



# Effect of phosphate additives on the hydration process of magnesium silicate cements: thermal and spectroscopic characterization

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## Abstract

The role of phosphate additives on the hydration process of magnesium silicate cement pastes was investigated through a multi-technique approach. A MgO/SiO<sub>2</sub> mixture was hydrated for 28 days either in the absence or in the presence of sodium hexametaphosphate, trimetaphosphate or orthophosphate. Information on the kinetics of the hydration reaction was acquired by monitoring the free water index by means of differential scanning calorimetry, while the hydration products were thoroughly investigated by X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, scanning electron microscopy and <sup>29</sup>Si solid-state nuclear magnetic resonance spectroscopy. The overall results provide new insight into the effect of phosphates on the hydration reaction and on the structure of magnesium silicate hydrate cements. All additives showed a plasticizing effect and promoted the formation of the binding phase magnesium silicate hydrate (M–S–H), without significantly altering its structure. Sodium orthophosphate was found to be by far the best-performing additive, even better than sodium hexametaphosphate, which is commonly used in these cementitious formulations. For the first time, <sup>31</sup>P solid-state NMR investigation allowed orthophosphate ion to be identified as the effective species.

**Keywords** Magnesium silicate hydrate · Orthophosphate · Plasticizer · Hydration kinetics · Thermal analysis · MAS NMR

## Introduction

Magnesium silicate hydrate (M–S–H) is a colloidal gel obtained by hydration of reactive periclase (MgO) in the presence of silica (SiO<sub>2</sub>). Thanks to its cementitious properties, M–S–H represents an environmentally

convenient alternative to standard binders based on calcium silicate hydrate (C–S–H) [1, 2]. MgO/SiO<sub>2</sub> cement recently gained considerable attention in the scientific community as it resulted a good candidate for some peculiar applications, such as the cementification of problematic radioactive wastes, enhancing the durability of the deep repositories within the natural clay environment [3–7].

During the hydration of MgO/SiO<sub>2</sub>, several reactions can occur: dissolution of MgO to give Mg<sup>2+</sup> and OH<sup>-</sup> ions and precipitation of brucite (Mg(OH)<sub>2</sub>) when these ions reach the supersaturation point; silica hydration, which in basic conditions brings to the formation of silicate anions;

Monica Tonelli and Francesca Martini have contributed equally to this work.

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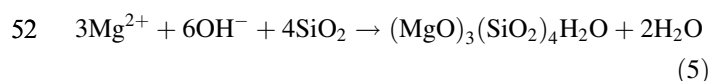
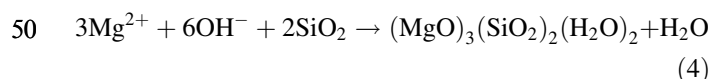
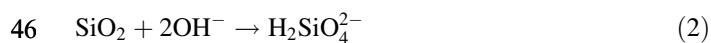
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42 reaction of hydrated silica with  $\text{Mg}^{2+}$  with formation of  
43 M–S–H gel [6–9]. These reactions can be schematized as  
44 [6, 9, 10]:



54 The last two reactions bring to the formation of ser-  
55 pentine and talc, respectively. Indeed, it has been shown  
56 that M–S–H is an amorphous phase with a sub-nanometric  
57 structure resembling that of Mg-phyllsilicate minerals:  
58 depending on the MgO and  $\text{SiO}_2$  relative content, their  
59 reactivity and the hydration conditions, serpentine-like and/  
60 or talc-like nanodomains were found in M–S–H [5, 10, 11].

61 When preparing cementitious pastes, the addition of  
62 admixtures is essential to achieve different goals, such as  
63 accelerate or retard setting or hardening, decrease the  
64 amount of water needed to obtain a proper workability,  
65 improve the mechanical performances and entrain air. For  
66 Portland-based cements, many different additives are  
67 commonly used to improve specific properties [12–17]. In  
68 the field of MgO/ $\text{SiO}_2$  cement, sodium hexametaphosphate  
69 ( $(\text{NaPO}_3)_6$ , HMP) has been the preferred plasticizer so far  
70 [5, 18–20]. Few works reported that the use of about  
71 1–2 wt% of HMP with MgO/ $\text{SiO}_2$  produces an effective  
72 reduction in the water/solid ratio and an improvement of  
73 the cement compressive strength [5, 18, 19]. Walling et al.  
74 stated that the addition of HMP does not alter the structure  
75 of M–S–H [5], but its role on M–S–H precipitation was not  
76 unraveled. Jia et al. investigated the effect of HMP on the  
77 hydration of MgO/ $\text{SiO}_2$  mixes and the formation of M–S–  
78 H [20]. They showed that HMP inhibits the formation of  
79 brucite when MgO is hydrated, and hypothesized that this  
80 is due to the adsorption of  $(6\text{MgOH}^+ \cdot (\text{PO}_3)_6^{6-})$  complexes  
81 on the MgO surface, which prevent the nucleation of  
82  $\text{Mg}(\text{OH})_2$ . The same authors reported that HMP determines  
83 a pH increase, which favors silica fume dissolution [21],  
84 and, when added in a proper amount, also leads to a rise of  
85  $\text{Mg}^{2+}$  concentration in solution (the authors speculate the  
86 presence of a  $[\text{Mg}_2(\text{PO}_3)_6]^{2-}$  species in solution),  
87 enhancing the formation of M–S–H. According to the  
88 hypotheses of Jia et al., the hexacycle phosphate molecule  
89 is the effective species affecting the properties of MgO/  
90  $\text{SiO}_2$  pastes. However, this has not been experimentally  
91 demonstrated yet, neither the effect of different phosphate-  
92 based additives has been explored so far.

To address these points, in the present work, MgO/ $\text{SiO}_2$  93  
pastes were prepared using three different phosphate salts, 94  
as shown in Fig. 1: sodium hexametaphosphate ( $(\text{NaPO}_3)_6$ , 95  
HMP), sodium trimetaphosphate ( $\text{Na}_3(\text{PO}_3)_3$ , TMP) and 96  
sodium orthophosphate ( $\text{Na}_3\text{PO}_4$ , OP). The combination of 97  
thermal and spectroscopic analyses is often essential to 98  
address the full characterization of cementitious materials' 99  
properties [22, 23]. In the present work, this multi-tech- 100  
nique approach allowed us to obtain a detailed character- 101  
ization of the samples, clarifying the influence of phosphate 102  
additives on the hydration reaction of MgO/ $\text{SiO}_2$  mixes and 103  
on the formation of M–S–H. In particular, we performed 104  
mini-slump tests [24, 25], free water index (FWI) deter- 105  
mination (by means of differential scanning calorimetry, 106  
DSC) [26–28], pH measurement, X-ray Diffraction (XRD), 107  
thermogravimetric analysis (TGA), Fourier transform 108  
infrared spectroscopy (FTIR) and scanning electron 109  
microscopy (SEM). The effects of the additives on the M– 110  
S–H structure were assessed by means of  $^{29}\text{Si}$  solid-state 111  
nuclear magnetic resonance spectroscopy (SSNMR) and, 112  
for the first time,  $^{31}\text{P}$  SSNMR was exploited to characterize 113  
the phosphate species present in the hydrated samples. The 114  
preparation of the specimens was specifically tailored to 115  
identify which phosphate species is actually responsible for 116  
the improving effects on the hydration reaction. In particu- 117  
lar, the additives were not pre-dissolved in water, so to 118  
avoid the hydrolysis of the hexacycle and the tricycle 119  
before the mixing with MgO and  $\text{SiO}_2$  powders. 120

