prehydration index for: (a) slope during the acceleration period, (b) heat flow value at the main heat peak and (c) inverse time required to achieve the main heat peak. The lower and upper dashed lines show linear fits to the data points associated with the plain OPC pastes prehydrated with water vapor or liquid, respectively.

The trends in the reaction rates are more clearly revealed in Fig. 5 by plotting parameters extracted from the calorimetric measurements as a function of the prehydration index, such as the slope during the acceleration period (Fig. 5a), the heat flow value at main heat peak (Fig. 5b), and the inverse of the time of the main heat peak (Fig. 5c). These calorimetric parameters all decrease with increasing prehydration, but the rate of decrease in the OPC's reactivity with prehydration is less severe for liquid exposure ( $\text{PI} \geq 2\%$ ) than water vapor exposure ( $\text{PI} \leq 2\%$ ). Further, quantifying calorimetric parameters in this manner also highlights the ability of *external* limestone to offset prehydration effects, with ever increasing success at lower PI.

## Effects on Compressive Strength

Fig. 6(b) shows the evolution of compressive strength in cement pastes made from as-received and prehydrated cement. The compressive strength decreases linearly with prehydration index, as shown in Fig. 6(c). The strength is also linearly correlated with the degree of reaction of the OPC and with the cumulative heat release normalized by the quantity of water in the system, as

indicated by the strength-heat master curves (SHMC) shown in Figs. 7(a) and 7(b) for both as-received and prehydrated materials [27,28,35]. For the latter, the normalization is based on the water mass in the mixture because this indicates the space that can be filled by the hydration product to achieve higher strengths [36]. These results are significant because they indicate that predicting the decrease in strength due to prehydration is reasonably straightforward if the prehydration index, degree of hydration or the heat release behavior of an OPC is known. This ability to forecast strength is especially important for binders containing substantial levels of OPC replacement by other materials because these binders often have both reduced ultimate strengths and slower rates of strength gain at early times [27,28].

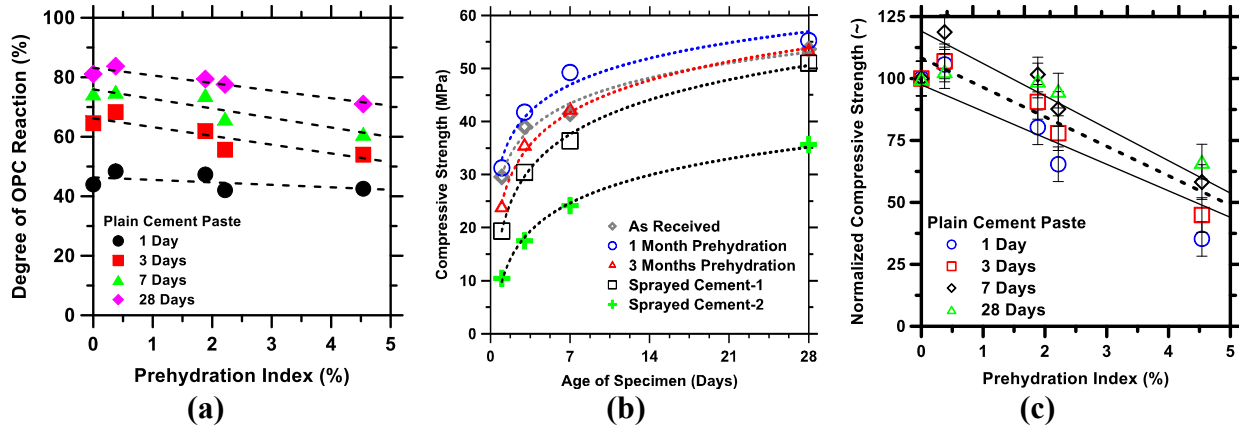


Figure 6 – (a) The degree of reaction of the OPC pastes quantified by thermogravimetric (TGA) analysis as a function of the prehydration index, (b) Compressive strength development of plain OPC pastes as a function of specimen age and (c) The normalized compressive strength of plain OPC pastes as a function 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.

