

The effect of alginates on the hydration of calcium aluminate cement

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ABSTRACT

The hydration of calcium aluminate cement (CAC) in the presence of sodium alginate which is known to slightly retard Portland cement, was studied using heat flow calorimetry and mortar strength testing. Most surprisingly, addition of alginate resulted in an earlier occurrence of the maximal heat release as well as an increased early strength, thus confirming that in CAC alginate acts as accelerator. The thickening effect of alginate was effectively compensated using a superplasticizer while retaining its accelerating property. An investigation of the pore solution composition indicated that in the presence of alginate the concentration of calcium ions was reduced. Such effect normally causes retardation of cement hydration and should delay the formation of C-A-H phases. Apparently, the strong calcium ion complexing ability of alginate promotes the formation of C-A-H via e.g. a templating effect. A combined application of alginates and lithium salts presents a viable option to reduce the lithium consumption in CAC acceleration.

1. Introduction

Calcium aluminate cements (CACs) have unique properties that include quick high early strength (faster strength development than from Portland cement) and a high acid and abrasion resistance. This makes CAC the cement of choice where those properties are required. Alumina cements are produced at higher temperatures than Ordinary Portland cement (OPC) because of their high content of Al_2O_3 and are sintered or molten at 1450°C and 1650°C , respectively (Bensted, 2002). Commercial products normally have an Al_2O_3 content of 35–85 wt.% depending on their field of application. The common hydraulic clinker phases of CACs include CA, CA_2 , C_{12}A_7 , C_4AF and C_2S . By mass, monocalcium aluminate is the most relevant phase present in calcium alumina cement. Hydration of the aluminous clinker phases proceeds via a dissolution and precipitation mechanism from solution. In the pore solution, Ca^{2+} and Al^{3+} are present at a molar ratio of about 0.55 - 0.6 which leads to the crystallisation and precipitation of metastable C-A-H phases (CAH_{10} , C_4AH_{13} or C_4AH_{19} and $\text{C}_2\text{AH}_8/\text{C}_2\text{AH}_{7.5}$) of which C_2AH_x is most important for the setting of CAC (Lothenbach, Pelletier-Chaignat, & Winnefeld, 2012; Scrivener & Capmas, 2003). Depending on the temperature, after months or years all metastable hydrates transform into the stable hydrogarnet C_3AH_6 phase (katoite). At low temperatures ($< 15^\circ\text{C}$) and room temperature ($15\text{--}25^\circ\text{C}$), the hydration of CAC either progresses through the formation of CAH_{10} (I) at first, followed by its transformation to C_2AH_8 (II), or

by direct formation of C_2AH_8 (III) (Scrivener & Capmas, 2003).



In CAC, most commonly lithium salts are used to accelerate its hydration. In particular, Li_2CO_3 is applied at dosages between 0.005 and 0.1 wt.-%, depending on the application and specific binder system. Lithium produces a strong accelerating effect in pure aluminate cement and in combinations with calcium sulphates (binary / ternary systems). According to a model presented by Goetz-Neunhoffer, Li^+ ions accelerate the hydration of the aluminate phases through six pathways: (1) improved dissolution of CA through an increased permeability of the aluminum hydroxo hydrate layer; (2) the thus increased $\text{Ca}^{2+}/\text{Al}^{3+}$ ratio in solution thermodynamically promotes the formation of C_2AH_8 ; (3) formation of $[\text{Li}_2\text{Al}_4(\text{OH})_{12}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}]$ layered double hydroxide (LDH) compound as seeding material which decreases the activation energy necessary for the crystallisation of C_2AH_8 ; (4) Li^+ ions are then continuously exchanged and replaced by Al^{3+} ions which then (5) reduces the Al^{3+} concentration in solution and (6) further fosters the dissolution of CA by the lower Al^{3+} content in solution (Götz-Neunhoffer, 2005).

However, the availability of lithium salts in general and for construction applications in particular is becoming increasingly

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

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problematic because of the high demand for lithium ion batteries. The fast growing market for mobile phones and electric cars drastically affected the price and the supply security for lithium compared in recent years (Speirs & Contestabile, 2018). Considering the key role which lithium is expected to play in future electromobility it appears to be irresponsible to use up such a precious element in flooring compounds and other CAC-based systems. Hence, a replacement for Li is highly needed.

In the context of another study, we observed an unexpected behaviour of alginates when tracking the hydration of alumina cement via heat flow calorimetry (de Reese, Sperl, Schmid, Sieber, & Plank, 2015). Most surprisingly it was found that alginates act as accelerator for CAC by prematurely triggering its hydration. This effect was not expected, because so far polysaccharides were only known to retard cement hydration.

