



HAL
open science

Synthesis and addition of Al-substituted Tobermorite particles to cement pastes

Marta Diez-Garcia, Juan J. Gaitero, Francisco Borja Aguirre Yagüe, Edurne Erkizia, Jose Tomas San-Jose, Cyril Aymonier, Jorge S. Dolado

► **To cite this version:**

Marta Diez-Garcia, Juan J. Gaitero, Francisco Borja Aguirre Yagüe, Edurne Erkizia, Jose Tomas San-Jose, et al.. Synthesis and addition of Al-substituted Tobermorite particles to cement pastes. *Journal of Materials in Civil Engineering*, 2022, 34 (12), 04022329 (10 p.). 10.1061/(ASCE)MT.1943-5533.0004486 . hal-03794387

HAL Id: hal-03794387

<https://hal.science/hal-03794387v1>

Submitted on 3 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Synthesis and addition of Al substituted tobermorite particles to cement pastes**

2 M. Diez-Garcia, J.J. Gaitero*, F.B. Aguirre, E. Erkizia, J.T. San-Jose, C. Aymonier and J.S. Dolado

3
4 Marta Diez-Garcia (marta1089@hotmail.com), doctoral student at:

5 - TECNALIA, Basque Research and Technology Alliance (BRTA), Parque Tecnológico de Bizkaia,
6 Astondo Bidea, Edificio 700, 48160, Derio (Spain)

7 - CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

8 - UPV/EHU, Dep. of Engineering in Mining, Metallurgical and Materials Science, Plaza Ingeniero
9 Torres Quevedo 1, 48013 Bilbao (Spain)

10 J.J. Gaitero (corresponding author, juanjose.gaitero@tecnalia.com), Senior researcher at:

11 - TECNALIA, Basque Research and Technology Alliance (BRTA), Parque Tecnológico de Bizkaia,
12 Astondo Bidea, Edificio 700, 48160, Derio (Spain)

13 F.B. Aguirre (francisco.aguirre@tecnalia.com), doctoral student at:

14 - TECNALIA, Basque Research and Technology Alliance (BRTA), Parque Tecnológico de Bizkaia,
15 Astondo Bidea, Edificio 700, 48160, Derio (Spain)

16 - CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

17 - UPV/EHU, Facultad de Química, Paseo Manuel Lardizabal 3, 20018 Donostia-San Sebastián
18 (Spain)

19 E. Erkizia (Edurne.erkizia@tecnalia.com), senior researcher at:

20 - TECNALIA, Basque Research and Technology Alliance (BRTA), Parque Tecnológico de Bizkaia,
21 Astondo Bidea, Edificio 700, 48160, Derio (Spain)

22 J.T. San-Jose (josetomas.sanjose@ehu.es), associate professor at:

23 - UPV/EHU, Dep. of Engineering in Mining, Metallurgical and Materials Science,
24 Plaza Ingeniero Torres Quevedo 1, 48013 Bilbao (Spain)

25 C. Aymonier (Cyril.Aymonier@icmcb.cnrs.fr), senior researcher at:

26 - CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

27 J.S. Dolado (jorge_dolado002@ehu.eus), senior researcher at:

28 - Centro de Física de Materiales, Centro Mixto CSIC-UPV/EHU, Paseo Manuel Lardizabal 5,

29 20018 San Sebastián (Spain)

30

31 **Abstract**

32 The last generation of cement hydration accelerators relies on the seeding effect induced by
33 amorphous calcium silicate hydrate particles. However, little is known about the effect of
34 variables like the degree of crystallinity, morphology, etc. on their performance. In this work,
35 particles with Ca/(Si+Al) molar ratio of 0.83 and different proportions of aluminum substitution
36 for silicon were synthesized under hydrothermal conditions. X-ray diffractograms, nuclear
37 magnetic resonance spectra and scanning electron images showed that this altered the degree
38 of crystallinity, the structure, and the morphology of the particles. Nevertheless, the addition
39 of the synthesis products to cement pastes and their subsequent study by isothermal
40 calorimetry and mechanical tests showed that the variables with the largest impact on cement
41 hydration are the dosage and the proper dispersion of the particles. In fact, the use of a
42 dispersing agent is highly recommended while drying of the particles should be avoided to
43 prevent irreversible agglomeration processes taking place.

44

45 **Keywords**

46 1.1nm tobermorite, Al substituted tobermorite, additions, cement paste, seeding effect,
47 cement hydration

48

49 **1. Introduction**

50 Accelerating admixtures reduce setting time and/or promote a faster strength development of
51 cement composites. Consequently, they are used by the precast industry and ready-mix
52 concrete producers to speed up construction, especially in cold weather conditions (Violetta et
53 al. 2016). Calcium chloride was the most widely used accelerating admixture for decades
54 because it was the most cost-effective (Violetta et al. 2016). However, since chloride affects
55 steel reinforcements causing corrosion, other compounds such as calcium nitrate, sodium
56 nitrate, triethanol-amine, calcium formate, and thiocyanate took its place (Violetta et al.
57 2016)(Edwards and Angstadt 1966)(Roskopf et al. 1975)(Gebler 1983). Nevertheless, these
58 alternatives have their own drawbacks such as toxicity, reduction of final strength and reduced
59 effectivity. Therefore, the pursue of the perfect admixture continues.

60 Over the last 20 years, the effect on hydration kinetics of a wide variety of nanoparticles (Kong
61 et al. 2018; Konsta-Gdoutos 2014; Land and Stephan 2015b; Rashad 2013; Zhao et al. 2020),
62 such as SiO₂ (Björnström et al. 2004; Gaitero et al. 2010; Kawashima et al. 2013; Yang et al.
63 2021), CaCO₃ (Kawashima et al. 2013; Sato and Diallo 2010), Al₂O₃ (Campillo et al. 2007), TiO₂
64 (Lee and Kurtis 2010) or nano-C-S-H gel (Alizadeh et al. 2009; Dittmar et al. 2013; Land and
65 Stephan 2015a), has also been studied. The key features of nanoparticles are particle size
66 smaller than 100nm and great surface area. There is a general agreement that nanoparticles
67 accelerate hydration reactions of Portland cement mainly by one of the following mechanisms:
68 the reaction with the ions dissolved from the cement grains, or the seeding effect. In the first
69 case, the most common process is the pozzolanic reaction of silica or clay nanoparticles with
70 dissolved Ca ions to give C-S-H gel (Björnström et al. 2004; Diez-Garcia et al. 2018; Gaitero et
71 al. 2008, 2010; Guerrero et al. 2014; Land and Stephan 2015b; Perez et al. 2015b; a; Yang et al.
72 2021). Nanoparticles are more reactive than larger particles of the same composition due to
73 the larger surface area. In addition, some authors (Björnström et al. 2004; Diez-Garcia et al.
74 2018; Perez et al. 2015a) have reported the presence of hydroxyl ions on the surface that
75 make them even more reactive. In the second case, the nanoparticles do not react chemically

