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

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## **Abstract**

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

## **Keywords**

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

## **1. Introduction**

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

Over the last 20 years, the effect on hydration kinetics of a wide variety of nanoparticles (Kong et al. 2018; Konsta-Gdoutos 2014; Land and Stephan 2015b; Rashad 2013; Zhao et al. 2020), such as  $\text{SiO}_2$  (Björnström et al. 2004; Gaitero et al. 2010; Kawashima et al. 2013; Yang et al. 2021),  $\text{CaCO}_3$  (Kawashima et al. 2013; Sato and Diallo 2010),  $\text{Al}_2\text{O}_3$  (Campillo et al. 2007),  $\text{TiO}_2$  (Lee and Kurtis 2010) or nano-C-S-H gel (Alizadeh et al. 2009; Dittmar et al. 2013; Land and Stephan 2015a), has also been studied. The key features of nanoparticles are particle size smaller than 100nm and great surface area. There is a general agreement that nanoparticles accelerate hydration reactions of Portland cement mainly by one of the following mechanisms: the reaction with the ions dissolved from the cement grains, or the seeding effect. In the first case, the most common process is the pozzolanic reaction of silica or clay nanoparticles with dissolved Ca ions to give C-S-H gel (Björnström et al. 2004; Diez-Garcia et al. 2018; Gaitero et al. 2008, 2010; Guerrero et al. 2014; Land and Stephan 2015b; Perez et al. 2015b; a; Yang et al. 2021). Nanoparticles are more reactive than larger particles of the same composition due to the larger surface area. In addition, some authors (Björnström et al. 2004; Diez-Garcia et al. 2018; Perez et al. 2015a) have reported the presence of hydroxyl ions on the surface that make them even more reactive. In the second case, the nanoparticles do not react chemically

with dissolved species, but they serve as heterogeneous nucleation agents for the deposition and growth of hydration products. Although Kong et al. (Kong et al. 2018) have recently put into question the seeding effect of  $\text{SiO}_2$  and  $\text{TiO}_2$  nanoparticles, most researchers (Konstadoudos 2014; Land and Stephan 2015b; Rashad 2013; Zhao et al. 2020) attribute the accelerating effect of some nanoparticles to this phenomenon. Apart from the particle size, heterogeneous nucleation also depends to a great extent on the chemical and structural compatibility between the seeds and precipitated species. If the compatibility is high, like in the case of C-S-H particles, dissolved ions might even deposit on the seeds layer by layer following the same structure (Kong et al. 2018). In fact, Alizadeh et al. (Alizadeh et al. 2009) proved that the average chain length of the precipitated C-S-H gel could be modified by varying the C/S ratio and silicate polymerization of the C-S-H seeds. In addition, they also observed that C-S-H particles were more effective if their C/S ratio was 0.8, i.e. in the range of tobermorite, rather than 1.2.

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

## **2. Materials and methods**

### **2.1 Synthesis and characterization of the additions**

Precursors employed for the synthesis of the additions were CaO (Sigma-Aldrich), nano-SiO<sub>2</sub> (AkzoNobel Levasil 100/45%) and nano-Al<sub>2</sub>O<sub>3</sub> (Nyacol Al20SD). Several degrees of substitution of aluminum for silicon (Al/(Si+Al)·100) were used (0%, 6%, 10%, 15% and 20%) because it is well known that Al substitution provides stability to the structure of 1.1nm tobermorite (Diez-Garcia et al. 2017; Mitsuda and Taylor 1975; Sakiyama and Mitsuda 1977; Shaw et al. 2000). The molar ratio Ca/(Si+Al) was in all cases 0.83 and CaO was calcined at 800°C for 4h before each synthesis. The reactions were carried out in a 2L hydrothermal batch reactor at 215°C and autogenous pressure for 4h. Solvent was in all cases distilled and degassed water (1.5L) and the liquid to solid ratio was approximately 200. Obtained products were either filtered and dried in an oven at 60°C for 12h or preserved in the synthesis media. The dried products were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to know their mineralogical composition and morphology.

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

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

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

the recycle time was 1s. The chemical shifts were referenced to an external standard of  $\text{AlNO}_3$  ( $\delta=0\text{ppm}$ ). The  $^{29}\text{Si}$  experiments were performed with a pulse length of  $4\mu\text{s}$ , and recycle time was 10s. The chemical shifts were referenced to an external standard of TSP (trimethylsilylpropanoic acid) ( $\delta=0\text{ppm}$ ).

## 2.2 Particle dispersion

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

## 2.3 Calorimetric tests

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

cases) and cement was done manually in a 20ml glass ampoule that was immediately sealed and introduced in the isothermal calorimeter (TA Instruments TAM air) for 24h. The measurement took place at a constant temperature of  $25\pm0.02^{\circ}\text{C}$  using water as a reference.

### 2.3 Mechanical tests

The mechanical strength of the pastes was determined by testing  $1\times1\times6\text{ cm}^3$  prismatic samples cast in steel molds. All samples were prepared at a water to cement ratio of 0.4 using the same materials as for the calorimetric tests. In this case, only synthesis products with 6 and 15% Al substitution were added in three different concentrations: 0%, 0.5% and 2% by weight of cement (see Table 2). Mixing was carried out on a tailor-made glass vessel using a mixer Heidolph RZR2102 control. The mixing process consisted of two cycles of mixing at 750r.p.m. for 90s, separated by a halt of 60s. Resulting cement pastes were subsequently used to fill the molds which were then stored in a wet chamber at  $20^{\circ}\text{C}$  and 100% humidity for either 24h or until the time of testing; whatever happened first. Test specimens were then demolded and immersed in water at room temperature until testing. The mechanical strength tests were performed after 6, 8, 16, 24, 40 and 72 hours from mixing using an electromechanical universal test machine Ibertest ELIB-10-W. Six prismatic specimens of 1cm side and 6cm long were tested at every age. Bending tests were carried out first (results not included), and then, each half of the samples was subjected to the compression test. Two different sets of loads were employed in the compression tests depending on the age of the specimens. In the case of the youngest, and as a consequence, weakest samples (6 and 8 hours), loading rate was 10N/s while for the rest of the samples (16, 24, 48 and 72 hours) it was increased to 100N/s to reduce measuring time. Although compressive strength may be affected by the change in loading rate, the increase in strength from 8h to 16h is so large that it does not have any effect on the discussion.



