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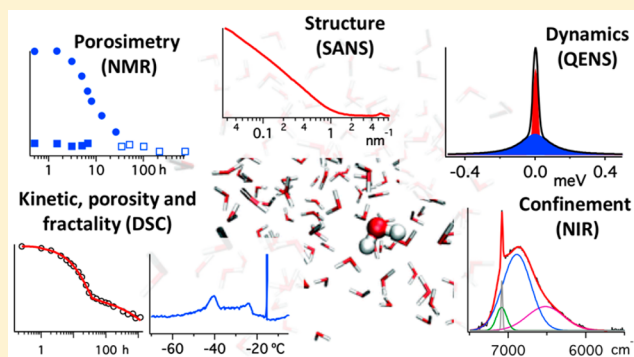
# Water as a Probe of the Colloidal Properties of Cement

Francesca Ridi,<sup>†</sup> Monica Tonelli,<sup>†</sup> Emiliano Fratini,<sup>\*,†</sup> Sow-Hsin Chen,<sup>‡</sup> and Piero Baglioni<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry “Ugo Schiff” and CSGI, University of Florence, via della Lastruccia 3-Sesto Fiorentino, I-50019 Florence, Italy

<sup>‡</sup>Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

**ABSTRACT:** Cement is produced by mixing mineral phases based on calcium silicates and aluminates with water. The hydration reaction of the mixture leads to a synthetic material with outstanding properties that can be used as a binder for construction applications. Despite the importance of cement in society, for a long time, the chemical reactions involved in its hydration remained poorly understood as a result of the complexity of hydration processes, nanostructure, and transport phenomena. This feature article reviews the recently obtained results using water as a probe to detail the essential features in the setting process. By examining the peculiar physicochemical properties of water, fundamental information on the evolving inorganic colloid matrix can be deduced, ranging from the fractal nanostructure of the inorganic silicate framework to the transport phenomena inside the developing porosity. A similar approach can be transferred to the investigation of a plethora of other complex systems, where water plays the main role in determining the final structural and transport properties (i.e., biomaterials, hydrogels, and colloids).



## 1. INTRODUCTION

The discovery of the pozzolanic reaction of volcanic materials mixed with lime and water was boasted as one of the most revolutionary innovations in history. Before the Romans, other ancient civilizations used nonhydraulic binders to build long-lasting structures such as the Great Wall in China and the Egyptian pyramids. The incredible benefits related to the addition of pozzolan to lime were the ability to set without the presence of carbon dioxide, even under water, and the impressive increase in mechanical properties. These characteristics enabled the construction of the renowned Roman aqueducts, bridges, and many other architectural structures that enormously contributed to the expansion of the Roman Empire. In modern times, three fundamental developments improved the Roman recipe for cement: the introduction of gypsum that avoids flash setting; the higher temperatures used to fire the raw materials, allowing for a more rapid setting process; and the advancement of the grinding process to increase the specific surface area available to hydration, which improves the setting process. With these changes, at the end of the XVIII century, modern Portland cement was finally formulated, and that original recipe (with few refinements) is still the most used hydraulic binder for building purposes.<sup>1</sup> Cement is a complex solid that is both structurally and chemically heterogeneous. The chemical and mineralogical composition of cement formulations is variable, depending on the composition of the raw materials extracted from quarries and on the addition of extra components aimed at tuning its reactivity. With the advancement in technical knowledge, the ordinary Portland cement composition has been modified,

producing several types of cements with different properties, to match specific applications. Today, a plethora of hydraulic cements are known and categorized. A summary of the most relevant is reported in Table 1. The compositions and properties of these systems are very different to cover very different applications ranging from building materials<sup>2,3</sup> to cement for biomedical purposes such as bone repair and orthodontics.<sup>4</sup> Currently, magnesium-based cements are suited for specialist applications to take advantage of their potential for CO<sub>2</sub> emission reduction. However, the high cost of the raw materials and the final pH not sufficiently high to passivate steel reinforcing bars limit their use and the possibility of replacing ordinary Portland cements.<sup>3</sup> Considering the field of cements for structural applications, magnesium silicate cement is an emerging material that finds application in the encapsulation of problematic radioactive wastes.<sup>5–7</sup> In addition, magnesium silicate cement is significant from a physicochemical point of view. Specifically, upon contact with water, it develops a hydrated phase (magnesium silicate hydrate, M–S–H) that is analogous to calcium silicate hydrate (C–S–H), the main binder of Portland cement. Therefore, cation substitution produces significant modifications in both the properties and structure of the hydrated phase.<sup>8,9</sup>

Water is one of the initial components of a cement paste and is progressively consumed during the development of the hydration products during the curing process. Therefore, the observation

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Table 1. Classification of Hydraulic Cements Based on Their Applications and Some of Their Main Hydration Reactions

construction and building applications		biomedical applications <sup>10</sup>	
material	main hydration reactions	material	main hydration reactions
Portland cement	$\text{Ca}_3\text{SiO}_5 + (1.3 + x)\text{H}_2\text{O} \rightarrow (\text{CaO})_{1.7}\text{SiO}_2(\text{H}_2\text{O})_x + 1.3\text{Ca}(\text{OH})_2$	calcium phosphate	apatitic cements: $3\alpha\text{-Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} \rightarrow \text{Ca}_9(\text{PO}_4)_5\text{HPO}_4\text{OH}$
	$\text{Ca}_2\text{SiO}_4 + (0.3 + x)\text{H}_2\text{O} \rightarrow (\text{CaO})_{1.7}\text{SiO}_2(\text{H}_2\text{O})_x + 0.3\text{Ca}(\text{OH})_2$		brushite-based cements: $\beta\text{-Ca}_3(\text{PO}_4)_2 + \text{Ca}(\text{H}_2\text{PO}_4)_2\text{H}_2\text{O} + 7\text{H}_2\text{O} \rightarrow 4\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$
	$2\text{Ca}_3\text{Al}_2\text{O}_6 + 12\text{H}_2\text{O} \rightarrow (\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$		$\beta\text{-Ca}_3(\text{PO}_4)_2 + \text{H}_3\text{PO}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$
Portland cement blends	$\text{Ca}_3\text{Al}_2\text{O}_6 + 3\text{CaSO}_4\cdot(\text{H}_2\text{O})_2 + 26\text{H}_2\text{O} \rightarrow (\text{CaO})_6\text{Al}_2\text{O}_3(\text{SO}_4)_3(\text{H}_2\text{O})_{32}$	calcium sulfate	$\text{CaSO}_4\cdot 0.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O}$
	$\text{Ca}_3\text{SiO}_5 + (1.3 + x)\text{H}_2\text{O} \rightarrow (\text{CaO})_{1.7}\text{SiO}_2(\text{H}_2\text{O})_x + 1.3\text{Ca}(\text{OH})_2$		$\text{CaSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O}$
	$\text{Ca}_2\text{SiO}_4 + (0.3 + x)\text{H}_2\text{O} \rightarrow (\text{CaO})_{1.7}\text{SiO}_2(\text{H}_2\text{O})_x + 0.3\text{Ca}(\text{OH})_2$		
magnesium phosphate cements	$2\text{Ca}_3\text{Al}_2\text{O}_6 + 12\text{H}_2\text{O} \rightarrow (\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$	calcium silicate	$\text{Ca}_3\text{SiO}_5 + (1.3 + x)\text{H}_2\text{O} \rightarrow (\text{CaO})_{1.7}\text{SiO}_2(\text{H}_2\text{O})_x + 1.3\text{Ca}(\text{OH})_2$
	$\text{Ca}_3\text{Al}_2\text{O}_6 + 3\text{CaSO}_4\cdot(\text{H}_2\text{O})_2 + 26\text{H}_2\text{O} \rightarrow (\text{CaO})_6\text{Al}_2\text{O}_3(\text{SO}_4)_3(\text{H}_2\text{O})_{32}$		
magnesium silicate hydrate cements	$2\text{MgO} + 2\text{NH}_4\text{H}_2\text{PO}_4 + 10\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{MgPO}_4\cdot 6\text{H}_2\text{O}$	magnesium phosphate	$2\text{MgO} + 2\text{NH}_4\text{H}_2\text{PO}_4 + 10\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{MgPO}_4\cdot 6\text{H}_2\text{O}$
magnesium oxychloride (Sorel) cements	$x\text{MgO} + y\text{H}_2\text{O} + \text{SiO}_2 \rightarrow (\text{MgO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_y$	magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2 + (\text{NH}_4)_2\text{HPO}_4 + 15\text{H}_2\text{O} \rightarrow 2\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O} + \text{MgHPO}_4\cdot 3\text{H}_2\text{O}$
	$3\text{MgO} + \text{MgCl}_2 + 11\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2\cdot \text{MgCl}_2\cdot 8\text{H}_2\text{O}$		
calcium sulfoaluminate cements	$(\text{CaO})_4(\text{Al}_2\text{O}_3)_3(\text{SO}_3) + \text{CaSO}_4 + 38\text{H}_2\text{O} \rightarrow (\text{CaO})_6\text{Al}_2\text{O}_3(\text{SO}_3)_3(\text{H}_2\text{O})_{32} + 4\text{Al}(\text{OH})_3$		
alkali-activated cements <sup>10–12</sup>	$\text{CaO} - \text{SiO}_2 - \text{MgO} - \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \text{ (activated with NaOH)} \rightarrow (\text{CaO})_y\text{SiO}_2(\text{H}_2\text{O})_x + (\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}) + \text{CaCO}_3 + \text{AFm phases}$		

76 of the physicochemical properties of water during hydration  
 77 allows monitoring of the reaction kinetics and structural/  
 78 dynamical features that are difficult to investigate by examining  
 79 the large number of products formed during the setting process.  
 80 The chemical reactions that form hydrated binding phases start  
 81 with a dissolution process, followed by the nucleation and growth  
 82 of hydrated phases, and continue until the rate of the reaction is  
 83 limited by the diffusion of water into the growing phases. These  
 84 two latter stages are responsible for the final cement properties.  
 85 Furthermore, cement is an exemplary system because most of the  
 86 characterization methods detailed in this feature article can be  
 87 applied to study different microporous and mesoporous water-  
 88 containing materials to obtain information on their properties.  
 89 In the following paragraphs, we will outline the major results  
 90 achieved using a multitechnique approach to monitor cement  
 91 characteristics at different length and time scales using water as  
 92 an in situ probe.

## 2. HYDRATION KINETICS

93 The hydration kinetics have a direct impact on the evolution of  
 94 the hydrated cement microstructure, which in turn influences the  
 95 mechanical properties and durability of the concrete, affecting  
 96 important characteristics such as strength, elastic moduli, tough-  
 97 ness, diffusivity, and permeability to liquids and gases.<sup>13</sup> The  
 98 complex reactions taking place between the anhydrous phases  
 99 and water can be considered to be the main cause of the setting  
 100 and hardening of cement pastes, and because of their exothermic  
 101 nature, the hydration process is usually monitored using calori-  
 102 metry, such as heat of solution calorimetry, semiadiabatic–  
 103 adiabatic calorimetry, and isothermal conduction calorimetry  
 104 (IC). From an industrial point of view, IC is probably the most  
 105 used technique to access the hydration kinetics in the cement  
 106 research field. However, this approach presents some drawbacks  
 107 because the hydration process can be followed only during the

early stage of hydration. A few days after mixing, the evolved heat  
 becomes too low to be distinguished from the instrumental  
 baseline, which prevents the use of IC in the case of slowly curing  
 cement formulations, such as those containing retarding agents.  
 To overcome this limit, we proposed an alternative method  
 based on differential scanning calorimetry (DSC),<sup>14,15</sup> where  
 the evolution of unreacted water can be quantified in terms of a  
 free or freezable water index (FWI).<sup>14,16</sup> In this approach,  
 cement pastes are periodically frozen at  $-60^\circ\text{C}$  and then melted  
 at a constant rate. Figure 1 shows the decrease in time of the

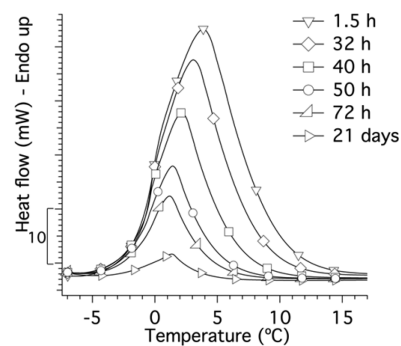


Figure 1. Evolution of the melting enthalpy of water during the hydration of a Portland cement sample ( $w/c = 0.4$ ).