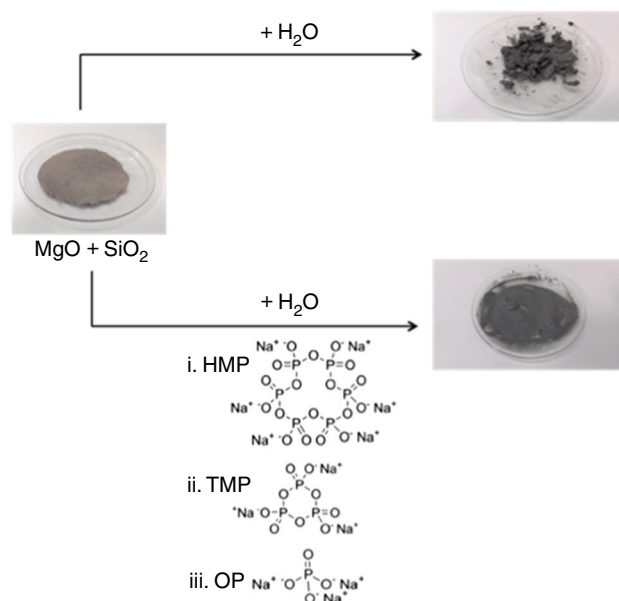


Fig. 1 Scheme of the preparation of MgO/ $\text{SiO}_2$  cement paste without (top) and with (bottom) HMP, TMP or OP additives

121 **Experimental**122 **Materials**

123 Highly reactive MgO (Magnesium oxide N 50, purity  $\approx$   
124 97%, BET surface area =  $150 \text{ m}^2 \text{ g}^{-1}$ ) was obtained from  
125 Lehmann&Voss&Co., SiO<sub>2</sub> (purity > 90%, BET surface  
126 area =  $4.33 \text{ m}^2 \text{ g}^{-1}$ ) from Elkem. HMP was purchased  
127 from CarloErba, TMP and OP from Aldrich.

128 **Samples**

129 Samples were prepared by mixing MgO and SiO<sub>2</sub> in a 1:1  
130 molar ratio ( $\pm 0.1$ ). When present, phosphate additives  
131 were dry mixed with MgO/SiO<sub>2</sub> at a P:Mg ratio of 0.01  
132 (corresponding to 1 wt% in the case of HMP). Then, the  
133 powders were gradually added to milliQ water at a water to  
134 solid weight ratio (w/s) of 0.8 and manually mixed. Sam-  
135 ples will be indicated throughout the paper as: MSH  
136 (without additives), MSH-HMP, MSH-TMP and MSH-OP.  
137 The sample labelled as MSH@pH = 11.8 was prepared by  
138 dry mixing MgO and SiO<sub>2</sub> and gradually adding the  
139 powder to a solution of milliQ water and NaOH at pH =  
140 11.8. The composition of this sample is analogous to  
141 MSH, but at same pH established by MSH-OP. For the  
142 mini-slump tests, a higher water to solid ratio (w/s = 2) and  
143 an automatic mixer were used.

144 Specimens for TGA, FTIR, SEM, XRD and SSNMR  
145 analyses were prepared by stopping the hydration reaction  
146 after  $n$  days ( $n$ : 1–28): about 1 g of paste was withdrawn,  
147 cooled in liquid nitrogen, and freeze-dried (50 mTorr,  
148  $-55 \text{ }^\circ\text{C}$ , 24 h).

149 **Methods**

150 For mini-slump tests, a miniature slump cone was fabri-  
151 cated in PMMA with a top diameter of 19 mm, a bottom  
152 diameter of 38 mm and a height of 57 mm, to maintain the  
153 same proportion of the slump cone described by ASTM  
154 C143 [29]. In the literature, the use of the miniature slump  
155 test was reported for Portland cement to compare the per-  
156 formances of water reducing admixtures and to evaluate  
157 the workability of the samples [5, 24, 35]. The cone was  
158 filled with freshly prepared paste and, after 1 min, lifted  
159 with a rapid motion. Thus, the spreading out diameter of  
160 the investigated sample was measured [30].

161 For DSC experiments, roughly 50 mg of each mixed  
162 paste was transferred in a steel pan (diameter 7.4 mm,  
163 capacity 60  $\mu\text{L}$ ) and sealed with a cover equipped with a  
164 neoprene O-ring, to avoid water leaking. The pan was  
165 maintained at  $20 \text{ }^\circ\text{C}$ , and samples were periodically ana-  
166 lyzed in a DSC Q2000 calorimeter from TA Instruments

(New Castle, DE, USA), with the following temperature  
167 program: equilibrate to  $-60 \text{ }^\circ\text{C}$ , isothermal for 4 min,  
168 ramp from  $-60 \text{ }^\circ\text{C}$  to room temperature at  $5 \text{ }^\circ\text{C min}^{-1}$ .  
169

170 FWI was determined following a procedure already  
171 reported in the literature [26, 27]. The method is based on  
172 the quantification of free, or freezable, water index by  
173 DSC. In this approach, the pastes are periodically frozen  
174 and then melted by heating at a constant rate in the DSC, as  
175 previously described. The melting peak of free, still unre-  
176 acted, water is integrated to obtain the melting enthalpy  
177 ( $\Delta H_{\text{exp}}$ ) and calculate FWI using Eq. (6):

$$\text{FWI} = \Delta H_{\text{exp}} / \varphi_w \Delta H_{\text{theor}} \quad (6)$$

179 where  $\varphi_w$  is the original weight fraction of water in the  
180 paste and  $\Delta H_{\text{theor}}$  is the theoretical value of the melting  
181 enthalpy of water ( $333.4 \text{ J g}^{-1}$ ).

182 pH measurements were taken, according to a method  
183 already established in the literature [10, 31], using a  
184 BASIC 20 CRISON pHmeter calibrated with three buffer  
185 solutions at pH 7.00, 9.21 and 10.90 (CRISON), at room  
186 temperature ( $22 \pm 1 \text{ }^\circ\text{C}$ ). In a polyethylene flask, 1 g of  
187 mixed solid and 10 g of distilled water were added. The  
188 container was sealed and constantly shaken in an orbital  
189 stirrer. At different time intervals, the solid particles were  
190 allowed to settle and the pH of the supernatant was  
191 measured.