76 with dissolved species, but they serve as heterogeneous nucleation agents for the deposition
77 and growth of hydration products. Although Kong et al. (Kong et al. 2018) have recently put
78 into question the seeding effect of SiO₂ and TiO₂ nanoparticles, most researchers (Konsta-
79 Gdoutos 2014; Land and Stephan 2015b; Rashad 2013; Zhao et al. 2020) attribute the
80 accelerating effect of some nanoparticles to this phenomenon. Apart from the particle size,
81 heterogeneous nucleation also depends to a great extent on the chemical and structural
82 compatibility between the seeds and precipitated species. If the compatibility is high, like in
83 the case of C-S-H particles, dissolved ions might even deposit on the seeds layer by layer
84 following the same structure (Kong et al. 2018). In fact, Alizadeh et al. (Alizadeh et al. 2009)
85 proved that the average chain length of the precipitated C-S-H gel could be modified by
86 varying the C/S ratio and silicate polymerization of the C-S-H seeds. In addition, they also
87 observed that C-S-H particles were more effective if their C/S ratio was 0.8, i.e. in the range of
88 tobermorite, rather than 1.2.

89 In an attempt to further understand the effect of the morphology, crystallinity and
90 composition of calcium silicate hydrate particles in their seeding capacity, in the current work
91 the effect of the addition of several synthetic calcium silicate hydrate particles, with Ca/(Si+Al)
92 molar ratio of 0.83 and different proportions of Al, were studied. In addition, other variables
93 such as the percentage of addition, the combination with a superplasticizer and the method of
94 preparation of particles dispersions, that may involve complete drying of the synthesis
95 products or not, were also considered. Scanning electron microscopy, X-ray diffraction and, ²⁹Si
96 and ²⁷Al nuclear magnetic resonance were used to characterize the synthesis products. The
97 effect of the particles on cement hydration was studied by isothermal calorimetry and
98 validated by mechanical strength tests.

99 **2. Materials and methods**

100 2.1 Synthesis and characterization of the additions

101 Precursors employed for the synthesis of the additions were CaO (Sigma-Aldrich), nano-SiO₂
102 (AkzoNobel Levasil 100/45%) and nano-Al₂O₃ (Nyacol Al20SD). Several degrees of substitution
103 of aluminum for silicon (Al/(Si+Al)·100) were used (0%, 6%, 10%, 15% and 20%) because it is
104 well known that Al substitution provides stability to the structure of 1.1nm tobermorite (Diez-
105 Garcia et al. 2017; Mitsuda and Taylor 1975; Sakiyama and Mitsuda 1977; Shaw et al. 2000).
106 The molar ratio Ca/(Si+Al) was in all cases 0.83 and CaO was calcined at 800°C for 4h before
107 each synthesis. The reactions were carried out in a 2L hydrothermal batch reactor at 215°C
108 and autogenous pressure for 4h. Solvent was in all cases distilled and degassed water (1.5L)
109 and the liquid to solid ratio was approximately 200. Obtained products were either filtered and
110 dried in an oven at 60°C for 12h or preserved in the synthesis media. The dried products were
111 studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to know their
112 mineralogical composition and morphology.

113 XRD measurements were carried out with a Bruker D8 Advance Series II from 5° to 90°
114 2θ, with a step size of 0.03°, using Cu K-alpha radiation. Obtained results were processed
115 with DIFFRAC.EVA for phase identification, and TOPAS for the quantitative analysis by Rietveld
116 refining method. For the quantitative analysis, the samples were mixed with 10% of highly
117 crystalline quartz that was used as internal standard.

118 The SEM used was a Jeol JSM-7000F with Wolfram filament. It has a beam voltage of 300V-
119 30kV and a resolution of 1.2 nm. The samples were directly deposited on a carbon tape and
120 coated with platinum.

121 Finally, solid state nuclear magnetic resonance (NMR) was used to study the local chemical
122 environment of Si and Al atoms. High-resolution solid-state NMR spectra were recorded at
123 298K and rotating frequency of 10KHz on a Bruker Avance 400 WB spectrometer at 9.4 T
124 equipped with a MAS/DVT probe, using 104.3MHz and 79.5MHz resonance frequencies for ²⁷Al
125 and ²⁹Si respectively. The ²⁷Al experiments were performed with pulse length of 0.45μs, and

126 the recycle time was 1s. The chemical shifts were referenced to an external standard of AlNO_3
127 ($\delta=0\text{ppm}$). The ^{29}Si experiments were performed with a pulse length of $4\mu\text{s}$, and recycle time
128 was 10s. The chemical shifts were referenced to an external standard of TSP
129 (trimethylsilylpropanoic acid) ($\delta=0\text{ppm}$).

130 2.2 Particle dispersion

131 Prior to the addition to cement, the synthesis products were dispersed in the mixing water. For
132 the experiments using the dry product (subsequently DRIED), the powder was just redispersed
133 with an ultrasonic tip (BANDELIN SONOPULS HD 2200 with probe VS 70 T) for two minutes at
134 30% power. By contrast, in the case of the particles preserved in the synthesis media
135 (thereafter CONC), the product was pre-concentrated up to the desired dosage of particles and
136 water needed for the preparation of the cement paste. To know the actual concentration of
137 the CONC product, a 20g aliquot of the reaction product was evaporated at 100°C up to
138 constant weight to determine the solid content (Thomas et al. 2009). With this information it
139 was possible to adjust the concentration of the dispersion to the value required for cement
140 paste preparation by simply evaporating the excess of water. In some cases, see Table 1 and
141 Table 2, 20% of superplasticizer (FOSROC Auracast 280) by weight of dry product was also
142 added to the resulting dispersion prior to mixing it with the cement.