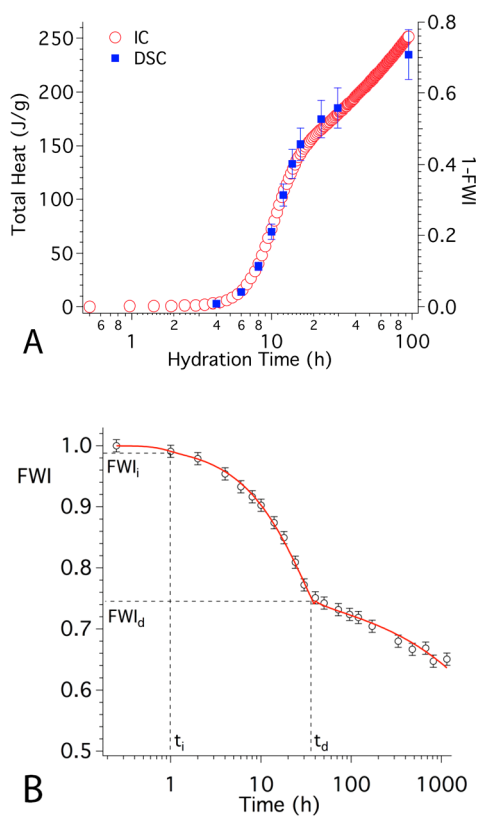
melting peak of the free, still unreacted, water for a Portland  
 cement paste.

The ice melting peak is integrated to extract the melting  
 enthalpy  $\Delta H_{\text{exp}}$  of water and to calculate the FWI

$$\text{FWI} = \frac{\Delta H_{\text{exp}}}{\phi_w \Delta H_{\text{theor}}} \quad (1)$$

123 where  $\phi_w$  is the original weight fraction of water in the paste and  
 124  $\Delta H_{\text{theor}}$  is the theoretical melting enthalpy of water (333.4 J/g).  
 125 In the original paper,<sup>14</sup> it was proven that FWI results are not  
 126 affected by freeze–thaw damage expansion taking place during  
 127 the DSC measurements.

128 Moreover, some of the authors<sup>15</sup> showed that hydration  
 129 kinetics obtained by DSC (see, for example, Figure 2B) fully



**Figure 2.** (A) Comparison between DSC and IC data monitoring of the hydration process of a tricalcium silicate paste ( $w/c = 0.4$ ). Reproduced with permission from ref 15. (B) Hydration kinetics of a MgO/SiO<sub>2</sub> paste reported as FWI vs time. Black markers represent the experimental data; the red line represents the global fitting curves according to the BNGM + diffusional model. Adapted with permission from ref 28.

130 agree with those achieved from the IC technique on the very  
 131 same cement paste (Figure 2A). Because DSC is based on  
 132 discrete measurements, it is not limited by the evolved heat or  
 133 baseline stability allowing the acquisition of data until the very  
 134 end of the hydration process. Similar to IC, the DSC technique is  
 135 able to capture the effect of parameters such as the water/cement  
 136 ratio or temperature on the hydration kinetics.

137 Kinetic analysis was used to obtain information on activation  
 138 energies and rate constants of the developing hydrated phases.  
 139 The hydration of cement powders is a complex multistage pro-  
 140 cess with a well-known scheme: an initial hydration process,  
 141 when the wetting of highly hygroscopic particles occurs; an  
 142 induction period, when the reaction is quiescent; an accelera-  
 143 tion period, when the nucleation and growth processes greatly  
 144 increase the rate of the hydration reaction and the formation of  
 145 several colloidal phases; a deceleration period; and finally, a  
 146 diffusional period, where the reaction proceeds at a slower rate  
 147 and the rate-limiting process is the diffusion of water through the  
 148 hydrated products toward the anhydrous cores.<sup>11,15,17,18</sup> In past  
 149 decades, the nucleation and growth stage taking place during the

hydration of tricalcium silicate (C<sub>3</sub>S) was modeled using Avrami-  
 Erove'ev (AE) kinetic law<sup>19–22</sup> to extract the rate constants of the  
 processes. In this framework, the DSC method was applied to  
 investigate the effect of some of the most used cement additives,  
 using the AE law for the acceleration period and a three-  
 dimensional diffusion equation for the final part of the FWI  
 curve.<sup>16</sup> More recently, some authors noted that the AE equation  
 cannot completely explain the cement hydration process. Above  
 all, the assumption that the probability of nucleation of the  
 hydrating phases is the same elsewhere is not appropriate  
 because it is commonly accepted that it occurs preferentially at  
 the grain boundaries.<sup>23</sup> The boundary nucleation and growth  
 model (BNGM) derived by Thomas overcomes this inconsis-  
 tency.<sup>24,25</sup> This model, which was originally developed for  
 solid-phase transformation,<sup>26</sup> can properly describe the process  
 of cement hydration, even using fewer parameters than in the AE  
 model. BNGM describes the hydration kinetics with two  
 independent rate constants:  $k_B$ , which “describes the rate at  
 which the surfaces become covered with hydration product” and  
 $k_G$ , which is the “rate at which the pore space between the  
 particles fills in with product”.<sup>24,25</sup> Then, the original BNGM  
 approach developed for IC was modified to directly analyze the  
 time evolution of FWI as accessed by the DSC protocol.  
 In particular, an extra independent parameter was added to  
 estimate the fraction of unreacted water, and any assumption on  
 the hydration reaction stoichiometry was avoided. It was shown  
 that the application of the model on kinetic profiles obtained by  
 IC and DSC provides comparable results, which further validates  
 the FWI approach.<sup>15</sup> Therefore, DSC was applied by our group  
 to investigate the effects of particle size, temperature,<sup>15</sup> and  
 additive addition<sup>27</sup> on the hydration reaction in cement pastes  
 even for very long processes, such as those obtained with the  
 so-called superplasticizing additives.

Some of the authors of this article recently proposed the  
 application of BNGM<sup>25</sup> combined with a three-dimensional  
 diffusional model to quantitatively describe the nucleation and  
 growth processes during the hydration of the new green cements  
 based on MgO/SiO<sub>2</sub> formulations.<sup>28</sup> Figure 2B shows the FWI vs  
 time for the MgO/SiO<sub>2</sub> sample together with the best-fit curve  
 obtained using the BNGM + diffusional combined model. The  
 model accurately describes all three hydration periods. The curve  
 shows the short initial induction period lasting until  $t_i$  is reached,  
 where FWI remains  $\sim 1$ ; the nucleation and growth period, with  
 a consistent decrease in FWI, which lasts up to  $\sim 40$  h; and  
 the final diffusional period, starting at time  $t_d$  where the change  
 in the curve slope suggests that the rate-limiting step becomes a  
 diffusion-limited process, similar to the Portland case. These  
 results agree with <sup>1</sup>H NMR relaxometry that follows the kinetics  
 using the evolution of the transverse ( $T_2$ ) spin relaxation time  
 signal in MgO/SiO<sub>2</sub> pastes.<sup>29</sup>

The kinetics profiles associated with a curing cement paste  
 simply detail the overall hydration reaction. During the different  
 stages, the hydrated phases develop to yield the well-known  
 porous structure, which is typical for cement systems. The  
 characterization of the pore structure (i.e., total porosity, pore  
 size distribution, and eventually specific surface area) is one of  
 the key factors in the prediction of the final performances of  
 cement. For example, it is known that a highly durable cement/  
 concrete will have mostly gel pores (<5 nm) hydraulically  
 isolated from each other.<sup>30–32</sup> However, accessing the porosity in  
 detail is not trivial because of the complexity of the pore size  
 distribution, which, in the case of a cement paste, ranges from a  
 few nanometers to tens of micrometers, and even because many



213 techniques require a dried sample with possible changes in the  
 214 original porous structure. For these given reasons, experimental  
 215 techniques that do not need a drying step (i.e., DSC, small-angle  
 216 scattering, nuclear magnetic resonance, etc.) have a significant  
 217 advantage with respect to all others (i.e., gas sorption, mercury  
 218 intrusion, electron microscopy, etc.).

### 3. POROSITY AND FRACTALITY OF HYDRATING PHASES

220 Thermoporometry enables the characterization of a porous  
 221 material, i.e., pore sizes, by analyzing the conditions of the solid–  
 222 liquid phase transition of a condensate inside a porous matrix.<sup>33</sup>  
 223 The method relies on the experimental evidence that when a  
 224 pure substance is confined in nanometric cavities the equilibrium  
 225 conditions of its solid, liquid, and gas phases depend on the  
 226 curvature of the interface.<sup>34</sup> Therefore, the solidification/melting  
 227 temperature of a liquid confined in a porous material changes  
 228 with the size of the pores, and the energy involved in the phase  
 229 transition is directly related to the pore volume, assuming that  
 230 the liquid saturates all of the porosity. Furthermore, thermo-  
 231 porometry can also provide information on the shape of the  
 232 pores by comparing the cooling and heating thermograms  
 233 obtained in the temperature range from ambient to  $-80\text{ }^{\circ}\text{C}$  (low-  
 234 temperature differential scanning calorimetry, LTDSC).<sup>33,35–38</sup>  
 235 LTDSC was used to characterize the porosity of cement.<sup>39–45</sup>

236 Bager and Sellevold investigated the formation of ice in mature  
 237 Portland cement, evaluating the effect of different moisture con-  
 238 tents, drying, and resaturation in the volume of large (capillary)  
 239 and small pores.<sup>39–41</sup> Later, Bentz investigated the percola-  
 240 tion of capillary porosity, which is of utmost importance in  
 241 the transport properties and durability of cement structures.<sup>42</sup>  
 242 More recently, our group investigated the properties of water  
 243 confined in hydrating cement pastes,<sup>43</sup> showing that LTDSC  
 244 thermograms can be fully explained considering the C–S–H  
 245 microstructure, as described in Jennings' colloidal model II<sup>46</sup>  
 246 (see next paragraph). LTDSC allows us to investigate matrixes  
 247 with saturated porosity and can be used to estimate the volume of  
 248 the meso/macroporosity, the depercolation threshold of  
 249 capillary porosity (i.e., the separation of capillary pores due to  
 250 the growth of hydrated phases or in other words the porosity  
 251 whereby the volume fraction of connected pores in the cement  
 252 paste decreases to zero), and the fractal dimension of hydrated  
 253 cementitious samples, with results compatible with those  
 254 obtained using more sophisticated techniques such as small-  
 255 angle neutron or X-ray scattering. For example, an in-depth  
 256 LTDSC investigation evidenced the differences in the micro-  
 257 structure and porosity among  $\text{C}_3\text{S}$  pastes hydrated in pure water  
 258 and in the presence of organic superplasticizers (i.e., poly-  
 259 carboxylic backbone with grafted PEO chains) used in advanced  
 260 cement formulations.<sup>44</sup>

261 The DSC heating scan, as reported in Figure 3A, shows a  
 262 single hump in the  $-50\text{ }^{\circ}\text{C}/0\text{ }^{\circ}\text{C}$  temperature range as a direct  
 263 consequence of the pore size distribution of cement micro-  
 264 structure spanning from the nanometer to micrometer scale.  
 265 During heating, melting of the ice progressively occurs from the  
 266 fractions confined in the smallest cavities to the fractions present  
 267 in the largest ones, thus generating the hump. Conversely, the  
 268 freezing process occurs in a discontinuous way, and the cooling  
 269 scan shows specific peaks (e.g., Figure 3B). This peculiar  
 270 behavior is usually attributed to the combination of homoge-  
 271 neous and heterogeneous freezing mechanisms. The homoge-  
 272 neous nucleation is an activated process where a free-energy  
 273 barrier must be overcome for a critical crystallization nucleus to

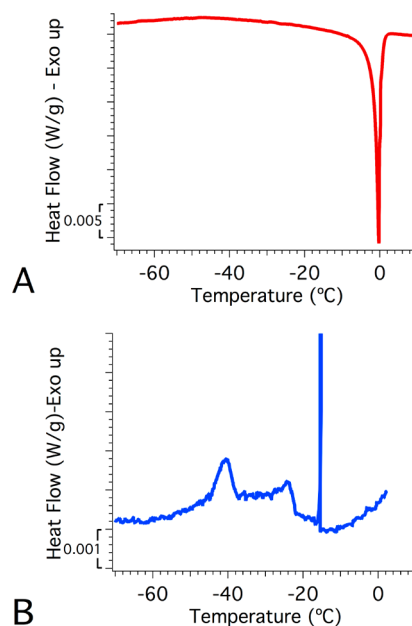


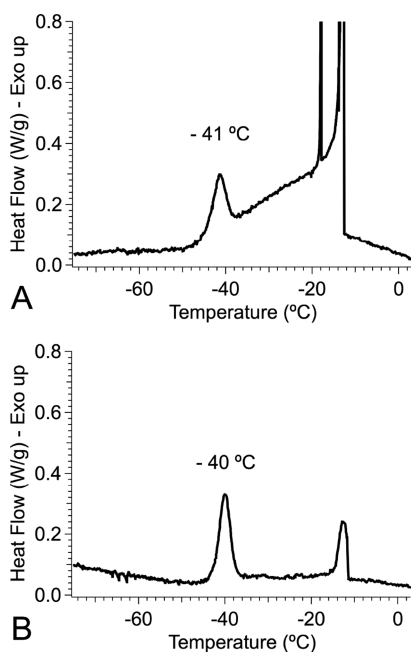
Figure 3. Heating (A) and cooling (B) scans recorded using LTDSC on a cementitious sample saturated with water. Adapted with permission from ref 44.