192 X-ray diffractograms were recorded with an XRD Bru-  
193 ker New D8 Da Vinci instrument operating at 40 kV and  
194 40 mA, with a Cu source (emitting radiation  $\lambda = 1.54 \text{ \AA}$ ).  
195 Data were collected in the  $5^\circ$ – $70^\circ$   $2\theta$  range, with an  
196 increment of  $0.05^\circ$ , at 0.5 s per step.

197 TGA measurements were performed by means of a SDT  
198 Q600 analyzer from TA Instruments (New Castle, DE,  
199 USA) on approximately 10 mg of each sample, in alumina  
200 pans, heating from room temperature to  $1000 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C}$   
201  $\text{min}^{-1}$ , in nitrogen flux ( $100 \text{ ml min}^{-1}$ ).

202 FTIR spectra were acquired with a BioRad FTS-40  
203 spectrometer (Biorad, Cambridge, MA, USA), between  
204 400 and  $4000 \text{ cm}^{-1}$ , with a resolution of  $2 \text{ cm}^{-1}$ , accu-  
205 mulating 32 scans. For the analysis, 1 mg of each sample  
206 was homogenized with 100 mg of KBr and pressed to  
207 obtain a pellet.

208 SEM images were collected on uncoated fracture sur-  
209 faces with a field-emission SIGMA (Carl Zeiss) micro-  
210 scope, with an accelerating potential of 5 kV.

211 SSNMR experiments were carried out on a Varian  
212 InfinityPlus 400 spectrometer, working at Larmor fre-  
213 quencies of 400.34 MHz, 79.54 MHz and 162.06 MHz for  
214  $^1\text{H}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  nuclei, respectively, exploiting a CP-MAS  
215 probehead accommodating rotors with outer diameter of  
216 7.5 mm. All spectra were obtained using a direct excitation  
217 (DE) pulse sequence under high-power decoupling from  $^1\text{H}$   
218 nuclei and magic-angle spinning (MAS), using air as

219 spinning gas and working at room temperature.  $^{29}\text{Si}$  DE-  
 220 MAS spectra were recorded at a MAS frequency of  
 221 5.5 kHz, with a recycle delay of 20 s and accumulating  
 222 4300 transients.  $^{31}\text{P}$  DE-MAS spectra were recorded at  
 223 MAS frequencies between 4 and 6.2 kHz, accumulating  
 224 4–180 transients separated by a recycle delay of 20 s for  
 225 pristine phosphates and 15,000–40,000 transients with a  
 226 recycle delay of 5 s for MSH-additive samples.  $^{31}\text{P}$  iso-  
 227 tropic peaks were identified by comparing spectra recorded  
 228 at different MAS frequencies.  $^{31}\text{P}$  shielding tensors were  
 229 determined analyzing the spinning sidebands according to  
 230 the Herzfeld and Berger approach [32], using the HBA  
 231 software [33]. The Haerberlen convention was used [34],  
 232 which assigns the principal components  $\sigma_{ii}$  such that  
 233  $|\sigma_{33} - \sigma^{\text{iso}}| > |\sigma_{11} - \sigma^{\text{iso}}| \geq |\sigma_{22} - \sigma^{\text{iso}}|$ , where  
 234  $\sigma^{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ . The shielding anisotropy  $\Delta\sigma$  and  
 235 asymmetry  $\eta$  were calculated as  $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$   
 236 and  $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma^{\text{iso}})$ . Percentages of the dif-  
 237 ferent  $^{29}\text{Si}$  and  $^{31}\text{P}$  species were obtained from peak areas  
 238 rescaled on the basis of the respective measured  $T_1$ 's [10].  
 239 The  $^{29}\text{Si}$  chemical shift scale was referred to the signal of  
 240 3-(trimethylsilyl)-1-propane-sulfonic acid sodium salt at  
 241 1.46 ppm. For  $^{31}\text{P}$  spectra both the chemical shift and  
 242 shielding scales were referred to the signal of  $\text{H}_3\text{PO}_4$  (85%)  
 243 at 0 ppm.

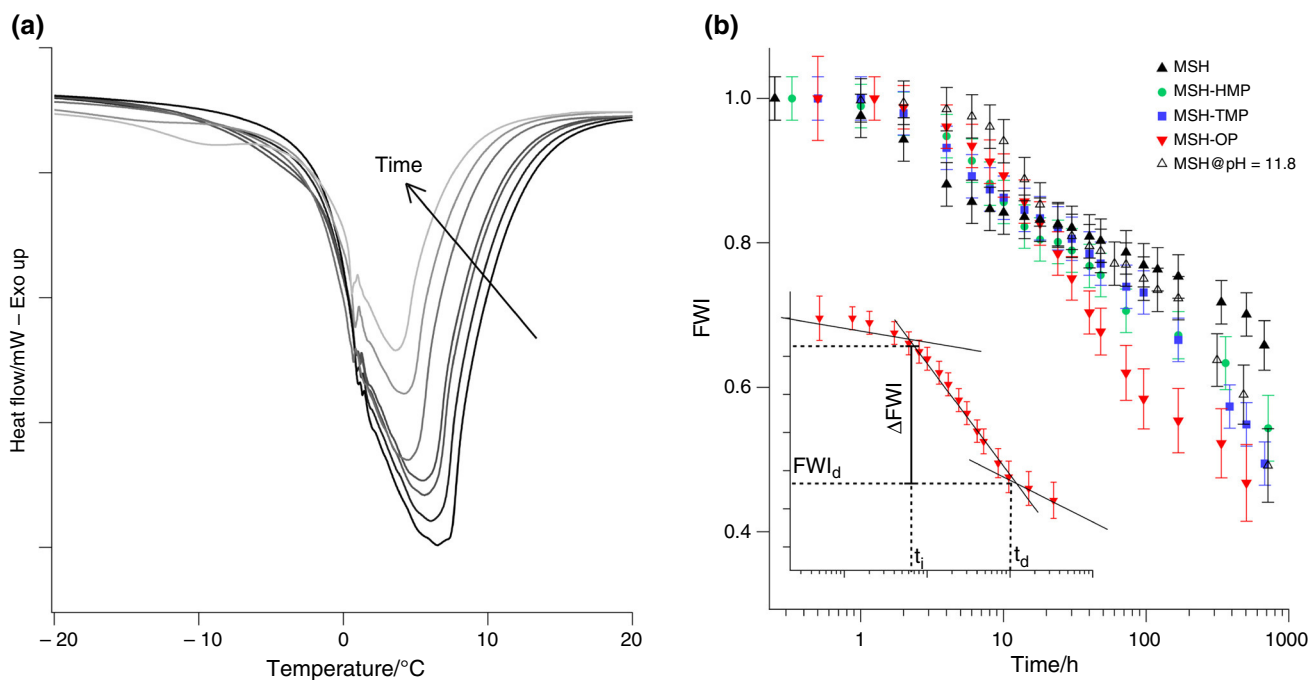
## 244 Results and discussion

245 HMP is usually added to the  $\text{MgO}/\text{SiO}_2$  formulations with  
 246 the aim of improving the fluidity without increasing the  
 247 water amount. The mini-slump tests performed on the  
 248 pastes under investigation (see Figure S11 and Table S11)  
 249 show that all the three phosphate additives improve the  
 250 plasticization, with OP being the most effective one.

