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## Water as a Probe of the Colloidal Properties of Cement

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ABSTRACT: Cement is produced by mixing mineral phases 7 based on calcium silicates and aluminates with water. The 8 hydration reaction of the mixture leads to a synthetic material 9 with outstanding properties that can be used as a binder for 10 construction applications. Despite the importance of cement in 11 12 society, for a long time, the chemical reactions involved in its 13 hydration remained poorly understood as a result of the com-14 plexity of hydration processes, nanostructure, and transport phenomena. This feature article reviews the recently obtained 15 results using water as a probe to detail the essential features in 16 the setting process. By examining the peculiar physicochemical 17 properties of water, fundamental information on the evolving 18 inorganic colloid matrix can be deduced, ranging from the 19 20



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

23 The discovery of the pozzolanic reaction of volcanic materials 24 mixed with lime and water was boasted as one of the most 25 revolutionary innovations in history. Before the Romans, 26 other ancient civilizations used nonhydraulic binders to build 27 long-lasting structures such as the Great Wall in China and 28 the Egyptian pyramids. The incredible benefits related to the 29 addition of pozzolan to lime were the ability to set without the 30 presence of carbon dioxide, even under water, and the impressive 31 increase in mechanical properties. These characteristics enabled 32 the construction of the renowned Roman aqueducts, bridges, and 33 many other architectural structures that enormously contributed 34 to the expansion of the Roman Empire. In modern times, three 35 fundamental developments improved the Roman recipe for 36 cement: the introduction of gypsum that avoids flash setting; the 37 higher temperatures used to fire the raw materials, allowing for a 38 more rapid setting process; and the advancement of the grinding 39 process to increase the specific surface area available to hydration, 40 which improves the setting process. With these changes, at the 41 end of the XVIII century, modern Portland cement was finally 42 formulated, and that original recipe (with few refinements) is still <sup>43</sup> the most used hydraulic binder for building purposes.<sup>1</sup>

44 Cement is a complex solid that is both structurally and 45 chemically heterogeneous. The chemical and mineralogical 46 composition of cement formulations is variable, depending on 47 the composition of the raw materials extracted from quarries and 48 on the addition of extra components aimed at tuning its 49 reactivity. With the advancement in technical knowledge, the 50 ordinary Portland cement composition has been modified, producing several types of cements with different properties, to 51 match specific applications. Today, a plethora of hydraulic 52 cements are known and categorized. A summary of the most 53 relevant is reported in Table 1. The compositions and properties 54 of these systems are very different to cover very different applica- 55 tions ranging from building materials<sup>2,3</sup> to cement for biomedical 56 purposes such as bone repair and orthodontics.<sup>4</sup> Currently, 57 magnesium-based cements are suited for specialist applications 58 to take advantage of their potential for  $CO_2$  emission reduction. 59 However, the high cost of the raw materials and the final pH not 60 sufficiently high to passivate steel reinforcing bars limit their use 61 and the possibility of replacing ordinary Portland cements.<sup>3</sup> 62 Considering the field of cements for structural applications, 63 magnesium silicate cement is an emerging material that finds 64 application in the encapsulation of problematic radioactive 65 wastes.<sup>5–7</sup> In addition, magnesium silicate cement is significant 66 from a physicochemical point of view. Specifically, upon contact 67 with water, it develops a hydrated phase (magnesium silicate 68 hydrate, M-S-H) that is analogous to calcium silicate hydrate 69 (C-S-H), the main binder of Portland cement. Therefore, 70 cation substitution produces significant modifications in both the 71 properties and structure of the hydrated phase.<sup>8,9</sup>

Water is one of the initial components of a cement paste and is 73 progressively consumed during the development of the hydra-74 tion products during the curing process. Therefore, the observation 75

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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	$Ca_{3}SiO_{5} + (1.3 + \alpha)H_{2}O \rightarrow (CaO)_{1.7}SiO_{2}(H_{2}O)_{\alpha} + 1.3Ca(OH)_{2}$	calcium phosphate	apatitic cements: $3\alpha$ -Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + H <sub>2</sub> O $\rightarrow$ Ca <sub>9</sub> (PO <sub>4</sub> ) <sub>5</sub> HPO <sub>4</sub> OH
	$Ca_2SiO_4 + (0.3 + x)H_2O \rightarrow (CaO)_{1.7}SiO_2(H_2O)_x + 0.3Ca(OH)_2$		brushite-based cements: $\beta$ -Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> O + 7H <sub>2</sub> O $\rightarrow$ 4CaHPO <sub>4</sub> 2H <sub>2</sub> O
	$2\text{Ca}_3\text{Al}_2\text{O}_6 + 12\text{H}_2\text{O} \rightarrow (\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$		$\beta$ -Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + H <sub>3</sub> PO <sub>4</sub> + 6H <sub>2</sub> O $\rightarrow$ 3CaHPO <sub>4</sub> 2H <sub>2</sub> O
	$\begin{array}{l} Ca_{3}Al_{2}O_{6}+3CaSO_{4}\cdot(H_{2}O)_{2}+26H_{2}O\rightarrow\\ (CaO)_{6}Al_{2}O_{3}(SO_{4})_{3}(H_{2}O)_{32} \end{array}$		
Portland cement blends	$Ca_3SiO_5 + (1.3 + x)H_2O \rightarrow (CaO)_{1.7}SiO_2(H_2O)_x + 1.3Ca(OH)_2$	calcium sulfate	$CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O$
	$Ca_2SiO_4 + (0.3 + x)H_2O \rightarrow (CaO)_{1.7}SiO_2(H_2O)_x + 0.3Ca(OH)_2$		
	$2\text{Ca}_3\text{Al}_2\text{O}_6 + 12\text{H}_2\text{O} \rightarrow (\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$		$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$
	$\begin{array}{c} Ca_{3}Al_{2}O_{6}+3CaSO_{4}\cdot(H_{2}O)_{2}+26H_{2}O \rightarrow \\ (CaO)_{6}Al_{2}O_{3}(SO_{4})_{3}(H_{2}O)_{32} \end{array}$		
magnesium phosphate cements	$2\text{MgO} + 2\text{NH}_4\text{H}_2\text{PO}_4 + 10\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{MgPO}_4 6\text{H}_2\text{O}$	calcium silicate	$Ca_3SiO_5 + (1.3 + x)H_2O \rightarrow (CaO)_{1.7}SiO_2(H_2O)_x + 1.3Ca(OH)_2$
magnesium silicate hydrate cements	$xMgO + yH_2O + SiO_2 \rightarrow (MgO)_x(SiO_2)(H_2O)_y$	magnesium phosphate	$2 \text{ MgO} + 2\text{NH}_4\text{H}_2\text{PO}_4 + 10\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{MgPO}_4 6\text{H}_2\text{O}$
			Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + 15H <sub>2</sub> O → 2 MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O + MgHPO <sub>4</sub> ·3H <sub>2</sub> O
magnesium oxychloride (Sorel) cements	$3MgO + MgCl_2 + 11H_2O \rightarrow 3 Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$		
calcium sulfoaluminate cements	$\begin{array}{l} (C_{aO})_{4}(Al_{2}O_{3})_{3}(SO_{3}) + CaSO_{4} + 38H_{2}O \rightarrow \\ (C_{aO})_{6}Al_{2}O_{3}(SO_{3})_{3}(H_{2}O)_{32} + 4Al(OH)_{3} \end{array}$		
alkali-activated cements <sup>10-12</sup>	$\begin{array}{l} CaO-SiO_2-MgO-Al_2O_3+H_2O \ (activated \ with \ NaOH) \rightarrow \\ (CaO)_ySiO_2(H_2O)_x + (Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O) + CaCO_3 + \\ AFm \ phases \end{array}$		