274 appear. Thus, the heterogeneous nucleation preferentially occurs  
 275 because the energy required by this process is smaller. According  
 276 to the molecular dynamics (MD) study on homogeneous ice  
 277 nucleation,<sup>47</sup> at a low degree of supercooling ( $-20\text{ }^{\circ}\text{C} < T < 277$   
 278  $0\text{ }^{\circ}\text{C}$ ), only heterogeneous nucleation is possible because of the  
 279 high free energy required for the homogeneous formation of a  
 280 critical nucleus (at  $T \approx -15\text{ }^{\circ}\text{C}$ , diameter  $\approx 8\text{ nm}$  corresponding  
 281 to  $\sim 8000$  molecules). For this reason, in a saturated system,  
 282 water freezes via heterogeneous nucleation even if it is confined  
 283 in cavities with dimensions that are large enough to host critical  
 284 nuclei isolated from the surface. Once the water in the large pores  
 285 (capillary pores) is frozen, the ice remains in contact with the  
 286 liquid water still present in the smaller cavities. By lowering the  
 287 temperature to below  $-20\text{ }^{\circ}\text{C}$ , the size of the critical cluster  
 288 sensibly decreases (at  $T \approx -35\text{ }^{\circ}\text{C}$ , diameter  $\approx 3.5\text{ nm}$  corre-  
 289 sponding to  $\sim 600$  molecules), and the nucleation free energy  
 290 barrier decreases, making the homogeneous process likely to  
 291 occur. Under these conditions, both the homogeneous and  
 292 heterogeneous nucleation mechanisms become accessible at  
 293 comparable rates. Then, freezing will occur in the pores whose  
 294 dimensions can host a critical ice cluster that is stable at that  
 295 temperature. However, the appearance of peaks in the cooling  
 296 curve indicate that the process starts at the pore entrance, where  
 297 the liquid water is in contact with the surrounding ice, which is a  
 298 preferential site for the nucleation. The dimensional range of  
 299 these freezing pores must be comparable to the size of their  
 300 entrance because, for the reasons given before, the water in larger  
 301 pores is already frozen at this stage, and the smaller pores cannot  
 302 host a critical ice nucleus. In the case of cement pastes, the  
 303 developing phases originate from three classes of nanometric  
 304 porosities on top of the capillary porosity. According to Jennings'  
 305 colloidal model II,<sup>46</sup> these are named the interlayer lamellar  
 306 porosity (IGP,  $<1\text{ nm}$ ), small gel pores (SGP,  $1\text{--}3\text{ nm}$ ), and large  
 307 gel pores (LGP,  $3\text{--}12\text{ nm}$ ). The water inside the lamellar IGP  
 308 of the primary unit cannot freeze (see paragraph on LTDSC),  
 309 and thus it cannot be detected using DSC. By integrating each  
 310 peak in the cooling scan (e.g., Figure 3B), the amount of water

311 contained in different classes of pores (SGP, LGP, and capillary)  
 312 can thus be obtained after considering the variation with  
 313 temperature of the standard enthalpy of the fusion of ice.<sup>48</sup>

314 It is important to stress here that, in addition to pore size  
 315 effects, the heterogeneous behavior of water crystallization at  
 316 low  $T$  can also be partially ascribed to the different chemical  
 317 environments experienced by the water molecules. Using the  
 318 reactive force field MD method, Hou et al.<sup>49</sup> demonstrated  
 319 that water molecules, which are confined in the nanopores of the  
 320 C–S–H gel, show heterogeneity in the structure and dynamic  
 321 behavior, respectively. Water molecules near the surface can react  
 322 with the high-energy nonbridging oxygen atoms, producing  
 323 Si–OH and Ca–OH (i.e., chemically bound water in the  
 324 developing C–S–H phase). Water molecules that are approx-  
 325 imately 1 nm away from the chemically bound water (i.e., close to  
 326 the surface) have a higher arrangement, longer exchange time,  
 327 and lower diffusion coefficient than bulk water because of both  
 328 the strong H-bond with oxygen atoms in silicate chains and the  
 329 ionic effect induced by the highly concentrated surface calcium  
 330 ions.<sup>49–51</sup> Because of the strong hydrophilic effect from the  
 331 C–S–H surface, more energy is needed for the surface-adsorbed  
 332 water molecules to overcome the energy barrier to transform into  
 333 ice crystals. This restriction is particularly pronounced for the  
 334 water molecules confined in the nanometer pores. Moreover,  
 335 the chemical composition of the C–S–H gel is also very  
 336 important for influencing the thermodynamic behavior of gel  
 337 pore water molecules.<sup>52</sup> Even if the pore size is the same,  
 338 C–S–H with a lower Ca/Si ratio can reduce the diffusion rate of  
 339 the interlamellar pore water to a greater extent because the  
 340 protruded bridging tetrahedron has a higher tendency to disturb  
 341 the transport channel that exists in the gel porosity.

342 The LTDSC method is useful for studying the porosity  
 343 of samples containing water regardless of their composition.  
 344 For example, Figure 4 shows two thermograms obtained from



**Figure 4.** LTDSC cooling scans recorded on (A) MgO/SiO<sub>2</sub> paste and (B) Portland cement paste; both with  $w/c = 2$ , hydrated for 28 days and saturated with water. Adapted with permission from ref 103.

345 cementitious samples hydrated for 28 days whose composition is  
 346 very different from the standard one (i.e., the water/solid ratio,

$w/c$ , is 2 instead of 0.4). In particular, Figure 4A shows the  
 cooling scan of MgO/SiO<sub>2</sub>; the shape of the curve indicates that,  
 similar to C–S–H-containing matrixes, this sample has a fraction  
 of water confined in large (capillary) pores where the liquid can  
 freeze via heterogeneous nucleation, and another fraction that is  
 confined in smaller pores gives rise to the large bump between  
 $-20$  and  $-35$  °C and to the sharp peak at  $-41$  °C. Figure 4B  
 shows Portland cement hydrated for the same time and with the  
 same  $w/c$ : the thermogram shows that when the amount of  
 water is high, only the capillary porosity remains, together with  
 the porosity in the 1–3 nm range (SGP), which is a structural  
 characteristic of the Portland-based samples. The significant  
 difference existing between the two thermograms (in the region  
 of  $-20$  °C/ $-40$  °C) can be further understood by considering  
 the difference existing in the structure and the enclosed porosity  
 of the two main hydration products (M–S–H and C–S–H), as  
 we will discuss later in this article.

As already mentioned, the pore size distribution,  $P(r)$ , deter-  
 mines the hump in the heating part of the thermogram. Thus, in  
 principle, it should contain information on the fractal arrange-  
 ment of the cementitious matrix, which is the result of how the  
 primary units are assembled into the volume generating the  
 porosity of the hydrated phase. Mass and surface fractal dimen-  
 sions ( $D_m$ ,  $D_s$ , respectively) are usually obtained using small-  
 angle scattering techniques, as reported in the literature for  
 various cement pastes.<sup>53–55</sup> The fractal nature of porous matrixes  
 can also be determined using DSC by relying on the fact that the  
 melting temperature of an ice crystal confined in a pore of radius  
 $R$  (with  $R = r - l$ , where  $r$  is the radius of the pore and  $l$  is the  
 thickness of the nonfreezable layer of water at the solid interface)  
 is depressed by a quantity  $\Delta T = T_m^0 - T_m$ . Previous estimations  
 from NMR measurements on porous glasses report a value for  $l$   
 of  $0.5 \pm 0.1$  nm.<sup>56</sup> This is the reason that the water confined in  
 IGP within the calcium silicate layers does not freeze, and the size  
 of these pores is approximately 1 nm. The Gibbs–Thomson  
 equation states that the melting temperature,  $T_m$ , and the pore  
 radius,  $R$ , are inversely related as follows

$$T_m = T_m^0 \left( \frac{1 - 2\gamma V_s}{\Delta H R} \right) \quad (2)$$

where  $T_m^0$  is the melting temperature of an ice crystal of infinite  
 dimension,  $\gamma$  is the solid–liquid interfacial tension,  $\Delta H$  is the  
 specific melting heat, and  $V_s$  is the specific volume of the solid.  
 Considering water (i.e.,  $T_m^0 = 273.15$  K,  $\gamma = 40 \times 10^{-3}$  N m<sup>-1</sup>,  
 $\Delta H = 334$  J g<sup>-1</sup>, and  $V_s = 1.02$  cm<sup>3</sup> g<sup>-1</sup>), eq 2 becomes

$$\Delta T = \frac{68.29}{R} \quad (3)$$

with  $R$  in nanometers.

When a water-saturated porous sample, with a pore size distri-  
 bution of  $P(r)$ , is heated from  $-80$  °C to room temperature, the  
 melting of the liquid confined in pores of progressively increasing  
 dimensions occurs. Then, the heat flux registered by DSC is  
 proportional to the incremental volume  $dV$  of the ice melting at  
 a given temperature,  $T_m$ . If the experimental heating rate is slower  
 than 2 °C/min, then the equilibrium conditions are satisfied<sup>57</sup> so  
 that the detected heat flow is independent of the heating rate and  
 its estimation is quantitative. The incremental pore volume per  
 solid mass can be written as  $dV = P(r) dr$ . To obtain  $dV$ , the  
 heating signal should be normalized by the total pore volume  $V_p$   
 obtained by integrating the melting peak, scaled by the bulk water  
 density value at 0 °C (0.9998 g/cm<sup>3</sup>). According to the

literature,<sup>57</sup> the heat flow,  $J_q$ , measured using DSC is related to  $\Delta T$  by a scaling law consistent with the fractal nature of the systems. The porous system can be regarded as a homogeneous solid of density  $\rho_s$ , where an incremental pore volume per solid unit mass  $dV$  was used to account for the change in the bulk density of the porous sample,  $\rho(r)$ , as a function of the pore-filling steps.<sup>58</sup> Mathematically, the process is described as

$$\frac{1}{\rho(r)} = \frac{1}{\rho_s} + \int_0^r P(r) dr \quad (4)$$

In the fractal regime, where  $a \leq r \leq \xi$ ,  $\rho(r)$  will scale with  $r$  as follows

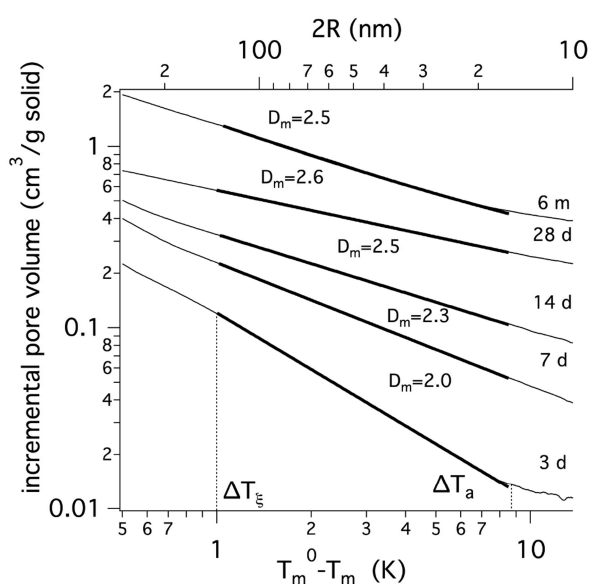
$$\rho(r) = \rho_s (r/a)^{D_m - 3} \quad (5)$$

where  $a$  is the characteristic dimension of the smallest repeating unit and  $\xi$  is the maximum correlation length of the fractal aggregate. Combining eqs 3 and 5,

$$dV = A(\Delta T)^{D_m - 3} \quad (6)$$

where  $A$  is the scaling factor.

Hence,  $D_m$  can be simply obtained from the fitting of the  $dV$  vs  $\Delta T$  log-log plots (Figure 5). This procedure enabled us to



**Figure 5.** Incremental pore volume per solid mass as a function of the melting depression,  $\Delta T = T_m^0 - T_m$  for a paste of  $C_3S$ /water during hydration. Reproduced with permission from ref 44.

investigate the effect of different superplasticizer on the fractality of  $C_3S$  pastes.<sup>44</sup> For example, Figure 5 shows the  $dV$  vs  $\Delta T$  log-log plots, and the fitting lines from  $\Delta T_\xi \cong 1$  K to  $\Delta T_a \cong 10$  K, corresponding to pores with a radius of between 100 and 10 nm (eq 3). The size range explored by DSC is very close to what is usually measured in a standard small-angle scattering experiment.