251 The hydration reaction of  $\text{MgO}/\text{SiO}_2$  was followed in  
 252 the first 28 days by measuring FWI at different hydration  
 253 times, to evaluate the influence of the additives on the  
 254 formation of the M–S–H phase. Figure 2 shows the DSC  
 255 curves recorded at different hydration times and the FWI  
 256 versus hydration time profiles of the investigated samples.  
 257 The decrease in the melting peak of water with time  
 258 (Fig. 2a) is related to the progress of the hydration reaction,  
 259 and through the integration of these signals, we calculated  
 260 the FWI values at each hydration time, thus obtaining the  
 261 kinetic curves of the process (Fig. 2b). The hydration of all  
 262 samples shows an induction period in which almost no  
 263 water reacts ( $\text{FWI} \approx 1$ ), followed by an acceleration per-  
 264 iod (starting at the induction time,  $t_i$ ), during which FWI  
 265 decreases because of the nucleation and growth of the  
 266 hydrated phases. Then, a change in the curve slope is  
 267 observed due to the modification of the rate-limiting  
 268 mechanism, from *nucleation and growth* to *diffusion-*

269 *limited* behavior, occurring at the diffusion time  $t_d$ . The  
 270 value of FWI at  $t_d$  ( $\text{FWI}_d$ ) represents a measurement of the  
 271 efficiency of the hydration reaction: the lower  $\text{FWI}_d$ , the  
 272 higher the water amount used to form hydrated phases  
 273 during the nucleation-and-growth step [28, 31]. The inset  
 274 of Fig. 2b illustrates the graphical method used to obtain  
 275 the  $t_i$ ,  $t_d$ ,  $\text{FWI}_d$  and  $\Delta\text{FWI}$  parameters reported in Table 1.  
 276 The presence of HMP slightly increases  $t_i$  and prolongs the  
 277 duration of the nucleation-and-growth step, while the  
 278 addition of TMP does not modify the induction and dif-  
 279 fusion times in a significant way with respect to the pristine  
 280 MSH sample. OP markedly retards the onset of the  
 281 nucleation and growth period and extends dramatically its  
 282 duration,  $t_i$  and  $t_d$  being much longer than for the other  
 283 samples (Table 1). It is known from the literature, espe-  
 284 cially in the field of refractory castables [16, 20, 35], that  
 285 phosphate ions are able to hinder  $\text{MgO}$  hydration, by easy  
 286 adsorption on its surface. The long  $t_i$  observed in MSH-OP  
 287 suggests that the interaction of orthophosphate ions with  
 288  $\text{MgO}$  surface is particularly favored in this sample. The  
 289  $\text{FWI}_d$  value is substantially the same for MSH, MSH-HMP  
 290 and MSH-TMP, which indicates that the efficiency of  
 291 water consumption during the nucleation-and-growth stage  
 292 is unaltered by these additives. On the other hand, in the  
 293 presence of OP,  $\text{FWI}_d$  is significantly lower, meaning that  
 294 the hydrated phases keep on precipitating at high rate of  
 295 formation until  $\sim 100$  h, consuming roughly 40% of the  
 296 initial water ( $\text{FWI}_d \sim 0.6$ ). The experimental values of  
 297  $\Delta\text{FWI}$  (Table 1) highlight that OP strongly enhances the  
 298 hydration reaction during the nucleation-and-growth step.

299 It was already reported that a high pH enhances M–S–H  
 300 precipitation by favoring the reactivity of silica. The pH of  
 301 the investigated samples is shown in the Supplementary  
 302 Material (Figure S12). In MSH sample, pH is initially  
 303 determined by the formation of  $\text{Mg}(\text{OH})_2$  ( $\text{pK}_a \approx 10.5$ )  
 304 and then it decreases to  $\sim 9$  because of the consumption  
 305 of brucite in the reaction with hydrated silica to give M–S–  
 306 H, as reported in the literature [21, 36, 37]. In the presence  
 307 of the additives, the trends are similar, but the values of pH  
 308 are higher over the entire investigated period, especially for  
 309 MSH-OP. Aqueous solutions of HMP, TMP and OP (with  
 310 the same concentrations as in the cement pastes) have pH  
 311 of 5.4, 6.8 and 11.8, respectively. It is worth noting that  
 312 despite the pH of water solutions of HMP and TMP is  
 313 lower than the pH of the paste, when these additives are  
 314 mixed to the cement, the final pH is higher than that of  
 315 MSH sample and only some tenths of pH unit lower than  
 316 that of MSH-OP sample. This observation suggests that in  
 317 the corresponding pastes, HMP and TMP undergo  
 318 hydrolysis, to some extent. An additional sample  
 319 “MSH@pH = 11.8” (prepared without any additive, but at  
 320 the same pH of MSH-OP) was investigated in order to  
 321 discriminate the effect on the hydration process arising



**Fig. 2** DSC curves of MSH sample at different hydration times (a) and FWI as a function of hydration time for all the investigated samples (b)

**Table 1** Parameters extracted from the FWI versus hydration time curves as explained in the inset of Fig. 2B

Sample	$t_i/h$	$t_d/h$	FWI <sub>d</sub> ( $\pm 0.05$ )	$\Delta$ FWI ( $\pm 0.01$ )
MSH	1 $\pm$ 0.5	6 $\pm$ 1	0.85	0.12
MSH-HMP	3 $\pm$ 1	18 $\pm$ 2	0.80	0.16
MSH-TMP	2 $\pm$ 0.5	8 $\pm$ 2	0.85	0.11
MSH-OP	6 $\pm$ 2	100 $\pm$ 10	0.58	0.35
MSH@pH = 11.8	6 $\pm$ 2	24 $\pm$ 3	0.82	0.12

