

Influence of Carboxylic Acids on the Nucleation of Cementitious Phases Studied by Titrimetric Methods

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Abstract

It is important to accurately control the setting of concrete and mortars. Functional admixtures such as hydroxy carboxylic acids can modify the hydration mechanism by influencing the dissolution of clinker phases and the crystallization of hydrate phases. While the crystallization of phases like CaCO_3 under the influence of various additives has been studied intensively, there is substantially less understanding with regard to the main products of cement hydration, i.e., C-S-H, portlandite, ettringite, etc. In this work a potentiometry based setup was used to study the influence of succinic, tartaric, and citric acid on the nucleation and growth of portlandite and C-S-H. We found that the investigated molecules not only lead to a significant delay in nucleation by stabilization of prenucleation clusters, but also show a strong influence on the process of crystal growth. Further the effect of these molecules on the hydration reaction of tricalcium silicate was examined using ex-situ calorimetry. We found a decent retarding effect on this reaction, even when there was almost no observable effect on the nucleation process in the previous experiments.

Keywords

Nucleation, Crystallization, Hydration, Retarding Additives, Portlandite, Calcium-Silicate-Hydrate, Tricalcium Silicate, Potentiometry, Calorimetry

1 Introduction

Today, the evolution of concrete is taking place under the influence of new challenges. Sustainability issues, environmental compatibility, and new processing techniques like 3D printing drive significant changes for the mix-design of concrete. To meet increased demands in terms of rheology, setting time and ecological footprint, a broad variety of chemical admixtures, like superplasticizers, viscosity-modifying admixtures or set-retarders are at the disposal of the engineer. It is desirable to increase the understanding of the structure-activity relationships of admixtures in cementitious materials [1–4].

The setting time, i.e., the time span between mixing cement with water and the onset of hardening, is one of the fundamentally important parameters of any concrete. According to the German standard (DIN EN 196-3), the onset of the hardening is defined by the vicat needle penetration depth. The setting time can be controlled using hydration control agents. Set retarders modify the kinetic pathway of dissolution and crystallization of the hydration processes and enable a predictable elongation of the setting time. Known retarders are sodium ligninsulfonates, inorganic and organic phosphonate derivatives, sugars (e.g., sucrose or glucose) or hydroxy carboxylic acids, like citric or tartaric acid [5–8]. Different interaction mechanisms have been described in the literature [8,9]. Possible mechanisms for the retardation are the dissolution inhibition of

clinker phases due to surface adsorption and the inhibition of nucleation of hydrate phases [6,10–12]. Generally, it is well known that functional polymers and molecules can strongly influence the crystallization and dissolution of mineral phases. This has been intensively studied for systems like calcium carbonate or calcium phosphate, but there is a lack of knowledge for cementitious systems like C-S-H, portlandite (CH) or ettringite [13–16]. The group of Cölfen pioneered the use of a titration setup to study crystallization. The non-classical crystallization mechanism of CaCO_3 was established using a titration system [17,18]. Such setups are well suited to study the influence of functional molecules onto nucleation of crystalline phases [19].

The cement hydration reaction follows a complex mechanism of simultaneous dissolution, nucleation, and crystal growth of mineral phases, like C-S-H, portlandite and ettringite. The slowest step of the sequence dissolution, nucleation and growth determines the overall rate of the hydration reaction. As of yet, it remains unclear which of these steps is most strongly influenced by the additives [4,13,15]. To reduce this knowledge gap, we used an adapted potentiometric titration setup to examine the influence of functional molecules on the nucleation and crystal growth of portlandite and C-S-H. In addition to the crystallization studies of individual hydrate phases, we used isothermal heat flow calorimetry of tricalcium silicate

(C₃S) to study the impact of the additives in a model system in which all the above-mentioned reactions are running parallel. As a start, we chose to study three compounds of close structural similarity, i.e., citric, tartaric, and succinic acid in the nucleation and hydration experiments outlined above.