143 2.3 Calorimetric tests

144 Cement pastes studied by calorimetry contained 0.5, 1, 2, 3, 4 and 5 percent of addition (dry
145 content) by weight of cement (Table 1). Two reference samples with no addition were also
146 analyzed for comparison. The only difference between them was that the content of
147 superplasticizer was 0% and 0.6% by weight of cement. This value was chosen because it is the
148 same amount used in the sample with 3% of addition, and it is approximately in the middle of
149 the range of values used. In all cases, a cement type CEM I- 52.5R was used with a water to
150 cement ratio (w/c) of 0.5. Mixing of the addition, mixing water, superplasticizer (only in some

151 cases) and cement was done manually in a 20ml glass ampoule that was immediately sealed
152 and introduced in the isothermal calorimeter (TA Instruments TAM air) for 24h. The
153 measurement took place at a constant temperature of $25\pm 0.02^{\circ}\text{C}$ using water as a reference.

154 2.3 Mechanical tests

155 The mechanical strength of the pastes was determined by testing $1\times 1\times 6\text{ cm}^3$ prismatic samples
156 cast in steel molds. All samples were prepared at a water to cement ratio of 0.4 using the same
157 materials as for the calorimetric tests. In this case, only synthesis products with 6 and 15% Al
158 substitution were added in three different concentrations: 0%, 0.5% and 2% by weight of
159 cement (see Table 2). Mixing was carried out on a tailor-made glass vessel using a mixer
160 Heidolph RZR2102 control. The mixing process consisted of two cycles of mixing at 750r.p.m.
161 for 90s, separated by a halt of 60s. Resulting cement pastes were subsequently used to fill the
162 molds which were then stored in a wet chamber at 20°C and 100% humidity for either 24h or
163 until the time of testing; whatever happened first. Test specimens were then demolded and
164 immersed in water at room temperature until testing. The mechanical strength tests were
165 performed after 6, 8, 16, 24, 40 and 72 hours from mixing using an electromechanical universal
166 test machine Ibertest ELIB-10-W. Six prismatic specimens of 1cm side and 6cm long were
167 tested at every age. Bending tests were carried out first (results not included), and then, each
168 half of the samples was subjected to the compression test. Two different sets of loads were
169 employed in the compression tests depending on the age of the specimens. In the case of the
170 youngest, and as a consequence, weakest samples (6 and 8 hours), loading rate was 10N/s
171 while for the rest of the samples (16, 24, 48 and 72 hours) it was increased to 100N/s to
172 reduce measuring time. Although compressive strength may be affected by the change in
173 loading rate, the increase in strength from 8h to 16h is so large that it does not have any effect
174 on the discussion.

175

176 **3. Results and discussion**

177 3.1 Characterization of the additions

178 The result of the syntheses was a white slurry with an important concentration gradient as a
179 function of height. However, no solid sediment was formed at the bottom of the container and
180 the slurry could be easily homogenized by gentle mixing. The pH of the liquid varied as a
181 function of the percentage of Al substitution for Si of the raw mix, see Table 3. This is due to
182 the lower oxidation number of Al that results in a charge imbalance that is compensated by
183 the incorporation of other ions to the structure (Liao et al. 2019). Considering the composition
184 of the slurry, such ions can only be Ca^{2+} or H^+ . In either case, this gives place to the release of
185 OH^- into the solution and, consequently, to an increase of the pH.

186 X-ray diffractograms of the synthesis products (Fig.1) revealed the presence of 1.1nm
187 tobermorite with low crystallinity, amorphous material and minor amounts of calcite. Since the
188 synthesis process took place in a closed vessel, calcite formation was attributed to the
189 carbonation of dissolved lime upon contact with environmental CO_2 during drying of the
190 reaction products. Comparison between the different samples showed a progressive shift of
191 the basal peak towards lower angles with increasing Al content. This can be attributed to Al
192 substitution for Si within the structure of 1.1nm tobermorite. In particular, to the larger radius
193 of Al^{3+} compared to Si^{4+} and to the need of incorporating counterions for charge balancing
194 (Liao et al. 2019). Rietveld refinement was used to quantify the relative proportion of each
195 phase in the samples (Table 3) using quartz as standard reference material. Tobermorite was
196 considered in all cases as a single phase due to the impossibility to distinguish 1.1nm
197 tobermorite from its Al substituted counterpart. Obtained results showed that the proportion
198 of tobermorite increased with increasing Al content from 48% to about 70%. This confirmed
199 that the use of nanoalumina as Al source for the hydrothermal synthesis of tobermorite favors
200 the crystallization (Mitsuda and Taylor 1975; Sakiyama and Mitsuda 1977; Shaw et al. 2000).

201 The large surface area of nanoalumina facilitates its reaction, and the crystallization rate along
202 the c-axis is accelerated by the incorporation of Al into the silicate chains (Biagioni et al. 2015;
203 Liao et al. 2019; Matsui et al. 2009), giving place to stiffer tobermorite (Li et al. 2020).

204 ²⁹Si NMR spectra showed the typical shape of Al substituted tobermorite (Liao et al. 2019, Li et
205 al. 2020), see Fig.2. The absence of Q₄ peak at -110 ppm suggests that nanosilica reacted
206 completely and, in consequence, the amorphous phase of Rietveld analysis must be
207 tobermorite-like C-S-H gel. In addition, the presence of two peaks at approximately -84ppm
208 (Q₂Al) and -93.5ppm (Q₃Al) confirms the incorporation of Al into the silicate structure,
209 although Li et al. reported that the latter could also appear in absence of Al. It is widely
210 accepted that Al substitutes for Si preferentially into the bridging and branching positions of C-
211 S-H gel and tobermorite, see for example (Sun et al. 2006), although it can also enter into
212 pairing positions (Manzano et al. 2008, 2009). Taking into account the structure of tobermorite
213 (Biagioni et al. 2015), incorporation of Al solely into branching positions would result in a
214 maximum Al/Si ratio of 1/6, i.e. lower than the ratio of the sample with the highest Al content.
215 In the case of substitution into the bridging positions of linear silicate chains with dreierketten
216 structure, the maximum Al/Si ratio increases to 1/3. Therefore, the composition of the samples
217 is compatible with having a mixture of particles with both structures.

