

Impact of sand and filler materials on the hydration behavior of calcium aluminate cement

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Abstract

In earlier work, we have observed discrepancies relating to the early hydration of calcium aluminate cement (CAC) when comparing data from heat flow calorimetry of CAC paste with results from mortar strength tests using the crushing method. Here, we investigated on this phenomenon and found that the sand which is used as a filler exerts a major influence on CAC hydration resulting in acceleration. Furthermore, in particular fine filler materials such as, for example, microsilica, fine limestone powder, and especially α - and γ - Al_2O_3 also produced a strong hydration accelerating effect which is dependent on their specific surface area. The mechanism underlying the acceleration is that under alkaline conditions their negative surface charge attracts calcium ions as was confirmed via inductively coupled plasma atomic emission measurements. Such a layer generates favourable conditions for the nucleation of CAC hydration products (C-A-H phases). The resulting crystalline hydrates which form on the surface of the filler particles submerged in CAC cement pore solution were visualized via SEM imaging. This way, specifically selected fillers can significantly accelerate CAC hydration and save precious lithium salts which are commonly used to boost the early strength of CAC.

KEYWORDS

acceleration, calcium aluminate cement, filler materials, hydration, mortar calorimetry

1 | INTRODUCTION

The set behavior of cements such as ordinary Portland cement (OPC) or calcium aluminate cement (CAC) in the presence of various admixtures like superplasticizers,¹⁻³ latex polymers,^{4,5} retarders,^{6,7} or accelerators including nano C-S-H^{8,9} or biopolymers, for example, alginate¹⁰⁻¹² has been investigated extensively. Most often, heat flow calorimetry in cement paste and mortar strength tests are applied to study the impact of admixtures on the hydration reaction of the binder.

It is generally known that heat flow calorimetry only presents insight into exothermic hydration reactions which are not necessarily linked to the strength development of the binder. One such example is the so-called “sulfate depletion peak.”^{13,14} This reaction which includes the conversion of ettringite to monosulfoaluminate does not much contribute to the specimen's strength which mostly originates from C-S-H formation. Another observation is that calorimetric results from cement pastes often do not match with data on actual strength development of mortar or concrete obtained from

Abbreviations: A, Al_2O_3 ; C, CaO; F, Fe_2O_3 ; H, H_2O ; M, MgO; S, SiO_2 ; T, TiO_2 .

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TABLE 1 Physical properties of different filler materials (particle size, Brunauer-Emmett-Teller-Analysis (BET) value, alkali content and *Blaine* value according to supplier's information)

Product name	APYRAL 200SM	ACTILOX 200SM	NABALOX NO 221-30	NABALOX NO 783	NABALOX NO 784	SILMIKRON 805/10-1	AEROXIDE P25	PRECARB 100	MILLISIL W 12	QUARZ- SAND F 36
Filler material	Al(OH) ₃	AlO(OH)	γ-Al ₂ O ₃	α-Al ₂ O ₃	α-Al ₂ O ₃	SiO ₂	TiO ₂	CaCO ₃	SiO ₂	SiO ₂
Purity (wt%)	99.3	98.5	>99	≥99.7	≥99.8	99	≥99.5	99	99	99.3
Alkali content (wt%)	≥0.04	—	—	≤0.3	≤0.1	0.4	—	—	0.3	—
<i>d</i> ₁₀ (μm)	0.3	0.2	—	0.4	0.4	0.2	0.2 ^a	—	—	—
<i>d</i> ₅₀ (μm)	0.4	0.3	30	0.8	0.8	0.5	2.7 ^a	1.0	16	160
<i>d</i> ₉₀ (μm)	0.8	0.6	50	2.0	2.0	1.0	9.2 ^a	—	—	—
BET (m ² /g)	15	17	75	12	7	20	50	9	0.9	—
<i>Blaine</i> (cm ² /g)	39 500 ^a	—	3700 ^a	23 500 ^a	—	—	—	—	3800	—

Values were determined by ourselves using a *Blaine* instrument or a laser granulometer model 1064 (CILAS Instruments).^a

crushing tests. This discrepancy has been addressed for example by *Cottin and George* when investigating the setting time of a CAC paste as compared to a CAC concrete.¹⁵ The authors report a difference for the initial setting time of up to 5 hours between both systems, depending on the reaction temperature.

In previous works, we have investigated the accelerating effect of alginate and similarly structured biopolymers on CAC.^{10,11} As working mechanism for these unusual accelerators, we proposed a heterogeneous surface crystallization process facilitated by alternating layers of Ca²⁺ and [Al(OH)₄]⁻ ions deposited along the molecular chain of the biopolymers.¹² Furthermore, in this study a discrepancy between heat flow calorimetry using paste and strength data collected from mortar was observed. For example, calorimetry suggested that in the presence of alginate the maximum heat release occurs 20%-50% earlier as in the neat cement paste. In the case of one cement sample (Ternal LC), this presented a reduction of the induction period of ≈ 4.5 hours (max. heat release of neat cement at 9.1 hours vs 4.7 hours in the presence of alginate).¹⁰ However, mortar strength testing using this cement revealed that after 6 hours of curing the neat mortar already had developed ≈ 10 N/mm² of compressive strength.¹⁰ Whereas, according to the calorimetry performed in paste, the neat mortar should not yet have hardened at 6 hours after preparation.