2 Experimental Procedure

2.1 Materials

Tricalcium silicate was made from analytical grade CaCO₃ and fused silica (Amosil 510, HPF Minerals) following the procedure in [20]. The overall molar ratio of Ca/Si was set to 3 and the dry components were homogenized with water ($w/s = 2$) in a ball mill (90 min, 70 rpm, 12.5 mm ZrO₂ balls). The obtained paste was filled into four circular moulds. Before sintering, the hardened green bodies were unmoulded, transferred to platinum crucibles, and dried to constant weight at 120 °C. The cylinders were sintered at 1550 °C for 10 h using a high temperature furnace. The solid-state reaction was quenched at 1550 °C using pressurized air. The cold discs were crushed in a jaw crusher and finely ground using a ball mill (90 min, 70 rpm, 12.5 mm ZrO₂ balls). The obtained product contains mainly C₃S with small quantities of C₂S and free lime (s. Table 1).

Table 1 Phase Composition of C₃S based on Rietveld analysis.

Phase	Content (wt.%)
C ₃ S	97.2
C ₂ S beta	2.4
Free Lime/CaO	< 0.5

All chemicals were purchased from different suppliers in analytical quality and used as received. To avoid excessive carbonate contamination, all solutions were prepared daily using degassed water. The degassing was done by heating ultrapure water (NANOpure Diamond, Barnstead) to the boil for 20 min followed by sparging with nitrogen for another 20 min.

To study the nucleation and crystal growth processes a titration setup (OMNIS, Metrohm) equipped with two automatic burettes (20 mL), pH (Unitrode, 6.0259.100) and Ca ion selective electrodes (Combined polymer membrane electrode, 6.0510.100) was used (Figure 1). To enable a constant solution temperature of 25 ± 0.1 °C an in-house built double jacketed reaction vessel coupled to a thermostat (JULABO 200F) was used. To avoid carbonation during the experiment, the reaction vessel was closed with a lid (Titration vessel lid with 5 openings, 6.1414.010) and a gentle flow of dry nitrogen was applied.

2.2 Methods

2.2.1 Nucleation Experiments

For Ca(OH)₂ nucleation experiments, the reaction vessel contained 150 mL degassed water or carboxylic acid solution. CaCl₂ (0.5 M) and NaOH (1 M) were added in a parallel titration at a constant speed of 0.4 mL min⁻¹.

For C-S-H nucleation experiments 100 mL of sodium metasilicate (3.7 mM) solution was added to the titration vessel and 20 mL NaOH (1 M) was dosed to achieve an initial pH of 13.0. To investigate the influence of the carboxylic acids, the corresponding amount of acid was added to the metasilicate solution prior to the experiment. CaCl₂ (30 mM) was added at a constant speed of 0.08 mL min⁻¹.

Prior to each measurement, the Ca-ISE was calibrated three times by dosing CaCl₂ (0.5 M / 30 mM) in 150 mL water (portlandite) or 120 mL water/NaOH (pH 13) (C-S-H) under the same conditions as for the respective experiment. The pH electrode was calibrated daily using three standard buffers of pH 4.0, 7.0 and 10.0.

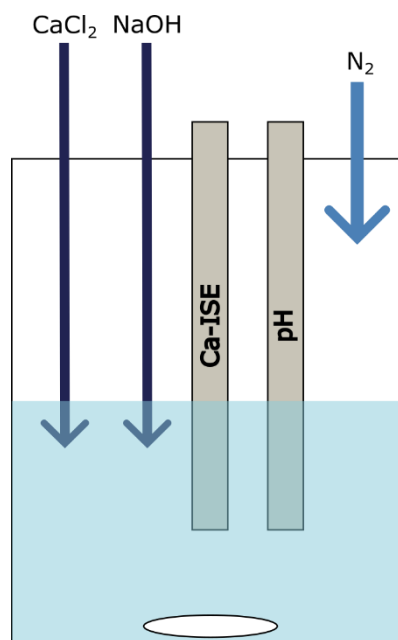


Figure 1 Titration setup equipped with two automatic burettes, Calcium ISE and pH Electrode for the online monitoring of nucleation processes.