218 ²⁷Al NMR analysis (Fig.2) showed two overlapping peaks centered at about 56 and 64 ppm.
219 These peaks are generally attributed to Al substitution for Si in branching (Q₃) and bridging (Q₂)
220 positions respectively (Guo et al. 2017; Houston et al. 2009; Komarneni et al. n.d.; Schneider et
221 al. 2001). Al placed in pairing positions gives place to a resonance peak centered at about 72
222 ppm not observed in this study (Pardal et al. 2012). The spectrum of the sample with the
223 largest proportion of Al, i.e. 20% Al, shows also the presence of a small proportion of
224 octahedrally coordinated Al. There is no consensus in the literature on the assignation of this
225 signal, which has been attributed to the incorporation of Al into the interlayer space (Guo et al.

226 2017), on C-S-H particles' surface (Sun et al. 2006), and even in silicate chain ends (Pardal et al.
227 2012). In this work, this signal could also be due to rests of unreacted Al_2O_3 coming from the
228 nanoalumina used in the synthesis. In any case, the fact that such peak only appears in the
229 sample with the largest proportion of Al agrees with the preferential incorporation of Al into
230 bridging and branching positions.

231 The degree of Al substitution had also an effect on the shape of the obtained particles (Fig.3).
232 For 0% substitution particle shape was less defined but, as the proportion of Al increased,
233 crystals became larger and more homogeneous. Three different morphologies were identified:
234 amorphous "cloud like" particles, thin plates, and fibers. In general, the typical clouds of C-S-H
235 gel (Torelli and Lees 2019) were predominant for low Al contents, while they were replaced by
236 the characteristic plates of tobermorite (Megaw and Kelsey 1956) as Al substitution increased.
237 Fibrous morphologies might also be present in Al rich samples, but their presence would
238 always be scarce, and they might in fact be just tobermorite plates seen from the side.
239 Although the thickness of the plates and fibers was nanometric, their larger dimension was
240 always in the range of tenths of micrometers.

241 3.2 Calorimetric study

242 The calorimetric curves of the samples containing redispersed additions (DRIED) showed an
243 accelerating effect compared to the reference (Fig.4). The acceleration was made evident by
244 the increase of the intensity of the heat flow peak and the displacement of the whole
245 calorimetric curves to the left, similar to results observed in previous studies using C-S-H seeds
246 (Thomas et al. 2009). The effect was quite subtle for the samples with the smallest dosages,
247 but it was very clear for the other ones. However, independently of the dosage no tendency
248 was observed in the samples as a function of Al content with one exception, namely, the
249 curves of the samples with no Al (0% Al) which were always a bit more displaced to the left.

250 Similarly, the use of concentrated additions (CONC) also induced certain acceleration of the
251 hydration process. Nevertheless, the tendency was not so clear in this case because the
252 displacement of the calorimetric curves to the left was accompanied in some cases by a
253 reduction of the intensity of the heat flow peak. This could be due to improper mixing of the
254 pastes because of their poor workability. In fact, these samples were a lot less fluid than the
255 DRIED ones making it impossible to obtain a proper cement paste. In any case, this was not
256 completely unexpected since it was already observed during the preparation of the dispersions
257 for mixing with the cement that CONC samples absorbed a lot more water than the DRIED
258 ones. The dispersions containing CONC additions had a gel like texture while the other ones
259 were completely liquid. The smaller water absorption of DRIED additions suggests that
260 irreversible agglomeration took place during the drying process, reducing the surface area of
261 the particles. Twenty percent of superplasticizer by weight of dry content of addition was
262 added to CONC samples to eliminate such workability difference. It is important to add as little
263 superplasticizer as possible because polymer containing surfaces are not active for the seeding
264 process (Krautwurst et al. 2018; Nicoleau et al. 2013). In fact, polymeric dispersants such as
265 polycarboxylates have been used to control the particle size during C-S-H synthesis
266 (Kanchanason and Plank 2017). To assess the effect of the superplasticizer itself on cement
267 hydration, a reference sample with 0.6% of superplasticizer by weight of cement was also
268 prepared. Such value was chosen because it is approximately in the middle of the range of
269 values used in this study 0.1-1%, and it coincides with the amount added to the sample with
270 3% of concentrated addition. Calorimetric curves (Fig.5) showed two different effects. The
271 superplasticizer induced a clear retardation of the hydration process in the reference sample,
272 increasing the induction period by about 3h. The addition of the superplasticizer resulted in an
273 enhanced acceleration of the pastes containing concentrated additions (CONC) in comparison
274 with the samples without superplasticizer. Once again, the magnitude of the acceleration
275 showed almost no variation as a function of Al content of the addition. The only exception was

276 the sample with no Al at all that showed, again, a further reduction of a few minutes in the
277 induction period, although this was also accompanied by a slightly smaller increase in the
278 intensity of the peak. These results add to the findings of Begarin et al. (Begarin et al. 2011)
279 who reported that the addition of C-S-H particles containing Al did not accelerate C_3S and alite
280 hydration due to the “poisoning effect” of Al. Such effect seems to be strongly related to the
281 presence of Al with octahedral coordination in the surface of C-S-H particles (Sun et al. 2006)
282 or at the end of silicate chains (Pardal et al. 2012) because they hinder the growth of C-S-H
283 particles. However, in our case, Al is almost always in bridging and branching positions,
284 therefore no interfering with particle growth. The only exception was the sample with 20% Al
285 that showed a low intensity signal of octahedral Al but no detrimental effect. The reason was
286 probably the small proportion “poisoned particles” that can be inferred from the relatively
287 small area of the peak.