In the work presented here, we investigated upon this discrepancy between results obtained from paste and mortar, and probed into the cause behind this effect. At first, the heat release in calorimetry was determined in cement paste as well as in mortar, especially taking into account the impact of admixtures like, for example, alginate. Thereafter, the relationship between calorimetric data obtained from mortar calorimetry and actual mortar strength development was qualitatively correlated. Furthermore, in the next step, the impact of sand and filler materials in general on the setting behaviour and strength development of CAC was investigated via calorimetry and compressive strength testing of mortar specimens. Finally, a mechanistic study was conducted to further elucidate the role of sand and fillers in CAC hydration by analyzing the cement pore solution composition via ICP-OES and characterization of the filler particle surface after imbibition in cement pore solution via Scanning electron microscopy (SEM) imaging.

2 | EXPERIMENTAL PROCEDURE

2.1 | Cement samples

Different CACs (*Secar 51*, *Secar 71*, and *Secar 712*, produced by Imerys Aluminates) and an ordinary Portland cement (CEM I 52.5 N, *HeidelbergCement*, Milke plant) were

utilised in this study. Information regarding their mineralogical phase composition, particle size, and *Blaine* value has been provided previously.^{10,16}

2.2 | Materials

Different filler materials (CaCO_3 , SiO_2 , TiO_2 , Al_2O_3 , $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$) were supplied by *Nabaltec*, *Quarzwirke*, *Schaefer Kalk*, and *Evonik*. Their chemical composition, alkali/earth alkali content (Na_2O , K_2O , CaO , and MgO), particle size and specific surface area (SSA) are displayed in Table 1.

In all experiments, deionised water obtained from a *Barnstead Nanopore Diamond* purification system (Werner Reinstwassersysteme) was used. Mortars were prepared using European Committee for Standardization (Comité Européen de Normalisation) standard sand (Normensand GmbH).

Alginate sample *XEA 5036* (Eurogum; for properties refer to¹⁰) was used as accelerator for CAC while anhydrous citric acid (≥ 99.5 wt%, Bernd Kraft GmbH) was added as retarder for OPC. As superplasticizer, an MPEG-type Polycarboxylate ester (PCE) exhibiting high anionic character and possessing a long side chain was utilized. Its properties are described in.¹⁰

2.3 | Experimental methods

2.3.1 | Isothermal heat-flow calorimetry

Paste calorimetry was performed in accordance with DIN EN 196-11¹⁷ using sealable 10 mL glass ampoules. Four grams of cement were filled into the ampoule and dry-blended with previously placed alginate powder, solid citric acid, or filler material.

Mortar calorimetry was conducted utilizing sealable 20 mL glass ampoules. First, alginate or citric acid were placed into the ampoule, followed by precisely four grams of cement and the norm sand/filler material ($s + f = 12$ g).

Deionised water was added to the mixture, the ampoule was sealed and homogenized for 2 minutes using a vortex mixer (VWR) before placement into an isothermal heat flow conduction calorimeter *TAM air model 3116-2* (Thermometric). Measurements were conducted at 20°C until heat evolution ceased.

2.3.2 | Mortar tests

Mortar testing was conducted according to DIN EN 196-1¹⁸ (strength testing) and DIN EN 1015-3¹⁹ (workability). Strength values were determined using a *ToniNORM*

instrument setup (Toni Technik) consisting of a *power-box model 2010* equipped with two load frames (*model 1543* and *model 1544*). Using a *ToniMIX* eccentric agitator (Toni Technik), the mortar was automatically prepared whereby the water containing the superplasticizer as well as one drop of defoamer (Dowfax DF 141; Dow Chemical) were first placed in the mixer cup. The mortar prisms ($4 \times 4 \times 16$ cm) were compacted using a *ToniVib* vibrating table (Toni Technik) and stored at 20°C until demoulding. Mortar density was calculated from the size and weight of the prisms.

Mortar tests were performed using the same shipment of each cement and the prisms were produced in one test series. This precaution was taken because CAC is quite sensitive to aging.