Alginates are biopolymers composed of mannuronic (M) and guluronic (G) acid that are glycosidically connected via α -1 \rightarrow 4 and β -1 \rightarrow 4 linkages, forming linear copolymers with average molecular weights between 10,000 and 600,000 Da. The carbohydrate monomer units (M and G) can be linked in different tactical sequences such as MM, GM and GG which leads to different steric arrangements (Fig. 1, top). The ratio between those blocks and the molecular weight (\sim viscosity) are mostly responsible for the properties (gel strength/syneresis) of aqueous solutions of the polymer. Furthermore, it is known that especially GG blocks are essential for the strong ionotropic gelling properties of alginates in the presence of divalent cations, like e.g. Ca^{2+} (Imeson, 2011; Plank, 2003). Due to its characteristic appearance, this complexation mode with Ca^{2+} is generally referred to as the “egg-box” model (Fig. 1, bottom), first introduced by Grant, Morris, Rees, Smith, and Thom (1973).

Alginates are biopolymers of natural origin and are harvested via extraction from brown algae *Phaeophyceae*. Depending on the species of algae, their growth conditions and processing after harvest, their chemical composition and molecular weight can vary.

The aim of this research was to investigate and understand this unusual property of alginate in CAC. In order to elucidate the effect of alginates of diverse natural origin, a series of commercial sodium alginate products exhibiting different properties were received from different companies and tested. Additionally, their accelerating effect on

alumina cements of various Al_2O_3 contents was examined. This program was developed because CACs can exhibit different mineralogical compositions resulting mainly from the ratio of $\text{CaO}/\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ present in the raw meal for CAC production. In order to compensate for the loss of workability resulting from the thickening effect of the biopolymer a superplasticizer was used. Moreover, the accelerating mechanism of the alginate was investigated by applying pore solution analysis.

2. Experimental

2.1. Cement samples

A variety of calcium aluminate cements (*Ciment Fondu, Secar 41, Secar 51, Secar 71, Secar 712, Secar 80 as well as Ternal SE, Ternal LC and Ternal EP*) produced by *Imerys Aluminates* were utilised. Their oxide composition (Table S-1 in supporting information) was determined using XRF (Axios, PANalytical, Kassel, Germany) while their mineralogical composition (Table 1) was investigated using XRD (*D8 advance*, Bruker AXS, Karlsruhe, Germany). Average particle size was analysed by laser granulometry (*Cilas 1064*, Cilas Instruments, Orleans, France). Here, particle size was measured three times after complete dispersion in isopropanol using ultrasonic, and the mean value was calculated. The specific surface area was determined according to *Blaine's* method.

2.2. Chemicals

In all experiments deionised water obtained from a *Barnstead Nanopore Diamond Water purification system* (Werner Reinstwassersysteme, Leverkusen, Germany) was used. As reference accelerator lithium carbonate (*Chemetal*) and as retarders trisodium citrate (*Merck*) as well as potassium sodium tartrate (Rochelle salt, *Jungbunzlauer*) were utilised. Li_2CO_3 ($< 40 \mu\text{m}$) was pre-blended at 1/40 wt./wt. ratio with calcium carbonate ($\approx 14 \mu\text{m}$, *Merck*) to ensure accurate dosing.

2.2.1. Alginates

Over thirty alginate samples were provided by *KIMICA, Eurogum, FMC* (through *IMCD*), *Roepel, Cargill, Danisco* and *Polygal*. Those varied