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 watercontaining materials to obtain information on their properties. 88 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

<sup>93</sup> The hydration kinetics have a direct impact on the evolution of <sup>94</sup> the hydrated cement microstructure, which in turn influences the <sup>95</sup> mechanical properties and durability of the concrete, affecting <sup>96</sup> important characteristics such as strength, elastic moduli, tough-<sup>97</sup> ness, diffusivity, and permeability to liquids and gases.<sup>13</sup> The <sup>98</sup> complex reactions taking place between the anhydrous phases <sup>99</sup> and water can be considered to be the main cause of the setting <sup>100</sup> and hardening of cement pastes, and because of their exothermic <sup>101</sup> nature, the hydration process is usually monitored using calori-<sup>102</sup> metry, such as heat of solution calorimetry, semiadiabatic– <sup>103</sup> adiabatic calorimetry, and isothermal conduction calorimetry <sup>104</sup> (IC). From an industrial point of view, IC is probably the most <sup>105</sup> used technique to access the hydration kinetics in the cement <sup>106</sup> research field. However, this approach presents some drawbacks <sup>107</sup> because the hydration process can be followed only during the early stage of hydration. A few days after mixing, the evolved heat 108 becomes too low to be distinguished from the instrumental 109 baseline, which prevents the use of IC in the case of slowly curing 110 cement formulations, such as those containing retarding agents. 111 To overcome this limit, we proposed an alternative method 112 based on differential scanning calorimetry (DSC),<sup>14,15</sup> where 113 the evolution of unreacted water can be quantified in terms of a 114 free or freezable water index (FWI).<sup>14,16</sup> In this approach, 115 cement pastes are periodically frozen at  $-60 \,^{\circ}$ C and then melted 116 at a constant rate. Figure 1 shows the decrease in time of the 117



**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 118 cement paste. 119

The ice melting peak is integrated to extract the melting 120 enthalpy  $\Delta H_{\rm exp}$  of water and to calculate the FWI 121

$$FWI = \frac{\Delta H_{exp}}{\phi_{w} \Delta H_{theor}}$$
(1) 122

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

<sup>128</sup> Moreover, some of the authors<sup>15</sup> showed that hydration <sup>129</sup> 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.

Kinetic analysis was used to obtain information on activation Kinetic analysis was used to obtain information on activation The hydration of cement powders is a complex multistage proto cess with a well-known scheme: an initial hydration process, when the wetting of highly hygroscopic particles occurs; an induction period, when the reaction is quiescent; an acceleration period, when the nucleation and growth processes greatly kincrease the rate of the hydration reaction and the formation of several colloidal phases; a deceleration period; and finally, a diffusional period, where the reaction proceeds at a slower rate and the rate-limiting process is the diffusion of water through the hydrated products toward the anhydrous cores.<sup>11,15,17,18</sup> In past decades, the nucleation and growth stage taking place during the hydration of tricalcium silicate  $(C_3S)$  was modeled using Avrami- 150 Erove'ev (AE) kinetic law<sup>19-22</sup> to extract the rate constants of the  $_{151}$ processes. In this framework, the DSC method was applied to 152 investigate the effect of some of the most used cement additives, 153 using the AE law for the acceleration period and a three- 154 dimensional diffusion equation for the final part of the FWI 155 curve.<sup>16</sup> More recently, some authors noted that the AE equation 156 cannot completely explain the cement hydration process. Above 157 all, the assumption that the probability of nucleation of the 158 hydrating phases is the same elsewhere is not appropriate 159 because it is commonly accepted that it occurs preferentially at 160 the grain boundaries.<sup>23</sup> The boundary nucleation and growth 161 model (BNGM) derived by Thomas overcomes this incon- 162 sistency.<sup>24,25</sup> This model, which was originally developed for 163 solid-phase transformation,<sup>26</sup> can properly describe the process 164 of cement hydration, even using fewer parameters than in the AE 165 model. BNGM describes the hydration kinetics with two 166 independent rate constants:  $k_{\rm B}$ , which "describes the rate at 167 which the surfaces become covered with hydration product" and 168  $k_{\rm G}$ , which is the "rate at which the pore space between the 169 particles fills in with product".<sup>24,25</sup> Then, the original BNGM 170 approach developed for IC was modified to directly analyze the 171 time evolution of FWI as accessed by the DSC protocol. 172 In particular, an extra independent parameter was added to 173 estimate the fraction of unreacted water, and any assumption on 174 the hydration reaction stoichiometry was avoided. It was shown 175 that the application of the model on kinetic profiles obtained by 176 IC and DSC provides comparable results, which further validates 177 the FWI approach.<sup>15</sup> Therefore, DSC was applied by our group 178 to investigate the effects of particle size, temperature,<sup>15</sup> and 179 additive addition<sup>27</sup> on the hydration reaction in cement pastes 180 even for very long processes, such as those obtained with the 181 so-called superplasticizing additives. 182