288 Although Al content did not seem to significantly affect the performance of the additions as
289 accelerating admixtures, samples with the same Al content were compared to study the effect
290 of the dosage in more detail. For the samples with DRIED additions, it was evident (Fig.6a) that
291 the accelerating effect increased with increasing dosage. On the contrary, the tendency was
292 not so clear for the samples with CONC additions (Fig.6b); which was attributed to improper
293 mixing of the pastes due to their poor workability. Although the addition of 20wt.% of
294 superplasticizer solved this issue, it also added a new variable to the system that made more
295 difficult the extraction of conclusions. For small dosages (Fig.6c), almost no difference was
296 observed in the calorimetric curves because the workability was still not very affected. That is
297 to say, the slight improvement induced by the superplasticizer was counterbalanced by its
298 retarding effect. On the contrary, for the largest dosages (Fig.6d) the superplasticizer clearly
299 enhanced the accelerating effect of CONC additions. And not only that, the improvement was
300 so significant that these samples largely outperformed the samples with dried seeds and no
301 superplasticizer. Thomas et al. (Thomas et al. 2009) already reported that the addition of C-S-H

302 seeds could negate the retarding effect of retarding admixtures, like sucrose, on C_3S hydration.
303 This was so because sucrose prevented the nucleation of C-S-H gel, and the added seeds
304 provided an alternative pathway for the hydration process. In the same line, Nicoleau et al.
305 concluded that, although the absorption of polymers into C-S-H particles' surface reduced the
306 activity as seed of the area covered by the polymer, it also improved the dispersion of the
307 particles resulting in a net increase of the active area and the overall activity (Nicoleau et al.
308 2013). Therefore, the smaller acceleration of the dried additions compared to the combination
309 of the concentrated ones with superplasticizer can be attributed to two reasons: to the
310 irreversible agglomeration processes that take place during drying, and to the improved
311 dispersion of the addition due to the superplasticizer. To estimate the efficiency gain of the
312 combination of the concentrated additions (CONC) with the superplasticizer, compared to the
313 dry ones (DRIED), we used the relative acceleration A defined by Nicoleau et al. (Nicoleau et al.
314 2013). A is the slope of the linear part of the acceleration period of the heat flow curves of the
315 samples containing the addition, divided by the equivalent slope obtained from the reference
316 sample. As can be observed in Fig.7, A is proportional in both cases to the amount of addition
317 used, but it is about 80% larger in the samples containing CONC additions than DRIED.
318 Nicoleau et al. reported values of relative acceleration A per gram of addition lower than $3.5g^{-1}$
319 for C-S-H dispersions with 0.35% solid content. If we use the linear fits of A (Fig.7) to calculate
320 the relative acceleration per gram of addition for the case of 0.35% of addition, we obtain a
321 value of $3.5g^{-1}$ for CONC and $3.1g^{-1}$ for DRIED. Therefore, these values are close to the best
322 results obtained by Nicoleau et al. even though he used mechanisms to control the specific
323 surface area of the particles.

324 3.3 Mechanical performance

325 Mechanical strength tests were performed to verify that the effect of the addition of the
326 synthesized particles in the calorimetric curves translated into a variation of the strength

327 development rate at early ages. The same variables as in the calorimetric tests were
328 considered: the Al content of the particles, the dosage and the method of preparation of
329 particles dispersions, that may involve complete drying of the synthesis products (DRIED) or
330 not (CONC). However, the number of samples was considerably reduced (see Table 2) based
331 on the results of the calorimetric tests. Water to cement ratio was reduced to 0.4 and 20% of
332 superplasticizer by weight of addition was added to all dispersions (Table 2) to ensure that all
333 cement pastes had a consistency suitable for preparing the test specimens.

334 Compression strength values along the first 72h of curing (Fig.8-9) increased because of the
335 addition of the synthesized particles. For the smallest dosage (0.5% b.w.c.), no strength gain in
336 comparison to the reference was observed until 16h from mixing. When the amount of
337 addition was increased to 2% b.w.c., the strength gain was clear from the very first moment
338 (6h). However, the final value after 72h from mixing was just slightly larger than with 0.5% of
339 addition. This is due to the change in the dominant process involved in each step of cement
340 hydration. During the first half of the acceleration period, hydration is mainly controlled by
341 nucleation and growth processes (Thomas et al. 2011) but this changes at later stages. In
342 particular, the beginning of the acceleration period is attributed to the formation of the first
343 nucleuses and the beginning of C-S-H gel growth. Consequently, the addition of particles that
344 can act as additional nucleuses for the heterogeneous growth of C-S-H gel reduces the
345 induction period and accelerates the initial growth rate. However, as we approach the
346 maximum of the calorimetric peak other phenomena come into play and the effect of the
347 seeding additions disappears.

348 Comparison of samples containing additions with 6 and 15% of Al substitution, Fig.8, shows
349 that Al content does not affect their acceleration capacity, in good agreement with the results
350 of the calorimetric tests.

351 When CONC additions are compared to the DRIED ones (Fig.9), it is made evident that the first
352 ones were considerably more active during the first hours. In fact, obtained values of strength
353 after 6h, were two and three times larger for 0.5% and 2% of addition, respectively. However,
354 the difference becomes smaller over time until it completely disappears after 24h from mixing.
355 This confirms that the drying process reduces the effectivity of the addition. Nicoleau et al.
356 (Nicoleau et al. 2013) proved that one of the key parameters of the seeding effect is the active
357 surface area. It was observed in this work during the dispersion of the additions in the mixing
358 water that DRIED additions absorbed less water than the CONC ones. Therefore, it is
359 reasonable to think that the drying process reduced the active surface area of the particles due
360 to an irreversible aggregation process.

361

362 **4. Conclusions**

363 Based on the experimental results obtained from this work the following conclusions were
364 extracted:

365 *The hydrothermal reaction of nanoalumina, nanosilica and CaO at a $Ca/(Si+Al)=0.83$ gave
366 place to the formation of a mixture of 1.1nm tobermorite and C-S-H gel particles. The
367 crystallinity of the product increased with increasing Al content due to the incorporation of Al
368 in bridging and branching positions. The sample with the largest proportion of Al (20%) also
369 contained a small proportion of Al with octahedral coordination.

370 *The addition of the synthesis products to cement pastes accelerated the first stages of the
371 hydration process, presumably, due to a seeding effect. The acceleration was proved by a
372 rapid growth of the calorimetric peak. However, the effect disappeared soon after the
373 maximum of the peak, i.e. at the beginning of the so-called deceleration period. This is
374 compatible with the hypothesis of the seeding effect because along that time kinetics are

375 mainly controlled by nucleation and growth processes. Therefore, added particles would act as
376 nucleuses for the growth of hydration products.

377 *According to the obtained results, the Al content of the addition has little effect in the
378 performance as hydration accelerator, despite the differences on the degree of crystallinity
379 and morphology of the obtained products. The absence of the “poisoning effect” reported by
380 other researchers can be attributed to the incorporation of Al in bridging and branching
381 positions, no interfering therefore in particle growth.