2.2.2 Hydration Reaction

The hydration reaction of C₃S was investigated by isothermal heat-flow calorimetry measurements following the procedure described by Nicoleau et al. [21]. 1.5 g of ultrapure water was added to 3.0 g of C₃S (water to binder ratio, $w/b = 0.5$) and manually mixed with a spatula for 30 seconds. About 1.5 g of the paste was weighed into a plastic vial, sealed with a cap, and inserted into the calorimeter (8-channel isothermal heat-flow calorimeter, TAM Air, TA Instruments). The temperature was controlled at 20 °C. The crystalline additives were dissolved in water and the dosages are indicated in mmol per liter of total water.

3 Results and Discussion

In this work, we investigated the impact of hydroxy carboxylic acids on the nucleation of portlandite and calcium silicate hydrate from homogeneous solutions. To study the effects of the additives, the crystallization of pure portlandite was investigated first. The result of this experiment is shown as black curves in Figures 2A to C and marked as reference experiment. The blue dashed line in the graphs marks the theoretical Ca curve, according to the added amount of calcium. The curve of the measured Ca follows the theoretical curve at the beginning of the experiment but starts to deviate as more calcium and hydroxide is added (Figure 2A, Phase I). This discrepancy between the theoretical and measured Ca concentration was first reported and explained by Cölfen et al. for the non-classical crystallization of CaCO_3 [14,17,18]. In contrast to the classical crystallization theory, i.e., formation and growth of nuclei in supersaturated solution, liquid droplets of higher ion-concentration (prenucleation clusters, PNC) and mesocrystals are formed, even at undersaturated conditions for the non-classical crystallization pathway [17].

Therefore, the slope of the Ca curve depends to the equilibrium of free calcium ions in solution and the formation of PNCs. Hence the first part of the curves provides information about the effect of the additives on this equilibrium prior to the nucleation. A flatter slope of the Ca curve indicates a stabilizing effect, similar to colloidal stabilization which hinders the nucleation by preventing the clustering of the PNCs [19,22]. While citric (Figure 2A) and tartaric acid (Figure 2B) hardly changes the slope of the calcium curve, the slope of the curve for succinic acid (Figure 2C) is steeper than the reference curve, which intends, that the additive destabilizes the PNCs in the solution [23].

The maximum in Ca concentration marks the onset of the nucleation at a certain level of supersaturation (Figure 2A, *). The equilibrium concentration of Ca in the saturated solution at the given parameters, i.e., pH of 12.5, temperature of 25 °C and a precipitate of $\text{Ca}(\text{OH})_2$, was calculated to 19.40 mmol L^{-1} using PHREEQC and the cemdata18 database [24]. The major effect of the additives can be seen by an increase in the maximum of the measured Ca concentration in solution, i.e., shift to a higher level of supersaturation. This shift is quantified in