Some of the authors of this article recently proposed the 183 application of BNGM<sup>25</sup> combined with a three-dimensional 184 diffusional model to quantitatively describe the nucleation and 185 growth processes during the hydration of the new green cements 186 based on MgO/SiO<sub>2</sub> formulations.<sup>28</sup> Figure 2B shows the FWI vs 187 time for the  $MgO/SiO_2$  sample together with the best-fit curve 188 obtained using the BNGM + diffusional combined model. The 189 model accurately describes all three hydration periods. The curve 190 shows the short initial induction period lasting until  $t_i$  is reached, 191 where FWI remains  $\sim$ 1; the nucleation and growth period, with 192 a consistent decrease in FWI, which lasts up to ~40 h; and 193 the final diffusional period, starting at time  $t_d$  where the change 194 in the curve slope suggests that the rate-limiting step becomes a 195 diffusion-limited process, similar to the Portland case. These 196 results agree with <sup>1</sup>H NMR relaxometry that follows the kinetics 197 using the evolution of the transverse  $(T_2)$  spin relaxation time 198 signal in MgO/SiO<sub>2</sub> pastes.<sup>29</sup> 199

The kinetics profiles associated with a curing cement paste 200 simply detail the overall hydration reaction. During the different 201 stages, the hydrated phases develop to yield the well-known 202 porous structure, which is typical for cement systems. The 203 characterization of the pore structure (i.e., total porosity, pore 204 size distribution, and eventually specific surface area) is one of 205 the key factors in the prediction of the final performances of 206 cement. For example, it is known that a highly durable cement/ 207 concrete will have mostly gel pores (<5 nm) hydraulically 208 isolated from each other.<sup>30–32</sup> However, accessing the porosity in 209 detail is not trivial because of the complexity of the pore size 210 distribution, which, in the case of a cement paste, ranges from a 211 few nanometers to tens of micrometers, and even because many 212

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 219 PHASES

220 Thermoporometry enables the characterization of a porous <sup>221</sup> 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 °C (low-234 temperature differential scanning calorimetry, LTDSC).<sup>33,35-</sup> LTDSC was used to characterize the porosity of cement.<sup>39-45</sup> 235 236 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 <sup>245</sup> 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 C<sub>3</sub>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>

The DSC heating scan, as reported in Figure 3A, shows a single hump in the -50 °C/0 °C temperature range as a direct consequence of the pore size distribution of cement microtemperature spanning from the nanometer to micrometer scale. During heating, melting of the ice progressively occurs from the fractions confined in the smallest cavities to the fractions present fractions confined in the smallest cavities to the fractions present freezing process occurs in a discontinuous way, and the cooling scan shows specific peaks (e.g., Figure 3B). This peculiar behavior is usually attributed to the combination of homogeneous and heterogeneous freezing mechanisms. The homogeneous nucleation is an activated process where a free-energy 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.

appear. Thus, the heterogeneous nucleation preferentially occurs 274 because the energy required by this process is smaller. According 275 to the molecular dynamics (MD) study on homogeneous ice 276 nucleation,<sup>47</sup> at a low degree of supercooling (-20 °C < T < 277 0  $^{\circ}$ C), only heterogeneous nucleation is possible because of the 278 high free energy required for the homogeneous formation of a 279 critical nucleus (at  $T \approx -15$  °C, diameter  $\approx 8$  nm corresponding 280 to ~8000 molecules). For this reason, in a saturated system, 281 water freezes via heterogeneous nucleation even if it is confined 282 in cavities with dimensions that are large enough to host critical 283 nuclei isolated from the surface. Once the water in the large pores 284 (capillary pores) is frozen, the ice remains in contact with the 285 liquid water still present in the smaller cavities. By lowering the 286 temperature to below -20 °C, the size of the critical cluster 287 sensibly decreases (at  $T \approx -35$  °C, diameter  $\approx 3.5$  nm corre- 288 sponding to ~600 molecules), and the nucleation free energy 289 barrier decreases, making the homogeneous process likely to 290 occur. Under these conditions, both the homogeneous and 291 heterogeneous nucleation mechanisms become accessible at 292 comparable rates. Then, freezing will occur in the pores whose 293 dimensions can host a critical ice cluster that is stable at that 294 temperature. However, the appearance of peaks in the cooling 295 curve indicate that the process starts at the pore entrance, where 296 the liquid water is in contact with the surrounding ice, which is a 297 preferential site for the nucleation. The dimensional range of 298 these freezing pores must be comparable to the size of their 299 entrance because, for the reasons given before, the water in larger 300 pores is already frozen at this stage, and the smaller pores cannot 301 host a critical ice nucleus. In the case of cement pastes, the 302 developing phases originate from three classes of nanometric 303 porosities on top of the capillary porosity. According to Jennings' 304 colloidal model II,<sup>46</sup> these are named the interlayer lamellar 305 porosity (IGP, <1 nm), small gel pores (SGP, 1-3 nm), and large 306 gel pores (LGP, 3-12 nm). The water inside the lamellar IGP 307 of the primary unit cannot freeze (see paragraph on LTDSC), 308 and thus it cannot be detected using DSC. By integrating each 309 peak in the cooling scan (e.g., Figure 3B), the amount of water 310 311 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>

It is important to stress here that, in addition to pore size 314 315 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.49 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 the strong H-bond with oxygen atoms in silicate chains and the 328 329 ionic effect induced by the highly concentrated surface calcium 330 ions.<sup>49-51</sup> Because of the strong hydrophilic effect from the C-S-H surface, more energy is needed for the surface-adsorbed 331 332 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 extend because the 340 protruded bridging tetrahedron has a higher tendency to disturb the transport channel that exists in the gel porosity. 341

