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Nucleation Seeding with Calcium Silicate Hydrates – A Review

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Abstract

The development of green cements, with the aim of reducing CO₂ emissions, often results in reduced hydration activity, especially during the first hours and days. Nucleation seeding with C-S-H has enormous potential to accelerate hydration, which can compensate for the above-mentioned effect, without compromising the long-term strength of seeded cements. In this work, the effects of calcium silicate hydrates are reviewed in detail, with a focus on synthesis, as well as their influence on the hydration mechanism and the development of mechanical properties, such as early and long-time compressive strength and porosity.

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1. Introduction

Portland cement based concrete, is the most widely used synthetic material on the planet [1,2]. The cement industry currently contributes approx. 8% of the global anthropogenic CO₂ emissions., Today's global cement production of >4 Billion tons expected to increase further as a consequence of an increased demand for housing and infrastructure projects (Figure 1) [3–5]. Concerning portland clinker the calcination of limestone, the main raw material in cement, contributes approximately 60% of the CO₂ emissions, with and the related thermal and electrical energy needed for burning and grinding [6,7] makes ~40%. Strong efforts have been made to reduce CO₂ emissions, through the use of alternative fuels (e.g. biomass), and more effective kilns, as well as by improving clinker mineralogy, which allows a reduction of the clinker content of the final cement [3].

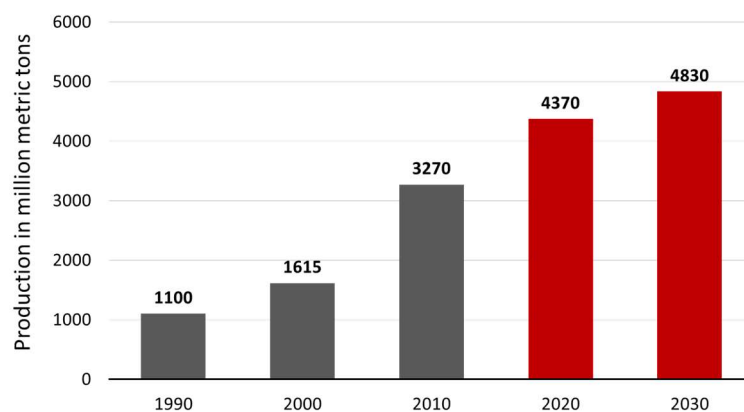


Figure 1: Global cement production in million metric tons from 1990 to 2010 and projections for 2020 and 2030 [5].

While the reduction of CO₂ emissions during production requires considerable effort and may heavily impact the economies of cement plants, the reduction of the clinker share in blended cements is less invasive. Thus, alternatives to ordinary Portland cement (OPC), that could result in an overall reduction of CO₂, are of great interest. There are several developments ongoing and reported in the literature [8–11]. On the other hand, a reduction of the clinker share impacts the early strength development of

concrete which may have negative consequences on the economic interests of the construction companies and end-users [12,13].

Although OPC has been used for more than a century, the mechanisms of cement hydration are still controversially discussed [14–17].

Tricalcium silicate (C_3S) is the most significant component of Portland cement, because it is mainly controlling hardening and strength development, as well as the durability of cement pastes, mortars and concretes. The C_3S hydration process is commonly divided into 4 or 5 phases, which are differentiated by their hydration activity (Figure 2) [18]. Stage I, the induction period, shows rapid hydration activity that lasts only for a few minutes and ends at the dormant period (II). Stage III is the acceleration period, which ends with a peak of hydration activity. For common cements, this maximum is usually reached after several hours. The deceleration period (IV), characterized by a decreasing reaction rate, descends into the last hydration period (V), which is characterized by continuous reaction kinetics, which end when all water is consumed, either by reaction or otherwise [15,18,19].

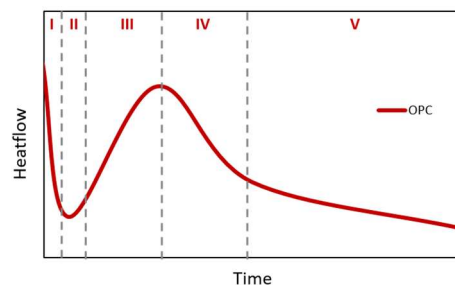


Figure 2: Schematic representation of the rate of heat evolution of pure C_3S . The hydration process steps: I – Induction period, II – Dormant period, III – Acceleration period, IV – Deceleration period, V – continuous slow hydration. Adapted from [18].

The mechanisms leading to the characteristic hydration curve are still under debate. The termination of the induction period, as well as the beginning of the acceleration period which follows the dormant period, are of particular interest. Since it is not our intention to review the cement hydration process we refer to the works by Gartner et al. and more recently Bullard et al. and Scrivener et al. [15,18,20].

A common theory for the termination of the induction period relates to the formation of a metastable C-S-H passivation layer around the clinker, which inhibits further C_3S dissolution [21,22]. However, while several authors showed the initial formation of silicate monomers on the C_3S surface after contact with water, the direct experimental evidence of a continuous layer and the impact of this metastable barrier on C_3S dissolution is still missing [17,21,23–26]. Other theories, resulting from the early works of Barret et al., have assumed the formation of a superficially hydroxylated layer on the C_3S surface in contact with water, slowing down its dissolution [27]. Nonat et al. have further refined this theory by stating, that the solubility of this superficially hydroxylated layer is significantly lower than that of C_3S , which especially at higher calcium concentrations, lowers the driving force of tricalcium silicate dissolution drastically [28–30]. More recently, Juilland and Nicoleau et al. have developed a thermodynamic framework, coupled with kinetic rate laws, which helped to describe the dissolution behavior of C_3S . The observed formation of etch pits on the surface of C_3S , enhancing the available reactive surface area, may further explain the increased dissolution rate during acceleration period [28,31]. In 2010 a dissolution theory, which correlates the hydration periods with the concentration of the pore solution with respect to the dissolving phase, was proposed and has gained wide spread popularity [32].

Further older theories regarding the end of the dormant period address rate-controlled nucleation and the growth of either portlandite or C-S-H, with Taylor et al. proposing that the nuclei of stable C-S-H are already formed during the induction period and that they grow with an almost exponential rate and hence that no real dormant period exists in a pure system [18,33].

1.1 Nucleation and growth of C-S-H

Tricalcium silicate dissolves rapidly in water to release calcium, silicon and hydroxide ions. The concentration of the solution increases to critical supersaturation with respect to C-S-H triggering its precipitation with a significantly lower Ca/Si ratio than C_3S , resulting in a decrease of silica concentration and increased calcium levels in the pore solution. Garrault et al. have demonstrated that

C-S-H nucleation during C_3S hydration occurs heterogeneously, with experiments using different heterogeneous nucleation sites showing that C_3S is more favorable for C-S-H nucleation than C_2S or calcium carbonate [29]. The duration of the period prior to precipitation, has been observed to be dependent on the number of initial nuclei formed [29]. Two distinct growth modes, parallel and perpendicular to the surface, have been observed with SEM and AFM by Gauffinet et al. and Garraut et al. who found that the ratio of parallel to perpendicular growth rate is determined by Ca^{2+} concentration, at a low lime concentration the rate of reaction slowed down earlier, due to the resulting surface coverage from enhanced parallel growth [22,39]. Recently Plank et al. have demonstrated that the C-S-H precipitation in the presence of poly carboxylate superplasticizers does follow a non-classical nucleation mechanism, and Picker et al. were able to prepare C-S-H mesocrystals in the presence of poly (1-vinylpyrrolidone-co-acrylic acid) supporting Plank et al.'s conclusions [91,92]. The nucleation of C-S-H in a polymer-free system has been investigated in detail by Krautwurst et al. in 2018, showing that the nucleation follows a non-classical two-step pathway via spherical amorphous precursors that most likely are the location of crystallization [40].

