Nucleation seeding with calcium silicate hydrate – A review

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ABSTRACT

The development of green cements, with the aim of reducing CO_2 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 hydrate 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-term compressive strength and porosity.

1. Introduction

Portland cement based concrete is the most widely used synthetic material on the planet [1,2]. The cement industry is currently responsible of approx. 8% of the global anthropogenic CO_2 emissions. Today's global cement production of > 4 billion tons is expected to increase further as a consequence of an increased demand for housing and infrastructural projects (Fig. 1) [3–5]. Concerning Portland clinker the calcination of limestone, the main raw material in cement, contributes approximately 60% of the CO_2 emissions, and the related thermal and electrical energy needed for burning and grinding makes ~40% [6,7]. Strong efforts have been made to reduce CO_2 emissions, through the use of alternative fuels (e.g. biomass), more effective kilns, as well as by improving clinker mineralogy which allows a reduction of the clinker content of the final cement [3].

While the reduction of CO_2 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 CO_2 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 cements, mortars and concretes. The C_3S hydration process is commonly divided into 4 or 5 phases, which are differentiated by their hydration activity (Fig. 2) [18]. Stage I, the induction period, shows rapid hydration activity that lasts only for a few minutes and ends with 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].

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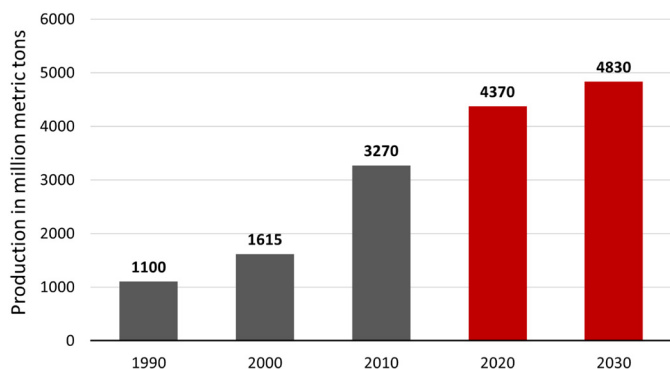
Fig. 1. Global cement production in million metric tons from 1990 to 2010 and projections for 2020 and 2030 [5].
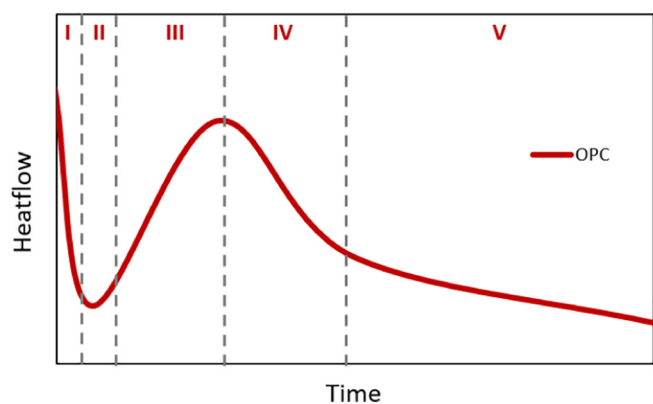

Fig. 2. Schematic representation of the rate of heat evolution of pure C_3S. The hydration process steps: I – Induction period, II – Dormant period, III – Acceleration period, IV – Deceleration period, V – continuous slow hydration. Adapted from [18].

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 the 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 a 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 the 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 represent 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 [41,42].

1.2. Nanoparticle additions 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 all mainly accelerate hydration physically. Small particles might provide heterogeneous nucleation sites and/or relatively more space in to which hydration products can grow (Fig. 3) [21,50]. 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].

The second group describes reactive additives that express 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 $Ca(OH)_2$ concentration of the pore solution. The addition of ultra-fine calcium hydroxide accelerates cement hydration significantly. Besides providing nucleation sites, it works through rapid saturation of the pore solution with respect to calcium and hydroxide ions [55]. 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, $CaCO_3$ forms carboaluminates and stabilizes ettringite which may be beneficial for concrete performance [53,54].

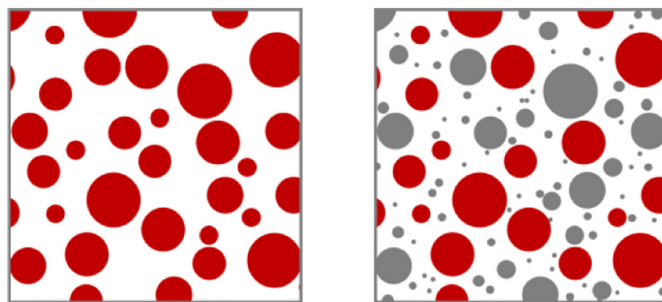Both additive groups might additionally adsorb ions from the pore

Fig. 3. 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].