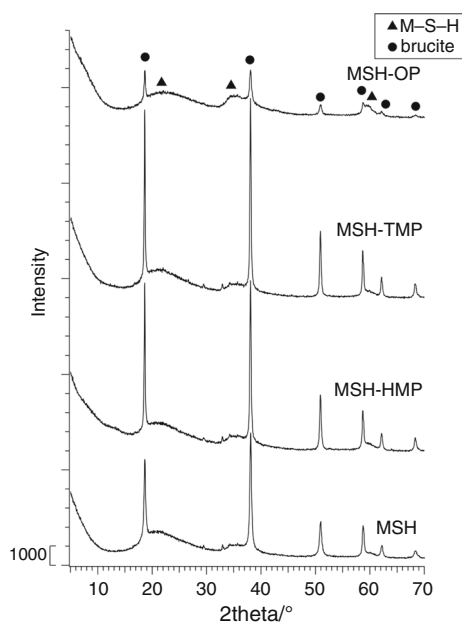
322 from the additives from that of pH. Looking at Fig. 2b and  
 323 Table 1, it is evident that the onset of the nucleation and  
 324 growth period is strongly retarded in “MSH@pH = 11.8”  
 325 sample (long  $t_i$ ), but the efficiency of the reaction is much  
 326 lower if compared to that of MSH-OP (lower  $\Delta$ FWI),  
 327 indicating that the presence of OP strongly affects the  
 328 efficiency of the hydration reaction.

329 To obtain information on the effects of the different  
 330 additives on the composition, morphology and structure of  
 331 cured pastes, we carried out XRD, TGA, FTIR, SEM and  
 332  $^{29}\text{Si}$  SSNMR experiments.

333 In the XRD diffractograms of the investigated samples  
 334 freeze-dried after 28 days of hydration (Fig. 3), no MgO  
 335 peaks can be recognized, indicating that MgO completely  
 336 reacted in the first month. The observed narrow peaks (at  
 337 19°, 38°, 51°, 59°, 62° and 68°) are due to brucite, the main  
 338 crystalline phase of the samples, while the broad peaks at  
 339 about 23°, 35° and 59° are consistent with the XRD pattern  
 340 of the amorphous M–S–H phase [20, 38]. In the presence of  
 341 OP, a low amount of brucite is present, as confirmed by the

quantitative estimation performed with the TG analysis  
 reported in Fig. 4.

342  
 343  
 344 Figure 4a shows the thermogravimetric profiles of the  
 345 analyzed samples. The deconvolution of the corresponding  
 346 differential thermogravimetric (DTG) curves (Fig. 4b) was  
 347 performed in the 200–800 °C temperature range to quan-  
 348 tify the relative amount of brucite in the samples hydrated  
 349 for 28 days [39–42]. In this region, the well-defined weight  
 350 loss at about 375 °C (peak #1) is due to the dehydroxy-  
 351 lation of  $\text{Mg}(\text{OH})_2$  [10]. The broad peak observed in the  
 352 DTG curves (#2) is attributed to multiple weight losses:  
 353 M–S–H silanols, hydroxyl groups and strongly adsorbed  
 354 water of the gel phase [10, 11]. For this reason, it cannot be  
 355 used for a quantitative estimation of the binder phase.  
 356 However, it is clear that the relative amount of brucite in  
 357 MSH-OP is significantly lower than in the other samples  
 358 (Table 2). Considering that the FWI data revealed that OP  
 359 increases the amount of “hydrated phases” and that DTG  
 360 and XRD results show a very low amount of brucite in  
 361 MSH-OP, we can infer that the presence of orthophosphate  
 362 enhances the formation of the M–S–H gel.

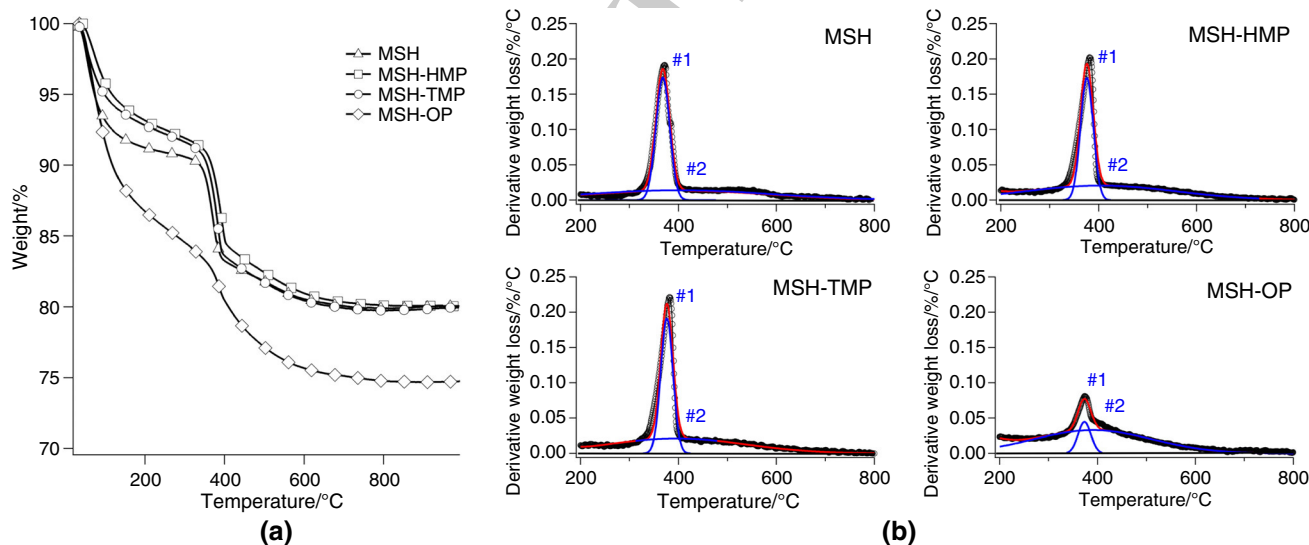


**Fig. 3** XRD diffractograms of the investigated samples freeze-dried after 28 days of hydration

363 The evolution with time of the hydrated phases was also  
 364 followed by means of FTIR spectroscopy. Figure 5 reports  
 365 the FTIR spectra in the  $3900\text{--}2500\text{ cm}^{-1}$  range, which is  
 366 particularly informative because it includes the frequencies  
 367 of the OH vibrations [43]. As expected from the literature

368 for the hydration of MgO and  $\text{SiO}_2$  [11, 44], all samples  
 369 show the sharp Mg-OH stretching vibration of brucite at  
 370  $3696\text{ cm}^{-1}$  and the OH vibrations attributed to the struc-  
 371 tural hydroxyl groups of the M-S-H phase at  $3300\text{ cm}^{-1}$ .  
 372 The signal at  $3300\text{ cm}^{-1}$  increases with time in all samples,  
 373 confirming the formation of the binder gel phase. In the  
 374 presence of OP, this signal is particularly intense, confir-  
 375 ming the enhancement of M-S-H precipitation disclosed  
 376 by FWI and TG/DTG results. In all the samples, the  
 377 amount of brucite decreases as time increases, because of  
 378 its consumption in the reaction with silica to form M-S-H.  
 379 The SEM images (Fig. 6) show the heterogeneous  
 380 complex morphology of the samples. It is possible to rec-  
 381 ognize the spherical shape of unreacted silica particles, the  
 382 amorphous morphology of M-S-H and brucite platelets  
 383 [10, 45]. Interestingly, in the MSH-OP sample, many  
 384 spherical holes were identified. (One of them is displayed  
 385 in the zoom.) Their presence is the clear demonstration that  
 386 silica acts as a “mold” for M-S-H formation, occurring by  
 387 the dissolution and re-precipitation process previously  
 388 hypothesized in the literature [46–48].