Additionally, it was shown by Mota-Gasso et al. as well as Nonat et al. that the addition of sulfate in form of gypsum or sodium salts alters the initial growth of C-S-H also [41,42].

1.2 The addition of nano particles to cement

The addition of nanoparticles typically accelerates cement hydration, which offers economic and ecological advantages such as compensation for reduced hydration activity resulting from the use of supplementary cementitious materials (SCMs) [43].

Nanoparticle accelerators are divided into two groups, based on their general mechanisms of action. The first group includes oxides like TiO_2 [44,45], ZrO_2 [46], and Fe_2O_3 [47,48], or nanoparticles like carbon nano-tubes [49], which mainly accelerate hydration physically. Small particles might provide heterogeneous nucleation sites and/or relatively more space in to which hydration products can grow (Figure 4) [21,50], and bigger aggregates that do not offer large surfaces for product growth have

recently been shown to increase the shearing conditions of pastes, which results in the generation of more initial nucleation sites on cement surfaces [51].

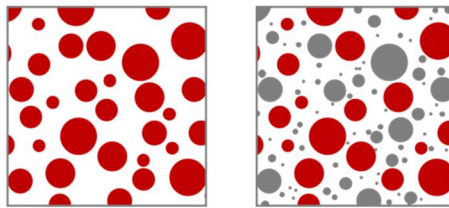


Figure 4: An illustration of the filler effect. In relation to clinker quantity, more space for hydration products is available when filler particles (right side) are present. Adapted from Scrivener et al. [21].

The second group describes reactive additives have an influence on the pore solution, in addition to their filler effect. Pozzolanic additives like nano-silica are able to form hydration products and hence change the $\text{Ca}(\text{OH})_2$ concentration of the pore solution. The addition of ultra-fine calcium hydroxide accelerates cement hydration significantly [55]. Besides providing nucleation sites, $\text{Ca}(\text{OH})_2$ works through rapid saturation of the pore solution with respect to calcium and hydroxide ions. Calcium carbonate has been shown to accelerate C-S-H formation, since apparently calcite surfaces are crystallographically an excellent growth template for C-S-H [51,52]. In addition, due to the chemical interaction with alumina rich phases, it forms carboaluminates and stabilizes ettringite which may be beneficial for concrete performance [53,54].

Both additive groups might additionally adsorb ions from the pore solution, as it has been shown for nano-silica additions [56,57]. The adsorption of ions from the solution, as well as product growth on the additive instead of on the clinker surface, may also create local concentration gradients which might alter dissolution mechanisms in cementitious systems [22,23,56–58].

2. The acceleration of cement hydration with calcium silicate hydrates

Calcium silicate hydrate is the main hydration product of the calcium silicates (alite and belite) in OPC, to which the material properties of concrete are primarily attributed [59]. As such, it plays a very important role with respect to seeding-additives for cementitious materials. C-S-H particles are clearly

distinct from other seeding agents, since they should be ideal nucleation substrates for C-S-H products [36,60].

Calcium silicate hydrates are able to incorporate additional calcium or aluminum ions into their structure, with an uptake of sodium and potassium ions being observed as well. [58,61–64].

Calcium silicate hydrates can be divided into two groups: semi crystalline C-S-H gels and crystalline C-S-H phases. Hydrated Portland cement consist of up to 80% gel-like C-S-H which is, like C-A-S-H, also the main constituent of hydrated slag and fly ash cements, but with a high amount of incorporated aluminium in its structure [64–66]. The most important C-S-H phases are displayed in figure 5, according to their position in the CaO-SiO₂-H₂O system. The ellipses describe the composition areas for the phases of C-S-H gels (I and II), zeolites, 11Å tobermorite and the solid-solution series of kilchoanite and C₂S [65].

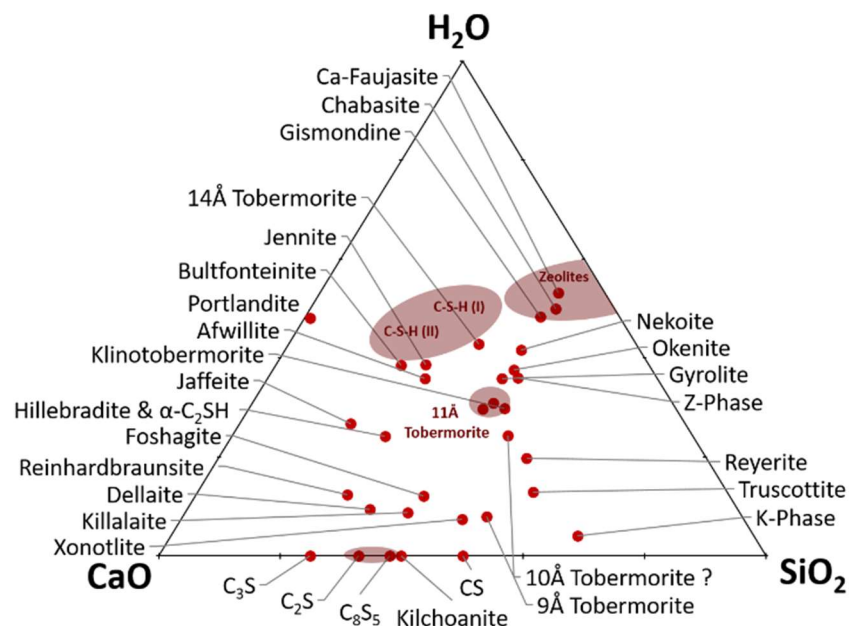


Figure 5: The orientation of calcium silicate hydrates in the SiO₂-CaO-H₂O system. The ellipses describe the composition areas for the phases of C-S-H gels (I and II), zeolites, 11Å tobermorite and the solid-solution series of kilchoanite and C₂S. Adapted from Garbev et al. [65].

The calcium to silicon ratio of C-S-H follows a function of the available calcium and silica contents in solid and solution. Lothenbach and Nonat have compared the experimental data of various authors

and concluded that under a Ca/Si of 0.7, amorphous silica will be present in synthetic C-S-H, while by exceeding a Ca/Si of 1.45-1.6 calcium hydroxide occurs (Figure 6A) [63]. By controlling the synthesis conditions carefully, it has recently been possible to prepare pure C-S-H exceeding a Ca/Si of 1.6 (see chapter 2.1 – Synthesis methods) [67].

The water to silicon ratio ranges from 0.5 to 3.5 depending on the drying method and the Ca/Si ratio, while a higher calcium to silicon ratio results in a higher water content (Figure 6B) [61]. When investigating the effects of various synthetic C-S-H phases on cement hydration, the impact of SiO₂ or Ca(OH)₂ residues must be taken into account carefully.