As is reported in Figure 5, a  $C_3S$ /water paste ( $w/c = 0.4$ ) has a fractal dimension that increases from 2.0 to 2.6 in the first 28 days of curing.<sup>44</sup> These results are in good agreement with previous SAXS investigations,<sup>53</sup> which reported  $D_m$  for a similar paste to vary from 1.9 to 2.8 in the same time interval. The same approach was also used on  $C_3S$ /water samples containing superplasticizers to highlight their effect on both C-S-H nanostructure and porosity. The  $D_m$  values for pastes cured for 1 month in the presence of superplasticizers resulted in lower values than in the

$C_3S$ /water case, indicating that the presence of superplasticizers causes the formation of a more open nanoscale structure with respect to a pristine sample.

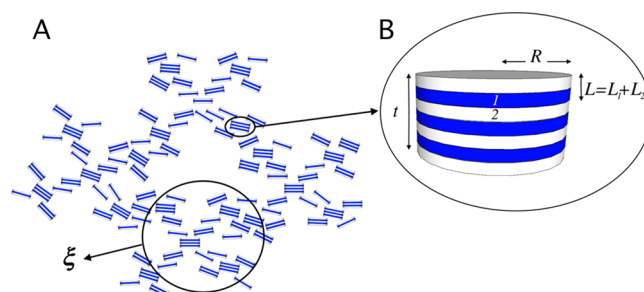
Even if the exact nanostructure of the C-S-H gel is still an active topic of research, Jennings colloidal model CM-II<sup>46,59</sup> represents one of the best micro/nanoscale descriptions reconciling the colloidal nature of cement-based systems with a large amount of experimental data available in the literature. Very recently, CM-II was used as a starting point to work out a detailed mathematical equation that is able to depict the hierarchy of pore sizes giving rise to the fractal structure property of the C-S-H phase,<sup>60</sup> even including the internal structure of the globule.<sup>61</sup> In general, the scattering intensity distribution related to an assembly of anisotropic units can be written as

$$I(Q) = N \langle \overline{P(Q)} \rangle S(Q)_c + \text{bkg} \quad (7)$$

where  $N$  is a scaling constant considering the number density and the probe interaction of the globules,  $\langle \overline{P(Q)} \rangle$  is the normalized intraparticle structure factor averaged over the distribution of the size and all possible orientations of the globules,  $S(Q)_c$  accounts for the interglobule structure factor coming from the fractal arrangement corrected for the polydispersity of the system,  $Q$  is the scattering vector, and bkg is the background term.  $\langle \overline{P(Q)} \rangle = \langle |F(Q)|^2 \rangle$  takes into account the internal layered structure of the primary globules (i.e.,  $F(Q)$  is the particle form factor; in the case of C-S-H, it describes the scattering of the disklike unit).<sup>60</sup> If the size, orientation, and position of the basic units are uncorrelated, then  $S(Q)_c = 1 + \beta(Q)[S(Q) - 1]$  with  $\beta(Q) = \langle |F(Q)|^2 \rangle / \langle |F(Q)|^2 \rangle$ . The interparticle structure factor for the fractal arrangement can be expressed as

$$S(Q) = 1 + \left( \frac{\xi}{R_c} \right)^{D_m} \Gamma(D_m + 1) \frac{\sin[(D_m - 1)\tan^{-1}(Q\xi)]}{(D_m - 1)[1 + (Q\xi)^2]^{[D_m - 1/2]}(Q\xi)} \quad (8)$$

where  $R_c(3\pi R^2 L/4)^{1/3}$  is the equivalent radius (where  $\bar{n}$  is average number of stacks in a disklike unit and  $R$  and  $L$  are defined in Figure 6) and  $D_m$  and  $\xi$  are the mass fractal and cutoff dimension of the aggregate, as already defined in the LT DSC section.



**Figure 6.** Interparticle (A) and intraparticle (B) structures associated with the fractal arrangement property of the disklike C-S-H units. Adapted with permission from ref 61.

This equation was used to model small-angle scattering curves (from either neutrons or X-rays) with the aim of unveiling the globule shape and size distribution as well as the fractal dimension and correlation distance characteristic of the overall arrangement in the case of the C-S-H phase. It turns out that the disklike shape of the globular unit assumed in CM-II is experimentally confirmed. This approach was used to investigate the effect of the water content<sup>61</sup> and of the addition of comb-shaped superplasticizers<sup>62</sup> on C-S-H synthetic phases.



481 The decrease in the water content from 30 to 10% caused the  
 482 shrinkage of the lamellar space characteristic of the IGP and  
 483 concurrently an increase in the mass fractal dimension from 2.58  
 484 to 2.75, which is associated with a reduction in the average  
 485 globule size from 18 to 12 nm.<sup>61</sup> Moreover, the addition of comb-  
 486 type superplasticizers resulted in an increase in the average  
 487 silicate chain length of the C–S–H building block that in the end  
 488 linearly translated into an increase in dimensions of the globule.<sup>62</sup>  
 489 Using the same approach, some of the authors were also able  
 490 to reconstruct the microstructure of synthetic M–S–H, the  
 491 principal binding phase in MgO-based cements. In the case of  
 492 M–S–H, the globule turned out to be spherical in shape, and  
 493 more importantly, when a mixed M–S–H/C–S–H system is  
 494 prepared, the two distinct morphologies are still present in the  
 495 sample,<sup>8</sup> evidencing that these hydrates are not compatible even  
 496 on the nanoscale. In both cases, a fractal arrangement of the  
 497 globules is retained. However, globules pack more compactly in  
 498 M–S–H but in a less extended way ( $\xi$ ), resulting in a greater  
 499 fractal exponent than in the C–S–H case. The intrinsic shape  
 500 difference between the two types of globules in C–S–H and  
 501 M–S–H gels also reflects in their morphology from submi-  
 502 crometer to micrometer levels and more importantly can be a key  
 503 parameter in understanding the different mechanical behavior of  
 504 the MgO-based cements with respect to the better-performing  
 505 CaO-based equivalent.

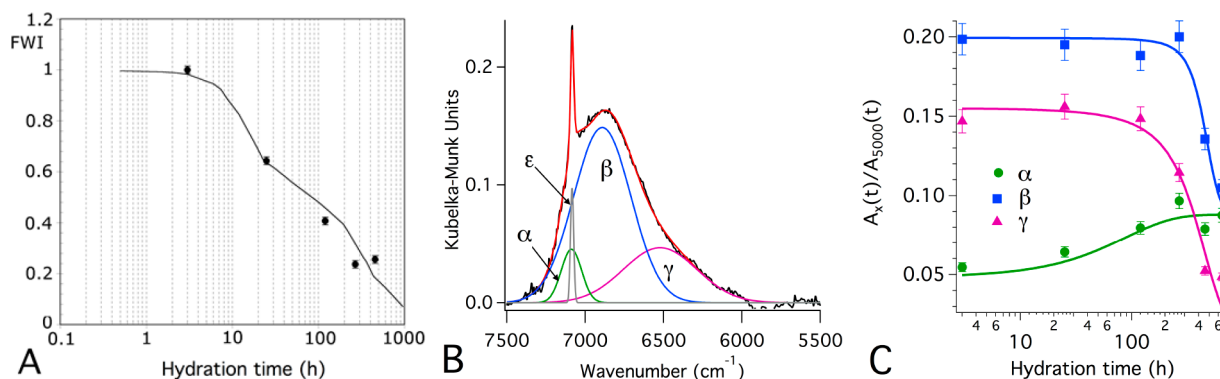
#### 4. STATE OF THE WATER: NEAR-INFRARED SPECTROSCOPY, NIR

507 The confinement and interaction of water within the host system  
 508 result in different types of water molecules being present in the  
 509 cement paste (i.e., bulklike, surface-interacting or constrained,  
 510 and structural). Near-infrared spectroscopy (NIR), which uses  
 511 wavenumbers from 14 000–4000  $\text{cm}^{-1}$ , provides information on  
 512 the vibrational modes of stretching and bending of bonds where  
 513 hydrogen is involved and, in particular, on the overtone and  
 514 combination vibrations.<sup>63</sup> The absorption bands in the NIR  
 515 region (and in particular the first overtone of the symmetric and  
 516 antisymmetric O–H stretching mode of water at  $\sim 7000 \text{ cm}^{-1}$ )  
 517 are excellent probes of the state of water because both the  
 518 strength and geometry of O–H bonds affect the frequency of  
 519 these peaks.<sup>64–66</sup> Moreover, because of the smaller extinction  
 520 coefficients with respect to IR, the analysis of samples containing  
 521 large amounts of water is feasible in the NIR region (i.e.,  
 522 saturation of the signal is not crucial). This characteristic enables

the direct analysis of bulk cementitious samples with  $w/c = 0.4$  or  
 even higher. The NIR technique, probing thin layers of the  
 samples, can provide information representative of the bulk  
 properties only if the specimen is well-homogenized. According  
 to the literature,<sup>67</sup> the absorption of water in the NIR region can  
 be attributed to two different classes of O–H oscillators, the  
 so-called weakly hydrogen bonded (WHB) and strongly  
 hydrogen bonded (SHB) oscillators. The SHB oscillator has a  
 broad absorption at lower wavenumbers, whereas the WHB  
 oscillator is sharper and centered at higher wavenumbers.  
 A significant increment of the WHB intensity is registered as a  
 result of the increase in temperature<sup>67</sup> or the increase in the  
 confinement effects due to a solid matrix.<sup>65</sup> The existence of two  
 classes of hydrogen bonds in a C–S–H/H<sub>2</sub>O system has also  
 been validated by MD simulations<sup>51</sup> showing that the structural  
 hydrogen bond (formed between silicate oxygen atoms and  
 water molecules) has a longer lifetime than the hydrogen bond  
 formed between neighboring water molecules. In the first case,  
 the hydrogen bond is more persistent even if the interaction with  
 the surface induces a change in the local water topology resulting  
 in a reduction in the number of hydrogen bonds<sup>68</sup> (i.e., WHB  
 the previous notation).

When applied to a hydrating tricalcium silicate paste,<sup>69</sup> the  
 NIR technique allowed the assessment of hydration kinetics  
 by monitoring the decrease with time in the intensity of the  
 5000  $\text{cm}^{-1}$  combination band: this trend follows the hydration  
 profile as obtained using DSC (Figure 7A). The time evolution  
 of the 7000  $\text{cm}^{-1}$  overtone band accounts for the evolution of  
 the two types of water coexisting in the matrix: the surface-  
 interacting and the bulklike water. The quantification of these  
 two species was possible by deconvoluting the 7000  $\text{cm}^{-1}$  band  
 into Gaussian components, as shown in Figure 7B. Figure 7C  
 shows that the two Gaussian peaks are directly connected to the  
 bulk water; the strongly hydrogen bonded (SHB, named  $\beta$  and  $\gamma$ )  
 component decreases in time, and the  $\alpha$  component, associated  
 with the surface-interacting water, weakly hydrogen bonded  
 (WHB) contribution, sensibly increases as a result of the  
 developing surface area.

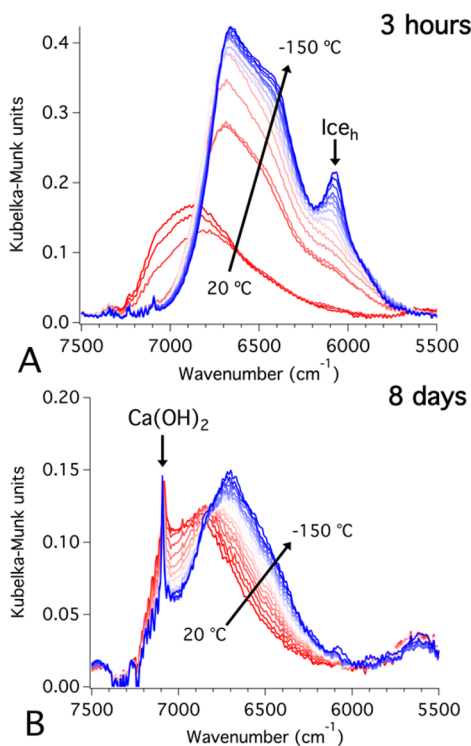
NIR spectroscopy is also particularly powerful in assessing the  
 state of the confined water. This is possible by taking advantage  
 of the temperature dependence of the NIR bands of water and  
 ice. The behavior of the hexagonal ice NIR bands with tem-  
 perature is well described in the literature, particularly for the  
 determination of the temperature of icy regions on remote



**Figure 7.** (A) Hydration kinetics of the C<sub>3</sub>S + water paste, as monitored by the 5000  $\text{cm}^{-1}$  peak area (black circles) compared to the FWI vs time curve obtained using DSC (line). (B) Deconvolution of the 7000  $\text{cm}^{-1}$  band of the sample C<sub>3</sub>S + water hydrated for 24 h at 20 °C: the  $\alpha$ ,  $\beta$ , and  $\gamma$  Gaussians account for the water, and the sharp  $\epsilon$  Gaussian is linked to the OH vibrations in Ca(OH)<sub>2</sub>. (C) Plot of the area vs time of the three Gaussian components describing the water contribution. Reproduced with permission from ref 69.