389 A clear picture of the structure of the amorphous silicate  
 390 phases present in the samples after 28 days of hydration is  
 391 provided by  $^{29}\text{Si}$  SSNMR spectra (Fig. 7). The spectrum of  
 392 MSH shows the typical signals of the M-S-H phase, whose  
 393 structure at the sub-nanometric scale is known to resemble  
 394 that of magnesium phyllo-silicates [5, 10, 37, 38]. It is

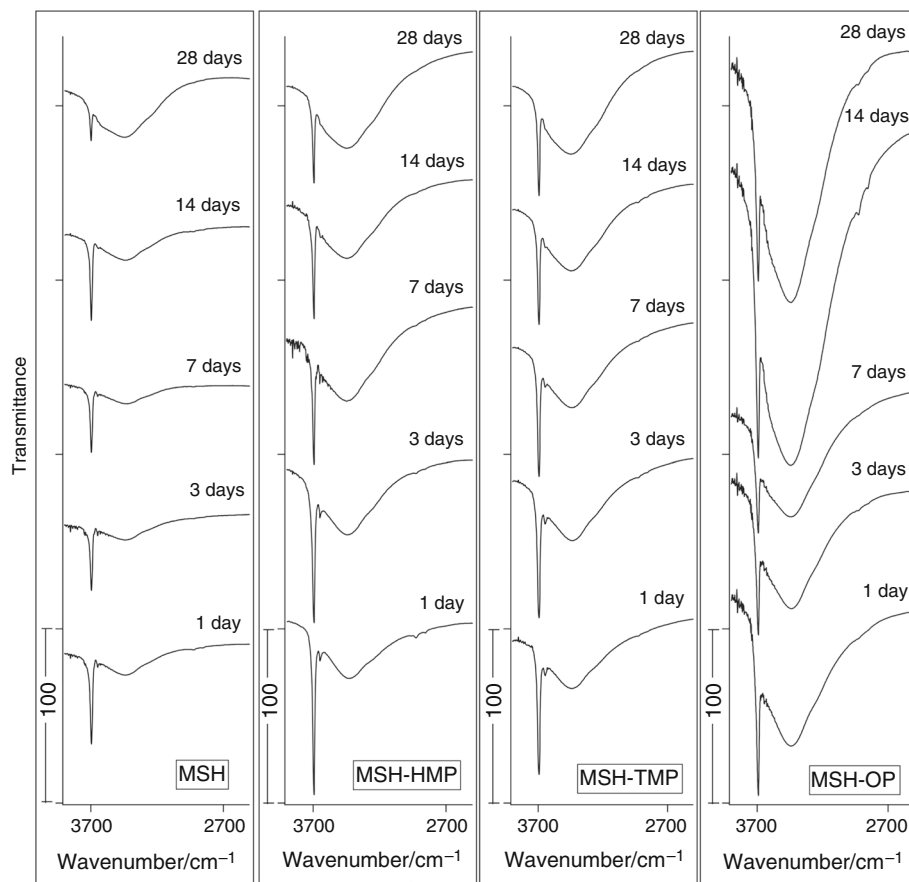


**Fig. 4** TG curves (a) and deconvolution of the DTG curves (b) of the samples freeze-dried after 28 days of hydration. Black markers represent the experimental data; red lines are the global fitting curves; blue lines are the Gaussian peaks obtained by the fitting procedure

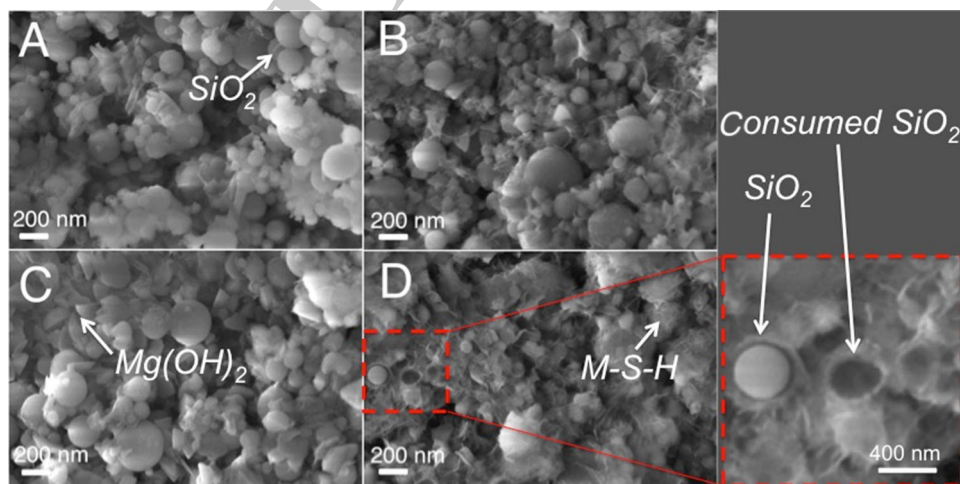
**Table 2** Position and percentage area of the Gaussian peak #1 resulting from the deconvolution of DTG curves

	MSH	MSH	MSH-HMP	MSH-TMP	MSH-OP
Peak 1	$T_{\text{max}}/\text{°C}$	$374 \pm 1$	$376 \pm 1$	$376 \pm 1$	$373 \pm 1$
	Area/%	$6.6 \pm 0.1$	$5.6 \pm 0.1$	$6.0 \pm 0.1$	$1.5 \pm 0.1$

**Fig. 5** FTIR spectra of the investigated samples at different hydration times in the  $3900\text{--}2500\text{ cm}^{-1}$  spectral range. Curves have been offset for the sake of clarity



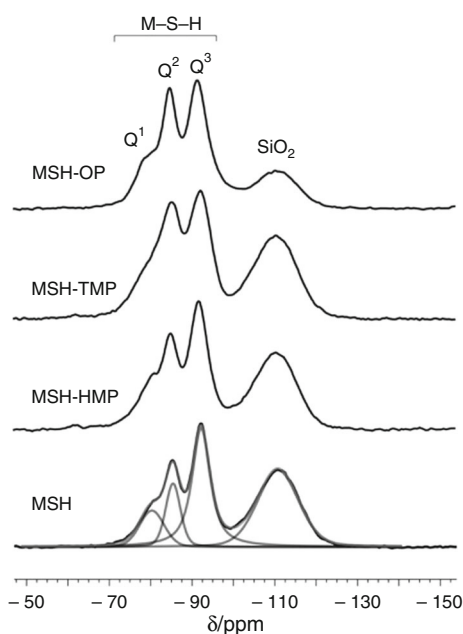
**Fig. 6** SEM images (magnification: 120 K X) of samples freeze-dried after 28 days of hydration: **a** MSH; **b** MSH-HMP; **c** MSH-TMP; **d** MSH-OP