2.4 | Analytical methods

2.4.1 | Ion concentrations via inductively coupled plasma atomic emission

Extraction of a cement pore solution for analysis was performed via centrifugation (10 000 *g*, 15 minutes) of the cement paste which was prepared by admixing, for example, 20 g of Secar 51 dry-blended with 20 wt% filler in a centrifuge tube and subsequent homogenisation for 2 minutes utilizing a vortex mixer. The supernatant pore solution was filtrated using a 0.2 μm Polyethersulfone membrane filter, diluted 1:30 using an acidified (hydrochloric acid) solution and analyzed via inductively coupled plasma atomic emission spectroscopy on a *series 700* apparatus (Agilent Technologies). Resulting data were averaged and reported including an additional methodical error of 1% to account for deviations in sample preparation.

2.4.2 | SEM imaging

Sample material was fixated to the sample holder stub with *Leit Adhesive Carbon Tabs* (PLANO) and was sputtered with gold for improved conductivity after freeze-drying. SEM imaging was performed on a *XL-30 FEG* microscope (FEI) equipped with secondary and backscattered electron detectors at 15 or 25 kV accelerating voltage at a working distance of 10 mm.

2.4.3 | X-ray diffraction

Powder diffraction patterns were captured on a *D8 advance* instrument (Bruker AXS) equipped with a *VANTEC-1* detector ($3^\circ - 45^\circ 2\theta$, 30 kV, 35 mA, 0.008° step, variable

divergence slit V6, *Bragg-Brentano* geometry and Cu K α source). Evaluation and processing of the diffraction patterns was performed using Bruker's *EVA V2* software.

3 | RESULTS AND DISCUSSION

3.1 | Hydration of cement paste and mortar investigated via calorimetry

As described in the introduction, in our previous investigation¹⁰ the results on the accelerating effect of alginate in CAC obtained from calorimetry using cement paste did not match with those from mortar strength testing. Therefore, either calorimetry in general or calorimetry performed using cement paste seems to be inappropriate to produce data which are representative of the setting behavior of mortar. To investigate on this subject, heat flow calorimetry was conducted by employing a CAC mortar consisting of three quarters of sand (12 g) and one quarter of cement (4 g). This approach of using a mortar containing sand for calorimetric measurements is not described in the standard DIN EN 169-11 which focuses on paste only.¹⁷

The results from this experiment are displayed in Figure 1. There, the heat flow curves from paste (top) and mortar (bottom) based on a neat CAC sample (Secar 71), admixed with or without 0.1 wt% of alginate are presented.

As is evident from the graphs, the setting behaviour (as expressed by the heat released during hydration) of a CAC paste or mortar diverge significantly. The system accelerated

by alginate yields comparable results while the neat paste and mortar exhibit a difference of nearly 3 hours for the time until maximum heat release occurs. Obviously, the addition of norm sand shifts the beginning of the acceleration period to a much earlier time, resulting in faster hardening of the mortar. This effect of sand needs to be taken into account and thus well explains the discrepancy observed in our previous investigations.

To check whether such an effect is specific only for aluminate cement, also an OPC was investigated via calorimetry (see Figure 2). Again, results achieved in paste as well as in mortar were compared, and the system without or admixed with 0.1 wt% of citric acid retarder were looked at. Also here, as was noticed in the case for CAC before, an accelerating effect of the norm sand regarding the time of maximum heat release was observed which however was less pronounced than in CAC, but still significant enough.

To validate mortar calorimetry as a method which better represents the actual hydration behaviour and strength development of CAC mortar, additional tests were performed employing two different CAC samples and comparing the results from mortar heat flow calorimetry with those from mortar strength testing. As CAC samples, one exhibiting a long induction period (Secar 712) and one possessing a short induction period (Ternal LC) were probed. Moreover the mortars were admixed with biopolymer accelerator (alginate or carrageenan). In the case of Secar 712, a PCE superplasticizer was admixed to improve workability of the mortar.

As is evident from Figure 3, mortar calorimetry produces results which qualitative match the strength development of the