567 planets.<sup>70,71</sup> The NIR spectra registered in the 20/−150 °C  
568 temperature range on a hydrated sample containing bulk water  
569 ( $w/c = 0.4$ ) appears as shown in Figure 8A:<sup>43</sup> a sudden change in



**Figure 8.** NIR spectra acquired from −150 to +20 °C from cement paste cured for (A) 3 h and (B) 8 days. Reproduced with permission from ref 43.

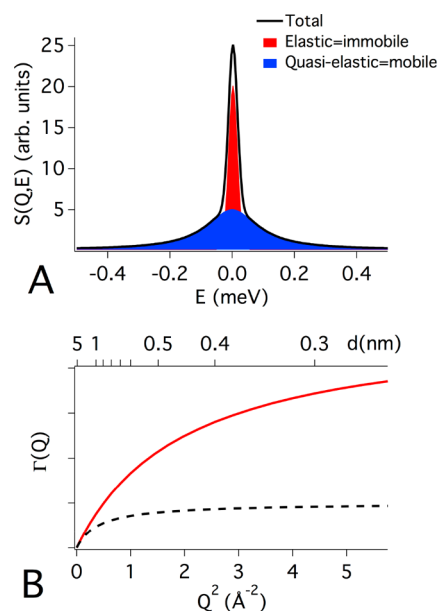
570 the shape of the 7000  $\text{cm}^{-1}$  band occurs when liquid water  
571 freezes, with a net red shift of the entire band and the appearance  
572 of a new band centered near 6080  $\text{cm}^{-1}$ , which is commonly  
573 considered to be a fingerprint of hexagonal ice. After a week, the  
574 trend in the spectra with temperature is similar to that shown in  
575 Figure 8B: the figure clearly shows that hexagonal ice formation is  
576 inhibited, indicating that water still present in the  $\text{C}_3\text{S}$  paste  
577 solidifies in an amorphous state. This is particularly interesting  
578 when compared to the LTDC experiments (section 3) because  
579 it indicates that water confined in the nanometric porosity of the  
580 cement matrix is not able to crystallize but solidifies in an  
581 amorphous state.

## 5. STATE OF THE WATER: WATER RELAXATION DYNAMICS

582  
583 **5.1. Quasi-Elastic Neutron Scattering.** Quasi-elastic  
584 neutron scattering (QENS) is a technique especially suited for  
585 the in situ investigation of relaxation dynamics of hydrogenated  
586 species, from the picosecond to nanosecond time scale  
587 corresponding to an energy window from a few  $\mu\text{eV}$  to tenths  
588 of a  $\text{meV}$ .<sup>72</sup> In complex systems containing water, this technique  
589 allows us to characterize the actual state of the water molecules  
590 from bulk/confined to completely immobile. QENS experi-  
591 ments on cementitious pastes are particularly informative about  
592 water dynamics because the incoherent scattering cross section  
593 of hydrogen is 10 times larger than that of other elements con-  
594 stituting the cement powder (oxygen, calcium, aluminum, iron,  
595 and silicon).<sup>21,73</sup> Thus, the QENS signal from a cement paste is  
596 dominated by the hydrogen self-dynamics term,<sup>74</sup> allowing for a

precise description of both the water state and the transport  
properties on the nanoscale. *The diffusion processes are of*  
*fundamental importance in predicting the service life (durability) of*  
*cement based systems since corrosive mechanisms involve the*  
*permeation of substances, such as aggressive ions, gases or just*  
*water, into the concrete.*<sup>74,75</sup>

A QENS spectrum usually contains two main contribu-  
tions: an elastic and a quasi-elastic component (Figure 9A).<sup>73,77</sup>



**Figure 9.** (A) Example of a QENS spectrum showing the two characteristic contributions: elastic and quasi-elastic, with an experimental resolution of 40  $\mu\text{eV}$ . (B) Broadening of the quasi-elastic component as a function of  $Q^2$  and the probed dimension,  $d$ . Passing from the continuous line (red) to the dashed line (black), the diffusion coefficient decreases, and the characteristic relaxation time increases. This is usually the evolution in time observed in a hydrating cement paste and reflects the conversion from bulk/capillary water into gel-confined water.

The elastic component is easily recognizable because it has the  
same width of resolution of the QENS spectrometer (and it is on  
the order of few tenths of a  $\mu\text{eV}$ ). This component gathers all  
neutrons scattered elastically (i.e., no exchange in energy) by the  
nuclei that are immobile in the sample or, in other words, that  
relax with characteristic times longer than hundreds of ns (i.e., a  
time longer than the one associated with the resolution of the  
instrument). In the case of a cement paste, the immobile fraction  
accounts for the hydrogenated species (mainly chemically bound  
water) contained in the hydrated phases ( $\text{CH}$ ,  $\text{C-S-H}$ , etc.).  
This quantity can be used to follow and detail the hydration  
kinetics in both the nucleation and growth stage and in the  
diffusional regime,<sup>78</sup> as already seen in the DSC case.

In the case of mobile atoms, the neutron–nuclei interaction  
results in an exchange of energy, and the QENS signal shows a  
broadening associated with the main relaxation processes of the  
sample (mainly water translational and rotational motions).  
In general, in the range of interest of a QENS investigation,  
 $t > 0.1$  ps, the scattering equation for the mobile part can be gen-  
erally written as  $S(Q, E) = \exp(-\langle u^2 \rangle Q^2/3) \otimes T(Q, E) \otimes R(Q, E)$ ,  
where the first term is the so-called Debye–Waller factor  
accounting for the mean square displacement of hydrogen in  
the O–H species,  $T(Q, E)$  represents the contribution of the

translational motion, and  $R(Q, E)$  is the contribution of the rotational motion. In the case where  $Q < 1 \text{ \AA}^{-1}$ , only translational motion is considered, which greatly simplifies the modeling of the quasi-elastic component<sup>74,79,80</sup> when compared to the cases where larger  $Q$  vectors are considered.<sup>81,82</sup> Moreover, the dependence of the broadening as a function of  $Q$  gives additional information on the type of motion (free diffusion, random jump diffusion, free diffusion in a confined geometry, etc.) allowing the calculation of the diffusion coefficient and eventually the residence times and associated jump lengths (Figure 9B). For a detailed review of the fitting models of both the mobile and immobile water fraction, the reader can refer to the literature.<sup>83</sup> However, current approaches tend to ignore the fact that part of the elastic signal comes from liquid water even without the presence of structural water because the  $Q$  dependence of the elastic fraction, especially at very low  $Q$  (typically  $Q < 1 \text{ \AA}^{-1}$ ), contains information on the form factor of the confining volume. Very recently, to overcome this limit, a new global fitting approach has been proposed<sup>84</sup> where all of the QENS spectra at a given time are simultaneously modeled over a  $Q$  range covering the decay of the elastic incoherent structure factor. This novel improved analysis method can accurately extract the structural water fraction and the associated spatial information directly linked to the confinement of the matrix.

The quasi-elastic component is a key feature in disclosing the evolution of the confinement imposed by the developing C–S–H nanoporosity. Therefore, Fratini et al.<sup>82</sup> clearly evidenced that in the random jump diffusion approximation the average diffusion coefficient for the mobile water fraction decreases by approximately 1 order of magnitude (from  $4.0 \times 10^{-9}$  to  $4.0 \times 10^{-10} \text{ m}^2/\text{s}$ ) for the  $\text{C}_3\text{S}/\text{H}_2\text{O}$  model system in 2 days of curing. Not surprisingly, MD simulations for water on the surface of model C–S–H<sup>68</sup> resulted in an average diffusion coefficient on the order of  $10^{-10} \text{ m}^2/\text{s}$  for all surface-associated molecules, which is in agreement with our QENS investigation and with water dynamics in the  $^1\text{H}$  NMR field cycling relaxation experiments.<sup>85,86</sup> The same decrease was evidenced by Bordallo et al.<sup>87</sup> by decoupling water dynamics of the capillary pores from that of the gel pores. In addition, the increase in confinement imposed by the developing inorganic matrix causes a reduction of the average jump length from 6 Å to approximately 4 Å in the first 2 days of curing.<sup>82</sup> Thus, the quantitative results obtained using the QENS experiment on hydrating cement pastes consist of the conversion of bulklike water (mainly contained in the capillary pores) in favor of constrained (i.e., strongly interacting with the surface, confined mainly in gel porosity) and bound water (i.e., being part of the hydration products, such as C–S–H and CH). Recently, Bordallo et al.<sup>88,89</sup> disclosed very important aspects related to the hydration of cement-based systems. By following water dynamics in a 28-cured sample and in the same sample rehydrated after drying at 105 °C, they clearly found that the water reabsorbed into the dried cement paste was more mobile than the water in the pristine cured sample. This suggests that water, once reabsorbed, goes initially into capillary pores and eventually will be admitted into the gel pores only at longer times, as recently confirmed by Pinson et al. using water sorption measurements.<sup>90</sup> Moreover, the initial situation can also be impossible to be restored if the drying process irreversibly damaged the C–S–H nanostructure and the associated porosity. As a matter of fact, QENS can differentiate among bound, constrained, and free water because their relaxation dynamics are quite distinct (i.e., they move differently). The advantage of this technique is twofold: it monitors the conversion of water in the

hydration products and simultaneously detects the water state during the hydration of the cement paste, being able to differentiate between capillary and gel-confined water.

**5.2. Porosimetry via NMR Relaxometry.** The dynamics of water in a porous system can also be probed using nuclear magnetic resonance (NMR), which is noninvasive, non-destructive, and quantitative.<sup>91</sup> In particular, NMR relaxometry is a well-established method of characterizing pore size distributions, specific surface areas, binder phase densities, water fractions, and dynamics. This technique has been applied to calcium-based cements for decades to study the formation and characteristics of cement microstructure and to monitor the evolution of water within them. One of the main advantages of NMR experiments is that they provide highly detailed information concerning the microstructure of both crystalline and amorphous phases.<sup>91,92</sup>

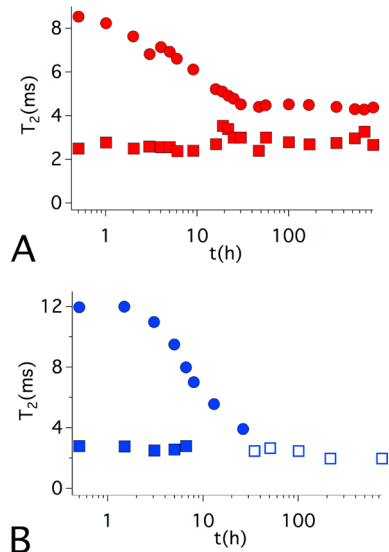
The use of combined Carr–Purcell–Meiboom–Gill (CPMG) and quad-echo pulse sequences was recently reported in the literature as an effective method to measure and quantify all hydrogen protons in different environments such as crystalline phases, interlayer water, gel pore water, and capillary water.<sup>91</sup> The measurement of the transverse ( $T_2$ ) and longitudinal ( $T_1$ ) spin relaxation time can be used to estimate the size of the pores, to gain information on the pore network evolution during the hydration process, and to monitor the kinetics of formation of hydrogen-containing solid phases.<sup>92–95</sup> This technique relies on the dependence of the  $T_2$  values of the pore water on the surface/volume ratio and on the specific surface relaxation. In the cement research field, a tool to quantitatively discriminate different populations of water has been demonstrated.<sup>91,96–98</sup> By assuming the fast diffusion regime,<sup>99,100</sup> the relationship

$$\frac{1}{T_2} \approx \frac{\epsilon S}{V} \frac{1}{T_2^{\text{surf}}} \quad (9)$$

can be applied, in which  $T_2$  is the measured spin–spin relaxation time,  $T_2^{\text{surf}}$  is the  $T_2$  value for water molecules adsorbed on the surface,  $\epsilon$  is the thickness of the adsorbed water layer, and  $S$  and  $V$  are the pore surface area and volume, respectively. Under this condition, from the experimental value of  $T_2$ , it is possible to obtain information on the  $S/V$  ratio and therefore on the pore size dimensions, distribution, and evolution in different phases.<sup>101,102</sup>

Similarly, this approach was further used, for the first time, with MgO/SiO<sub>2</sub> cements to discriminate different populations of water and to correlate their evolution with the hydration kinetics.<sup>103</sup>  $T_2$  measurements were performed at different times, ranging from ~0.5 h to 1 month, during the hydration of the investigated samples. In this study, several mixtures of Portland cement and MgO/SiO<sub>2</sub> were investigated, and important differences were highlighted. The two binder gel phases, magnesium silicate hydrate (M–S–H) and calcium silicate hydrate (C–S–H), showed significantly different pore size distributions. In the MgO/SiO<sub>2</sub> sample, three peaks were present soon after mixing with water. The peak at the shortest  $T_2$  is due to embedded water, which broadened with increasing hydration time. The other signals were assigned to free water with different mobilities in the spaces between powder grains. The so-called less-mobile water contribution broadened, and the more-mobile water moved to shorter values and decreased with time. In the Portland cement sample, two populations of free water, less mobile and more mobile, appear soon after mixing with water. In the first 6 h, two separate peaks were present, and then they

merged into a single signal that decreased and shifted to shorter  $T_2$  with increases in the hydration time to up to 30 h. After 1 day of hydration, an additional signal was observed as a result of water in the gel pores and interlayer spacing, and then, at a longer hydration time, a peak assigned to water in C–S–H interlayer spaces started to be resolved, and its relative intensity increased in the first month of hydration. Figure 10 shows the



**Figure 10.** Evolution of hydrogen  $T_2$  relaxation time as a function of hydration time: (A) MgO/SiO<sub>2</sub> and (B) Portland cement. Filled symbols (● and ■) are for the more-mobile and less-mobile free water components, and the open symbol (□) is for free water at longer hydration times, becoming water in the interhydrate spaces. Adapted with permission from ref 103.