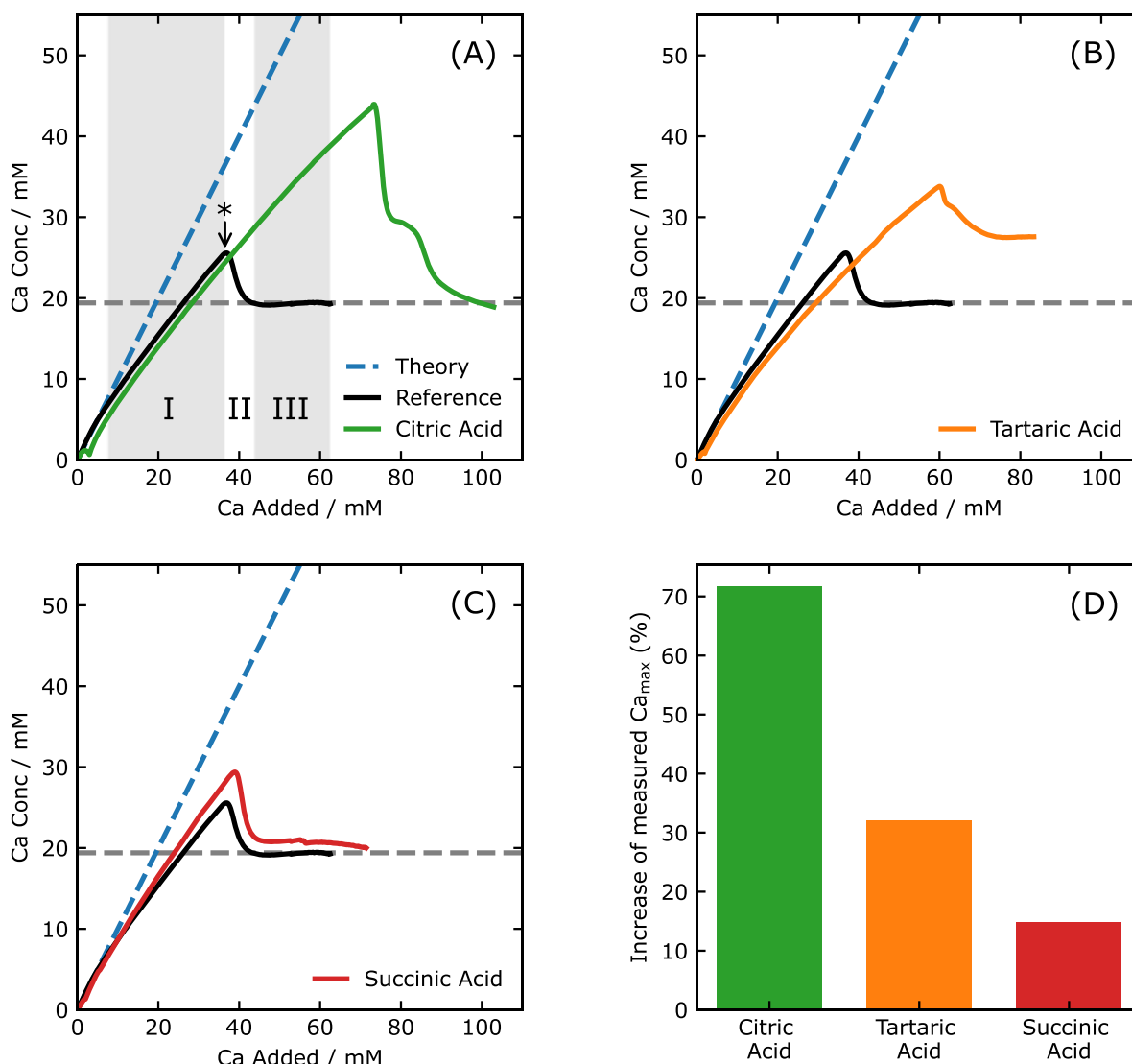


Figure 2 Crystallization of Portlandite under the influence of 2 mM hydroxy carboxylic acid. (A) Citric, (B) Tartaric, (C) Succinic Acid. (D) Shows the increase of the measured maximum Ca concentration induced by the different additives. The horizontal grey-dashed line shows the equilibrium concentration of Ca at the given conditions. The different phases of the crystallization are marked in plot (A) as I -Prenucleation, II - Crystal growth, III - Equilibrium. The asterisk marks the onset of nucleation.

Figure 2D. Citric acid leads to an increase of the maximum Ca concentration of 72%, while tartaric acid, at 32%, does not quite reach half of the value. Succinic acid shows only a small shift of about 15%. The thermodynamic supersaturation of the maximum calcium concentration with regard to portlandite was calculated using PHREEQC and is found in Table 2.

Table 2 Supersaturation at the maximum calcium concentration for the portlandite crystallization experiments.

Additive	Supersaturation
Reference	0.32
Citric Acid	1.26
Tartaric Acid	0.74
Succinic Acid	0.51

These observations coincide with the stability constants of the corresponding Ca-ligand complexes with decreasing

stability in the order of Ca-citrate > Ca-tartrate > Ca-succinate, reported in the literature [13,25].