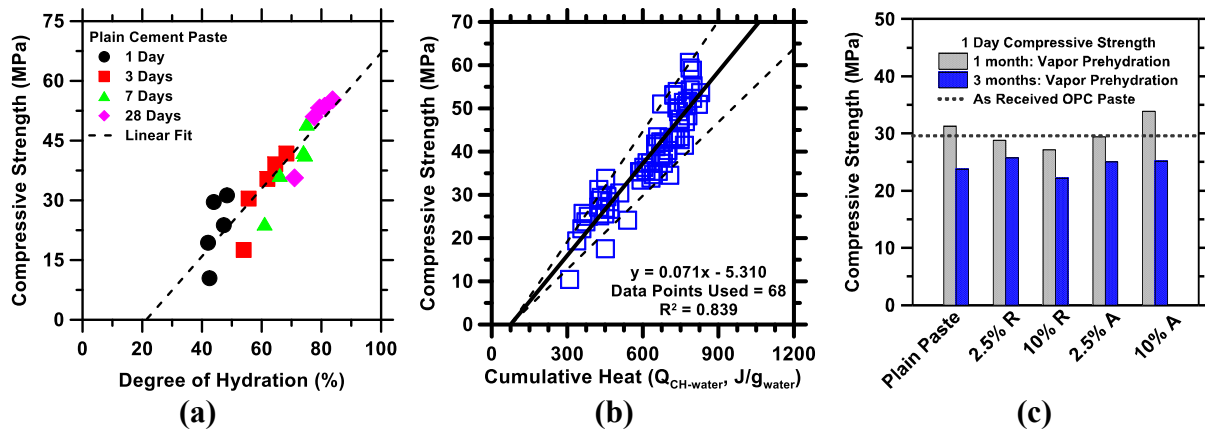


Figure 7 – (a) Compressive strength as a function of the degree of hydration for the plain cement pastes; (b) strength-heat master curve (SHMC) for the as received and prehydrated systems after 1 d, 3 d, 7 d, and 28 d of hydration, where the dashed lines denote a  $\pm 15\%$  bound; (c) compressive strength development at 1 d of hydration for varying levels of prehydration and various replacement levels of OPC by fine limestone. R denotes OPC replacement and A denotes external limestone additions to OPC. The dashed line represents the 1 d strength of as received

457 *OPC. The largest variation in the strength, degree of hydration and cumulative heat is  $\pm 7\%$ ,  $\pm$*   
458  *$2\%$ , and  $\pm 2\%$ , respectively.*

459  
460 Compressive strengths of the prehydrated systems remain inferior to those of pastes made from  
461 the as-received powder even at 28 d, as shown in Fig. 6(b). This suggests that the effects of  
462 prehydration are evident not only at early times, but also longer times where they continue to  
463 prevent an equivalence in properties. It is not yet clear if these depressive effects are only a  
464 function of reaction progress or if aspects of the microstructure of prehydrated systems (*e.g.*,  
465 changes in pore size distributions, or phase compositions as caused by elevated temperature  
466 curing [37]) may be different. However, it is clear that externally provisioned limestone offsets  
467 the detrimental effects of prehydration on strength evolution especially at early times (see Fig.  
468 7c) in spite of the fact that limestone replacement for OPC increases the ratio of the water filled  
469 pore volume to cementing material (since limestone contributes very slightly to binding product  
470 formation); this is a dilution effect which normally would decrease strength.

## 471 472 473 **SUMMARY AND CONCLUSIONS**

474  
475 Experiments have been described that fully investigate the nature of cement prehydration.  
476 Exposure to either water vapor or liquid water causes a loss in the subsequent hydraulic  
477 reactivity. The extent of prehydration relative to an as-received OPC powder can be quantified,  
478 using thermogravimetric measurements, by a prehydration index (PI) that is defined here for the  
479 first time. Carbonation during prehydration is minimal in all cases except extended exposure to  
480 water vapor for three months. Therefore, we attribute the loss of reactivity after prehydration to  
481 the formation of a layer of hydrated (*i.e.*, water inclusive) solids on the cement particles. The  
482 hypothesized prehydration layer acts as a mass transport barrier that impedes the progress of  
483 chemical reactions when the cement is subsequently introduced into the mixing water. The  
484 severity of suppression of the OPC reaction scales with the duration of exposure to either water  
485 vapor or liquid water. In both cases, the activity of water is sufficient to cause surface reactions  
486 with the aluminate components in the OPC to form aluminosulfate hydrates. The reduced  
487 availability and chemical activity of water during vapor phase OPC prehydration probably  
488 inhibits the formation of the *typical C-S-H* phase formed during normal hydration, although a  
489 precursor silicate hydrate likely forms on the surfaces of the anhydrous silicate phases. In  
490 contrast, liquid water prehydration likely enables formation of a product that is somewhat similar  
491 to *typical C-S-H* formed during normal OPC hydration, and that is certainly less effective at  
492 inhibiting the dissolution of the cement grains. Consequently the hydration progress of liquid  
493 prehydrated powders is similar to an as-received OPC. These broad inferences are supported by  
494 the experiments, which were designed to test the influences of the two types of barrier layers  
495 thought to be formed during prehydration by water vapor or liquid water. Detailed information  
496 regarding the composition, location, and properties of the prehydration products is needed to  
497 confirm these conclusions. The results of this work, nevertheless, shed light on the nature and  
498 mechanisms of prehydration as well as its influences on the hydration kinetics of OPC, and other  
499 materials that are sensitive to moisture exposure.