$T_2$  evolution vs the hydration time for the investigated MgO/SiO<sub>2</sub> (Figure 10A) and Portland cement (Figure 10B). When M–S–H is the binder phase, the porous structures evolve during the entire investigated period, and the final pore distribution confirms the globular structure previously proposed in the literature.<sup>8</sup> However, with C–S–H as the main phase, the pore size distribution dramatically changes when this binder phase precipitates, i.e., when water remains segregated in the interlayer spaces and in gel pores.

**5.3. Dielectric Relaxation.** Various dielectric relaxation experiments were conducted on cement pastes and mortars. Depending on the frequency range, several relaxation processes can be followed during the hydration reaction. Typically, three components are monitored: a low relaxation occurring near 1 MHz, a medium relaxation at approximately 100 MHz, and a high relaxation in the GHz regime.<sup>104</sup> The main experimental evidence is that the relaxation strength of free water at high frequency (~10 GHz) decreases rapidly as the curing time passes, which enables us to follow the hydration reaction kinetics in these types of systems. The two components observed at lower frequencies (i.e., ~100 and 1 MHz) are usually distinctive of the reorientation of water constrained in the C–S–H phase.<sup>105</sup>

Cervený et al.<sup>106</sup> studied the influence of the water level on the dielectric response of the synthetic C–S–H phase. Even in this case, three different relaxation processes related to water are present at room temperature. The effect of the temperature (110–260 K) was investigated as a function of the water level (6–15 wt %) to evidence the activation mechanism behind these

relaxations. All three relaxations exhibited Arrhenius behavior at low water content (<10 wt %). With increasing water level, the process associated with water in small gel pores (medium frequency) shows a crossover from Arrhenius to super-Arrhenius (i.e., the motions become cooperative) as the water level reaches 10 wt % or in other words more than one monolayer is present. In the case of the water confined in large gel pores (high-frequency process), no crossover (from Arrhenius to super-Arrhenius) is present, and the super-Arrhenius behavior testifies to a cooperative relaxation for high water content. The two populations described agree with the findings reported using LT-NIR and DSC by some of the authors of the present paper.<sup>43</sup> More interesting, the crossover from Arrhenius to super-Arrhenius behavior was reported in the translational relaxation dynamics as obtained using QENS in C–S–H, M–S–H,<sup>107</sup> and various cement pastes.<sup>108,109</sup>

## 6. CONCLUDING DISCUSSION

The physicochemical properties of water can be a fundamental and unique resource to investigate complex porous matrixes. This feature article presented relevant results obtained on cement, which is a complex inorganic nanocomposite with structural characteristics (such as the pore size range and the dimension of the basic building block generating the fractal microstructure) that undoubtedly allow its allocation among the vast class of colloidal systems.<sup>73</sup> Furthermore, the number of innovative hydraulic cement formulations both for building and biomedical applications is going to increase, and the characterization of their kinetics and structural properties will become crucial for their improvement and formulation. The colloidal nature of cement suggests that the approach of using water as a probe can be extended to several other colloidal systems with very different chemical composition, where water plays a key role in the structure of the material (i.e., water is the main constituent). For example, in nonevolving systems with pores in the nanometer range, such as zeolites, clays, carbon nanotubes, or other inorganic matrixes, the thermal behavior evaluation of water is a method to infer their properties in terms of porosity, whereas the combination of QENS, NIR, NMR relaxometry, and dielectric relaxation allows one to study the translational, vibrational, and rotational motions of the confined liquid, thus evidencing the transport properties of the host material. However, biological molecules such as proteins, polysaccharides, and DNA always display behavior that is dictated by the presence of water as in the case of the plasticizing effect of water on the glass transition of biopolymers, and the study of water dynamics often yields precious information on their structure and activity. In addition, hydrogels can be successfully investigated by studying the properties of water, which directly regulates the transport phenomena of ions, molecules, and even gases through them.

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: emiliano.fratini@unifi.it.

\*E-mail: piero.baglioni@unifi.it.

### ORCID

Francesca Ridi: 0000-0002-6887-5108

Emiliano Fratini: 0000-0001-7104-6530

Sow-Hsin Chen: 0000-0001-6588-2428

Piero Baglioni: 0000-0003-1312-8700



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849 The authors declare no competing financial interest.

850 **Biographies**

851 From left to right: Sow-Hsin Chen, Piero Baglioni, Francesca Ridi,  
852 Monica Tonelli, and Emiliano Fratini

854 Sow-Hsin Chen, a condensed matter physicist, is a professor emeritus in  
855 the Department of Nuclear Science and Engineering at MIT (a faculty  
856 member at MIT since 1968). His main research area is thermal neutron,  
857 synchrotron X-ray, and laser light scattering spectroscopies of soft  
858 condensed matter. His recent work mainly involves molecular dynamics  
859 of various types of confined water in deeply supercooled states under  
860 high pressure, including water in MCM-41 porous silica, in cement  
861 pastes, in carbon nanotubes, and hydration water near surfaces of  
862 proteins, DNA, and RNA. He is the author of more than 450 publica-  
863 tions in condensed matter physics.

864 Piero Baglioni has been a full professor of physical chemistry in the  
865 Department of Chemistry at the University of Florence since 1994 and is  
866 an MIT affiliate. He was appointed as a visiting scientist/professor by the  
867 University of Houston, the Weizmann Institute, the Collège de France,  
868 and MIT. He is the Director of CSGI, and he is on the editorial/advisory  
869 boards of several international journals and a member of the scientific  
870 board of several national and international institutions and societies.  
871 He is the author of more than 450 publications and 25 patents in the  
872 field of colloids and interfaces and a pioneer in the application of soft  
873 matter to the conservation of cultural heritage.

874 Francesca Ridi is a researcher in the Department of Chemistry at the  
875 University of Florence. She received her Ph.D. in chemical sciences at  
876 the University of Florence. Her research is focused on the investigation  
877 of the physicochemical processes occurring during the hydration  
878 reaction of hydraulic cements both for construction and building  
879 materials and for bone tissue engineering applications.

880 Monica Tonelli received her B.S. in chemistry and M.S. in chemical  
881 sciences at the University of Florence, where she is currently a Ph.D.  
882 student in chemical sciences. Her research interests include magnesium-  
883 based cements with a focus on the use of nanotubular reinforcing fibers  
884 and phosphate-based additives. She is also working in collaboration with  
885 Italcementi SpA on the physicochemical characterization of Portland-  
886 based formulations.

887 Emiliano Fratini is an associate professor of physical chemistry in the  
888 Department of Chemistry of the University of Florence. His research  
889 topics include multifunctional nanocomposites, novel hydrogels and  
890 organogels, water dynamics in confining matrices, new mesoporous

silica scaffolds for catalysis and actives delivery, and structural and  
dynamical characterization of nanomaterials and soft matter. 891 892

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■ **ABBREVIATIONS** 898

NMR, nuclear magnetic resonance; CPMG, Carr–Purcell– 899  
Meiboom–Gill; LTDCS, low-temperature differential scanning 900  
calorimetry; C<sub>3</sub>S, tricalcium silicate; PEO, poly(ethylenoxide); 901  
DSC, differential scanning calorimetry; SGP, small gel pores; 902  
LGP, large gel pores; IGP, interlamellar gel pores; FWI, free 903  
water index; AE, Avrami-Eroev; BNGM, boundary nucleation 904  
and growth model; NIR, near-infrared spectroscopy; WHB, 905  
weakly hydrogen bonded; SHB, strongly hydrogen bonded; 906  
QENS, quasi-elastic neutron scattering; SANS, small-angle 907  
neutron scattering 908

■ **REFERENCES** 909

- (1) Hewlett, P. *Lea's Chemistry of Cement and Concrete*, 4th ed.; Elsevier, 1998. 910
- (2) Khatib, J. *Sustainability of Construction Materials*; Woodhead Publishing, 2016. 911
- (3) Walling, S. A.; Provis, J. L. Magnesia-Based Cements: A Journey of 150 Years, and Cements for the Future? *Chem. Rev.* **2016**, *116* (7), 912–916. 912
- (4) Sinitina, O. V.; Veresov, A. G.; Putlayev, V. I.; Tretyakov, Y. D.; Ravaglioli, A.; Krajewski, A.; Mazzocchi, M. Cements for Biomedical Applications. *Mendeleev Commun.* **2004**, *14* (4), 179–180. 913
- (5) Brew, D. R. M.; Glasser, F. P. Synthesis and Characterisation of Magnesium Silicate Hydrate Gels. *Cem. Concr. Res.* **2005**, *35* (1), 85–98. 914
- (6) Zhang, T.; Cheeseman, C. R.; Vandeperre, L. J. Development of Low pH Cement Systems Forming Magnesium Silicate Hydrate (M-S-H). *Cem. Concr. Res.* **2011**, *41* (4), 439–442. 915
- (7) Zhang, T.; Vandeperre, L. J.; Cheeseman, C. R. Magnesium-Silicate-Hydrate Cements for Encapsulating Problematic Aluminium Containing Wastes. *J. Sustainable Cem.-Based Mater.* **2012**, *1* (1–2), 34–45. 916
- (8) Chiang, W.-S.; Ferraro, G.; Fratini, E.; Ridi, F.; Yeh, Y.-Q.; Jeng, U. S.; Chen, S.-H.; Baglioni, P. Multiscale Structure of Calcium-and Magnesium-Silicate-Hydrate Gels. *J. Mater. Chem. A* **2014**, *2* (32), 12991–12998. 917
- (9) Lothenbach, B.; Nied, D.; L'Hôpital, E.; Achiedo, G.; Dauzères, A. Magnesium and Calcium Silicate Hydrates. *Cem. Concr. Res.* **2015**, *77*, 60–68. 918
- (10) Hughes, E.; Yanni, T.; Jamshidi, P.; Grover, L. M. Inorganic Cements for Biomedical Application: Calcium Phosphate, Calcium Sulphate and Calcium Silicate. *Adv. Appl. Ceram.* **2015**, *114* (2), 65–76. 919
- (11) Taylor, H. *Cement Chemistry*; Thomas Telford Publishing: London, 1997. 920
- (12) Wang, S.-D.; Scrivener, K. L. Hydration Products of Alkali Activated Slag Cement. *Cem. Concr. Res.* **1995**, *25* (3), 561–571. 921
- (13) Pane, I.; Hansen, W. Investigation of Blended Cement Hydration by Isothermal Calorimetry and Thermal Analysis. *Cem. Concr. Res.* **2005**, *35* (6), 1155–1164. 922
- (14) Damasceni, A.; Dei, L.; Fratini, E.; Ridi, F.; Chen, S.-H.; Baglioni, P. A Novel Approach Based on Differential Scanning Calorimetry Applied to the Study of Tricalcium Silicate Hydration Kinetics. *J. Phys. Chem. B* **2002**, *106* (44), 11572–11578. 923
- (15) Ridi, F.; Fratini, E.; Luciani, P.; Winnefeld, F.; Baglioni, P. Hydration Kinetics of Tricalcium Silicate by Calorimetric Methods. *J. Colloid Interface Sci.* **2011**, *364* (1), 118–124. 924