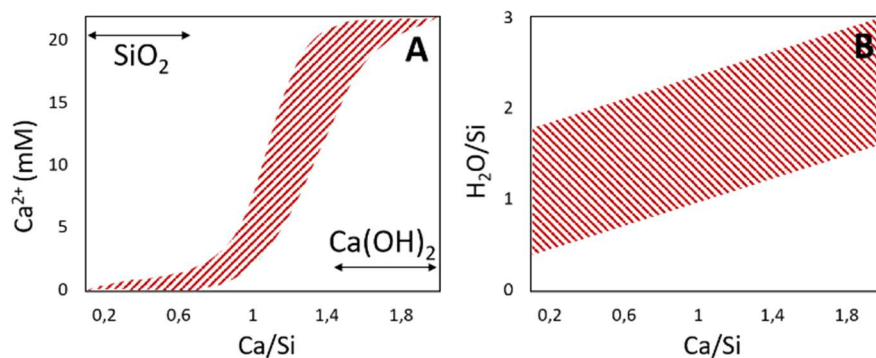


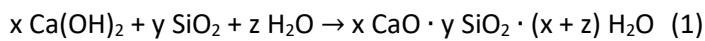
Figure 6: A – The relationship between the Ca/Si ratio of synthetic C-S-H phases and the calcium ion content of the aqueous phase in equilibrium. The arrows mark calcium to silicon ratios outside the solubility borders, where silicon dioxide or calcium hydroxide remain in the system. B – The relationship between the water content and the calcium to silicon ratio for different drying methods. The bottom line of the area represents C-S-H samples dried harshly at 110°C, whilst the upper end of the area refers to samples dried via solvent extraction. Compiled experimental data adapted from Nonat et al. [63].

2.1 Synthesis of calcium silicate hydrates

Various methods for synthesising C-S-H phases for nucleation seeding, have been applied in the literature. The common synthesis routes use the pozzolanic, sol-gel and precipitation methods.

2.1.1 The pozzolanic method

The pozzolanic reaction is described as the chemical reaction of calcium hydroxide with silicon dioxide and water to form calcium silicate hydrate (Equation 1).



The reaction allows control of the calcium to silicon ratio, via the ratio of the starting materials, in a range given by the solubility of the C-S-H system. The silicon source can be varied within a broad range in terms of particle size and crystallinity (e.g. amorphous silica or quartz glass). The crystallinity of the C-S-H product, as well as the speed of the reaction, are determined by the reaction conditions.

Ambient conditions

Reactions at room temperature have very low equipment requirements; the starting materials are simply mixed to the desired Ca/Si ratio with water and the reaction runs in a sealed vessel, under inert gas, to avoid carbonation. The water-solid ratio is higher than with other methods, to ensure a homogenous mixing of the reactants. The biggest disadvantage of the method is that a complete turnover to a semi crystalline C-S-H gel, takes between a number of weeks to a month. The simplicity of the system nevertheless offers only very few possibilities to vary the properties of the product. A semi crystalline C-S-H gel is obtained as a product [58,68].

Mechanochemical synthesis

Compared to the pozzolanic reaction under ambient conditions the mechanochemical method leads to a significantly quicker turnover of the reactants. Typical reaction times for complete reaction are in the range of a few hours to a few days, depending on the milling equipment. The starting materials are mixed under ambient conditions, but the reaction takes place in a mill, which allows a lower water/solid ratio. During milling, the reaction products forming at the surface of the silicon dioxide are removed repeatedly, thus uncovering any unreacted silica and enhancing the turnover speed (Figure 7).

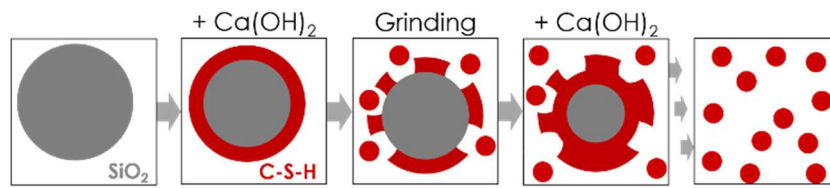


Figure 7: Schematic representation of the mechanochemical synthesis of C-S-H gel. C-S-H forms at the surface of the silicon dioxide particles and gets removed during the grinding process until complete turnover is achieved.

The grinding time, and the water/solid and Ca/Si ratios can be tuned, to change the product. Since a complete turnover can be achieved under optimized reaction conditions, the Ca/Si of the starting materials equals the Ca/Si of the produced C-S-H phase, in the range of the system solubility (See figure 6). A grinding setup can additionally be used for the hydration of tricalcium silicate, which might result in the formation of afwillite instead of C-S-H under controlled conditions [69]. The hydration of C_3S results in the formation of excess calcium hydroxide that needs to be removed through leaching during or after synthesis [70,71].

The disadvantages of the mechanochemical method are the high equipment requirements and long reaction time nonetheless [72–74].

Hydrothermal synthesis

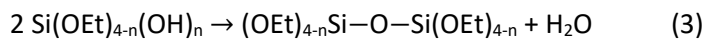
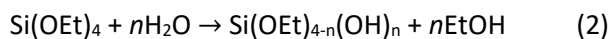
Hydrothermal synthesis routes are typically used to form crystalline C-S-H. They take place in a sealed autoclave, where a saturated steam atmosphere forms during heating. Elevated temperatures and pressure enable the formation of crystalline phases. The starting materials are either the same as for the other pozzolanic reactions or a C-S-H gel. The product is tunable via the Ca/Si ratio (refer to the phase diagram in figure 5), reaction temperature and reaction time. Typical reaction times range from days to a few weeks, depending on the desired phase. Not every C-S-H phase can be obtained with good purity, with mixed phases yielded often [65,75]. The use of surfactants and templates allows one to vary the nano-structure of the prepared C-S-H phase. Tobermorite nano-wires and platelets have been prepared using EDTA/ Ca^{2+} , as chelating agent and with a novel micro-emulsion method using cetyl

tert ammonium bromide as a surfactant [76,77]. Xonotlite nano-wires have even been prepared without surfactants by rotating the autoclave at 100 rpm during treatment [78].

The product variability of the hydrothermal method is advantageous, but the reaction time and the energy demand are high compared to the previously described methods. Additionally, it should be mentioned that during hydrothermal reactions, particle size grows, such that after synthesis grinding of the product material might be necessary, to get an efficient accelerator for cement hydration. All these methods are also applicable to the formation of C-S-H from the hydration of tricalcium silicate [69,79].

2.1.2 Sol-gel method

Sol-gel synthesis is a poly condensation of metal alkoxides hydrolyzed with water (Equation 2 and 3). A commonly used Si-precursor for C-S-H synthesis is tetraethyl orthosilicate (TEOS).



Product formation during sol-gel synthesis is dependent on the pH of the solution and the salts present. A gel network forms if the pH is lower than 7 or if salts are present. A colloidal sol is formed when the pH is above 7 in the absence of salts (Figure 8).

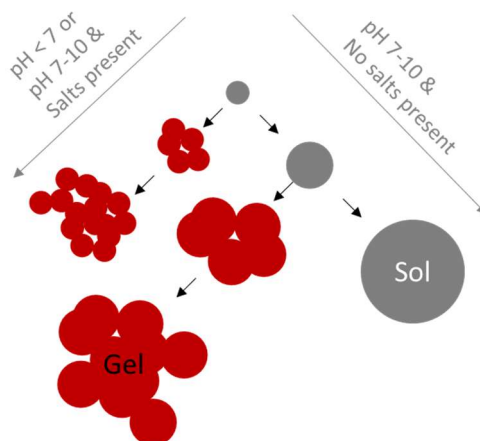


Figure 8: Schematic representation of the products of the sol gel process. Below a pH of 7 or with salts present, gel networks form [80]. In the absence of salts in the pH range of 7-10, larger sol particles can grow (Stöber process) [81].