The last part of the curve is attributed to a combination of crystal growth and secondary nucleation (Figure 2A, Phase II). All three acids lead to a similar curve after the nucleation event. The step in the decreasing calcium concentration is attributed to blocking of the just formed crystal surfaces by the additive, resulting in a second rise in Ca concentration, until the energy barrier to further nucleation is surpassed again and nucleation and crystal growth continues until the equilibrium concentration (Figure 2A, Phase III) is reached [26]. In contrast to the other two molecules, succinic acid shows only minor effects onto the crystallization processes. The flat end of the curves indicates that a state of equilibrium has been reached at the end of the experiment. While citric- and succinic acid do not show any effect on the equilibrium of the saturated lime solution, it is so far unclear, when the equilibrium state (i.e., the equilibrium concentration) would be reached for tartaric acid. As the experiment was aborted due to the limited volume of the beaker, the plateau at the end of the curve might be attributed to the step like pattern, similar to the observations made for citric acid.

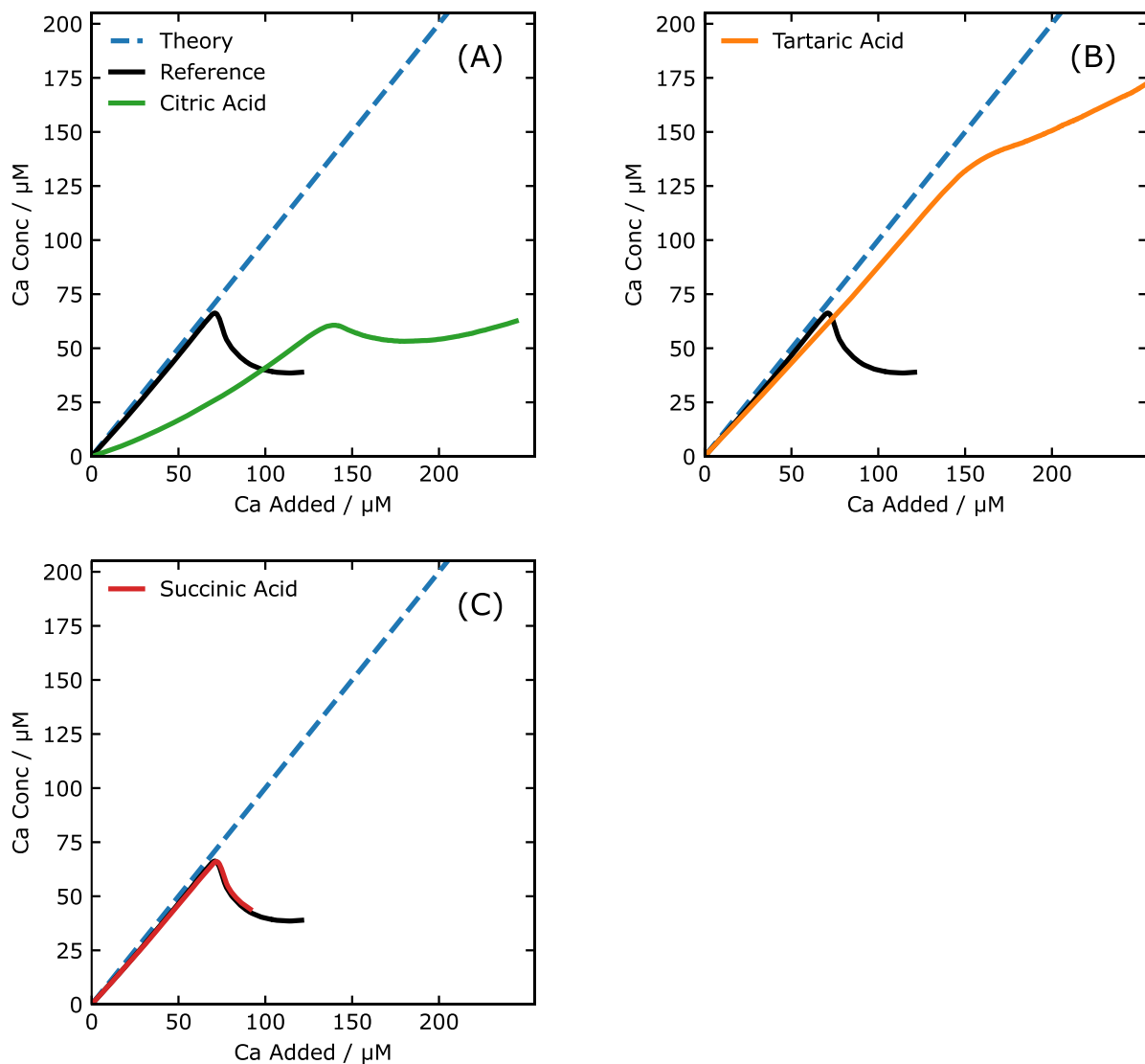


Figure 3 Crystallization of C-S-H phases under the influence of 2 mM hydroxy carboxylic acid. The individual subplots show the impact of (A) Citric, (B) Tartaric, and (C) Succinic Acid.