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 347 cooling scan of MgO/SiO<sub>2</sub>: the shape of the curve indicates that, 348similar to C-S-H-containing matrixes, this sample has a fraction 349 of water confined in large (capillary) pores where the liquid can 350 freeze via heterogeneous nucleation, and another fraction that is 351 confined in smaller pores gives rise to the large bump between 352 -20 and -35 °C and to the sharp peak at -41 °C. Figure 4B 353 shows Portland cement hydrated for the same time and with the 354 same w/c: the thermogram shows that when the amount of 355 water is high, only the capillary porosity remains, together with 356 the porosity in the 1-3 nm range (SGP), which is a structural 357characteristic of the Portland-based samples. The significant 358 difference existing between the two thermograms (in the region 359 of  $-20 \text{ }^{\circ}\text{C}/-40 \text{ }^{\circ}\text{C}$ ) can be further understood by considering 360 the difference existing in the structure and the enclosed porosity 361 of the two main hydration products (M–S–H and C–S–H), as 362 we will discuss later in this article. 363

As already mentioned, the pore size distribution, P(r), deter- 364 mines the hump in the heating part of the thermogram. Thus, in 365 principle, it should contain information on the fractal arrange- 366 ment of the cementitious matrix, which is the result of how the 367 primary units are assembled into the volume generating the 368 porosity of the hydrated phase. Mass and surface fractal dimen- 369 sions ( $D_{\rm m}$ ,  $D_{\rm s}$ , respectively) are usually obtained using small- 370 angle scattering techniques, as reported in the literature for 371 various cement pastes. 53-55 The fractal nature of porous matrixes 372 can also be determined using DSC by relying on the fact that the 373 melting temperature of an ice crystal confined in a pore of radius 374 *R* (with R = r - l, where *r* is the radius of the pore and *l* is the 375 thickness of the nonfreezable layer of water at the solid interface) 376 is depressed by a quantity  $\Delta T = T_{\rm m}^0 - T_{\rm m}$ . Previous estimations 377 from NMR measurements on porous glasses report a value for l 378 of  $0.5 \pm 0.1$  nm.<sup>56</sup> This is the reason that the water confined in 379 IGP within the calcium silicate layers does not freeze, and the size 380 of these pores is approximately 1 nm. The Gibbs-Thomson 381 equation states that the melting temperature,  $T_{\rm m}$ , and the pore 382 radius, R, are inversely related as follows 383

$$T_{\rm m} = T_{\rm m}^0 \left( \frac{1 - 2\gamma V_{\rm s}}{\Delta HR} \right) \tag{2}_{384}$$

where  $T_{\rm m}^0$  is the melting temperature of an ice crystal of infinite 385 dimension,  $\gamma$  is the solid–liquid interfacial tension,  $\Delta H$  is the 386 specific melting heat, and  $V_{\rm s}$  is the specific volume of the solid. 387 Considering water (i.e.,  $T_{\rm m}^0 = 273.15$  K,  $\gamma = 40 \times 10^{-3}$  N m<sup>-1</sup>, 388  $\Delta H = 334$  J g<sup>-1</sup>, and  $V_{\rm s} = 1.02$  cm<sup>3</sup> g<sup>-1</sup>), eq 2 becomes 389

$$\Delta T = \frac{68.29}{R}$$
(3) 390

with *R* in nanometers.

When a water-saturated porous sample, with a pore size distribution 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 spits estimation is quantitative. The incremental pore volume per 400 solid mass can be written as dV = P(r) dr. To obtain dV, the 401 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 404

391

412

405 literature,<sup>57</sup> the heat flow,  $J_{qr}$  measured using DSC is related to 406  $\Delta T$  by a scaling law consistent with the fractal nature of the 407 systems. The porous system can be regarded as a homogeneous 408 solid of density  $\rho_S$ , where an incremental pore volume per solid 409 unit mass dV was used to account for the change in the bulk 410 density of the porous sample,  $\rho(r)$ , as a function of the pore-411 filling steps.<sup>58</sup> Mathematically, the process is described as

$$\frac{1}{\rho(r)} = \frac{1}{\rho_{\rm S}} + \int_0^r P(r) \, \mathrm{d}r \tag{4}$$

<sup>413</sup> In the fractal regime, where  $a \le r \le \xi$ ,  $\rho(r)$  will scale with r as <sup>414</sup> follows

$$\rho(r) = \rho_{\rm S}(r/a)^{D_{\rm m}-3} \tag{5}$$

416 where *a* is the characteristic dimension of the smallest repeating 417 unit and  $\xi$  is the maximum correlation length of the fractal 418 aggregate. Combining eqs 3 and 5,

$$dV = A(\Delta T)^{D_{\rm m}-3}$$
(6)

420 where *A* is the scaling factor.

Hence,  $D_{\rm m}$  can be simply obtained from the fitting of the dV vs 422  $\Delta T$  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<sub>3</sub>S/water during hydration. Reproduced with permission from ref 44.

423 investigate the effect of different superplasticizer on the frac-424 tality of C<sub>3</sub>S pastes.<sup>44</sup> For example, Figure 5 shows the dV vs 425  $\Delta T$  log-log plots, and the fitting lines from  $\Delta T_{\xi} \cong 1$  K to  $\Delta T_{a} \cong$ 426 10 K, corresponding to pores with a radius of between 100 and 427 10 nm (eq 3). The size range explored by DSC is very close to what 428 is usually measured in a standard small-angle scattering experiment. As is reported in Figure 5, a C<sub>3</sub>S/water paste (w/c = 0.4) has a 429 430 fractal dimension that increases from 2.0 to 2.6 in the first 28 days 431 of curing.<sup>44</sup> These results are in good agreement with previous 432 SAXS investigations, <sup>53</sup> which reported  $D_m$  for a similar paste to 433 vary from 1.9 to 2.8 in the same time interval. The same approach 434 was also used on C<sub>3</sub>S/water samples containing superplasticizers 435 to highlight their effect on both C-S-H nanostructure and 436 porosity. The  $D_{\rm m}$  values for pastes cured for 1 month in the 437 presence of superplasticizers resulted in lower values than in the