During the reaction calcium ions can be intercalated into the silicon network, through an ion exchange with the weakly acidic silanol group [80] (Equation 4). As a calcium precursor, calcium ethylate ($\text{Ca}(\text{OEt})_2$) is often used [72,80,82].



The calcium ethylate precursor is obtained by reacting elementary calcium with ethanol, with the silicon precursor then added to the stirred solution and condensation being induced by the addition of water. A gel forms in a time range from a few minutes to a few hours, depending on the reaction conditions. Residues are removed from the product by repeatedly washing the gel with ethanol and water [72]. For calcium containing systems, a gel is usually formed. The synthesis of colloidal C-S-H phases has not been reported so far [83,84].

Sol-gel synthesis require several chemicals as well as laboratory equipment but have the advantage of short reaction times in the range of a few hours [72]. The gel obtained is x-ray amorphous.

2.1.3 Precipitation method

The synthesis of C-S-H phases through precipitation is a fast, cheap and simple preparation method. The combination of sodium silicate solution (Na_2SiO_3) and calcium nitrate solution ($\text{Ca}(\text{NO}_3)_2$), or calcium chloride solution (CaCl_2), results in the immediate precipitation of calcium silicate hydrate [73,85,86]. The calcium to silicon ratio can be adjusted via the concentrations of the precursor solutions. To avoid decalcification, excess sodium and nitrate ions are removed, by washing the precipitate with a calcium hydroxide solution of a concentration similar to that of the desired C-S-H [86].

The disadvantage of this synthesis is that, like for the pozzolanic reaction at ambient temperatures, the number of impact factors for tuning the product, especially particle size control is very limited.

Precipitation in the presence of polymers

Inspired by nature the preparation of composite materials from polymers and inorganic matter has been an intensively studied topic aimed at improving and tuning the resultant material properties [35,87,92]. To create C-S-H/polymer composite materials, precipitation is carried out in the presence of a polymer, under controlled conditions.

Matsuyama and Young were the first to report the intercalation of polymers non-covalently into calcium silicate hydrates, but it was demonstrated later, by Merlin et al., that C-S-H does not swell in water and that the intercalation of polymers is not effective, either during precipitation or the pozzolanic reaction, nor as a treatment after synthesis [88–90]. Franceschini et al. have synthesized 2007 covalently bound C-S-H/polymer composites via T-silane functionalities at the C-S-H surface and were able to incorporate noticeable amounts of polymer. They have confirmed the fact that the intercalation of polymers into C-S-H sheets does not always occur [91]. As mentioned in chapter 1.1 Plank et al. have demonstrated that the C-S-H precipitation in the presence of poly carboxylate superplasticizers does follow a non-classical nucleation mechanism, and Picker et al. were able to give support to Plank et al.'s conclusions through the preparation of C-S-H mesocrystals in the presence of poly (1-vinylpyrrolidone-co-acrylic acid) [92,93]. With the aim of creating effective accelerators for cement hydration, recent studies have focused on the preparation of C-S-H/superplasticizer nanocomposites [94]. Different approaches towards particle size control have been studied. Kanchanason et al. have successfully tuned particle size via the sidechain length of methacrylic acid-co- ω -methoxy poly(ethylene glycol) methacrylate esters, whilst Sun et al. have controlled particle size by manipulating the reaction conditions during precipitation and, by applying latex particles as templates Phattharachindanuwong et al. have prepared hollow C-S-H spheres of uniform nanometer size [95-97]

The incorporation of polymers offers unique possibilities for controlling synthesis, especially the inhibition of agglomeration and Ostwald ripening of the nanoparticles. However, this great advantage of the co-precipitation method is offset by the fact that the preparation of polymer composites includes long stirring and pumping times, ranging from several hours up to a number of days [95,97].

Additionally, one must take into account the significantly more expensive starting materials, as compared to methods using solely calcium and silicon oxide as sources. Since the addition of these composite materials to cement results in a more complex reaction mechanism, their benefit for fundamental hydration studies is limited, as it is assumed that polymer surface coverage and desorption exert a strong influence on acceleration performance.

Ultrasonic Treatment

The preparation of C-S-H particles under ultrasonic treatment offers a unique possibility for tailoring shape. Mehrali et al. have prepared needle-like C-S-H in the absence of additives by ultrasonic irradiation, after mixing the precursor solutions. They were able to show that the addition of surfactants has a significant influence on the morphology of the precipitated C-S-H, by synthesizing sheet-like structures in the presence of SDS (sodium dodecyl sulfate) [98]. The impact of other surfactants during irradiation has also been investigated; Zhang et al. have been able to prepare hollow C-S-H spheres by co-precipitation, in the presence of cetyltrimethylammonium bromide (CTAB), whereas Moghaddam et al. have produced cubes and dendritic structures by varying precursor and surfactant (CTAB) concentrations [99].

Despite the relatively high costs of the surfactants involved, the authors claim that the improved material properties and resulting benefits of the seeded cement justify the use of this synthesis method [92,100].

Precipitation with pH Control

Synthetic calcium silicate hydrates with a Ca/Si higher than 1.4-1.6 usually coexist with a calcium hydroxide phase [63]. In 2017 Kumar et al. have been able to prepare C-S-H with a defined Ca/Si of 1.75 and 2 under controlled pH conditions, which equal the real cement system, and a very high level of supersaturation. The preparation of uniform C-S-H with a Ca/Si up to 2, allowing the precise investigation of the structural and chemical environment, has led to the proposal of a novel structure model with interlayer calcium sites, bridging terminal Q_1 silicate units [67].

2.1.4 Advantages and limitations of the synthesis methods

The extent of product control is strongly dependent on the preparation method used in C-S-H synthesis. The Ca/Si ratio can be tuned exactly through mechanochemical synthesis, since no further processing steps are necessary after milling, but nevertheless in the absence of further additives, neither morphology nor effective size control can be achieved. Precise control over particle size can be achieved by precipitation in the presence of polymers and additionally, ultrasonic irradiation in the presence of polymers offers further and a very interesting possibility for controlling shape. Nevertheless, the possible influence of the polymers in hydration complicates the investigations of the effects of C-S-H seeding. Crystalline C-S-H phases can be obtained almost solely by hydrothermal reactions and their defined stoichiometry and morphology are advantageous in investigating their effect as admixtures. Morphology directing polymers could also be applied in the synthesis of crystalline C-S-H.

2.1.5 Application as nucleation seeds

C-S-H gels are commonly used in suspensions and either need to be stabilized properly or intensively homogenized, before application as effective accelerators, the industry, nevertheless also provides C-S-H seeds applicable as powder [47,82,86,101]. Due to a different mechanism of action, crystalline C-S-H seeds have proven to be applicable as powders, as shown by Horgnies et al. [69].

The stability of C-S-H depends on the method of stabilization used. Due to Ostwald ripening, the agglomeration and carbonation of nano C-S-H, without any stabilization, the seeds will become less effective over time. To avoid ripening and carbonation processes, pure C-S-H suspensions should be stored under inert gas and used as soon as possible after preparation [72,102,103].

2.2 Nucleation seeding in cement

Calcium silicate hydrates incorporated in cement pastes have been studied early, because of their potential to drastically accelerate cement hydration [104-106]. In many studies, the resulting economic benefits are a focus, but environmental advantages, resulting from a reduction of the proportion of cement in concrete, are also of great interest. Seeding effects have also been studied to obtain a more fundamental understanding of cement hydration processes.