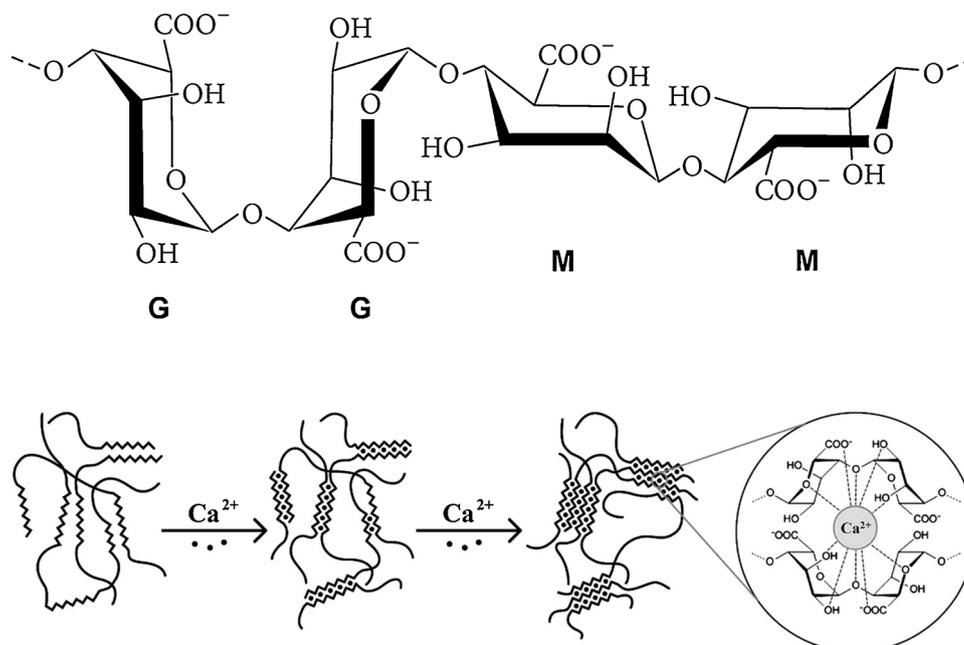


Fig. 1. Top: General chemical structure of the alginate molecule composed of guluronic (G) and mannuronic (M) acid as building blocks; Bottom: Complexation of calcium ions by alginate molecules (“egg-box” model) resulting in gel formation (adapted from Stolarz (2003) and Pistone, Qoragllu, Smistad, and Hiorth, (2015)).

Table 1

Typical contents (wt.%) of hydraulic clinker phases in alumina cement samples used in the study, according to quantitative X-ray diffraction analysis including Rietveld refinement performed by TUM in conjunction with reported literature values.

Phase	Ternal EP	Ciment Fondu Ternal SE	Secar 41	CAC sample (wt.%)		
				Secar 51 Ternal LC	Secar 71 Secar 712	Secar 80
CA	1–5 ¹	47–57 ^{1,2}	54–66 ¹	64–74 ^{1,2,3,4,5}	54–64 ^{1,2,7}	35–45 ^{1,7}
CA ₂	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	36–44 ^{1,7}	22–30 ^{1,7}
C ₂ AS	<i>n.d.</i>	1–10 ¹	10–22 ¹	18–22 ^{1,3,4,5}	< 1 ^{1,7}	<i>n.d.</i>
C ₄ AF	10–20 ¹	10–20 ¹	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
C ₂ S	10–20 ¹	1–10 ¹	1–10 ¹	1–5 ^{1,3,4,5}	<i>n.d.</i>	<i>n.d.</i>
C ₁₂ A ₇	55–65 ¹	1–5 ^{1,2}	1–5 ¹	< 1 ^{1,3,5}	< 1 ^{1,7}	< 1 ^{1,7}
other	C ₃ A, CT	C ₃ FT, C ₂₀ A ₁₃ M ₃ S ₃ ⁶	CT, C ₃ FT, C ₂₀ A ₁₃ M ₃ S ₃	CT, C ₃ FT	α-Al ₂ O ₃ ^{1,7} (< 2)	α-Al ₂ O ₃ ^{1,7} (35 - 45)

¹ Own analysis.

² Data from Parr, Bin, Alt, and Wohrmeyer (2006).

³ Data from Puerta-Falla et al. (2015).

⁴ Data from Bizzozero, Gosselin, and Scrivener (2014).

⁵ Data from Gosselin and Scrivener (2008).

⁶ Data from Touzo, Gloter, and Scrivener (2001).

⁷ Data from Ostrand and Schmid (2015).

in purity (food grade or technical grade), particle size, viscosity grade and M/G ratio. In the following work, the commercial alginate products XEA 5036 (Eurogum), ALGIN (KIMICA), S 900 NS (Cargill), FD 170 (Danisco) and Protanal LF 200 FTS (FMC) were utilised (properties shown in Table 3).

The ratio between mannuronic and guluronic acid was determined via IR spectroscopy. From commercial samples of known composition a calibration curve between the M/G ratio and the ratio of the IR absorptions at about 1025 cm⁻¹ and 1085 cm⁻¹ was established (Sellimi et al., 2015) (see Table S-2 and Figure S-1 in supporting information). The investigated samples had M/G ratios in the range between 0.4 and 1.6, according to our analysis.

2.2.2. PCE superplasticizer

A polycarboxylate (PCE) superplasticizer based on ω-methoxy poly (ethylene oxide) methacrylate and methacrylic acid was utilised to reduce the viscosity and water demand of the CAC pastes. It was self-prepared via aqueous free radical copolymerisation at 80 °C as described in literature (Plank, Zouaoui, Andres, & Schaefer, 2014). In the PCE copolymers, the molar ratio of the monomers was 6 : 1 (MAA : Ester) and the side chain was composed of 114 ethylene oxide units. Molecular properties of the PCE sample was collected by GPC analysis which revealed a macromonomer conversion of 95 %, resulting in a copolymer with a mass average molecular weight of 33,800 Da and a PDI of 2.26.