 $C_3S$ /water case, indicating that the presence of superplasticizers 438 causes the formation of a more open nanoscale structure with 439 respect to a pristine sample. 440

Even if the exact nanostructure of the C–S–H gel is still an <sup>441</sup> active topic of research, Jennings colloidal model CM-II<sup>46,59</sup> <sup>442</sup> represents one of the best micro/nanoscale descriptions <sup>443</sup> reconciling the colloidal nature of cement-based systems with a <sup>444</sup> large amount of experimental data available in the literature. Very <sup>445</sup> recently, CM-II was used as a starting point to work out a detailed <sup>446</sup> mathematical equation that is able to depict the hierarchy of pore <sup>447</sup> sizes giving rise to the fractal structure property of the C–S–H <sup>448</sup> phase,<sup>60</sup> even including the internal structure of the globule.<sup>61</sup> <sup>449</sup> In general, the scattering intensity distribution related to an <sup>450</sup> assembly of anisotropic units can be written as

$$I(Q) = N\langle P(Q) \rangle S(Q)_{c} + bkg$$
(7) 452

where *N* is a scaling constant considering the number density and 453 the probe interaction of the globules,  $\langle \overline{P(Q)} \rangle$  is the normalized 454 intraparticle structure factor averaged over the distribution of the 455 size and all possible orientations of the globules,  $S(Q)_c$  accounts 456 for the interglobule structure factor coming from the fractal 457 arrangement corrected for the polydispersity of the system, Q is 458 the scattering vector, and bkg is the background term.  $\langle \overline{P(Q)} \rangle = 459$  $\langle |F(Q)|^2 \rangle$  takes into account the internal layered structure of the 460 primary globules (i.e., F(Q) is the particle form factor; in the case 461 of C–S–H, it describe the scattering of the disklike unit).<sup>60</sup> If the 462 size, orientation, and position of the basic units are uncorrelated, 463 then  $S(Q)_c = 1 + \beta(Q)[S(Q) - 1]$  with  $\beta(Q) = |\langle F(Q) \rangle|^2 / \langle |F(Q)|^2 \rangle$ . 464 The interparticle structure factor for the fractal arrangement can be 465 expressed as

$$S(Q) = 1 + \left(\frac{\xi}{R_{\rm e}}\right)^{D_{\rm m}} \Gamma(D_{\rm m} + 1) \frac{\sin[(D_{\rm m} - 1)\tan^{-1}(Q\xi)]}{(D_{\rm m} - 1)[1 + (Q\xi)^2]^{[D_{\rm m} - 1/2]}(Q\xi)}$$
(8) 467

where  $R_{\rm e}(3\overline{n}R^2L/4)^{1/3}$  is the equivalent radius (where  $\overline{n}$  is aver-468 age number of stacks in a disklike unit and R and L are defined in 469 Figure 6) and  $D_{\rm m}$  and  $\xi$  are the mass fractal and cutoff dimension 470 of the aggregate, as already defined in the LTDSC section. 471



**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 472 (from either neutrons or X-rays) with the aim of unveiling 473 the globule shape and size distribution as well as the fractal 474 dimension and correlation distance characteristic of the overall 475 arrangement in the case of the C–S–H phase. It turns out that 476 the disklike shape of the globular unit assumed in CM-II is 477 experimentally confirmed. This approach was used to investigate 478 the effect of the water content<sup>61</sup> and of the addition of comb- 479 shaped superplasticizers<sup>62</sup> on C–S–H synthetic phases. 480

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 <sup>488</sup> linearly translated into an increase in dimensions of the globule.<sup>62</sup> Using the same approach, some of the authors were also able 489 490 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 <sup>495</sup> sample,<sup>8</sup> evidencing that these hydrates are not compatible even 496 on the nanoscale. In both cases, a fractal arrangement of the globules is retained. However, globules pack more compactly in 497 498 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 506 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 s11 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 s16 antisymmetric O–H stretching mode of water at  $\sim$ 7000 cm<sup>-1</sup>) 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 523 even higher. The NIR technique, probing thin layers of the 524 samples, can provide information representative of the bulk 525 properties only if the specimen is well-homogenized. According 526 to the literature,<sup>67</sup> the absorption of water in the NIR region can 527 be attributed to two different classes of O-H oscillators, the 528 so-called weakly hydrogen bonded (WHB) and strongly 529 hydrogen bonded (SHB) oscillators. The SHB oscillator has a 530 broad absorption at lower wavenumbers, whereas the WHB 531 oscillator is sharper and centered at higher wavenumbers. 532 A significant increment of the WHB intensity is registered as a 533 result of the increase in temperature<sup>67</sup> or the increase in the 534 confinement effects due to a solid matrix.<sup>65</sup> The existence of two 535 classes of hydrogen bonds in a C-S-H/H<sub>2</sub>O system has also 536 been validated by MD simulations<sup>51</sup> showing that the structural 537 hydrogen bond (formed between silicate oxygen atoms and 538 water molecules) has a longer lifetime than the hydrogen bond 539 formed between neighboring water molecules. In the first case, 540 the hydrogen bond is more persistent even if the interaction with 541 the surface induces a change in the local water topology resulting 542 in a reduction in the number of hydrogen bonds<sup>68</sup> (i.e., WHB in 543 the previous notation). 544

When applied to a hydrating tricalcium silicate paste,<sup>69</sup> the 545 NIR technique allowed the assessment of hydration kinetics 546 by monitoring the decrease with time in the intensity of the 547  $5000 \text{ cm}^{-1}$  combination band: this trend follows the hydration 548 profile as obtained using DSC (Figure 7A). The time evolution 549 of the 7000 cm<sup>-1</sup> overtone band accounts for the evolution of 550 the two types of water coexisting in the matrix: the surface- 551 interacting and the bulklike water. The quantification of these 552 two species was possible by deconvoluting the 7000 cm<sup>-1</sup> band 553 into Gaussian components, as shown in Figure 7B. Figure 7C 554 shows that the two Gaussian peaks are directly connected to the 555 bulk water; the strongly hydrogen bonded (SHB, named  $\beta$  and  $\gamma$ ) 556 component decreases in time, and the  $\alpha$  component, associated 557 with the surface-interacting water, weakly hydrogen bonded 558 (WHB) contribution, sensibly increases as a result of the 559 developing surface area. 560