2.2.1 Hydration

The addition of well dispersed nano-sized calcium silicate hydrates into cement pastes results in an enhanced hydration rate, and shortens induction and dormant period, with the maximum of the hydration rate becoming higher and shifting to earlier times [43,72,82,86,95,96,107–111]. C-S-H additions to cement, ranging from 0.04 wt.-% up to 10 wt.-%, have been investigated in literature, but an upper limit for acceleration has been found to occur [72,108,109].

The strongest effect in cement has been recorded by Nicoleau, who added 4% X-Seed® to cement, resulting in an 85% earlier and 120% higher hydration maximum [109]. The strong effect of 4% C-S-H (prepared by coprecipitation) in C₃S, recorded by Thomas et al., resulted in an 80% earlier and 67% higher maximum [87,111] (Figure 9). However, the C-S-H gels prepared by the pozzolanic reaction by Land et al. and Alizadeh et al. do not show a strong acceleration performance (See figure 9) [58,72].

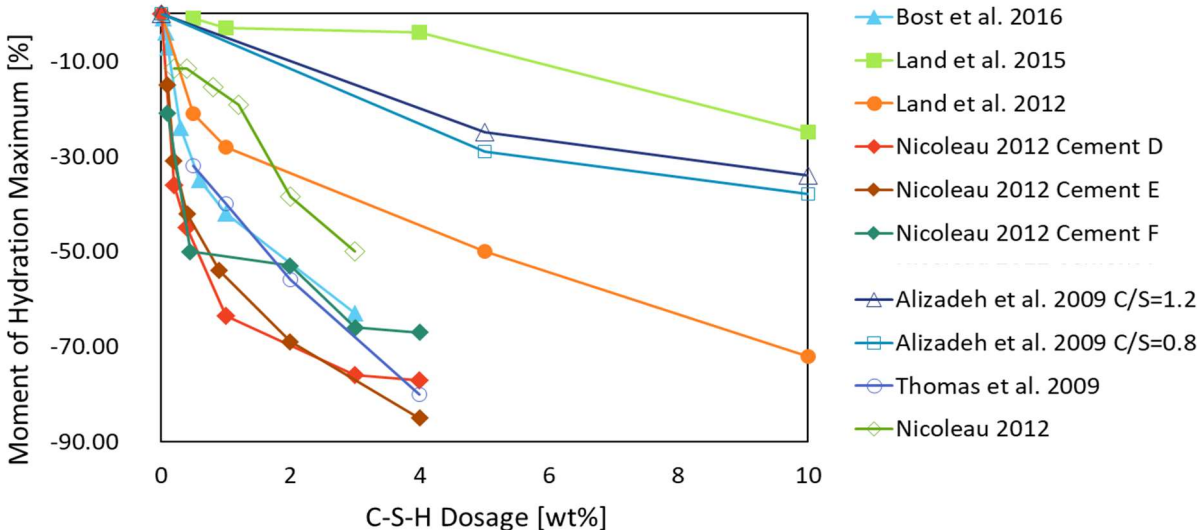


Figure 9: The relative acceleration of hydration (defined by the shift of the time of the maximum) as a function of the added weight percentage of C-S-H seed. Bost and Land et al. have investigated cement

while Alizadeh and Thomas et al. have investigated C_3S . Data adopted from sources [47,58,85,108,109,111] and [86].

The altered location of product formation was observed to be one of the predominant changes induced by nucleation seeding and discussed to be one reason for acceleration. C-S-H seeds have been shown to act directly as secondary nucleation or growth sites of further hydration products, leading the product formation process away from clinker particles [13,53,60,86,111–113]. Growth on the seeds, instead of on the clinker particles, has been found to reduce the inhibition of C_3S dissolution [13,86,111]. Additionally, nucleation in the pore space removes calcium and hydroxide ions from the solution, creating a local concentration gradient away from the clinker particles, which might accelerate C_3S dissolution [58] (Figure 10). With the stronger calcium and hydroxide ion flow, the aluminate hydration is accelerated as well, which was observed in an earlier sulfate depletion peak [109].

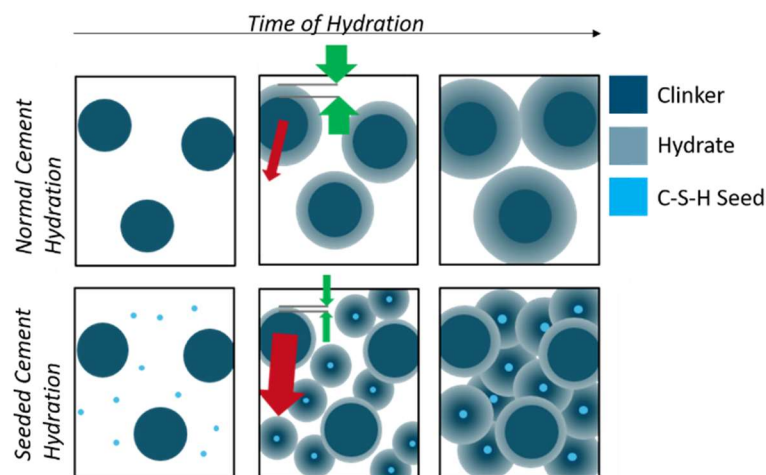


Figure 10: Schematic representation of cement hydration and the influence of nucleation seeding with C-S-H. The red arrows display concentration gradients while the green arrows highlight the different thickness of the hydrate formed around the clinker particles.

Kanchanason et al. have prepared C-S-H/ PCE composites with particle sizes ranging from 35 to 535 nm and compared their acceleration behavior [96]. Acceleration was enhanced when equal masses of

smaller seeds were used, as displayed in figure 11. Combined with the observation that a larger amount of C-S-H enhances acceleration, this indicates that the total number of seeds added, or the total surface provided, might be crucial factors.

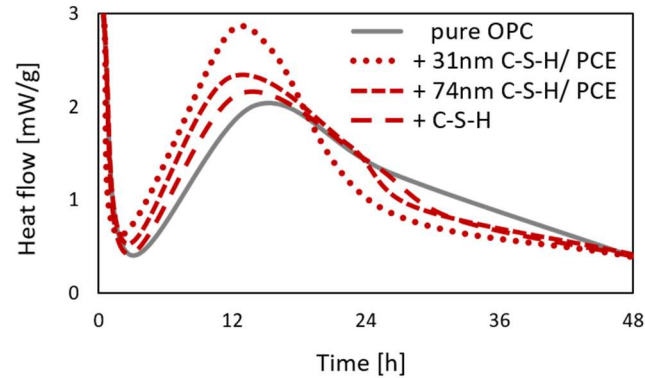


Figure 11: Hydration behavior of cements seeded with 31 or 74 nm C-S-H/ PCE composites compared to the effect of a pure C-S-H additive (550 nm) and OPC without additives. The more seeds added (smaller size), the more pronounced the acceleration. Adapted from Kanchanason et al. [96].

Nicoleau et al. have thoroughly investigated the correlation of seed quantity and acceleration with respect to cements mineralogy. They found 4 areas of accelerating behavior, depending on the amount of seeds added to different cement pastes. For overly small quantities in some cements (the dotted line in figure 12), an annihilation of acceleration was observed, leading to an initial plateau (P1), followed by quasi linear accelerating behavior (A1). For higher seed quantities, the previously mentioned upper limit was reached (P2, solid and dashed lines in figure 12). For some cements, the authors found a second acceleration after the plateau (A2, solid line in figure 12). It is of note that none of the investigated cements showed all four effects combined.