382 *On the contrary, complete drying of the particles at the end of the hydrothermal synthesis
383 process resulted in a reduction of their acceleration capacity. Such reduction was attributed to
384 an agglomeration process that could not be reversed by ultrasonic treatment. The
385 agglomeration was evidenced by the much smaller water absorption of the particles that
386 underwent drying. In fact, the large water absorption of the non-dried (CONC) additions made
387 the use of a superplasticizer necessary.

388 *Despite the well-known retarding effect of superplasticizers on cement hydration, its
389 combination with CONC additions had the opposite effect due to two possible reasons. Firstly,
390 due to the improvement in workability. Since mixing for the calorimetric test was manual and
391 particles absorbed so much water, it is likely that improper mixing diffculted wetting of
392 cement particles. This was solved with the addition of the superplasticizer. Secondly, the
393 polymer might also have improved the dispersion of the particles increasing the active surface
394 area readily available for seeding.

395 *Finally, the acceleration induced by the additions was proportional to the amount of addition
396 used. Furthermore, the efficiency of the synthesized additions was comparable to the values
397 obtained by other researchers using C-S-H seeds, and no saturation was observed despite of
398 adding up to 5% by weight of cement.

399

400 **Acknowledgements**

401 This study was carried out under the umbrella of the BASKRETE initiative and the Transnational
402 Common Laboratory “Aquitaine-Euskadi Network in Green Concrete and Cement-based
403 Materials” (LTC-Green Concrete). Economic support was provided by the Basque Government
404 under the ELKARTEK Program (project NEOMAT (KK-2021/00059)). In addition, Marta Diez-
405 Garcia is grateful to the University of the Basque Country (UPV/EHU) and the University of
406 Bordeaux for her pre-doctoral fellowship, within the framework of the Cross-Border
407 Euroregional Campus of International Excellence IDEX Bordeaux–Euskampus. Francisco B.
408 Aguirre acknowledges the funding received from Tecnalía to carry out his PhD in cotutelle
409 between the University of the Basque Country (UPV-EHU) and Université de Bordeaux within
410 the framework of the Cross-Border Euroregional Campus of International Excellence IDEX
411 Bordeaux–Euskampus. The authors wish also to express their gratitude to the SAREN Research
412 Group (IT-1619-22, Basque Government) and MCIN/AEI/10.13039/501100011033/ FEDER, UE
413 [PID2021-124203OB-I00].

414

415 **Data availability statement**

416 All data, models, and code generated or used during the study appear in the submitted article.

417

418 **References**

- 419 Alizadeh, R., Raki, L., Makar, J. M., Beaudoin, J., and Moudrakovski, I. (2009). “Hydration of
420 tricalcium silicate in the presence of synthetic calcium – silicate – hydrate.” 7937–7946.
- 421 Begarin, F., Garrault, S., Nonat, A., and Nicoleau, L. (2011). “Hydration of alite containing
422 aluminium.” *Advances in Applied Ceramics*.
- 423 Biagioni, C., Merlino, S., and Bonaccorsi, E. (2015). “The tobermorite supergroup: a new

424 nomenclature." *Mineralogical Magazine*.

425 Björnström, J., Martinelli, A., Matic, A., Börjesson, L., and Panas, I. (2004). "Accelerating effects
426 of colloidal nano-silica for beneficial calcium-silicate-hydrate formation in cement."
427 *Chemical Physics Letters*.

428 Campillo, I., Guerrero, A., Dolado, J. S., Porro, A., Ibáñez, J. A., and Goñi, S. (2007).
429 "Improvement of initial mechanical strength by nanoalumina in belite cements."
430 *Materials Letters*.

431 Diez-Garcia, M., Gaitero, J. J., Dolado, J. S., and Aymonier, C. (2017). "Ultra-Fast Supercritical
432 Hydrothermal Synthesis of Tobermorite under Thermodynamically Metastable
433 Conditions." *Angewandte Chemie - International Edition*, 56(12).

434 Diez-Garcia, M., Gaitero, J. J., Santos, J. I., Dolado, J. S., and Aymonier, C. (2018). "Supercritical
435 hydrothermal flow synthesis of xonotlite nanofibers." *Journal of Flow Chemistry*, 8(2).

436 Dittmar, S., Hauck, H. G., and König, R. (2013). "C-S-H: a state of the art concept to accelerate
437 concrete hardening." *bft international*, january, 44–51.

438 Edwards, G. C., and Angstadt, R. L. (1966). "The effect of some soluble inorganic admixtures on
439 the early hydration of portland cement." *Journal of Applied Chemistry*, John Wiley &
440 Sons, Ltd, 16(5), 166–168.

441 Gaitero, J. J., Campillo, I., and Guerrero, A. (2008). "Reduction of the calcium leaching rate of
442 cement paste by addition of silica nanoparticles." *Cement and Concrete Research*, 38(8–
443 9), 1112–1118.

444 Gaitero, J. J., Campillo, I., Mondal, P., and Shah, S. P. (2010). "Small Changes Can Make a Great
445 Difference." *Transportation Research Record: Journal of the Transportation Research
446 Board*, 2141(2141), 1–5.

447 Gebler, S. (1983). "EVALUATION OF CALCIUM FORMATE AND SODIUM FORMATE AS
448 ACCELERATING ADMIXTURES FOR PORTLAND CEMENT CONCRETE." *Journal of the*
449 *American Concrete Institute*, 80, 439–444.

450 Guerrero, A., Redondo, J. J. G., Quiñones, G. P. Á., and Elizalde, S. G. (2014). "Multi-scale
451 analysis of cement pastes with nanosilica addition." *Advances in Cement Research*.

452 Guo, X., Meng, F., and Shi, H. (2017). "Microstructure and characterization of hydrothermal
453 synthesis of Al-substituted tobermorite." *Construction and Building Materials*, 133, 253–
454 260.

455 Houston, J. R., Maxwell, R. S., and Carroll, S. a. (2009). "Transformation of meta-stable calcium
456 silicate hydrates to tobermorite: reaction kinetics and molecular structure from XRD and
457 NMR spectroscopy." *Geochemical transactions*, 10, 1.