NIR spectroscopy is also particularly powerful in assessing the 561 state of the confined water. This is possible by taking advantage 562 of the temperature dependence of the NIR bands of water and 563 ice. The behavior of the hexagonal ice NIR bands with tem- 564 perature is well described in the literature, particularly for the 565 determination of the temperature of icy regions on remote 566



**Figure 7.** (A) Hydration kinetics of the  $C_3S$  + water paste, as monitored by the 5000 cm<sup>-1</sup> peak area (black circles) compared to the FWI vs time curve obtained using DSC (line). (B) Deconvolution of the 7000 cm<sup>-1</sup> band of the sample  $C_3S$  + water hydrated for 24 h at 20 °C: the  $\alpha$ ,  $\beta$ , and  $\gamma$  Gaussians account for the water, and the sharp  $\varepsilon$  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.

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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.

s70 the shape of the 7000 cm<sup>-1</sup> band occurs when liquid water s71 freezes, with a net red shift of the entire band and the appearance s72 of a new band centered near 6080 cm<sup>-1</sup>, which is commonly s73 considered to be a fingerprint of hexagonal ice. After a week, the s74 trend in the spectra with temperature is similar to that shown in s75 Figure 8B: the figure clearly shows that hexagonal ice formation is s76 inhibited, indicating that water still present in the C<sub>3</sub>S paste s77 solidifies in an amorphous state. This is particularly interesting s78 when compared to the LTDSC experiments (section 3) because s79 it indicates that water confined in the nanometric porosity of the s80 cement matrix is not able to crystallize but solidifies in an s81 amorphous state.

## 5. STATE OF THE WATER: WATER RELAXATION 582 DYNAMICS

**5.1. Quasi-Elastic Neutron Scattering.** Quasi-elastic neutron scattering (QENS) is a technique especially suited for the in situ investigation of relaxation dynamics of hydrogenated species, from the picosecond to nanosecond time scale corresponding to an energy window from a few  $\mu$ eV to tenths of a meV.<sup>72</sup> In complex systems containing water, this technique allows us to characterize the actual state of the water molecules from bulk/confined to completely immobile. QENS experi- ments on cementitious pastes are particularly informative about water dynamics because the incoherent scattering cross section of hydrogen is 10 times larger than that of other elements con- stituting the cement powder (oxygen, calcium, aluminum, iron, and silicon).<sup>21,73</sup> Thus, the QENS signal from a cement paste is dominated by the hydrogen self-dynamics term,<sup>74</sup> allowing for a precise description of both the water state and the transport 597 properties on the nanoscale. The diffusion processes are of 598 fundamental importance in predicting the service life (durability) of 599 cement based systems since corrosive mechanisms involve the 600 permeation of substances, such as aggressive ions, gases or just 601 water, into the concrete.<sup>74,75</sup>

A QENS spectrum usually contains two main contribu- 603 tions: an elastic and a quasi-elastic component (Figure 9A).<sup>73,77</sup> 604



**Figure 9.** (A) Example of a QENS spectrum showing the two characteristic contributions: elastic and quasi-elastic, with an experimental resolution of 40  $\mu$ 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 605 same width of resolution of the QENS spectrometer (and it is on 606 the order of few tenths of a  $\mu$ eV). This component gathers all 607 neutrons scattered elastically (i.e., no exchange in energy) by the 608 nuclei that are immobile in the sample or, in other words, that 609 relax with characteristic times longer than hundreds of ns (i.e., a 610 time longer than the one associated with the resolution of the 611 instrument). In the case of a cement paste, the immobile fraction 612 accounts for the hydrogenated species (mainly chemically bound 613 water) contained in the hydrated phases (CH, C–S–H, etc.). 614 This quantity can be used to follow and detail the hydration 615 kinetics in both the nucleation and growth stage and in the 616 diffusional regime,<sup>78</sup> as already seen in the DSC case.

In the case of mobile atoms, the neutron-nuclei interaction 618 results in an exchange of energy, and the QENS signal shows a 619 broadening associated with the main relaxation processes of the 620 sample (mainly water translational and rotational motions). 621 In general, in the range of interest of a QENS investigation, 622 t > 0.1 ps, the scattering equation for the mobile part can be gen- 623 erally written as  $S(Q, E) = \exp(-\langle u^2 \rangle Q^2/3) \otimes T(Q, E) \otimes R(Q, E)$ , 624 where the first term is the so-called Debye–Waller factor 625 accounting for the mean square displacement of hydrogen in 626 the O–H species, T(Q, E) represents the contribution of the 627

628 translational motion, and R(Q, E) is the contribution of the 629 rotational motion. In the case where Q < 1 Å<sup>-1</sup>, only the  $_{630}$  translational motion is considered, which greatly simplifies the  $_{631}$  modeling of the quasi-elastic component  $^{74,79,80}$  when compared 632 to the cases where larger Q vectors are considered.<sup>81,82</sup> More-633 over, the dependence of the broadening as a function of Q gives 634 additional information on the type of motion (free diffusion, 635 random jump diffusion, free diffusion in a confined geometry, 636 etc.) allowing the calculation of the diffusion coefficient and 637 eventually the residence times and associated jump lengths 638 (Figure 9B). For a detailed review of the fitting models of both 639 the mobile and immobile water fraction, the reader can refer to 640 the literature.<sup>83</sup> However, current approaches tend to ignore the 641 fact that part of the elastic signal comes from liquid water even 642 without the presence of structural water because the Q depen-643 dence of the elastic fraction, especially at very low Q (typically 644 Q < 1 Å<sup>-1</sup>), contains information on the form factor of the 645 confining volume. Very recently, to overcome this limit, a new 646 global fitting approach has been proposed<sup>84</sup> where all of the 647 QENS spectra at a given time are simultaneously modeled over a 648 Q range covering the decay of the elastic incoherent structure 649 factor. This novel improved analysis method can accurately 650 extract the structural water fraction and the associated spatial 651 information directly linked to the confinement of the matrix.