Contrary to the portlandite experiments, the reference experiment of the C-S-H crystallization shows no formation of PNCs (Figure 3). This observation was explained by Picker et al., as silicate monomers in solution of pH 13.0 are stabilized against oligomerization and therefore the formation of PNCs is inhibited [27]. The impact of the three acids onto the crystallization of C-S-H exhibits differences in comparison to the portlandite experiments. The slope of the Ca curve prior to the nucleation of C-S-H is hardly changed by the presence of tartaric acid (Figure 3B), but citric acid (Figure 3A) decreases the initial slope significantly. Both acids lead to a similar retardation of the nucleation, i.e., the local maximum of the curve, in terms of the added amount of Calcium by a factor of three, compared to the reference experiment. Nevertheless, their effect on the supersaturation before nucleation, i.e., the first maximum of the measured Ca concentration in solution, is significantly different. While citric acid shows hardly any effect, tartaric acid increases the maximum measured calcium concentration by a factor of two. In summary, citric acid mainly influences the calcium equilibrium in the PNC stage while tartaric acid massively inhibits the nucleation of C-S-H and enables a very large supersaturation with regard to C-S-H. In contrast to the other two substances, succinic acid does not show any impact on the nucleation of C-S-H, as the curve follows the same path as the reference curve.

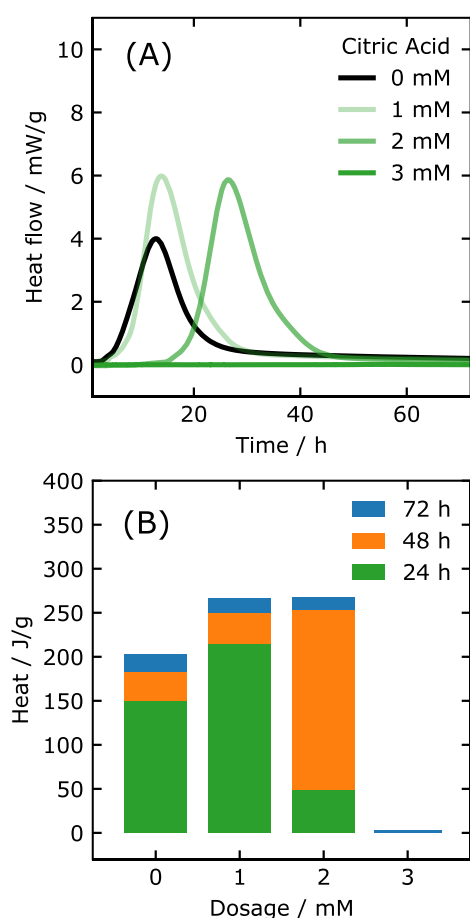


Figure 4 Heat flow curve of the hydration reaction of C_3S with various amounts of citric acid at $w/s = 0.5$ (A). Cumulative heat after 24 and 48 hours correlated with the dosed amount of citric acid (B).