395 possible to recognize signals of  $Q^3$  ( $\text{Si}(\text{OMg})(\text{OSi})_3$ ),  $Q^2$   
 396 ( $\text{Si}(\text{OMg})(\text{OSi})_2\text{OH}$ ) and  $Q^1$  ( $\text{Si}(\text{OMg})(\text{OSi})(\text{OH})_2$ ) sites at  
 397 about  $-92$ ,  $-85$  and  $-80$  ppm, respectively [10, 38]. It  
 398 is worth noticing that, differently from M-S-H previously  
 399 obtained [5, 10, 38, 44], which showed two or more distinct  
 400  $Q^3$  signals ascribed to serpentine- and talc-like structures,  
 401 here a sole  $Q^3$  signal is observed with a chemical shift  
 402 typical of serpentines. Moreover, an intense broad signal

403 ascribable to unreacted silica is present in the spectra at  
 404 about  $-111$  ppm. The relatively scarce reactivity of silica  
 405 can explain the preferential formation of serpentine  
 406 domains for which the Si:Mg ratio is lower than in talc (2:3  
 407 vs. 4:3). Samples prepared with additives show the same  
 408 signals as MSH, although with different relative intensities.

409 From the relative amounts of the different silicon spe-  
 410 cies (Table 3), indicated as “ $Q^i$ ” and “silica” in Eqs. 7 and



**Fig. 7**  $^{29}\text{Si}$  DE-MAS spectra of the indicated samples after 28 days of hydration. The peak assignment to different silicon species is reported on the spectrum of MSH-OP. For MSH, the spectral deconvolution is also shown in gray

8, it is possible to calculate the silica reaction degree (RD) and the condensation degree (CD) of M-S-H as [10]:

$$\text{RD} = 100 \times (Q^1 + Q^2 + Q^3) / (Q^1 + Q^2 + Q^3 + \text{silica}) \quad (7)$$

$$\text{CD} = 100 \times (3Q^3 + 2Q^2 + Q^1) / 3(Q^3 + Q^2 + Q^1) \quad (8)$$

Values of RD (Table 3) confirm and quantify the indications obtained from the other characterization techniques on the enhanced formation of M-S-H in the presence of phosphates: OP has the strongest effect, increasing by  $\sim 30\%$  the amount of reacted silica, while HMP and TMP determine smaller and similar increases (2–7%). On the other hand, the comparison between the CD values

obtained in the presence and in the absence of additives indicates that they do not substantially modify the structure of M-S-H: In all cases, M-S-H with a serpentine-like subnanometric structure is obtained, with a slightly lower CD in the presence of TMP and a slightly higher one in the presence of HMP and OP.

In order to clarify the different effects of the investigated additives, we carried out a detailed analysis of the phosphorus containing species present in the samples by means of  $^{31}\text{P}$  SSNMR. The analysis was extended also to the pristine additives, to better highlight the chemical and structural modifications they underwent during the hydration of  $\text{MgO}/\text{SiO}_2$ . All the  $^{31}\text{P}$  DE-MAS spectra (shown in Fig. 8) were analyzed to obtain, for each phosphorous species, the isotropic chemical shift ( $\delta^{\text{iso}}$ ), the shielding tensor and the relative amount (Table 4).

The spectrum of OP, in agreement with the literature [34, 49, 50], shows only one signal with isotropic chemical shift of 7.7 ppm and very weak first-order spinning sidebands. These features are determined by the high symmetry of the local electronic environment of phosphorus nuclei in the orthophosphate ( $\text{PO}_4^{3-}$ ) groups. In a commonly accepted nomenclature, according to which phosphorus nuclei in phosphate moieties are denoted with  $Q^n$ , where  $n$  is the number of P-O-P bonds, only  $Q^0$  sites are present in OP. The spectra of TMP and HMP show several signals with quite broad spinning sideband patterns. In particular, TMP displays three narrow signals with  $\delta^{\text{iso}}$  of  $-15.8$ ,  $-18.5$ ,  $-19.5$  ppm and quite similar shielding tensors (Table 4), due to  $Q^2$  sites of the TMP rings. The presence of three different signals was already reported in the literature and attributed to either inequivalent sites in the crystals or multiple solid forms [34]. Very weak and broad signals with  $\delta^{\text{iso}}$  of about  $-5$  and  $+5$  ppm are ascribable to impurities. The spectrum of HMP shows three signals at  $\delta^{\text{iso}}$  of 2.5,  $-7.6$  and  $-19.5$  ppm. Peaks are broad, in agreement with the amorphous character of HMP, and show quite different spinning sideband patterns. The signal

**Table 3** Percentages (I) and isotropic chemical shift values ( $\delta^{\text{iso}}$ ) of the different silicon species in the  $^{29}\text{Si}$  SSNMR spectra

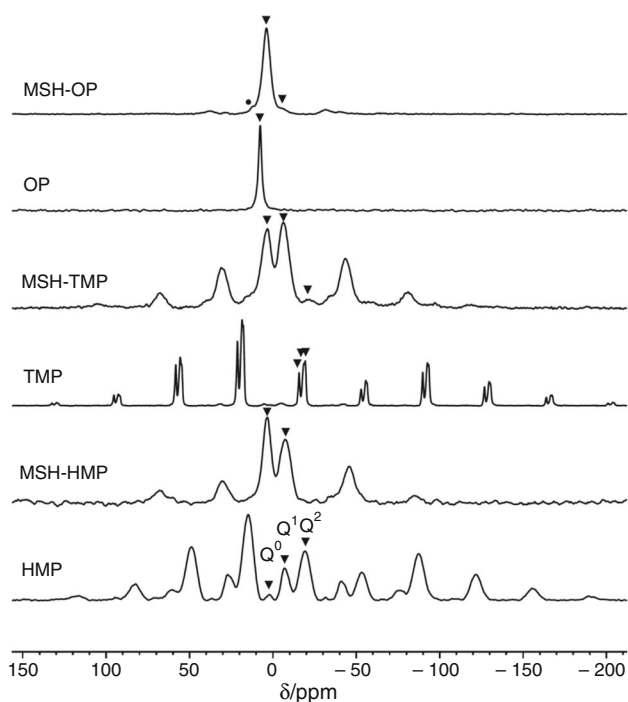
Silicon species	$\delta^{\text{iso}}/\text{ppm}^a$	I/%			
		MSH	MSH-HMP	MSH-TMP	MSH-OP
$Q^1$	$-80.2$	9	8	13	12
$Q^2$	$-85.2$	10	6	15	13
$Q^3$	$-92.0$	31	37	29	51
Silica	$-111.0$	50	49	43	24
RD/% <sup>b</sup>		50	52	57	76
CD/% <sup>b</sup>		81	85	76	84