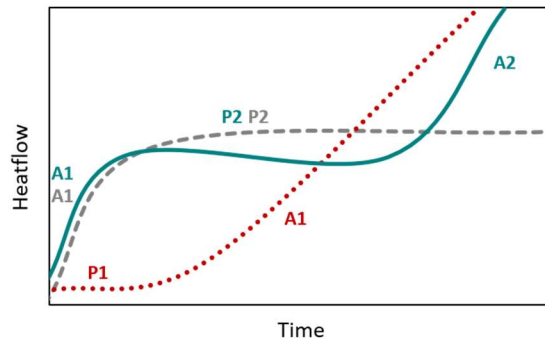


Figure 12: Schematic representation of the lower (P1) and upper limit (P2) of addition, as well as the first acceleration (A1) and second acceleration (A2), in cement pastes seeded with C-S-H. The effects depend on cement composition. Adapted from Nicoleau [109].

With respect to cement composition, Nicoleau et al. have found that sulfate and alkali concentrations are the most important parameters. Overly low sulfate or alkali contents result in the annihilation of the first nuclei, resulting in a plateau (P1). The beginning and end of plateau (P2) are strongly correlated with the sulfate content of the cement as well; the lower the gypsum content, the more C-S-H seeds are required to reach plateau (P2) and the earlier a second acceleration (A2), after the plateau, achieved.

Gypsum is assumed to contribute to the pore solution buffer system and prevents a decrease of calcium ions; this was found to be one reason for an acceleration through C-S-H seeds [41].

Besides cement mineralogy, the influence of cement fineness has also been investigated. It has been found that, with an enlarged C_3S surface, acceleration is lowered when adding the same seed content. This contradicts the hypothesis that cement hydration is controlled purely by nucleation and growth and highlights the importance of C_3S dissolution [109].

The influence of other seed parameters is under debate. The impact of the calcium to silicon ratio (Ca/Si) is the most controversial property of the seeds. Land et al. has found that seeds with a high Ca/Si ratio are advantageous in cement, while the opposite has been found for C_3S (Chapter 2.3) [58,72]. However, the authors have only presented seeds prepared with a Ca/Si ratio of 0.4 and 2, which is outside the borders of the CaO-SiO₂-H₂O system [68]. With a ratio of 0.4, unreacted silicon

oxide will remain in the product and for a Ca/Si of 2, calcium hydroxide will remain (under the reaction conditions given). In both cases, the real quantity of the C-S-H added becomes distorted and for the remaining calcium hydroxide, the pore solution (calcium and hydroxide concentration) and hence the C₃S dissolution of the cement might change. Additionally, particle size, which is known to be a crucial factor, was not determined.

2.2.2 Mechanical properties and microstructure

With hydration, microstructure formation and consequent setting and hardening of pastes is accelerated [13,47,72,82,95,96,108,110,111,114]. These effects are attributed to faster product formation. Sun et al. have found that after 12 hours, 18% less clinker phase was remaining in the investigated OPC paste containing 0.6 wt.-% of C-S-H/PCE composite seeds, compared to an unseeded cement. Nevertheless, this effect nevertheless is relativized after 3 days to 5% [95].

In figure 13, the effects of different types of C-S-H additives on the early strength of different cements, with and without SCMs, are summarized in comparison to samples prepared without C-S-H additives. By far the strongest effect was accomplished by the addition of X-Seed to cement, as reported in the patent from Reichenbach et al. (2011) and by Land et al. (2012) [111,115]. Other authors have used either co-precipitated C-S-H (CP C-S-H) or additives prepared in sol-gel synthesis (SG C-S-H) with an average strength gain of 30% with 1% additive [82,85]. The strength loss with higher amounts of C-S-H (Owens et al. 4% compared to 2%; Reichenbach et al. 1.5% compared to 0.3%) indicates the existence of an upper limit for the beneficial addition of C-S-H, dependent on cement mineralogy, as it has been described by Nicoleau et al. (2009) [109].

	Binder System	Additive Specification	Quantity [wt%]	1d Strength Gain [%]
Reichenbach et al. 2011	Lafarge Class H Cement	X-Seed	0.30	270
Land et al. 2012	Cement (CEM I, 42.5R)		0.35	263
Reichenbach et al. 2011	Lafarge Class H Cement		1.50	230
			0.15	116
			0.07	94
Jiang Ling-fei et al. 2017	Cement + GB 1596 Class I FA	SG C-S-H	2.00	67
	Cement GB175-2007 42.5R	C-S-H/ PCE	2.00	53
Sun et al. 2017	J. Onoda Type II-52.5	CP C-S-H	0.60	37
Jiang Ling-fei et al. 2017	Cement GB175-2007 42.5R	SG C-S-H	1.00	33
	+ GB 1596 Class I FA		2.00	33
			1.00	33
K. Owens et al. 2014	CEM I 42.5N + GGBS	Unknown	2.00	33
Land et al. 2015	CEM I 42.5R	SG C-S-H	0.50	32
Hubler et al. 2011	Lafarge Type I OPC	CP C-S-H	1.00	30
Jiang Ling-fei et al. 2017	Cement GB175-2007 42.5R	CP C-S-H/ PCE	1.00	25
K. Owens et al. 2014	CEM I 42.5N	Unknown	2.00	21
	+ 10mm Limestone / Sand		2.00	15
	CEM I 42.5N		4.00	9

Figure 13: Compressive Strength gains, as reported by various authors, with different C-S-H seed types (CP C-S-H = Coprecipitated C-S-H; SG C-S-H = Sol-Gel C-S-H). Obviously, the commercially available C-S-H composite material X-Seed led to the strongest strength gain with very small amounts of additive (in proportion to the active C-S-H in X-Seed suspension) [72,82,85,95,108,111,115].

More controversial results have been found regarding long term compressive strength. While Ling-Fei et al. have found nearly no differences to an unseeded cement after 28 days Ludwig et al. recorded a 6% enhanced compressive strength in OPC whilst Owens et al. have found a 12% decrease in strength [82,108,114]. Nevertheless, all of these authors agree that the compressive strength gain of seeded cement is relativized with time [111].

A possible explanation for the strength development is the change of the microstructure of the resulting cement stone. Various authors have reported a more homogenous, denser cement microstructure when seeds are incorporated. This is attributed to the filler effect, enhanced product growth in the pore space, faster filling of the voids between clinker particles and reduction of porosity [95].

The roentgenographic structure of the seeded cement has not been observed to have changed [95,114].

2.3 Nucleation seeding in pure C_3S

Tricalcium silicate is the major mineral phase of cement and it is attributed to setting and early strength development, since it forms the majority of C-S-H phases during cement hydration [15]. The use of pure alite offers the possibility to investigate a less complex cement hydration subsystem. Pure triclinic C_3S has been investigated in the literature.

2.3.1 Hydration

Some effects of calcium silicate hydrate seeds in cement, such as a higher hydration rate with an earlier maximum and an enhancement of the acceleration proportional with the amount of seed, have also been observed for C_3S [58,69,72]. The effect of seeding on the induction period is more pronounced in C_3S than in OPC. Thomas et al. have observed an elimination of the induction period with C-S-H seeding. Additionally, the formation of a shoulder in the hydration curve with C-S-H seed added, has been observed (see figure 14). Simulation experiments (see chapter 2.5) support the authors' theory that two nucleation and growth processes occur in parallel; the growth on the clinker particles and the growth on seeds, which is in accordance with Nicoleau et al.'s results, as well as Alizadeh et al.'s findings regarding the formation of two different C-S-H phases [58,60,86].