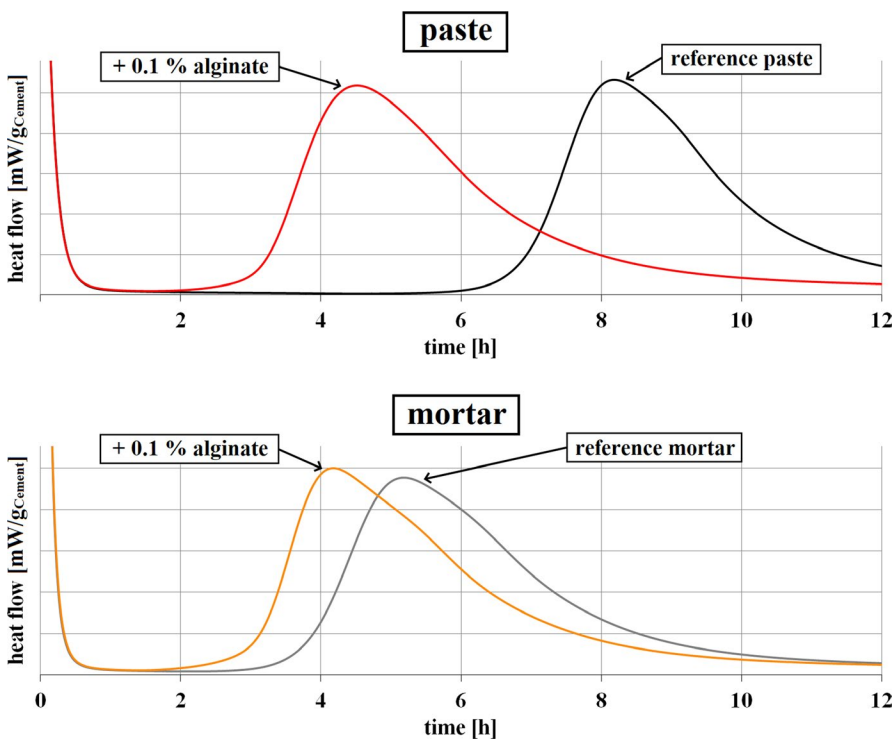


FIGURE 1 Comparison of heat evolution from cement paste (top, $w/c = 0.5$) or mortar (bottom, $w/c = 0.55$) of a calcium aluminate cement sample (Secar 71), neat or admixed with 0.1 wt.% alginate (sample XEA 5036) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 2 Comparison of heat evolution from cement paste or mortar of an ordinary Portland cement (OPC) sample (CEM I 52.5 N, $w/c = 0.5$), neat (top) or in the presence of 0.1 wt% citric acid retarder (bottom) [Color figure can be viewed at wileyonlinelibrary.com]

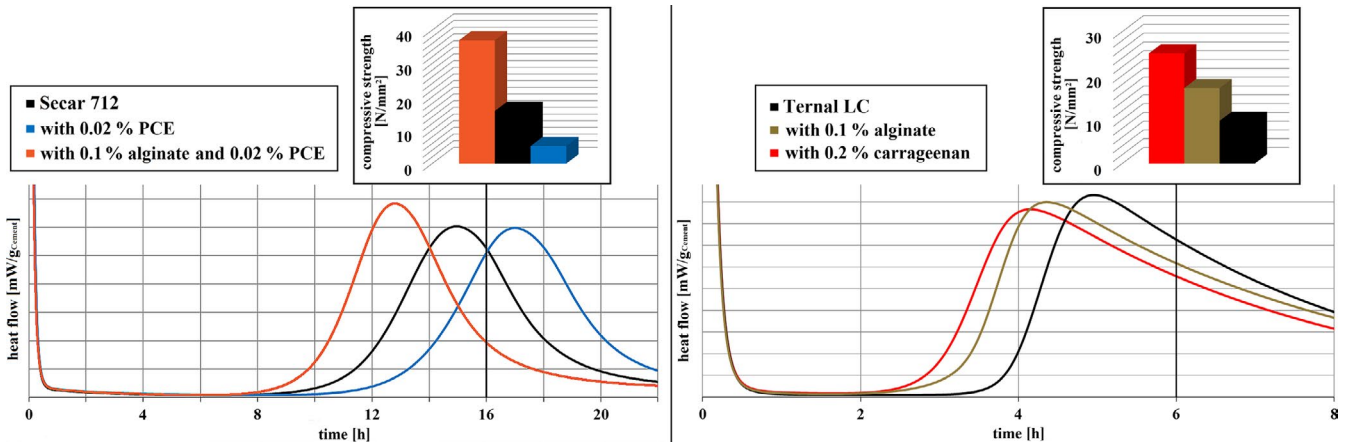
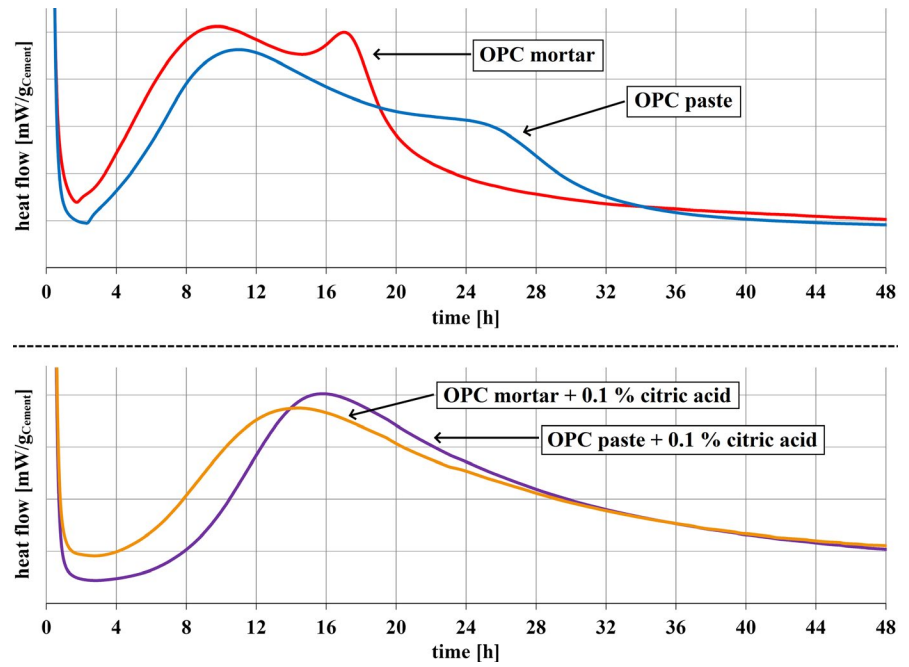