The quasi-elastic component is a key feature in disclosing 653 the evolution of the confinement imposed by the developing 654 C-S-H nanoporosity. Therefore, Fratini et al.<sup>82</sup> clearly evi-655 denced that in the random jump diffusion approximation the 656 average diffusion coefficient for the mobile water fraction  $_{657}$  decreases by approximately 1 order of magnitude (from 4.0  $\times$ 658  $10^{-9}$  to  $4.0 \times 10^{-10}$  m<sup>2</sup>/s) for the C<sub>3</sub>S/H<sub>2</sub>O model system in 659 2 days of curing. Not surprisingly, MD simulations for water on 660 the surface of model  $C-S-H^{68}$  resulted in an average diffusion  $_{661}$  coefficient on the order of  $10^{-10}$  m<sup>2</sup>/s for all surface-associated 662 molecules, which is in agreement with our QENS investigation <sup>663</sup> and with water dynamics in the <sup>1</sup>H NMR field cycling relaxation <sup>664</sup> experiments.<sup>85,86</sup> The same decrease was evidenced by Bordallo 665 et al.<sup>87</sup> by decoupling water dynamics of the capillary pores from 666 that of the gel pores. In addition, the increase in confinement 667 imposed by the developing inorganic matrix causes a reduction of 668 the average jump length from 6 Å to approximately 4 Å in the first 669 2 days of curing.<sup>82</sup> Thus, the quantitative results obtained using 670 the QENS experiment on hydrating cement pastes consist of the 671 conversion of bulklike water (mainly contained in the capillary 672 pores) in favor of constrained (i.e., strongly interacting with the 673 surface, confined mainly in gel porosity) and bound water (i.e., 674 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 675 676 related to the hydration of cement-based systems. By following 677 water dynamics in a 28-cured sample and in the same sample 678 rehydrated after drying at 105 °C, they clearly found that the 679 water reabsorbed into the dried cement paste was more mobile 680 than the water in the pristine cured sample. This suggests that 681 water, once reabsorbed, goes initially into capillary pores and 682 eventually will be admitted into the gel pores only at longer 683 times, as recently confirmed by Pinson et al. using water sorption 684 measurements.<sup>90</sup> Moreover, the initial situation can also be 685 impossible to be restored if the drying process irreversibly 686 damaged the C-S-H nanostructure and the associated porosity. As a matter of fact, QENS can differentiate among bound, 688 constrained, and free water because their relaxation dynamics are 689 quite distinct (i.e., they move differently). The advantage of this 690 technique is twofold: it monitors the conversion of water in the

hydration products and simultaneously detects the water state 691 during the hydration of the cement paste, being able to 692 differentiate between capillary and gel-confined water. 693

**5.2. Porosimetry via NMR Relaxometry.** The dynamics of 694 water in a porous system can also be probed using nuclear 695 magnetic resonance (NMR), which is noninvasive, non-696 destructive, and quantitative.<sup>91</sup> In particular, NMR relaxometry 697 is a well-established method of characterizing pore size distri-698 butions, specific surface areas, binder phase densities, water 699 fractions, and dynamics. This technique has been applied to 700 calcium-based cements for decades to study the formation and 701 characteristics of cement microstructure and to monitor the 702 evolution of water within them. One of the main advantages of 703 NMR experiments is that they provide highly detailed infor-704 mation concerning the microstructure of both crystalline and 705 amorphous phases.<sup>91,92</sup>

The use of combined Carr–Purcell–Meiboom–Gill (CPMG) 707 and quad-echo pulse sequences was recently reported in the 708 literature as an effective method to measure and quantify all 709 hydrogen protons in different environments such as crystalline 710 phases, interlayer water, gel pore water, and capillary water.<sup>91</sup> 711 The measurement of the transverse ( $T_2$ ) and longitudinal ( $T_1$ ) 712 spin relaxation time can be used to estimate the size of the pores, 713 to gain information on the pore network evolution during the 714 hydration process, and to monitor the kinetics of formation of 715 hydrogen-containing solid phases.<sup>92–95</sup> This technique relies on 716 the dependence of the  $T_2$  values of the pore water on the surface/ 717 volume ratio and on the specific surface relaxation. In the cement 718 research field, a tool to quantitatively discriminate different populations of water has been demonstrated.<sup>91,96–98</sup> By assuming the 720 fast diffusion regime,<sup>99,100</sup> the relationship 721

$$\frac{1}{T_2} \approx \frac{\varepsilon S}{V} \frac{1}{T_2^{\text{surf}}} \tag{9}_{722}$$

can be applied, in which  $T_2$  is the measured spin—spin relaxation 723 time,  $T_2^{\text{surf}}$  is the  $T_2$  value for water molecules adsorbed on the 724 surface,  $\varepsilon$  is the thickness of the adsorbed water layer, and S and V 725 are the pore surface area and volume, respectively. Under this 726 condition, from the experimental value of  $T_2$ , it is possible to 727 obtain information on the S/V ratio and therefore on the 728 pore size dimensions, distribution, and evolution in different 729 phases.<sup>101,102</sup> 730

Similarly, this approach was further used, for the first time, with 731 MgO/SiO<sub>2</sub> cements to discriminate different populations of 732 water and to correlate their evolution with the hydration 733 kinetics.<sup>103</sup>  $T_2$  measurements were performed at different times, 734 ranging from ~0.5 h to 1 month, during the hydration of the 735 investigated samples. In this study, several mixtures of Portland 736 cement and MgO/SiO<sub>2</sub> were investigated, and important differ- 737 ences were highlighted. The two binder gel phases, magnesium 738 silicate hydrate (M-S-H) and calcium silicate hydrate 739 (C-S-H), showed significantly different pore size distributions. 740 In the MgO/SiO<sub>2</sub> sample, three peaks were present soon after 741 mixing with water. The peak at the shortest  $T_2$  is due to 742 embedded water, which broadened with increasing hydration 743 time. The other signals were assigned to free water with different 744 mobilities in the spaces between powder grains. The so-called 745 less-mobile water contribution broadened, and the more-mobile 746 water moved to shorter values and decreased with time. In the 747 Portland cement sample, two populations of free water, less 748 mobile and more mobile, appear soon after mixing with water. 749 In the first 6 h, two separate peaks were present, and then they 750