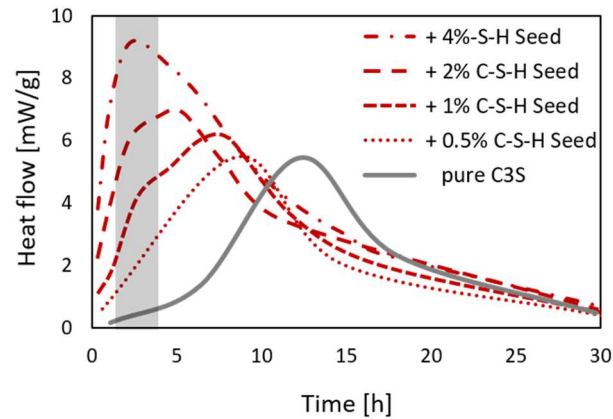


Figure 14: The rise of a shoulder (grey block) with the amount of C-S-H in C_3S indicating two parallelly occurring processes in seeded pastes. Adapted from Thomas et al. [86].

The impact of the calcium to silicon ratio of the seeds on the hydration rate is also controversial in regard to C_3S . Thomas et al. were not able to find any influence, while Alizadeh et al. have found that seeds prepared with a low Ca/Si ratio can be advantageous, which conflicts with the results of Land et al. in regard to Portland cement [58,72,86]. However, Alizadeh et al. used amounts of 20 wt.-% C-S-H in C_3S which is more than four times the amount needed for significant acceleration reported elsewhere. Horgnies et al. have found seeding with afwillite, a crystalline C-S-H phase with a calcium to silicon ratio of 1.5, to be more effective than seeding with C-S-H gel of a lower Ca/Si ratio. However, this effect is most likely attributable to a reduced blocking effect for later-age hydrates, due to reduced nano-porosity resulting from the growth of afwillite, rather than to the impact of the Ca/Si ratio [69]. The calcium to silicon ratio of C-S-H cannot be readily varied without altering many other properties of the particles, such as the silicate chain length, crystallinity and water content [33,116–120]. Further research is needed in regard to the separation of these effects.

Additional experiments with sucrose have confirmed that the nucleation location changes, and that two different nucleation processes take place when C-S-H seeds are added to C_3S . Pastes were inhibited by sucrose but reactivated with C-S-H seeds, which supports the theory that sucrose retards hydration by inhibiting nucleation on clinker particles, by blocking the surface, with C-S-H seeds providing an alternative nucleation location [86].

2.3.2 Influence of C-S-H seeds on the hydration product

The main difference of nucleation seeding in C_3S instead of in cement is that the hydration product is influenced by the seed, as has been proven [119,120].

The chemistry of calcium silicate hydrates is mostly determined by their calcium to silicon ratio and their crystal structure (see figure 5). Alizadeh et al. have investigated the impact of C-S-H gels of varying Ca/Si ratios on C_3S pastes, in regard to the hydration product. The authors used exothermal dehydration of C-S-H to β -wollastonite ($CaSiO_3$) at over 800 °C, as an indicator for the Ca/Si ratio of the C-S-H product formed [121]. This is because the β -wollastonite transition occurs at higher temperatures for higher calcium to silicon ratios [124]. In the DSC curve of the pastes they seeded (Ca/Si = 0.8 and 1.2), a second exothermic peak at higher temperatures developed after 3 hours. This thermal event was assigned to the C-S-H formed around the seeds, since in pure hydrated C_3S pastes no such exothermic event has been observed. The authors thus concluded that around every seed a calcium silicate hydrate gel is formed, with a higher Ca/Si ratio than the seeds [60].

The accelerating effect of crystalline C-S-H seeds in C_3S was first described by Seligmann et al. in 1969 [120]. They observed that relatively small quantities of afwillite induced the formation of crystalline afwillite, rather than C-S-H gel in C_3S . These results were confirmed by Davis et al. in 1975 and recently by Horgnies et al. [69,119]. All of these authors agree that the system is not adaptable to cement, since the formation of afwillite is easily disturbed by impurities.

The possibility of changing the crystalline phase of the hydration product with the seed, depends on the difference between the free energy of the pure C-S-H gel compared to free energy of the seed [120]. Afwillite might have a relatively small difference that is susceptible to being disturbed by impurities. The impact of other crystalline calcium silicate hydrates remains uninvestigated, except for the unpublished results of J. F. Young, which have been mentioned elsewhere [119].

Megaw et al. have pointed out the structural similarities of afwillite ($Ca_3 [SiO_3(OH)]_2 \cdot 2 H_2O$) and bultfonteinite ($Ca_3 [SiO_3(OH)]_2 \cdot 2 H_2O \cdot CaF_2$), with the fluoride ions in the described natural

bultfonteinite perhaps representing substituted hydroxide positions [123] (Figure 15). α -dicalcium silicate hydrate (α -C₂SH) is a metastable nesosilicate with structural similarities to afwillite and bultfonteinite. The silicate atoms are coordinated in a tetrahedral formation, like in afwillite and bultfonteinite, with three O²⁻ groups and one OH⁻ group and calcium polyhedrons forming layers through the structure.

The structural resemblance of these nesosilicates suggests that bultfonteinite and α -C₂SH might be able to tune product formation through seeding, like afwillite does. Bultfonteinite has not been synthesized so far, but α -C₂SH has been prepared from various starting materials [65,126].

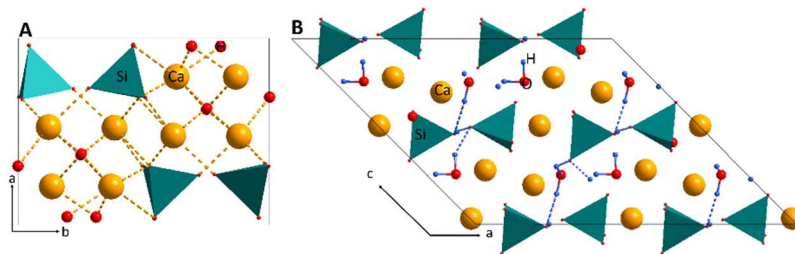


Figure 15: The crystallographic structures of bultfonteinite [124] (A) and afwillite [125] (B). In both structures, the silicon atoms are coordinated tetrahedrally by three O²⁻ groups and one OH⁻ group. Both structures are nesosilicates.

2.3.3 Mechanical properties and microstructure

It has been found that, while C-S-H (gel) seeding in cement reduces porosity, afwillite seeding significantly enhances the porosity of C₃S samples. Consequently, tensile and compressive strengths suffer a reduction. This effect is attributable to induced afwillite formation in the paste, through the seed [69,119].

2.4 Supplementary cementitious materials (SCMs)

While many studies have focused particularly on explaining the seeding effect, some publications have looked at the practical aspects. Ling-Fei et al. and Land et al. have investigated the influence of C-S-H seeding on the hydration of cement pastes containing supplementary cementitious materials (SCMs),

like fly ash (FA) and ground granulated blast-furnace slag (GGBS) [72,82,108]. The accelerating effect of calcium silicate hydrates in cements blended with SCMs partially compensates for the slowed down reaction rate and opens new fields of application for low CO₂ cements.

2.4.1 Ground granulated blast furnace slag

The effects found in cements blended with slag are comparable to cement and C₃S systems, with an accelerated hydration rate and enhanced early strength, with the long-term compressive strength being lower in seeded pastes, as compared to unseeded samples [72,110].