FIGURE 3 Comparison of compressive strength development of mortar ($w/c = 0.5$) and mortar heat flow monitored via calorimetry ($w/c = 0.55$) of calcium aluminate cement sample Secar 712 (left) and Ternal LC (right), neat and admixed with biopolymers (alginate or carrageenan) and/or a PCE superplasticizer [Color figure can be viewed at wileyonlinelibrary.com]

mortar at a given time and can be utilized to make a rule of thumb estimate. This is observed in the presence of the accelerating biopolymers as well of the retarding PCE superplasticizer, and also for a combination of these admixtures. Therefore, we conclude that mortar calorimetry presents a more reliable method to monitor actual hardening and strength development of CAC mortar than calorimetry in cement paste. In addition, we observed here that the accelerating effect of alginate which is based on providing a heterogeneous crystallization surface for C-A-H phases by attracting Ca^{2+} and $[\text{Al}(\text{OH})_4]^-$ ions and enriching them along the biopolymer's chain,¹² is still visible albeit less pronounced as compared to the effect recorded in CAC paste.¹⁰ This hints to a specific impact which presumably is owed to the sand particles.

In order to further investigate the impact of norm sand on the hydration behaviour of CAC as well as the associated

reduced effectiveness of alginate as accelerator, the general influence of filler materials on CAC hydration was probed in-depth whereby the cement was partially replaced by different kinds of fillers.

3.2 | Accelerating effect of fine fillers

A similar accelerating effect as observed before for the norm sand was recorded on addition of quartz sand (Millisil W12 or Frechen F36) to a CAC paste. Addition of 20 or 40 wt% of such fine sands (these portions only present a fraction of what is present in a norm mortar which contains as much as 75 wt% sand and 25 wt% cement) already resulted in an earlier maximum for the heat release. Moreover the addition of submicron filler particles (primary crystal and/or particle

size in the nanometer range) to the CAC paste strongly promoted the hydration to much earlier times (see Figure 4; Table 2). The effect clearly increases with increasing SSA of various filler materials which are tabulated in Table 2 along with the particle size and chemical composition of the product samples. The effectiveness of selected accelerating filler samples is presented in Figure 4. There, $\text{Al}(\text{OH})_3$ exhibiting a d_{50} value of $0.4 \mu\text{m}$ was identified as the most effective accelerator.

In a next step, the dosage dependence of the accelerating effect of all fillers listed in Table 1 was probed. There, substitution rates for CAC by filler of 0 - 75 wt% were studied. The results are tabulated in Table 2. It was found that (a) the accelerating effect of a filler clearly depends on its particle size/SSA (ie the smaller the particle or the higher the SSA, the stronger is the effect); and (b) higher addition rates of the fine fillers instigate a more pronounced acceleration (see Table 2).

The results from Table 2 suggest that the chemical composition of the filler material is less important than particle size and SSA. Only in the case of $\text{Al}(\text{OH})_3$ another factor comes into play which is represented by the solubility of the submicron powder. An increased $[\text{Al}(\text{OH})_4]^-$ content in the pore solution presumably promotes nucleation and crystal growth of C-A-H phases and this way accelerates CAC hydration. Furthermore, the nanoscale $\text{Al}(\text{OH})_3$ might also act as nucleation seed for hydration products.

To further confirm the accelerating effect of fine fillers, mortar calorimetry using $\gamma\text{-Al}_2\text{O}_3$ and $\text{Al}(\text{OH})_3$ as accelerator (see Figure S1, top) and mortar strength testing was performed on specimens holding $\gamma\text{-Al}_2\text{O}_3$ (sample NO 221-30, d_{50} $30 \mu\text{m}$, $75 \text{ m}^2/\text{g}$, primary crystal size 10 - 50 nm) which was found to present the best filler regarding dosage effectiveness (see Table 2). By using this filler, substitution of a small amount only of the norm sand with this filler resulted in a nine-fold increase of the early strength of Secar 71 mortar