- 953 (16) Ridi, F.; Dei, L.; Fratini, E.; Chen, S.-H.; Baglioni, P. Hydration  
954 Kinetics of Tri-Calcium Silicate in the Presence of Superplasticizers. *J.*  
955 *Phys. Chem. B* **2003**, *107* (4), 1056–1061.
- 956 (17) Kondo, R.; Ueda, S. *Kinetics of Hydration of Cements*; Cement  
957 Association of Japan: Tokyo, 1969; Vol. 2, pp 203–248.
- 958 (18) Jolicoeur, C.; Simard, M. Chemical Admixture-Cement  
959 Interactions: Phenomenology and Physico-Chemical Concepts. *Cem.*  
960 *Concr. Compos.* **1998**, *20*, 87.
- 961 (19) Brown, P. W.; Pommersheim, J.; Frohnsdorff, G. A Kinetic Model  
962 for the Hydration of Tricalcium Silicate. *Cem. Concr. Res.* **1985**, *15*, 35–  
963 41.
- 964 (20) Tarrida, M.; Madon, M.; Le Rolland, B.; Colombet, P. An in-Situ  
965 Raman Spectroscopy Study of the Hydration of Tricalcium Silicate. *Adv.*  
966 *Cem. Based Mater.* **1995**, *2* (1), 15–20.
- 967 (21) FitzGerald, S. A.; Neumann, D. A.; Rush, J. J.; Bentz, D. P.;  
968 Livingston, R. A. In Situ Quasi-Elastic Neutron Scattering Study of the  
969 Hydration of Tricalcium Silicate. *Chem. Mater.* **1998**, *10* (1), 397–402.
- 970 (22) Berliner, R.; Popovici, M.; Herwig, K. W.; Berliner, M.; Jennings,  
971 H. M.; Thomas, J. J. Quasielastic Neutron Scattering Study of the Effect  
972 of Water-to-Cement Ratio on the Hydration Kinetics of Tricalcium  
973 Silicate. *Cem. Concr. Res.* **1998**, *28* (2), 231–243.
- 974 (23) Garrault, S.; Behr, T.; Nonat, A. Formation of the C-S-H Layer  
975 during Early Hydration of Tricalcium Silicate Grains with Different  
976 Sizes. *J. Phys. Chem. B* **2006**, *110* (1), 270–275.
- 977 (24) Thomas, J. J. A New Approach to Modeling the Nucleation and  
978 Growth Kinetics of Tricalcium Silicate Hydration. *J. Am. Ceram. Soc.*  
979 **2007**, *90* (10), 3282–3288.
- 980 (25) Thomas, J. J.; Allen, A. J.; Jennings, H. M. Hydration Kinetics and  
981 Microstructure Development of Normal and CaCl<sub>2</sub>-Accelerated  
982 Tricalcium Silicate Pastes. *J. Phys. Chem. C* **2009**, *113* (46), 19836–  
983 19844.
- 984 (26) Cahn, J. W. The Kinetics of Grain Boundary Nucleated Reactions.  
985 *Acta Metall.* **1956**, *4* (5), 449–459.
- 986 (27) Ridi, F.; Fratini, E.; Luciani, P.; Winnefeld, F.; Baglioni, P.  
987 Tricalcium Silicate Hydration Reaction in the Presence of Comb-  
988 Shaped Superplasticizers: Boundary Nucleation and Growth Model  
989 Applied to Polymer-Modified Pastes. *J. Phys. Chem. C* **2012**, *116* (20),  
990 10887–10895.
- 991 (28) Tonelli, M.; Martini, F.; Calucci, L.; Geppi, M.; Borsacchi, S.; Ridi,  
992 F. Traditional Portland Cement and MgO-Based Cement: A Promising  
993 Combination? *Phys. Chem. Earth ABC* **2017**, *99*, 158–167.
- 994 (29) Martini, F.; Tonelli, M.; Calucci, L.; Geppi, M.; Ridi, F.; Borsacchi,  
995 S. Hydration of MgO/SiO<sub>2</sub> and Portland cement mixtures: a structural  
996 investigation of the hydrated phases by means of X-ray diffraction and  
997 Solid State NMR spectroscopy. *Cem. Concr. Res.* **2017**, *102*, 60.
- 998 (30) Bordallo, H. N.; Aldridge, L. P.; Desmedt, A. Water Dynamics in  
999 Hardened Ordinary Portland Cement Paste or Concrete: From  
1000 Quasielastic Neutron Scattering. *J. Phys. Chem. B* **2006**, *110* (36),  
1001 17966–17976.
- 1002 (31) Jacobsen, J.; Rodrigues, M. S.; Telling, M. T. F.; Beraldo, A. L.;  
1003 Santos, S. F.; Aldridge, L. P.; Bordallo, H. N. Nano-Scale Hydrogen-  
1004 Bond Network Improves the Durability of Greener Cements. *Sci. Rep.*  
1005 **2013**, *3*, 2667.
- 1006 (32) Bordallo, H. N.; Aldridge, L. P.; Fouquet, P.; Pardo, L. C.; Unruh,  
1007 T.; Wuttke, J.; Yokaichiya, F. Hindered Water Motions in Hardened  
1008 Cement Pastes Investigated over Broad Time and Length Scales. *ACS*  
1009 *Appl. Mater. Interfaces* **2009**, *1* (10), 2154–2162.
- 1010 (33) Brun, M.; Lallemand, A.; Quinson, J. F.; Eyraud, C. A New  
1011 Method for the Simultaneous Determination of the Size and the Shape  
1012 of Pores: The Thermoporometry. *Thermochim. Acta* **1977**, *21*, 59–87.
- 1013 (34) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface*  
1014 *Tension and Adsorption*; Longmans Green: London, 1966.
- 1015 (35) Landry, M. R. Thermoporometry by Differential Scanning  
1016 Calorimetry: Experimental Considerations and Applications. *Thermo-*  
1017 *chim. Acta* **2005**, *433* (1–2), 27–50.
- 1018 (36) Ishikiriyama, K.; Todoki, M. Pore Size Distribution Measure-  
1019 ments of Silica Gels by Means of Differential Scanning Calorimetry. *J.*  
1020 *Colloid Interface Sci.* **1995**, *171* (1), 103–111.
- (37) Ishikiriyama, K.; Todoki, M. Evaluation of Water in Silica Pores  
Using Differential Scanning Calorimetry. *Thermochim. Acta* **1995**, *256*  
(2), 213–226.
- (38) Ishikiriyama, K.; Todoki, M.; Motomura, K. Pore Size  
Distribution (PSD) Measurements of Silica Gels by Means of  
Differential Scanning Calorimetry: I. Optimization for Determination  
of PSD. *J. Colloid Interface Sci.* **1995**, *171* (1), 92–102.
- (39) Bager, D. H.; Sellevold, E. J. Ice Formation in Hardened Cement  
Paste, Part I — Room Temperature Cured Pastes with Variable  
Moisture Contents. *Cem. Concr. Res.* **1986**, *16* (5), 709–720.
- (40) Bager, D. H.; Sellevold, E. J. Ice Formation in Hardened Cement  
Paste, Part II — Drying and Resaturation on Room Temperature Cured  
Pastes. *Cem. Concr. Res.* **1986**, *16* (6), 835–844.
- (41) Bager, D. H.; Sellevold, E. J. Ice Formation in Hardened Cement  
Paste, Part III — Slow Resaturation of Room Temperature Cured  
Pastes. *Cem. Concr. Res.* **1987**, *17* (1), 1–11.
- (42) Bentz, D. P. Capillary Porosity Depercolation/Repercolation in  
Hydrating Cement Pastes Via Low-Temperature Calorimetry Measure-  
ments and CEMHYD3D Modeling. *J. Am. Ceram. Soc.* **2006**, *89* (8),  
2606–2611.
- (43) Ridi, F.; Luciani, P.; Fratini, E.; Baglioni, P. Water Confined in  
Cement Pastes as a Probe of Cement Microstructure Evolution. *J. Phys.*  
*Chem. B* **2009**, *113* (10), 3080–3087.
- (44) Ridi, F.; Fratini, E.; Baglioni, P. Fractal Structure Evolution during  
Cement Hydration by Differential Scanning Calorimetry: Effect of  
Organic Additives. *J. Phys. Chem. C* **2013**, *117* (48), 25478–25487.
- (45) Sun, Z.; Scherer, G. W. Pore size and shape in mortar by  
thermoporometry. *Cem. Concr. Res.* **2010**, *40* (5), 740–751.
- (46) Jennings, H. M. Refinements to Colloid Model of CSH in  
Cement: CM-II. *Cem. Concr. Res.* **2008**, *38* (3), 275–289.
- (47) Sanz, E.; Vega, C.; Espinosa, J. R.; Caballero-Bernal, R.; Abascal, J.  
L. F.; Valeriani, C. Homogeneous Ice Nucleation at Moderate  
Supercooling from Molecular Simulation. *J. Am. Chem. Soc.* **2013**, *135*  
(40), 15008–15017.
- (48) Hansen, E. W.; Gran, H. C.; Sellevold, E. J. Heat of Fusion and  
Surface Tension of Solids Confined in Porous Materials Derived from a  
Combined Use of NMR and Calorimetry. *J. Phys. Chem. B* **1997**, *101*  
(35), 7027–7032.
- (49) Hou, D.; Zhao, T.; Ma, H.; Li, Z. Reactive molecular simulation  
on water confined in the nanopores of the calcium silicate hydrate gel:  
structure, reactivity, and mechanical properties. *J. Phys. Chem. C* **2015**,  
*119* (3), 1346–1358.
- (50) Li, D. K.; Zhao, W. Y.; Hou, D. S.; Zhao, T. J. Molecular dynamics  
study on the chemical bound, physical adsorbed and ultra-confined  
water molecules in the nano-pore of calcium silicate hydrate. *Constr.*  
*Build. Mater.* **2017**, *151*, 563–574.
- (51) Youssef, M.; Pellenq, R. J. M.; Yildiz, B. Glassy nature of water in  
an ultraconfining disordered material: the case of calcium–silicate–  
hydrate. *J. Am. Chem. Soc.* **2011**, *133* (8), 2499–2510.
- (52) Qomi, M. J. A.; Bauchy, M.; Ulm, F. J.; Pellenq, R. J. M.  
Anomalous composition-dependent dynamics of nanoconfined water in  
the interlayer of disordered calcium-silicates. *J. Chem. Phys.* **2014**, *140*  
(5), 054515.
- (53) Kriechbaum, M.; Degovics, G.; Tritthart, J.; Laggner, P. Fractal  
Structure of Portland Cement Paste during Age Hardening Analyzed by  
Small-Angle X-Ray Scattering. *Prog. Colloid Polym. Sci.* **1989**, *79*, 101–  
105.
- (54) Livingston, R. A. Fractal Nucleation and Growth Model for the  
Hydration of Tricalcium Silicate. *Cem. Concr. Res.* **2000**, *30*, 1853–1860.
- (55) Winslow, D.; Bukowski, J. M.; Young, J. F. The Fractal  
Arrangement of Hydrated Cement Paste. *Cem. Concr. Res.* **1995**, *25*  
(1), 147–156.
- (56) Rault, J.; Neffati, R.; Judeinstein, P. Melting of Ice in Porous Glass:  
Why Water and Solvents Confined in Small Pores Do Not Crystallize?  
*Eur. Phys. J. B* **2003**, *36* (4), 627–637.
- (57) Neffati, R.; Rault, J. Pore Size Distribution in Porous Glass:  
Fractal Dimension Obtained by Calorimetry. *Eur. Phys. J. B* **2001**, *21*  
(2), 205–210.