### 3. Results and discussion

#### 3.1 Characterization of the additions

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

X-ray diffractograms of the synthesis products (Fig.1) revealed the presence of 1.1nm tobermorite with low crystallinity, amorphous material and minor amounts of calcite. Since the synthesis process took place in a closed vessel, calcite formation was attributed to the carbonation of dissolved lime upon contact with environmental  $\text{CO}_2$  during drying of the reaction products. Comparison between the different samples showed a progressive shift of the basal peak towards lower angles with increasing Al content. This can be attributed to Al substitution for Si within the structure of 1.1nm tobermorite. In particular, to the larger radius of  $\text{Al}^{3+}$  compared to  $\text{Si}^{4+}$  and to the need of incorporating counterions for charge balancing (Liao et al. 2019). Rietveld refinement was used to quantify the relative proportion of each phase in the samples (Table 3) using quartz as standard reference material. Tobermorite was considered in all cases as a single phase due to the impossibility to distinguish 1.1nm tobermorite from its Al substituted counterpart. Obtained results showed that the proportion of tobermorite increased with increasing Al content from 48% to about 70%. This confirmed that the use of nanoalumina as Al source for the hydrothermal synthesis of tobermorite favors the crystallization (Mitsuda and Taylor 1975; Sakiyama and Mitsuda 1977; Shaw et al. 2000).

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

<sup>29</sup>Si NMR spectra showed the typical shape of Al substituted tobermorite (Liao et al. 2019, Li et al. 2020), see Fig.2. The absence of Q<sub>4</sub> peak at -110 ppm suggests that nanosilica reacted completely and, in consequence, the amorphous phase of Rietveld analysis must be tobermorite-like C-S-H gel. In addition, the presence of two peaks at approximately -84ppm (Q<sub>2</sub>Al) and -93.5ppm (Q<sub>3</sub>Al) confirms the incorporation of Al into the silicate structure, although Li et al. reported that the latter could also appear in absence of Al. It is widely accepted that Al substitutes for Si preferentially into the bridging and branching positions of C-S-H gel and tobermorite, see for example (Sun et al. 2006), although it can also enter into pairing positions (Manzano et al. 2008, 2009). Taking into account the structure of tobermorite (Biagioni et al. 2015), incorporation of Al solely into branching positions would result in a maximum Al/Si ratio of 1/6, i.e. lower than the ratio of the sample with the highest Al content. In the case of substitution into the bridging positions of linear silicate chains with dreierketten structure, the maximum Al/Si ratio increases to 1/3. Therefore, the composition of the samples is compatible with having a mixture of particles with both structures.

<sup>27</sup>Al NMR analysis (Fig.2) showed two overlapping peaks centered at about 56 and 64 ppm. These peaks are generally attributed to Al substitution for Si in branching (Q<sub>3</sub>) and bridging (Q<sub>2</sub>) positions respectively (Guo et al. 2017; Houston et al. 2009; Komarneni et al. n.d.; Schneider et al. 2001). Al placed in pairing positions gives place to a resonance peak centered at about 72 ppm not observed in this study (Pardal et al. 2012). The spectrum of the sample with the largest proportion of Al, i.e. 20% Al, shows also the presence of a small proportion of octahedrally coordinated Al. There is no consensus in the literature on the assignation of this signal, which has been attributed to the incorporation of Al into the interlayer space (Guo et al.

2017), on C-S-H particles' surface (Sun et al. 2006), and even in silicate chain ends (Pardal et al. 2012). In this work, this signal could also be due to rests of unreacted  $\text{Al}_2\text{O}_3$  coming from the nanoalumina used in the synthesis. In any case, the fact that such peak only appears in the sample with the largest proportion of Al agrees with the preferential incorporation of Al into bridging and branching positions.

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

### 3.2 Calorimetric study

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

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

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

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

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

### 3.3 Mechanical performance

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

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

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

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

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

#### **4. Conclusions**

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

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

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



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

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

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

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

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

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## **Data availability statement**

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

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

Type of addition	w/c	Al Substitution respect to Si	Amount of addition	Amount of superplasticizer
		(%)	(% b.w.c) <sup>1</sup>	(% b.w.a) <sup>2</sup>
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 <sup>3</sup>

<sup>1</sup>Dry weight of addition by weight of cement.

<sup>2</sup>Weight of superplasticizer by dry weight of addition.

<sup>3</sup>In the case of the sample with 0% of addition 0.6% of superplasticizer by weight of cement was added.

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

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

<sup>1</sup>Dry weight of addition by weight of cement.

<sup>2</sup>Relative weight of Auracast by dry weight of addition, added to compensate for the workability loss induced by the addition.

<sup>3</sup>No superplasticizer was added to the reference sample without addition because the consistency of the paste was appropriate for the preparation of test specimens.

**Table 3.** Mineralogical composition of synthesis products, obtained by Rietveld refinement, 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

## Figure Captions List

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

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

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

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

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

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

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

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

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