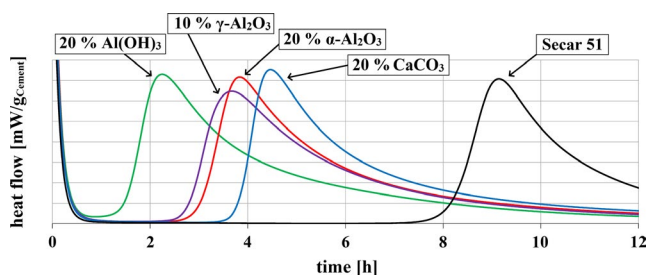


FIGURE 4 Accelerating effect of submicron filler particles on calcium aluminate cement (CAC) paste hydration, as determined via heat flow calorimetry of a mixture of cement (Secar 51, $w/c = 0.6$, 3.2 or 3.6 g CAC) substituted with 10 or 20 wt% (0.4 or 0.8 g) filler and compared to the neat CAC (4 g). $\text{Al}(\text{OH})_3$ = APYRAL 200SM, $\gamma\text{-Al}_2\text{O}_3$ = NO 221-30, $\alpha\text{-Al}_2\text{O}_3$ = NO 783, and CaCO_3 = PRECARB 100 [Color figure can be viewed at wileyonlinelibrary.com]

cured for 4 hours, and a 15-fold increase for Secar 51 mortar cured for 5 hours (see Tables S1 and S2).

The acceleration caused by fillers can well explain another observation which we previously had made when testing the alginate in CAC sample Secar 80.¹⁰ There, surprisingly we noticed only a minor accelerating effect of the biopolymer in this CAC. It is important to know that Secar 80 presents a formulated CAC which holds about 40 wt% $\alpha\text{-Al}_2\text{O}_3$ and possesses a *Blaine* value of $\approx 10\,600 \text{ cm}^2/\text{g}$. Thus, to obtain a similar mixture as in Secar 80, we blended Secar 71 with fine $\alpha\text{-Al}_2\text{O}_3$ (sample NO 783). Note that Secar 80 exhibits a similar clinker composition relative to the ratio of CA/CA_2 as is present in Secar 71,¹⁰ it only differs in that it is formulated with aluminium oxide. Already at a 20 wt% replacement of the cement with this fine filler, a major reduction in the time until maximum heat release occurred was found (Figure 5). Moreover, upon addition of alginate as an accelerator to this mixture, only minor effectiveness of the biopolymer was recorded. Therefore, we contemplate that the accelerating effect of fine filler materials is almost comparable to that of the accelerating biopolymer admixture. This explains why alginate is relatively less effective in such CAC formulated with a fine filler. Furthermore, it suggests that incorporation of expensive accelerating admixtures (e.g. lithium salts) can be reduced by pre-formulating the CAC with simple inorganic fillers such as silica or limestone powder (see Figure S1).

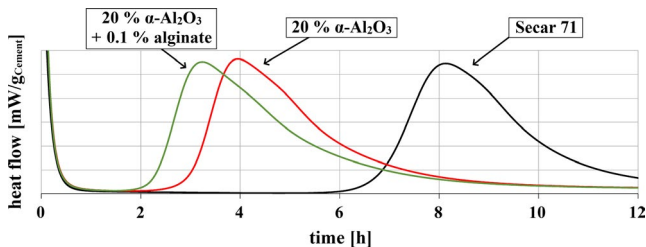
4 | MECHANISTIC STUDY

In a series of previous studies employing fine Al_2O_3 and SiO_2 Gessner et al²⁰⁻²³ already noticed that the addition of a fine filler material "...changes the nucleation mechanism..." and in CAC hydration produces "...a preferential nucleation of the hydration products..."²² They also identified the influence of the SSA, the Na_2O content as well as the concentration of acid sites on aluminium oxide as relevant parameters with respect to the acceleration. Similar observations were made by other researchers.²⁴⁻²⁶ In particular, Puerta-Falla et al showed "...that the number of product nuclei, formed at the end of the induction period, is linearly proportional to the additional surface area provided by the fillers. This suggests that CAC hydrated is enhanced by the provision of additional solid surface area for the heterogeneous nucleation of products. ..."²⁵

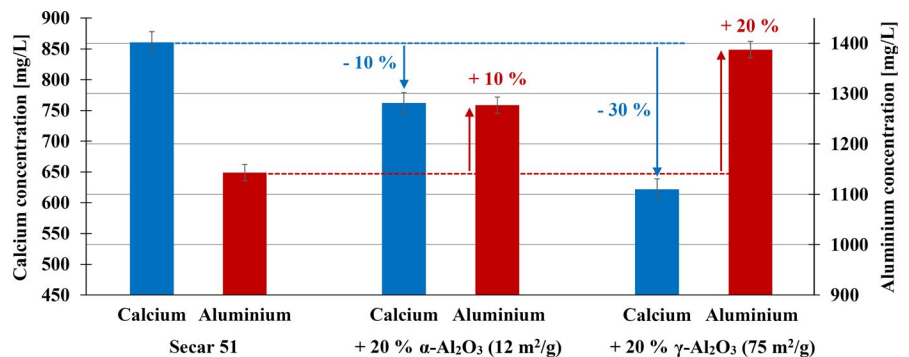
Our results fully confirm these previous findings and directed us to further investigate the working mechanism of these fine fillers, specifically taking into account the model proposed for the accelerating effect of alginate.¹² According to this, the negative charge along the alginate polymer chain attracts Ca^{2+} ions which are then bound and chelated by the biopolymer in a molecular cavity holding carboxylate groups. This way, the electric charge of the alginate reverses