500  
501 The effects of prehydration are evident not only in early stages of normal hydration, but also  
502 propagate to much later times by reducing the overall amount of reaction and the compressive

strength relative to materials made from the as-received powders. The magnitude of these effects is highly correlated with the prehydration index. Dosages of fine limestone powder are able to mitigate the effects of OPC prehydration. Such mitigation actions are probably both catalytic and chemical in nature: availability of preferable surface for nucleation catalyzes the precipitation of C-S-H, and increases in pH resulting from sorption of dissolved carbonate ions by the C-S-H enhance the driving force for C-S-H growth. When the extent of prehydration is modest, fine limestone can restore reaction rates and properties in prehydrated OPCs to nearly the same levels as for the as-received OPC powder(s). This has important implications on the addition of fine limestone to OPC, not only to reduce cement contents, but also to build in a *safety-valve* which can help overcome the detrimental effects of OPC prehydration, which are often experienced in field applications.

## REFERENCES

- (1) Theisen K.; Johansen V., Prehydration and strength development of portland cement, *Am. Ceram. Soc. Bull.* **1975**, 54,787-791.
- (2) Starinieri, V.; Hughes, D.; Gosselin, C.; Wilk, D.; Bayer, K., Pre-hydration as a technique for the retardation of Roman cement mortars. *Cem. Concr. Res.* **2013**, 46, 1-13.
- (3) Flatt, R. J.; Scherer, G. W.; Bullard, J. W., Why alite stops hydrating below 80% relative humidity. *Cem. Concr. Res.* **2011**, 41 (9), 987-992.
- (4) Jensen, O. M.; Hansen, P. F.; Lachowski, E. E.; Glasser, F. P., Clinker mineral hydration at reduced relative humidities. *Cem. Concr. Res.* **1999**, 29 (9), 1505-1512.
- (5) Ruiz-Agudo, E.; Kudłacz, K.; Putnis, C. V.; Putnis, A.; Rodriguez-Navarro, C., Dissolution and Carbonation of Portlandite [Ca(OH)<sub>2</sub>] Single Crystals. *Env. Sci. Technol.* **2013**, 47 (19), 11342-11349.
- (6) MacIntire, W. H., The carbonation of burnt lime in soils. *Soil Science* **1919**, 7 (5), 325-453.
- (7) Dubina, E.; Black, L.; Sieber, R.; Plank, J., Interaction of water vapour with anhydrous cement minerals. *Adv. App. Ceram.* **2010**, 109 (5), 260-268.
- (8) Dubina, E.; Wadsö, L.; Plank, J., A sorption balance study of water vapour sorption on anhydrous cement minerals and cement constituents. *Cem. Concr. Res.* **2011**, 41 (11), 1196-1204.
- (9) Whittaker, M.; Dubina, E.; Al-Mutawa, F.; Arkless, L.; Plank, J.; Black, L., The effect of prehydration on the engineering properties of CEM I Portland cement. *Adv. Cem. Res.* **2013**, 25 (1), 12-20.
- (10) Dubina, E.; Plank, J., Influence of moisture-and CO<sub>2</sub>-induced ageing in cement on the performance of admixtures used in construction chemisti. *ZKG international* **2012**, (10), 60-68.
- (11) Le Saoût, G.; Kocaba, V.; Scrivener, K., Application of the Rietveld method to the analysis of anhydrous cement. *Cem. Concr. Res.* **2011**, 41 (2), 133-148.
- (12) Garboczi, E.; Bullard, J., Shape analysis of a reference cement. *Cem. Concr. Res.* **2004**, 34 (10), 1933-1937.
- (13) ASTM International: *Annual Book of Standards*. [www.astm.org](http://www.astm.org). **2012**.
- (14) Zhang, J.; Scherer, G. W., Comparison of methods for arresting hydration of cement. *Cem. Concr. Res.* **2011**, 41 (10), 1024-1036.
- (15) Mounanga, P.; Khelidj, A.; Loukili, A.; Baroghel-Bouny, V., Predicting Ca (OH)<sub>2</sub> content and chemical shrinkage of hydrating cement pastes using analytical approach. *Cem. Concr. Res.* **2004**, 34 (2), 255-265.
- (16) Taylor, H. F. W. *Cement Chemistry*, 2 ed.; Thomas Telford Publishing: London, **1997**.
- (17) Beruto, D. T.; Barberis, F.; Botter, R., Calcium carbonate binding mechanisms in the setting of calcium and calcium–magnesium putty-limes. *J. cultural heritage* **2005**, 6 (3), 253-260.