- (58) Vollet, D.; Donatti, D.; Ruiz, A. I. Comparative Study Using Small-Angle X-Ray Scattering and Nitrogen Adsorption in the Characterization of Silica Xerogels and Aerogels. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *69* (6), 64202.
- (59) Jennings, H. M. A Model for the Microstructure of Calcium Silicate Hydrate in Cement Paste. *Cem. Concr. Res.* **2000**, *30* (1), 101–116.
- (60) Allen, A. J.; Thomas, J. J.; Jennings, H. M. Composition and Density of Nanoscale Calcium-Silicate-Hydrate in Cement. *Nat. Mater.* **2007**, *6* (4), 311–316.
- (61) Chiang, W.-S.; Fratini, E.; Baglioni, P.; Liu, D.; Chen, S.-H. Microstructure Determination of Calcium-Silicate-Hydrate Globules by Small-Angle Neutron Scattering. *J. Phys. Chem. C* **2012**, *116* (8), 5055–5061.
- (62) Chiang, W.-S.; Fratini, E.; Ridi, F.; Lim, S.-H.; Yeh, Y.-Q.; Baglioni, P.; Choi, S.-M.; Jeng, U.-S.; Chen, S.-H. Microstructural Changes of Globules in Calcium-silicate-hydrate Gels with and without Additives Determined by Small-Angle Neutron and X-Ray Scattering. *J. Colloid Interface Sci.* **2013**, *398*, 67–73.
- (63) Siesler, H. W. *Near-Infrared Spectroscopy: Principles, Instruments, Applications*; Wiley-VCH: Weinheim, 2002.
- (64) Andaloro, G.; Chiricò, P.; Guzzio, G.; Leone, M.; Palma-Vittorelli, M. B. Thermal Behavior of the near IR Absorption of H<sub>2</sub>O and NaClO<sub>4</sub> Aqueous Solutions. *J. Chem. Phys.* **1977**, *66* (1), 335–341.
- (65) Cupane, A.; Levantino, M.; Santangelo, M. G. Near-Infrared Spectra of Water Confined in Silica Hydrogels in the Temperature Interval 365–5 K. *J. Phys. Chem. B* **2002**, *106* (43), 11323–11328.
- (66) Czarnik-Matusiewicz, B.; Pilorz, S.; Hawranek, J. P. Temperature-Dependent Water Structural Transitions Examined by near-IR and Mid-IR Spectra Analyzed by Multivariate Curve Resolution and Two-Dimensional Correlation Spectroscopy. *Anal. Chim. Acta* **2005**, *544* (1–2), 15–25.
- (67) Angell, C. A.; Rodgers, V. Near Infrared Spectra and the Disrupted Network Model of Normal and Supercooled Water. *J. Chem. Phys.* **1984**, *80* (12), 6245–6252.
- (68) Hou, D.; Li, Z.; Zhao, T.; Zhang, P. Water transport in the nanopore of the calcium silicate phase: reactivity, structure and dynamics. *Phys. Chem. Chem. Phys.* **2015**, *17* (2), 1411–1423.
- (69) Ridi, F.; Fratini, E.; Milani, S.; Baglioni, P. Near-Infrared Spectroscopy Investigation of the Water Confined in Tricalcium Silicate Pastes. *J. Phys. Chem. B* **2006**, *110* (33), 16326–16331.
- (70) Grundy, W. M.; Schmitt, B. The Temperature-Dependent near-Infrared Absorption Spectrum of Hexagonal H<sub>2</sub>O Ice. *J. Geophys. Res. Planets* **1998**, *103* (E11), 25809–25822.
- (71) Grundy, W. M.; Buie, M. W.; Stansberry, J. A.; Spencer, J. R.; Schmitt, B. Near-Infrared Spectra of Icy Outer Solar System Surfaces: Remote Determination of H<sub>2</sub>O Ice Temperatures. *Icarus* **1999**, *142* (2), 536–549.
- (72) Bee, M. *Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, Biology and Materials Science*; Adam Hilger: Bristol, 1988.
- (73) Ridi, F.; Fratini, E.; Baglioni, P. Cement: A Two Thousand Year Old Nano-Colloid. *J. Colloid Interface Sci.* **2011**, *357*, 255–264.
- (74) Fratini, E.; Chen, S. H.; Baglioni, P.; Bellissent-Funel, M. C. Quasi-Elastic Neutron Scattering Study of Translational Dynamics of Hydration Water in Tricalcium Silicate. *J. Phys. Chem. B* **2002**, *106* (1), 158–166.
- (75) RILEM Technical Committee TC 116-PCD; *Relations between Transport Characteristics and Durability*; Hilsdorf, H., Kropp, J., Eds.; E & FN Spon: London, 1995.
- (76) Mindess, S.; Young, J. F.; Darwin, D. *Concrete*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 2003.
- (77) Harris, D. H. C.; Windsor, C. G.; Lawrence, C. D. Free and Bound Water in Cement Pastes. *Mag. Concr. Res.* **1974**, *26* (87), 65–72.
- (78) Del Buffa, S.; Fratini, E.; Ridi, F.; Faraone, A.; Baglioni, P. State of Water in Hydrating Tricalcium Silicate Pastes: The Effect of a Cellulose Ether. *J. Phys. Chem. C* **2016**, *120* (14), 7612–7620.
- (79) Fratini, E.; Chen, S. H.; Baglioni, P.; Bellissent-Funel, M. C. Age-Dependent Dynamics of Water in Hydrated Cement Paste. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2001**, *64* (2), 20201.
- (80) Fratini, E.; Chen, S. H.; Baglioni, P. Investigation of the Temporal Evolution of Translational Dynamics of Water Molecules in Hydrated Calcium Aluminate Pastes. *J. Phys. Chem. B* **2003**, *107* (37), 10057–10062.
- (81) Li, H.; Zhang, L.-L.; Yi, Z.; Fratini, E.; Baglioni, P.; Chen, S.-H. Translational and Rotational Dynamics of Water Contained in Aged Portland Cement Pastes Studied by Quasi-Elastic Neutron Scattering. *J. Colloid Interface Sci.* **2015**, *452*, 2–7.
- (82) Fratini, E.; Faraone, A.; Ridi, F.; Chen, S.-H.; Baglioni, P. Hydration Water Dynamics in Tricalcium Silicate Pastes by Time-Resolved Incoherent Elastic Neutron Scattering. *J. Phys. Chem. C* **2013**, *117* (14), 7358–7364.
- (83) Peterson, V. K. Studying the Hydration of Cement. In *Studying Kinetics with Neutrons: Prospects for Times-Resolved Neutron Scattering*; Springer Series in Solid-State Sciences; Springer, 2010; Vol. 161, pp 19–75.
- (84) Le, P.; Fratini, E.; Zhang, L.-L.; Ito, K.; Mamontov, E.; Baglioni, P.; Chen, S.-H. Quasi-Elastic Neutron Scattering Study of Hydration Water in Synthetic Cement: An Improved Analysis Method Based on a New Global Model. *J. Phys. Chem. C* **2017**, *121*, 12826–12833.
- (85) Kalinichev, A. G.; Wang, J.; Kirkpatrick, R. J. Molecular Dynamics Modeling of the Structure, Dynamics and Energetics of Mineral-water Interfaces: Application to Cement Materials. *Cem. Concr. Res.* **2007**, *37* (3), 337–347.
- (86) Korb, J.-P.; McDonald, P. J.; Monteilhet, L.; Kalinichev, A. G.; Kirkpatrick, R. J. Comparison of Proton Field-Cycling Relaxometry and Molecular Dynamics Simulations for Proton-water Surface Dynamics in Cement-Based Materials. *Cem. Concr. Res.* **2007**, *37* (3), 348–350.
- (87) Bordallo, H. N.; Aldridge, L. P.; Desmedt, A. Water Dynamics in Hardened Ordinary Portland Cement Paste or Concrete: From Quasielastic Neutron Scattering. *J. Phys. Chem. B* **2006**, *110* (36), 17966–17976.
- (88) Jacobsen, J.; Rodrigues, M. S.; Telling, M. T. F.; Beraldo, A. L.; Santos, S. F.; Aldridge, L. P.; Bordallo, H. N. Nano-Scale Hydrogen-Bond Network Improves the Durability of Greener Cements. *Sci. Rep.* **2013**, *3*, 2667.
- (89) Bordallo, H. N.; Aldridge, L. P.; Fouquet, P.; Pardo, L. C.; Unruh, T.; Wuttke, J.; Yokaichiya, F. Hindered Water Motions in Hardened Cement Pastes Investigated over Broad Time and Length Scales. *ACS Appl. Mater. Interfaces* **2009**, *1* (10), 2154–2162.
- (90) Pinson, M. B.; Masoero, E.; Bonnaud, P. A.; Manzano, H.; Ji, Q.; Yip, S.; Thomas, J. J.; Bazant, M. Z.; Van Vliet, K. J.; Jennings, H. M. Hysteresis from Multiscale Porosity: Modeling Water Sorption and Shrinkage in Cement Paste. *Phys. Rev. Appl.* **2015**, *3*, 064009.
- (91) Muller, A. C. A.; Scrivener, K. L.; Gajewicz, A. M.; McDonald, P. J. Use of Bench-Top NMR to Measure the Density, Composition and Desorption Isotherm of C–S–H in Cement Paste. *Microporous Mesoporous Mater.* **2013**, *178*, 99–103.
- (92) Valori, A.; McDonald, P. J.; Scrivener, K. L. The Morphology of C–S–H: Lessons from <sup>1</sup>H Nuclear Magnetic Resonance Relaxometry. *Cem. Concr. Res.* **2013**, *49*, 65–81.
- (93) Faure, P. F.; Rodts, S. Proton NMR Relaxation as a Probe for Setting Cement Pastes. *Magn. Reson. Imaging* **2008**, *26* (8), 1183–1196.
- (94) Korb, J.-P. NMR and Nuclear Spin Relaxation of Cement and Concrete Materials. *Curr. Opin. Colloid Interface Sci.* **2009**, *14* (3), 192–202.
- (95) Bortolotti, V.; Fantazzini, P.; Mongiorgi, R.; Sauro, S.; Zanna, S. Hydration Kinetics of Cements by Time-Domain Nuclear Magnetic Resonance: Application to Portland-Cement-Derived Endodontic Pastes. *Cem. Concr. Res.* **2012**, *42* (3), 577–582.
- (96) McDonald, P. J.; Rodin, V.; Valori, A. Characterisation of Intra- and Inter-C–S–H Gel Pore Water in White Cement Based on an Analysis of NMR Signal Amplitudes as a Function of Water Content. *Cem. Concr. Res.* **2010**, *40* (12), 1656–1663.
- (97) Pop, A.; Badea, C.; Ardelean, I. The Effects of Different Superplasticizers and Water-to-Cement Ratios on the Hydration of

- 1225 Gray Cement Using T<sub>2</sub>-NMR. *Appl. Magn. Reson.* **2013**, *44* (10), 1223–  
1226 1234.
- 1227 (98) Bligh, M. W.; d'Eurydice, M. N.; Lloyd, R. R.; Arns, C. H.; Waite,  
1228 T. D. Investigation of Early Hydration Dynamics and Microstructural  
1229 Development in Ordinary Portland Cement Using <sup>1</sup>H NMR  
1230 Relaxometry and Isothermal Calorimetry. *Cem. Concr. Res.* **2016**, *83*,  
1231 131–139.
- 1232 (99) Brownstein, K. R.; Tarr, C. E. Importance of Classical Diffusion in  
1233 NMR Studies of Water in Biological Cells. *Phys. Rev. A: At., Mol., Opt.*  
1234 *Phys.* **1979**, *19* (6), 2446–2453.
- 1235 (100) Halperin, W. P.; Jehng, J.-Y.; Song, Y.-Q. Application of Spin-  
1236 Spin Relaxation to Measurement of Surface Area and Pore Size  
1237 Distributions in a Hydrating Cement Paste. *Magn. Reson. Imaging* **1994**,  
1238 *12* (2), 169–173.
- 1239 (101) Gombia, M.; Bortolotti, V.; De Carlo, B.; Mongiorgi, R.; Zanna,  
1240 S.; Fantazzini, P. Nanopore Structure Buildup during Endodontic  
1241 Cement Hydration Studied by Time-Domain Nuclear Magnetic  
1242 Resonance of Lower and Higher Mobility <sup>1</sup>H. *J. Phys. Chem. B* **2010**,  
1243 *114* (5), 1767–1774.
- 1244 (102) Muller, A. C. A.; Scrivener, K. L.; Gajewicz, A. M.; McDonald, P.  
1245 J. Densification of C–S–H Measured by <sup>1</sup>H NMR Relaxometry. *J. Phys.*  
1246 *Chem. C* **2013**, *117* (1), 403–412.
- 1247 (103) Martini, F.; Calucci, L.; Geppi, M.; Tonelli, M.; Ridi, F.;  
1248 Borsacchi, S. Monitoring the Hydration of MgO-Based Cement and Its  
1249 Mixtures with Portland Cement by <sup>1</sup>H NMR Relaxometry. *Microporous*  
1250 *Mesoporous Mater.* **2017**, doi: [10.1016/j.micromeso.2017.05.031](https://doi.org/10.1016/j.micromeso.2017.05.031).
- 1251 (104) Hager, N. E.; Domszy, R. C. Monitoring of Cement Hydration  
1252 by Broadband Time-Domain-Reflectometry Dielectric Spectroscopy. *J.*  
1253 *Appl. Phys.* **2004**, *96* (9), 5117–5128.
- 1254 (105) Miura, N.; Shinyashiki, N.; Yagihara, S.; Shiotsubo, M.  
1255 Microwave Dielectric Study of Water Structure in the Hydration  
1256 Process of Cement Paste. *J. Am. Ceram. Soc.* **1998**, *81* (1), 213–216.
- 1257 (106) Cervený, S.; Arrese-Igor, S.; Dolado, J. S.; Gaitero, J. J.; Alegria,  
1258 A.; Colmenero, J. Effect of Hydration on the Dielectric Properties of C-  
1259 S-H Gel. *J. Chem. Phys.* **2011**, *134* (3), 034509.
- 1260 (107) Le, P.; Fratini, E.; Ito, K.; Wang, Z.; Mamontov, E.; Baglioni, P.;  
1261 Chen, S.-H. Dynamical Behaviors of Structural, Constrained and Free  
1262 Water in Calcium- and Magnesium-Silicate-Hydrate Gels. *J. Colloid*  
1263 *Interface Sci.* **2016**, *469*, 157–163.
- 1264 (108) Zhang, Y.; Lagi, M.; Fratini, E.; Baglioni, P.; Mamontov, E.;  
1265 Chen, S.-H. Dynamic Susceptibility of Supercooled Water and Its  
1266 Relation to the Dynamic Crossover Phenomenon. *Phys. Rev. E* **2009**, *79*  
1267 (4), 40201.
- 1268 (109) Li, H.; Chiang, W.-S.; Fratini, E.; Ridi, F.; Bausi, F.; Baglioni, P.;  
1269 Tyagi, M.; Chen, S.-H. Dynamic Crossover in Hydration Water of  
1270 Curing Cement Paste: The Effect of Superplasticizer. *J. Phys.: Condens.*  
1271 *Matter* **2012**, *24* (6), 064108.