The only deviating behavior can be observed in regard to sulfate depletion. The sharp sulfate depletion peak in cements blended with slag, shifts to later in time when C-S-H seeds are present, whilst in cement with no slag the peak occurs earlier [72].

The influence of C-S-H seeds on the hydration of pure alkali activated slag pastes was investigated by Hubler et al. in 2011 with comparable results. The authors concluded that AAS hydration follows a nucleation and growth mechanism like that of cement [85].

2.4.2 Fly ash

The effects in cement – fly ash blends are basically the same as those described for pure cement, except that the effect of seeds on the early strength of fly ash blends is greater than in pure cement, with the effect on the hydration rate being reduced [72,82].

2.5 Numerical simulations of nucleation seeding

The combination of computational and experimental methods is a versatile tool for extending and giving support to prevailing theories. Hence the hydration of tricalcium silicate has been addressed in various numerical simulations [30,127–129]. Recently these models have been expanded to include nucleation seeding.

Thomas et al. have used a three-dimensional grain boundary growth model, developed by Cahn et al. in 1956, as a base for modification and expansion [129]. Their model describes the growth of C-S-H at the internal planes of rectangular prisms defined by 3 perpendicular planes in a 3D cubic volume. The planes represent the C_3S surface while the prisms display the water-filled pore volume. Nucleation seeds are added by defining random nucleation sites through prismatic volumes (Figure 16A). Product growth is solely allowed on the internal planes and the nucleation sites. The growth rate for C-S-H formed at the planes and C-S-H formed at the seeds is kept constant. To simulate the effect of seeding, the number of random nucleation sites and the minimum distance (D) of these to the internal planes, is varied.

The boundary growth model is successfully able to reproduce the calorimetry data of C_3S in the presence and absence of calcium silicate hydrate seeds. For the formation of shoulders observed in the experiments (see figure 14), the distance parameter D has to be nonzero, which supports the theory of two parallel occurring growth processes [86,130].

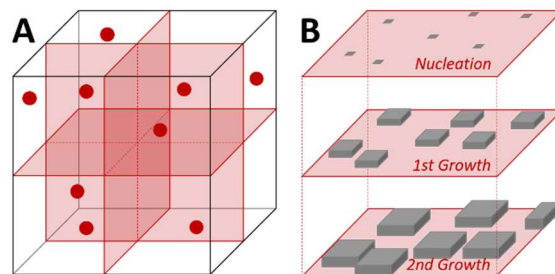


Figure 16: **A** – Schematic representation of the 3D boundary growth model, applied by Thomas et al., with perpendicular planes representing the C_3S surface and nucleation sites in the volume [86]. **B** – Growth model, applied by Nicoleau based on the Garrault model, with 3 iteration steps displayed. Seeding is simulated by the addition of an additional matrix [60].

Nicoleau has modified a particle agglomeration model based on Garrault et al.s, which defines the tricalcium silicate surface as a square, with nuclei randomly distributed over the matrix area. Nucleation seeding is implemented by a second matrix, with a size representing the seed concentration and a defined number of nucleation sites that display the ability of C-S-H to grow on the seed surface.

Growth is simulated after an induction period originating from the nucleation sites, with a parallel and perpendicular growth rate, until the defined matrix is covered, after which growth is solely perpendicular (Figure 16B).

By varying the parameters described, the authors were able to fit the model to different seeding agents. The model was tested with various additives, the C-S-H layer thickness on C_3S and the seeds were correlated with fitted calorimetry curves. It was found that for the simulation of portlandite additions, no additional matrix was needed while the addition of C-S-H seeds or calcium salts needed an additional matrix for simulation. Hence, it was concluded that the surface needing to simulate C-S-H and $CaCl_2$ seeding is a dummy surface that displays direct growth [60]. However, the boundary conditions of the model and the interpretation of the results are quite contested [131,132]. The main points of disagreement are the simplicity of a model which uses a 2D plane for simulation and cuboidal growth which requires an additional permeability parameter to simulate the reducing rate of reaction, after a uniform layer of nuclei is formed. Furthermore, the validation of the layer thickness through SEM images is questionable because of the irregularity of the C-S-H layer around the clinker grains and possible sectioning of the grains [131]. In reply to these issues, Nicoleau et al. have argued that a good standard deviation can be reached through repeated determination of layer thickness [132].

2.6 Health risks of nano C-S-H

The effect of nanoparticles on human health depends on numerous factors like genetics, exposure, particle chemistry, as well as shape, size and agglomeration state. Studies have shown that the macrophage clearance mechanism of the lungs works less effectively on inhaled nanoparticles than on bigger particles. This might cause serious lung damage and the nanoparticles might even translocate to many tissues and organs [133]. Using detailed in vivo testing, Brau et al. have established a benefit risk analysis of calcium silicate hydrate seeds. Five-day inhalation periods in rats were followed by 21-day recovery periods, after which the organ-specific toxicity, 71 endpoints of bronchoalveolar lavage (BAL) and blood, were carried out.

The results indicate a generally low toxicity, with no test related changes in the BAL analysis being recorded. A minimal increase in alveolar macrophages was observed in the lungs of all test animals, but this returned to control levels after 21 days.

In summary, the authors confirmed a favorable benefit-risk ratio for the C-S-H seed investigated, especially because it was used in an aqueous suspension instead of in powder [134]. The use of nano C-S-H powders needs to be examined separately, because of the higher inhalation risk.

3 Summary and outlook

Various publications have demonstrated that nucleation seeding with calcium silicate hydrates is a convincing method for accelerating the hydration rate of tricalcium silicate. The setting, hardening and development of the microstructure of seeded C_3S , OPC, mortar or concrete is accelerated, while a generally denser microstructure develops. The effect of supplementary cementitious materials, like fly ash and slag, can be compensated up to a certain ratio, but the direct effect of C-S-H seeds on SCMs has to be investigated in further detail. The most crucial factor of the seeds has been shown to be correlated to the total number of seeds added, varied according to either the number of particles or their size.

Seeds with varying properties, like Ca/Si and crystallinity, have been found to express a strong influence on product formation in C_3S , culminating in induced product formation, with the crystalline C-S-H phase afwillite as the seed. The impact of other crystalline C-S-H phases remains uninvestigated. Observation of the β -wollastonite transition, has revealed that the hydrate formed around seeds is different from the hydrate formed on C_3S particles. The reason for the relatively higher Ca/Si ratio of the hydrate around the seed needs further investigation and might offer the possibility of customizing the final hydrated cement. The impact of the Ca/Si ratio of the seeds on cement and C_3S is still controversial and needs to be evaluated free from any size effects.

Various mechanistic effects of C-S-H seeding have also been investigated and it has been shown, by both simulation and experiment, that the addition of extra growth sides offers an alternative pathway

for nucleation and growth occurring in parallel to nucleation on the clinker particles. The inhibition of further acceleration with rising seed content in calcium sulfate containing systems, has proven that C_3S hydration is dependent on combination of C-S-H nucleation and C_3S dissolution.

Compared to conventional acceleration additives C-S-H seeds can be prepared from cheap starting materials like amorphous silica and calcium oxide, which makes them very useful in industrial applications, with shape directing methods, like ultra-sonic irradiation, offering further possibilities for product control in seeded pastes. The health risks represented by nano-particles can be avoided by using seeds as aqueous suspensions.

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Conflicts of interest: none

Keywords: A - Acceleration, B - Calcium Silicate Hydrates (C-S-H), D - Cement, D - Ca_3SiO_5 , Seeding

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