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- (18) Lee, D. K., An apparent kinetic model for the carbonation of calcium oxide by carbon dioxide. *Chem. Eng. J.* **2004**, *100* (1), 71-77.
- (19) Mess, D.; Sarofim, A. F.; Longwell, J. P., Product layer diffusion during the reaction of calcium oxide with carbon dioxide. *Energy & Fuels* **1999**, *13* (5), 999-1005.
- (20) Dubina, E.; Korat, L.; Black, L.; Strupi-Šuput, J.; Plank, J., Influence of water vapour and carbon dioxide on free lime during storage at 80° C, studied by Raman spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2013**, *111*, 299-303.
- (21) Barret, P.; Ménétrier, D., Filter dissolution of C<sub>3</sub>S as a function of the lime concentration in a limited amount of lime water. *Cem. Concr. Res.* **1980**, *10* (4), 521-534.
- (22) Jennings, H. M., Aqueous solubility relationships for two types of calcium silicate hydrate. *J. Am. Ceram. Soc.* **1986**, *69* (8), 614-618.
- (23) Thomas, J. J.; Jennings, H. M.; Chen, J. J., Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement. *J. Phys. Chem. C* **2009**, *113* (11), 4327-4334.
- (24) Nicoleau, L.; Nonat, A.; Perrey, D., The di-and tricalcium silicate dissolutions. *Cem. Concr. Res.* **2013**, *47*, 14-30.
- (25) Alizadeh, R.; Raki, L.; Makar, J. M.; Beaudoin, J. J.; Moudrakovski, I., Hydration of tricalcium silicate in the presence of synthetic calcium-silicate-hydrate. *J. Mater. Chem.* **2009**, *19* (42), 7937-7946.
- (26) Scheetz, B.; Tikalsky, P.; Badger, S. In *Control of the microstructure of concrete: a case for nanometer-sized seeding*, Proceedings of the 11th International Congress on the Chemistry of Cement, ed. G. Grieve and G. Owens, Durban, South Africa, **2003**; pp 1692-1699.
- (27) Bentz, D. P.; Barrett, T.; De la Varga, I.; Weiss, W. J., Relating compressive strength to heat release in mortars. *Adv. Civ. Eng. Mater.* **2012**, *1* (1), 14.
- (28) Kumar, A.; Oey, T.; Kim, S.; Thomas, D.; Badran, S.; Li, J.; Fernandes, F.; Neithalath, N.; Sant, G., Simple methods to estimate the influence of limestone fillers on reaction and property evolution in cementitious materials. *Cem. Concr. Comp.* **2013**, *42*, 20-29.
- (29) Skapa, R., *Optimum sulfate content of portland cement*. PhD Dissertation, University of Aberdeen, Scotland, **2009**.
- (30) Kumar, A. *Modelling Hydration Kinetics of Cementitious Systems*. PhD Dissertation, École Polytechnique Fédérale de Lausanne, Switzerland, **2012**.
- (31) Sato, T.; Diallo, F., Seeding effect of nano-CaCO<sub>3</sub> on the hydration of tricalcium silicate. *Trans. Res. Rec.* **2010**, *2141* (1), 61-67.
- (32) Oey, T.; Kumar, A.; Bullard, J. W.; Neithalath, N.; Sant, G., The filler effect: the influence of filler content and surface area on cementitious reaction rates. *J. Am. Ceram. Soc.* **2013**, *96* (6), 1978-1990.
- (33) Matschei, T.; Lothenbach, B.; Glasser, F., The AFm phase in Portland cement. *Cem. Concr. Res.* **2007**, *37* (2), 118-130.
- (34) Lothenbach, B.; Le Saout, G.; Gallucci, E.; Scrivener, K., Influence of limestone on the hydration of Portland cements. *Cem. Concr. Res.* **2008**, *38* (6), 848-860.
- (35) Kumar, A.; Oey, T.; Falla, G. P.; Henkensiefken, R.; Neithalath, N.; Sant, G., A comparison of intergrinding and blending limestone on reaction and strength evolution in cementitious materials. *Const. Build. Mater.* **2013**, *43*, 428-435.
- (36) Lyse, I., *Tests on consistency and strength of concrete having constant water content*. Proceedings of the American Society for Testing and Materials, 32 (Paper: 60), **1932**, 629-636.
- (37) Gallucci, E.; Zhang, X.; Scrivener, K., Effect of temperature on the microstructure of calcium silicate hydrate (CSH). *Cem. Concr. Res.* **2013**, *53*, 185-195.