TABLE 2 Time period until the maximum of heat release is achieved in a paste ($w/c = 0.6$, 4 g CAC fixed) prepared from CAC cement (Secar 51) dry-blended with different filler materials

Material	Product name	d_{50} (μm)	BET (m^2/g)	Time until max. heat release at substitution rate (wt%) of cement by filler				
				5%	10%	20%	40%	75%
SiO_2	CEN standard sand	700	—	—	—	—	—	5.0 h
SiO_2	QUARZSAND F 36	160	—	—	—	7.2 h	6.6 h	4.9 h
SiO_2	MILLISIL W 12	16	0.9	—	—	6.9 h	6.0 h	—
$\alpha\text{-Al}_2\text{O}_3$	NABALOX NO 784	0.8	7	—	6.3 h	4.8 h	3.2 h	—
CaCO_3	PRECARB 100	1	9	—	5.9 h	4.5 h	2.6 h	—
SiO_2	SILMIKRON 805	0.5	20	—	5.1 h	4.2 h	—	—
$\alpha\text{-Al}_2\text{O}_3$	NABALOX NO 783	0.8	12	—	4.9 h	3.8 h	—	—
$\text{Al}(\text{OH})_3$	APYRAL 200SM	0.4	15	5.6 h	4.4 h	2.3 h	—	—
$\text{AlO}(\text{OH})$	ACTILOX 200SM	0.3	17	5.3 h	4.2 h	3.0 h	—	—
$\gamma\text{-Al}_2\text{O}_3$	NABALOX NO 221-30	30	75	4.5 h	3.6 h	3.4 h	—	—
TiO_2	AEROXID P25	2.7	50	3.9 h	3.0 h	—	—	—

**FIGURE 5** Heat release from neat calcium aluminate cement (CAC) (Secar 71, 4 g, $w/c = 0.62$) compared to a paste ($w/(c + f) = 0.62$) prepared from CAC (3.2 g) and fine $\alpha\text{-Al}_2\text{O}_3$ (sample NO 783, 0.8 g), admixed with alginate (sample XEA 5036) [Color figure can be viewed at wileyonlinelibrary.com]

from negative to positive and now is capable of attracting $[\text{Al}(\text{OH})_4]^-$ anions. Through this biotemplating effect involving alternating layers of calcium and aluminate ions, the alginate becomes a heterogeneous crystallization surface for C-A-H nuclei. This was further proven by SEM imaging of alginate which was imbibed into CAC pore solution. There, a much enhanced growth of C-A-H clusters on the surface of the biopolymer became visible.¹²

FIGURE 6 Ca^{2+} and Al^{3+} ion concentrations present in the pore solution of a calcium aluminate cement paste prepared from Secar 51 (20 g, $w/c = 0.7$), neat and dry-blended with additional 20 wt.% (4 g) of $\alpha\text{-Al}_2\text{O}_3$ (NO 783) or $\gamma\text{-Al}_2\text{O}_3$ (NO 221-30) [Color figure can be viewed at wileyonlinelibrary.com]

Relative to the fillers studied here, it is generally known that in alkaline medium Al_2O_3 , SiO_2 , TiO_2 and CaCO_3 exhibit negative zeta potentials (surface charges).^{27,28} Moreover in the presence of Ca^{2+} ions these cations can adsorb onto the surfaces of these fillers which—as is the case for alginates—leads to a reversal of the surface charge from negative to positive.²⁷⁻²⁹ For Al_2O_3 , this interaction with calcium causes an ion binding that has been reported to be proportional to the BET surface area.³⁰

To elucidate the interactions occurring in the presence of our fillers, we investigated the ionic composition of the pore solution of pastes from CAC sample Secar 51 dry-blended with two different fillers, namely $\alpha\text{-Al}_2\text{O}_3$ (BET surface area $12 \text{ m}^2/\text{g}$) and $\gamma\text{-Al}_2\text{O}_3$ (BET surface area $75 \text{ m}^2/\text{g}$). The results are presented in Figure 6.