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<sup>751</sup> merged into a single signal that decreased and shifted to shorter <sup>752</sup>  $T_2$  with increases in the hydration time to up to 30 h. After 1 day <sup>753</sup> of hydration, an additional signal was observed as a result of water <sup>754</sup> in the gel pores and interlayer spacing, and then, at a longer <sup>755</sup> hydration time, a peak assigned to water in C–S–H inter-<sup>756</sup> layer spaces started to be resolved, and its relative intensity <sup>757</sup> 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 ( $\bullet$  and  $\blacksquare$ ) are for the more-mobile and less-mobile free water components, and the open symbol ( $\Box$ ) is for free water at longer hydration times, becoming water in the interhydrate spaces. Adapted with permission from ref 103.

<sup>758</sup>  $T_2$  evolution vs the hydration time for the investigated MgO/ <sup>759</sup> SiO<sub>2</sub> (Figure 10A) and Portland cement (Figure 10B). When <sup>760</sup> M–S–H is the binder phase, the porous structures evolve during <sup>761</sup> the entire investigated period, and the final pore distri-<sup>762</sup> bution confirms the globular structure previously proposed in <sup>763</sup> the literature.<sup>8</sup> However, with C–S–H as the main phase, the <sup>764</sup> pore size distribution dramatically changes when this binder <sup>765</sup> phase precipitates, i.e., when water remains segregated in the <sup>766</sup> interlayer spaces and in gel pores.

5.3. Dielectric Relaxation. Various dielectric relaxation 767 768 experiments were conducted on cement pastes and mortars. 769 Depending on the frequency range, several relaxation processes 770 can be followed during the hydration reaction. Typically, three 771 components are monitored: a low relaxation occurring near 772 1 MHz, a medium relaxation at approximately 100 MHz, and a 773 high relaxation in the GHz regime.<sup>104</sup> The main experimental 774 evidence is that the relaxation strength of free water at high 775 frequency (~10 GHz) decreases rapidly as the curing time 776 passes, which enables us to follow the hydration reaction kinetics 777 in these types of systems. The two components observed at lower 778 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> 779 Cerveny et al.<sup>106</sup> studied the influence of the water level on the

Cerveny et al.<sup>106</sup> studied the influence of the water level on the r81 dielectric response of the synthetic C–S–H phase. Even in this r82 case, three different relaxation processes related to water are r83 present at room temperature. The effect of the temperature r84 (110–260 K) was investigated as a function of the water level r85 (6–15 wt %) to evidence the activation mechanism behind these relaxations. All three relaxations exhibited Arrhenius behavior at 786 low water content (<10 wt %). With increasing water level, the 787 process associated with water in small gel pores (medium 788 frequency) shows a crossover from Arrhenius to super-Arrhenius 789 (i.e., the motions become cooperative) as the water level reaches 790 10 wt % or in other words more than one monolayer is present. 791 In the case of the water confined in large gel pores (high- 792 frequency process), no crossover (from Arrhenius to super- 793 Arrhenius) is present, and the super-Arrhenius behavior testifies 794 to a cooperative relaxation for high water content. The two 795 populations described agree with the findings reported using 796 LT-NIR and DSC by some of the authors of the present 797 paper.<sup>43</sup> More interesting, the crossover from Arrhenius to super-798 Arrhenius behavior was reported in the translational relaxation 799 dynamics as obtained using QENS in C–S–H, M–S–H,<sup>107</sup> and 800 various cement pastes.<sup>108,109</sup>

#### 6. CONCLUDING DISCUSSION

The physicochemical properties of water can be a fundamental 802 and unique resource to investigate complex porous matrixes. 803 This feature article presented relevant results obtained on 804 cement, which is a complex inorganic nanocomposite with struc- 805 tural characteristics (such as the pore size range and the 806 dimension of the basic building block generating the fractal 807 microstructure) that undoubtedly allow its allocation among the 808 vast class of colloidal systems.<sup>73</sup> Furthermore, the number of 809 innovative hydraulic cement formulations both for building and 810 biomedical applications is going to increase, and the character- 811 ization of their kinetics and structural properties will become 812 crucial for their improvement and formulation. The colloidal 813 nature of cement suggests that the approach of using water as a 814 probe can be extended to several other colloidal systems with 815 very different chemical composition, where water plays a key role 816 in the structure of the material (i.e., water is the main consti- 817 tuent). For example, in nonevolving systems with pores in the 818 nanometer range, such as zeolites, clays, carbon nanotubes, or 819 other inorganic matrixes, the thermal behavior evaluation of 820 water is a method to infer their properties in terms of porosity, 821 whereas the combination of QENS, NIR, NMR relaxometry, and 822 dielectric relaxation allows one to study the translational, vibra- 823 tional, and rotational motions of the confined liquid, thus 824 evidencing the transport properties of the host material. How- 825 ever, biological molecules such as proteins, polysaccharides, and 826 DNA always display behavior that is dictated by the presence of 827 water as in the case of the plasticizing effect of water on the glass 828 transition of biopolymers, and the study of water dynamics often 829 vields precious information on their structure and activity. 830 In addition, hydrogels can be successfully investigated by study- 831 ing the properties of water, which directly regulates the transport 832 phenomena of ions, molecules, and even gases through them. 833

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#### Langmuir

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#### 848 Notes

849 The authors declare no competing financial interest.

#### 850 Biographies



851 From left to right: Sow-Hsin Chen, Piero Baglioni, Francesca Ridi, 853 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
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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 891 dynamical characterization of nanomaterials and soft matter. 892

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ABBREVIATIONS 898

NMR, nuclear magnetic resonance; CPMG, Carr–Purcell– 899 Meiboom–Gill; LTDSC, 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-Erove'ev; 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

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