As the previous section was focused on the isolated reactions of hydrating C_3S , i.e., the formation of portlandite and C-S-H, the following part combines all parallel occurring processes by using C_3S paste. The results of the heat flow calorimetry experiments are shown in the (A) plots of Figure 4 to Figure . The hydration reaction C_3S shows a characteristic time of low reactivity, i.e., the so-called induction- or dormant period, followed by a steep increase in the reactivity (acceleration period). The obtained data show a clear retarding effect, i.e., elongation of the induction period, of all applied additives to the silicate reaction of C_3S . While citric acid (Figure 4) at a small dosage of 1 mM leads to almost no observable retardation, tartaric acid (Figure) at the same concentration induces a shift of about 2 hours. Doubling the additive amount leads to an increased shift of the silicate reaction for both acids. Concentrations of 3 mM or higher lead to a complete inhibition of the reaction within the time-span of the experiment of 72 h for both molecules. Succinic acid shows a significantly smaller retarding effect to the hydration reaction of C_3S (Figure). While citric and tartaric acid show such strong retarding effects that the maximum applied concentration was 3 mM, the concentration for succinic acid had to be increased by a factor of 10, to achieve significant retarding effects. The (B) plots of Figure 4 to Figure show the effect of the different additives and dosages to the cumulative heat of the reactions after 24, 48 and 72 h. The plots at 48 and 72 h of citric acid show an increase in the total

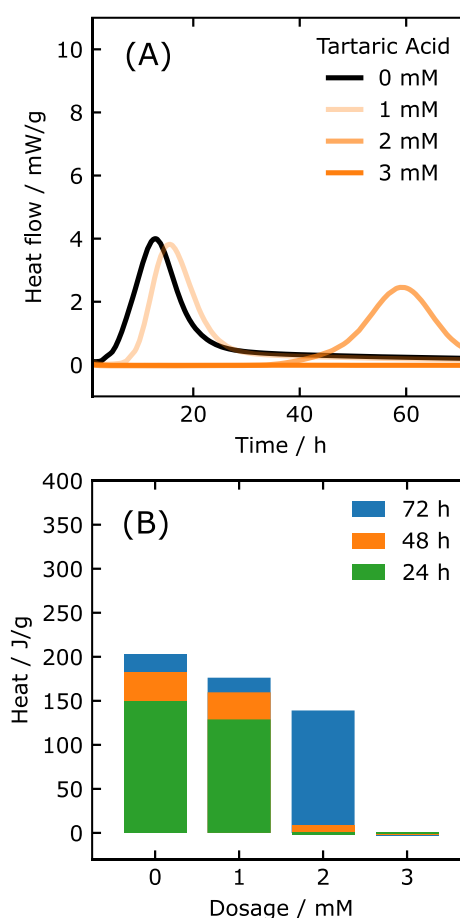


Figure 5 Heat flow curve of the hydration reaction of C_3S with various amounts of tartaric acid at $w/s = 0.5$ (A). Cumulative heat after 24 and 48 hours correlated with the dosed amount of tartaric acid (B).

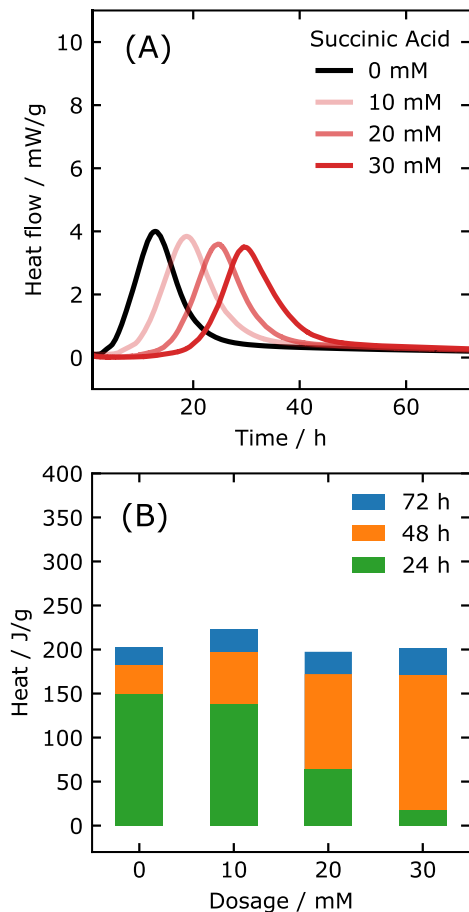


Figure 6 Heat flow curve of the hydration reaction of C_3S with various amounts of succinic acid at $w/s = 0.5$ (A). Cumulative heat after 24 and 48 hours correlated with the dosed amount of succinic acid (B).