458 Kanchanason, V., and Plank, J. (2017). "Role of pH on the structure, composition and
459 morphology of C-S-H–PCE nanocomposites and their effect on early strength
460 development of Portland cement." *Cement and Concrete Research*.

461 Kawashima, S., Hou, P., Corr, D. J., and Shah, S. P. (2013). "Modification of cement-based
462 materials with nanoparticles." *Cement and Concrete Composites*.

463 Komarneni, S., Roy, R., Roy, D. M., Fyfe, C. A., Kennedy, G. J., Bothner-By, A. A., Dadok, J., and
464 Chesnick, A. S. (n.d.). "27Al and 29Si magic angle spinning nuclear magnetic resonance
465 spectroscopy of Al-substituted tobermorites." *Journal of Materials Science*, 20(11), 4209–
466 4214.

467 Kong, D., Huang, S., Corr, D., Yang, Y., and Shah, S. P. (2018). "Whether do nano-particles act as
468 nucleation sites for C-S-H gel growth during cement hydration?" *Cement and Concrete*
469 *Composites*, Elsevier Ltd, 87, 98–109.

470 Konsta-Gdoutos, M. S. (2014). "Nanomaterials in self-consolidating concrete: A state-of-the-art

471 review." *Journal of Sustainable Cement-Based Materials*.

472 Krautwurst, N., Nicoleau, L., Dietzsch, M., Lieberwirth, I., Labbez, C., Fernandez-Martinez, A.,
473 Van Driessche, A. E. S., Barton, B., Leukel, S., and Tremel, W. (2018). "Two-Step
474 Nucleation Process of Calcium Silicate Hydrate, the Nanobrick of Cement." *Chemistry of*
475 *Materials*.

476 Land, G., and Stephan, D. (2015a). "Preparation and application of nanoscaled C-S-H as an
477 accelerator for cement hydration." *Nanotechnology in Construction*, 377–382.

478 Land, G., and Stephan, D. (2015b). "Controlling cement hydration with nanoparticles." *Cement*
479 *and Concrete Composites*, 57, 64–67.

480 Lee, B. Y., and Kurtis, K. E. (2010). "Influence of TiO₂ nanoparticles on early C3S hydration."
481 *Journal of the American Ceramic Society*, 93(10), 3399–3405.

482 Li, J., Zhang, W., Garbev, K., Beuchle, G., and Monteiro, P. J. M. (2020). "Influences of cross-
483 linking and Al incorporation on the intrinsic mechanical properties of tobermorite."
484 *Cement and Concrete Research*.

485 Liao, W., Li, W., Fang, Z., Lu, C., and Xu, Z. (2019). "Effect of different aluminum substitution
486 rates on the structure of Tobermorite." *Materials*.

487 Manzano, H., Dolado, J. S., and Ayuela, A. (2009). "Aluminum incorporation to dreierketten
488 silicate chains." *Journal of Physical Chemistry B*.

489 Manzano, H., Dolado, J. S., Griebel, M., and Hamaekers, J. (2008). "A molecular dynamics study
490 of the aluminosilicate chains structure in Al-rich calcium silicate hydrated (C-S-H) gels."
491 *Physica Status Solidi (A) Applications and Materials Science*, 205(6), 1324–1329.

492 Matsui, K., Ogawa, A., Kikuma, J., Tsunashima, M., Ishikawa, T., and Matsuno, S. (2009). "In situ
493 time-resolved X-Ray diffraction of tobermorite formation process under hydrothermal

494 condition: influence of reactive Al compound." *Denver X-ray conference on Applications*
495 *of X-ray Analysis*, 1–7.

496 Megaw, H. D., and Kelsey, C. H. (1956). "Crystal structure of tobermorite." *Nature*, 177, 390–
497 391.

498 Mitsuda, T., and Taylor, H. F. W. (1975). "Influence of aluminum on the conversion of calcium
499 silicate hydrate gels into 11 Å tobermorite at 90°C and 120°C." *Cem Concr Res*, 5, 203–
500 210.

501 Nicoleau, L., Gädt, T., Chitu, L., Maier, G., and Paris, O. (2013). "Oriented aggregation of
502 calcium silicate hydrate platelets by the use of comb-like copolymers." *Soft Matter*.

503 Pardal, X., Brunet, F., Charpentier, T., Pochard, I., and Nonat, A. (2012). "27Al and 29Si Solid-
504 State NMR Characterization of Calcium-Aluminosilicate-Hydrate." *Inorganic Chemistry*,
505 51(3), 1827–1836.

506 Perez, G., Erkizia, E., Gaitero, J. J., Kaltzakorta, I., Jiménez, I., and Guerrero, A. (2015a).
507 "Synthesis and characterization of epoxy encapsulating silica microcapsules and amine
508 functionalized silica nanoparticles for development of an innovative self-healing
509 concrete." *Materials Chemistry and Physics*, 165, 39–48.

510 Perez, G., Gaitero, J. J., Erkizia, E., Jimenez, I., and Guerrero, A. (2015b). "Characterisation of
511 cement pastes with innovative self-healing system based in epoxy-amine adhesive."
512 *Cement and Concrete Composites*, Elsevier Ltd, 60, 55–64.

513 Rashad, A. M. (2013). "Effects of ZnO₂, ZrO₂, Cu₂O₃, CuO, CaCO₃, SF, FA, cement and
514 geothermal silica waste nanoparticles on properties of cementitious materials - A short
515 guide for Civil Engineer." *Construction and Building Materials*, Elsevier Ltd, 48, 1120–
516 1133.

517 Roskopf, P., Linton, F., and Pepler, R. (1975). "Effect of Various Accelerating Chemical

518 Admixtures on Setting and Strength Development of Concrete." *Journal of Testing and*
519 *Evaluation*, 3(4), 322.

520 Sakiyama, M., and Mitsuda, T. (1977). "Hydrothermal reaction between C-S-H and kaolinite for
521 the formation of tobermorite at 180°C." *Cement and Concrete Research*, 7(6), 681–685.

522 Sato, T., and Diallo, F. (2010). "Seeding effect of nano-CaCO₃ on the hydration of tricalcium
523 silicate." *Transportation Research Record*.

524 Schneider, J., Cincotto, M. ., and Panepucci, H. (2001). "29Si and 27Al high-resolution NMR
525 characterization of calcium silicate hydrate phases in activated blast-furnace slag pastes."
526 *Cement and Concrete Research*, 31(7), 993–1001.