According to the results, a binding of calcium by the Al_2O_3 is clearly observed. For example, in the case of the $\gamma\text{-Al}_2\text{O}_3$ filler possessing a high SSA ($75 \text{ m}^2/\text{g}$) the concentration of initial free calcium decreases by $\approx 30\%$ (from 842 to 612 mg/L). This decrease in the Ca^{2+} concentration further fosters dissolution of the CA phase as a consequence of the solution equilibrium, resulting in higher Al^{3+} concentrations

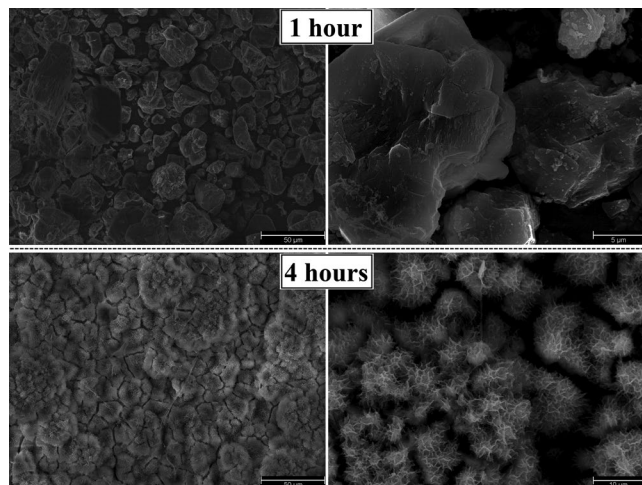


FIGURE 7 Surfaces of γ - Al_2O_3 submerged in calcium aluminate cement pore solution after 1 or 4 h of imbibition, as observed via SEM (left: magnification 500 \times ; SE detector; right: magnifications 4000 \times [top], 2000 \times [bottom]; Secondary electron (SE) [top], Backscattered electron (BSE) [bottom] detectors)

in the pore solution. A similar behaviour was observed for the working mechanism of alginate accelerator. Hence, it can be postulated that on the surface of the filler particles an electrochemical double layer composed of Ca^{2+} at first and a second layer of aluminate ions is formed, similar to the mechanism found for alginate. There, formation of C-A-H nuclei along the alginate molecular chains could be visualized via SEM imaging.

To investigate whether a similar layer of hydrate phases forms on the surface of the filler particles, γ - Al_2O_3 powder was fixed to a SEM sample holder, submerged in CPS and then analysed via SEM imaging. There, after 4 hours of contact time, massive overgrowth of the surface with crystalline cement hydration products exhibiting the characteristic morphology of C-A-H was observed, as is displayed in Figure 7. A more detailed image of these early C-A-H phases recorded at higher magnification is presented in Figure S2.

Furthermore, XRD analysis of the hydration products was performed on CAC paste samples hardened over 20 hours at 20 $^\circ\text{C}$. There, in the presence of fillers (e.g. α - Al_2O_3 sample NO 783) formation of a C-A-H phase (CAH_{10}) as early hydration product was observed (sample diffractograms for Al_2O_3 and CaCO_3 fillers shown in Figure S3). No other hydration products were observed which would indicate a different path of hydration taking place. These findings are consistent with previous reports on the application of accelerating filler materials on CAC hydration conducted via XRD and SEM analysis.^{21,25,31,32}

5 | CONCLUSION

Heat flow calorimetry using cement paste can produce results which are not consistent with actual mortar strength

development data from mortars. This effect is particularly pronounced for CACs. Their strength development is significantly impacted when heterogeneous crystallization surfaces are present. Utilizing heat flow calorimetry of a mortar instead of cement paste can mitigate this problem and produce a correlation between the time at which peak heat release occurs and mortar strength, the reason being that sand provides a heterogeneous crystallization surface.

Probing of different filler materials including SiO_2 , CaCO_3 , α -/ γ - Al_2O_3 , $\text{AlO}(\text{OH})$, $\text{Al}(\text{OH})_3$, and TiO_2 on CAC hydration affirmed the role of the specific surface area of the fillers, with high surface area prompting earlier hydration. For example, a γ - Al_2O_3 sample exhibiting a high BET surface (75 m^2/g) was found to significantly accelerate CAC hydration.

A mechanistic study involving pore solution analysis and SEM imaging revealed that the accelerating effect of the fillers is based on a similar mechanism as was proven before for alginate. In CAC pore solution, the initially negatively charged filler particles first adsorb Ca^{2+} ions which induces a charge reversal. Onto these layers of cations, another layer of $[\text{Al}(\text{OH})_4]^-$ anions is deposited. This electrochemical double layer presents the template for continued crystal growth of C-A-H phases which provide the strength to CAC.

Our study suggests that the dosages of accelerating admixtures such as lithium salts or alginates can be reduced substantially by formulating the CAC binder with suitable inorganic nano fillers (see Figure S1) while still achieving exceptionally high early strength values. However, these fine materials also actively promote the formation of C-A-H, the term “filler” might describe their function only partially as it usually refers to inert materials.

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CONFLICT OF INTEREST

The authors wish to declare that no conflicts of interest or competing interests exists.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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