Values of RD and CD, obtained by Eqs. 7 and 8, are also reported

<sup>a</sup> $\pm 0.2$  ppm

<sup>b</sup> $\pm 2\%$





**Fig. 8**  $^{31}\text{P}$  DE-MAS spectra of pristine additives and MSH-additive samples, as indicated in the figure. Isotropic signals are marked with full triangles, and the peak assignment to  $Q^1$  phosphorus species is indicated in the spectrum of HMP. The full circle indicates a weak signal at about 12 ppm ascribable to anhydrous OP [47]

at  $-19.5$  ppm, characterized by the largest shielding anisotropy, arises from  $Q^2$  sites of HMP rings [49]. The other two peaks (2.5 and  $-7.6$  ppm, accounting for about 17% of phosphorus nuclei in the sample) can be ascribed to  $Q^0$  and  $Q^1$  sites of orthophosphate and pyrophosphate

( $\text{P}_2\text{O}_7^{4-}$ ) moieties, respectively, present as impurities in the sample.

The  $^{31}\text{P}$  spectra of MSH-additive samples show two signals with  $\delta^{\text{iso}}$  of about 4 and  $-7$  ppm, although with quite different relative intensities. For MSH-TMP a weak  $Q^2$  signal ( $\delta^{\text{iso}} = -22$  ppm) is also detected. On the basis of the values of  $\delta^{\text{iso}}$  and shielding tensors, the main signals can be ascribed to hydrated orthophosphate ( $Q^0$ ) and pyrophosphate ( $Q^1$ ) anions [39, 49]. The hydrated environments can be envisaged as water included in the solids or OH groups of M-S-H. In analogy to what already reported for orthophosphate ions in calcium silicate hydrate [51], it is possible that phosphate ions interact with the layers of the M-S-H structure. Moreover, the presence of amorphous magnesium orthophosphates cannot be ruled out [50, 52]. The comparison between the spectra of MSH-additives and those of pristine additives unambiguously highlights that, during cement hydration, the most condensed metaphosphate species ( $Q^2$ ) present in HMP and TMP rings almost completely dissociate into ortho- and pyrophosphate ( $Q^0$  and  $Q^1$ ) ions, due to the alkaline pH [53, 54]. Signal intensities (Fig. 8 and Table 4) indicate that the amount of orthophosphate species decreases in the order MSH-OP > MSH-HMP > MSH-TMP, while pyrophosphates are most abundant in MSH-TMP.

All this considered, these results clearly demonstrate that there is a strong correspondence between higher amount of orthophosphate ions available during cement hydration and better additive performances, in terms of retarding and plasticizing effects and efficiency of M-S-H formation. This can be ascribed to the combination of the following factors: the favored interaction between orthophosphate ions and MgO surface, the increased

**Table 4** Isotropic chemical shifts ( $\delta^{\text{iso}}$ ), percentages (I) and parameters of the shielding tensors of the  $^{31}\text{P}$  species in pristine additives and MSH-additive samples

Sample	$Q^n$	$\delta^{\text{iso}}/\text{ppm}$	I/%	$\sigma_{11}/\text{ppm}$	$\sigma_{22}/\text{ppm}$	$\sigma_{33}/\text{ppm}$	$\Delta\sigma/\text{ppm}$	$\eta$
OP	$Q^0$	7.7	100	ND <sup>a</sup>	ND	ND	ND	ND
TMP	$Q^2$	$-15.8$	36	$-90$	$-38$	175	239	0.33
	$Q^2$	$-18.5$	46	$-82$	$-35$	173	232	0.31
	$Q^2$	$-19.5$	18	$-101$	$-13$	173.0	230	0.57
HMP	$Q^0$	2.5	<1	ND	ND	ND	ND	ND
	$Q^1$	$-7.6$	17	$-68$	$-1$	92	127	0.80
	$Q^2$	$-19.5$	83	$-90$	$-23$	172	229	0.44
MSH-OP	$Q^0$	3.9	95	ND	ND	ND	ND	ND
	$Q^1$	$-5.2$	5	ND	ND	ND	ND	ND
MSH-TMP	$Q^0$	3.9	21	ND	ND	ND	ND	ND
	$Q^1$	$-6.6$	72	83	14	$-76$	$-125$	0.83
	$Q^2$	$-22.0$	7	ND	ND	ND	ND	ND
MSH-HMP	$Q^0$	3.8	38	ND	ND	ND	ND	ND
	$Q^1$	$-7.6$	62	72	24	$-73$	$-121$	0.60

<sup>a</sup>Shielding tensors could not be determined for signals showing very low intensity or few spinning sidebands

499 availability of  $Mg^{2+}$  ions in solution, and the higher silica  
500 reactivity. In conclusion, orthophosphate ion was identified  
501 as the most active species, and thus OP as the best-per-  
502 forming additive.

## 503 Conclusions

504 In this study, the effects on the formation and structure of M–  
505 S–H have been assessed for three phosphate salts: HMP,  
506 already used as plasticizer in  $MgO/SiO_2$  cement pastes, TMP  
507 and OP, here explored for the first time. By means of a  
508 combined thermal and spectroscopic analyses, we found that  
509 all the tested additives increase the fluidity of the pastes and  
510 enhance the formation of M–S–H, inducing minor modifica-  
511 tions on its structure. In particular, the free water index versus  
512 time curves, obtained by DSC measurements, allowed us to  
513 assess the hydration kinetics of pastes prepared with the dif-  
514 ferent additives, evidencing that OP is the most efficient one  
515 in enhancing the formation of hydrated phases. The results of  
516 TGA, XRD, FTIR and  $^{29}Si$  SSNMR experiments demon-  
517 strated in particular that the formation of M–S–H is strongly  
518 increased by the presence of OP. The detailed analysis of the  
519 phosphorus species in the pastes, here performed for the first  
520 time by means of  $^{31}P$  SSNMR, highlighted that the condensed  
521 phosphate additives undergo hydrolysis, giving rise to ortho-  
522 and pyrophosphate species. A clear correspondence was  
523 found between additive best performances and highest  
524 amount of orthophosphate ions, making us to conclude that  
525 these are the species really responsible for the enhancement of  
526 M–S–H formation.

527 As a consequence of our investigation, we propose that  
528 OP could substitute HMP as a plasticizer of  $MgO/SiO_2$   
529 cement, since its performances are clearly better and its use  
530 does not imply cost drawback.

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