527 Shaw, S., Clark, S. M., and Henderson, C. M. B. (2000). "Hydrothermal formation of the calcium
528 silicate hydrates , tobermorite and xonotlite : an in situ synchrotron study." *Chemical*
529 *Geology*, 167, 129–140.

530 Sun, G. K., Young, J. F., and Kirkpatrick, R. J. (2006). "The role of Al in C–S–H: NMR, XRD, and
531 compositional results for precipitated samples." *Cement and Concrete Research*, 36(1),
532 18–29.

533 Thomas, J. J., Biernacki, J. J., Bullard, J. W., Bishnoi, S., Dolado, J. S., Scherer, G. W., and Luttge,
534 A. (2011). "Modeling and simulation of cement hydration kinetics and microstructure
535 development." *Cement and Concrete Research*.

536 Thomas, J. J., Jennings, H. M., and Chen, J. J. (2009). "Influence of nucleation seeding on the
537 hydration mechanism of tricalcium silicate and cement." *J Phys Chem c*, 113, 4327–4334.

538 Torelli, G., and Lees, J. M. (2019). "Fresh state stability of vertical layers of concrete." *Cement*
539 *and Concrete Research*, Elsevier, 120(October 2018), 227–243.

540 Violetta, B. K., Kari L. Yuers, Aldred, J. M., Berke, N. S., Bognacki, C. J., Brown, M. L., Cook, L. J.,

541 Durning, T., Eller, R., Farzam, H., Fisher, D., Folks, T. S., Helle, B., Ludirdja, D., Martin, R. S.,
542 Nkinamubanzi, P.-C., Phelan, W. S., Pistilli, M. F., Roberts, L. R., Sompura, K. R., Stokes, D.
543 B., and Winters, A. T. (2016). *Report on Chemical Admixtures for Concrete*.

544 Yang, H., Monasterio, M., Zheng, D., Cui, H., Tang, W., Bao, X., and Chen, X. (2021). "Effects of
545 nano silica on the properties of cement-based materials: A comprehensive review."
546 *Construction and Building Materials*.

547 Zhao, Z., Qi, T., Zhou, W., Hui, D., Xiao, C., Qi, J., Zheng, Z., and Zhao, Z. (2020). "A review on
548 the properties, reinforcing effects, and commercialization of nanomaterials for cement-
549 based materials." *Nanotechnology Reviews*.

550

551

552

553

554

555

556

557

558

559

560

561

562

563

564

565

566

567

568 **Table 1.** Composition of the mixes studied by isothermal calorimetry

Type of addition	w/c	Al Substitution	Amount of addition	Amount of
		respect to Si (%)	(% b.w.c) ¹	superplasticizer (% b.w.a) ²
DRIED	0.5	0, 6, 10, 15, 20	0, 0.5, 1, 2, 3, 4, 5	0
CONC	0.5	0, 6, 10, 15, 20	0, 0.5, 1, 2, 3, 4, 5	0, 20 ³

569 ¹Dry weight of addition by weight of cement.

570 ²Weight of superplasticizer by dry weight of addition.

571 ³In the case of the sample with 0% of addition 0.6% of superplasticizer by weight of cement
572 was added.

573

574 **Table 2.** Composition of the samples prepared for the mechanical strength tests.

Type of addition	w/c	Al Substitution	Amount of	Amount of
		respect to Si (%)	addition (% b.w.c) ¹	superplasticizer (% b.w.a) ²
DRIED	0.4	6, 15	0 ³ , 0.5, 2	20
CONC	0.4	6, 15	0 ³ , 0.5, 2	20

575 ¹Dry weight of addition by weight of cement.

576 ²Relative weight of Auracast by dry weight of addition, added to compensate for the
577 workability loss induced by the addition.

578 ³No superplasticizer was added to the reference sample without addition because the
579 consistency of the paste was appropriate for the preparation of test specimens.

580

581 **Table 3.** Mineralogical composition of synthesis products, obtained by Rietveld refinement,
582 and pH of the slurries.

Al Content (%)	pH	Calcite (wt. %)	Tobermorite (wt. %)	Amorphous (wt. %)
0	10.07	5.8	48.4	45.8
6	10.43	5.3	59.6	35.1
10	10.58	7.6	56.1	36.3
15	10.77	1.1	73.5	25.4
20	11.01	1.0	79.0	20.0

583

584

585

586

587

588

589

590

591

592

593

594

595

596

597

598 **Figure Captions List**

599 **Fig. 1.** X-ray diffraction patterns of the synthesis products with different Al contents. Red lines
600 represent the position and intensity of the main peaks of 1.1nm tobermorite PDF 00-045-1480.

601 **Fig. 2.** ^{29}Si NMR (left) and ^{27}Al NMR spectra (right) of the synthesis products with different
602 contents of Al.

603 **Fig. 3.** Scanning electron microscopy images of synthesis products with different Al contents.

604 **Fig. 4.** Calorimetric curves of the cement pastes with redispersed (DRIED) and concentrated
605 (CONC) additions with different proportions of Al. Dosages range from 0.5 to 5% b.w.c..

606 **Fig. 5.** Calorimetric study of cement pastes with 5% of CONC additions with different Al
607 contents. Solid and dashed lines correspond to pastes without and with superplasticizer
608 respectively.

609 **Fig. 6.** Calorimetric measurements of: cement pastes with different proportions of a) DRIED
610 and b) CONC additions with 15% of Al, c) reference, 1% DRIED addition, and 1% of CONC
611 addition with and without superplasticizer, and d) reference, 5% DRIED addition and 5% CONC
612 addition with and without superplasticizer.

613 **Fig. 7.** Relative acceleration (Nicoleau et al. 2013) as a function of the proportion of addition
614 used by weight of cement. Rhomboid and square dots represent experimental values while
615 dashed lines correspond to the linear fit.

616 **Fig. 8.** Compressive strength of samples with DRIED additions with 6% and 15% of Al at
617 different curing times. The amount of addition used was 0.5% b.w.c (left) and 2% b.w.c. (right).

618 **Fig. 9.** Compressive strength of samples containing CONC and DRIED additions with 6% of Al as
619 a function of curing time. The amount of addition used was 0.5% (left) and 2% b.w.c. (right).

620