heat, while tartaric and succinic acid lower the amount of heat. Furthermore, one can see, that the individual dosages of 1 and 2 mM citric acid lead to a significant shift of the silicate peak, but the total heat after 48 or 72 h is similar. The higher amount of released heat in combination with the steeper slope of the heat flow curves indicate, that the molecules at low dosages act similar to sucrose as “delayed accelerant” as reported in the literature [28]. This effect might be attributed to an enhanced solubilization of the silicate species inducing an increase in the produced amount of early hydration products with structural changes to the formed C-S-H phases [7,29]. As there was no measurable reaction in the observation period of 72 h, the cumulative heat for the experiments using 3 mM citric or tartaric acid shows values near to zero. Contrary to citric acid, higher concentrations of tartaric or succinic acid result in a decrease of the released heat, which indicates a suppressing effect to the hydration reaction.

4 Discussion

At the end of the induction period the hydration reaction of tricalcium silicate to form C-S-H and portlandite accelerates. It has been shown in the past, that the end of the induction period goes along with a massive formation of portlandite, but it is by now unclear if there is a direct causality between this crystallization and the ending of the dormant period [10,11]. The acceleration period is controlled by a combination of C-S-H and CH crystallization

[30,31]. It has been reported that superplasticizers or set-retarding additives, like polysaccharides, lignosulfonate or polyacrylate show a significant effect on the kinetics of portlandite via a non-classical crystallization pathway with the formation of liquid and/or amorphous PNCs [31]. Recent studies did also show strong effects of small molecules, like gluconate or hexitol on the nonclassical crystallization of C-S-H, via adsorption of the additives on the surface of the PNCs and therefore sterically hindering their aggregation and crystallization [32]. The second effect of these molecules was their enhancing effect on the solubility of C-S-H via the formation of aqueous calcium complexes and polynuclear silicate species [33]. Our results show a strong influence of citric and tartaric acid on the crystallization of both phases. These results agree with the strong retarding effect, observed in the calorimetry experiments of C_3S paste. As the C_3S reaction is a combination of C-S-H and CH formation, it is not unambiguously possible to interpret the additive controlled hydration kinetics of C_3S in terms of the exact contributions of the calcium hydroxide and C-S-H nucleation. In the case of citric and tartaric acid, both additives inhibit the nucleation of both CH and C-S-H. While there are specific differences, their exact contribution to the full hydration process cannot be quantified based on the currently available data. However, as citric acid shows a strong increase in the acceleration of the C-S-H formation (calorimetry data) and basically no increase in supersaturation for the nucleation of C-S-H (titration data), it is tempting to speculate that the influence of citric acid on the retardation of C_3S is mainly driven by the inhibition of the nucleation of CH while tartaric acid inhibits both the CH and the C-S-H nucleation. The retarding effect of succinic acid on the C_3S hydration reaction is much smaller than the effect of citric acid and tartaric acid. Succinic acid does not influence C-S-H nucleation at all (based on titration data) while it shows a small increase in the necessary supersaturation for the nucleation of portlandite. In this case, one could argue that the retardation of succinic acid, as observed in calorimetry, is mostly driven by the small inhibition of the nucleation of portlandite.

5 Conclusions

In this work, it has been shown that citric- and tartaric acid have great influence on the nucleation and crystal growth of the main reaction products of cement hydration, i.e., portlandite and C-S-H. This inhibition is manifest in the retardation of C_3S pastes as determined with isothermal calorimetry. Even though succinic acid shows a close structural similarity to the other two molecules, the retardation of the C_3S hydration was smaller which is tentatively ascribed to a small inhibition of the nucleation of portlandite. It was further shown that citric acid shows a “delayed acceleration” of the hydration reaction of C_3S . This work is still to be complemented with additional experiments regarding the characterisation of the formed crystals in terms of morphology, crystal structure and chemical composition. Furthermore, the influence of the additives on the dissolution of C_3S needs to be investigated to complete the experimental data of the individual reaction steps of the hydration reaction.

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