2.3. Experimental methods

2.3.1. Isothermal heat-flow calorimetry

Calorimetry was performed following DIN EN 196-11 (2019). Four gram of cement were filled into sealable 10 mL glass ampoules and dry-blended with previously placed alginate powder until a homogenous mixture was achieved. This blend was mixed with deionised water at room temperature and homogenised with a vortex mixer VWT 1419 (VWR, Ismaning, Germany) for two minutes. The ampoule was placed in an isothermal conduction calorimeter TAM air model 3116-2 (Thermometric, Järfälla, Sweden) for monitoring of the heat flow. Measurements were conducted at 20 °C until heat evolution was concluded and repeated at least twice.

2.3.2. Mortar tests

Mortar testing was conducted according to DIN EN 196-1 (2016) and strength values were determined at different times of hydration using a ToniNORM instrument setup (Toni Technik, Berlin, Germany). The mortar was composed of three parts of norm sand and one part of

cement which was pre-blended with the alginate powder. Using a ToniMIX eccentric agitator (Toni Technik, Berlin, Germany) the mortar was automatically prepared whereby the water containing the superplasticizer as well as one drop of defoamer (Dowfax DF 141, Dow Chemical) was first placed in the mixer cup. The mortar prisms (4 × 4 × 16 cm) were compacted using a ToniVib vibrating table (Toni Technik, Berlin, Germany), stored at 20 °C / 90 % relative humidity and demolded 10 min prior to measuring their compressive and tensile strength. Mortar density was calculated from the size and weight of the prisms. Mortar tests were performed from 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 ageing.

2.3.2.1. Mortar spread flow. The spread flow of the mortar was determined according to DIN EN 1015-3 (2007). First, the mortar was added in two steps into a Vicat cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm) and slightly compacted. Each layer was compacted 10 times with a tamping rod. Thereafter, the cone was removed vertically and the flow table was lifted up 40 mm and then dropped 15 times, causing the mortar to spread out. The resulting spread was measured twice, the second measurement being at a 90° angle to the first and averaged to report the mean value.

2.3.2.2. Compressive and tensile strengths. Compressive and tensile strengths were determined according to DIN EN 196-1. For measurement of the tensile strength, three specimens of each sample were used and the average was calculated. The compressive strength was assessed using the broken specimens from the tensile strength testing. The mean value for the compressive strength was calculated from the measured results of the six pieces. Measurements were performed on a ToniNORM powerbox model 2010 equipped with two load frames model 1543 and model 1544.

2.4. Analytical methods

2.4.1. FT-IR spectroscopy

Infrared spectra of the polymers were measured with an attenuated total reflectance Fourier transform spectrophotometer (ATR-FTIR) (Vertex 70, Bruker Optics, Karlsruhe, Germany). It was acquired in transmittance mode on a Diamond ATR crystal cell (MPV-Pro, Harrich Scientific Products, Pleasantville, USA) by accumulation of 20 scans with a resolution of 0.5 cm⁻¹ and a spectral range of 2000–650 cm⁻¹. Evaluation of the spectra was performed using Bruker's OPUS 6.5 software after background correction and normalization.

2.4.2. Ion concentrations via ICP-OES

Inductively coupled plasma atomic emission (ICP-OES) spectroscopy was performed on a *series 700* apparatus (Agilent Technologies, Santa Clara, CA, USA). The cement paste was prepared by admixing e.g. 20 g Ciment Fondu blended with 0.1 wt.% alginate in a centrifuge tube and subsequent homogenisation for two minutes utilizing a vortex mixer *VWT 1419* (VWR, Ismaning, Germany). The cement paste was centrifuged (8500 rpm, 15 min) and the supernatant pore solution was filtrated using a 0.2 μm PES membrane filter. The resulting solution was diluted accordingly (1/30) and automatically measured five times to capture the Ca^{2+} and Al^{3+} content in the pore solution. Calibration was performed at concentrations of 1, 10 and 50 mg/L using an ICP multi-element standard (standard IV, Merck) and data was collected at several wavelengths. Results were averaged and deviation was calculated including an additional methodical error of 1 % to account for errors resulting from e.g. weighting and pipetting.

3. Results and discussion

3.1. Effect of alginate on CAC hydration

As is generally known, the addition of various polysaccharides to CAC including Xanthan gum, Welan gum etc. normally results in a retardation of cement hydration. In the course of this study, we surprisingly found that only a few specific polysaccharides (e.g. Gellan Gum or Karaya Gum) have no retarding effect or even produce a weak acceleration under specific circumstances. In contrast to those polymers, an alginate sample was found to strongly accelerate alumina cement. Moreover, other randomly selected sodium alginates showed similar accelerating properties.

In the following, the accelerating effect of four randomly selected alginate samples with different properties on the hydration of a commercial CAC is presented (Fig. 2). Of those samples shown only #1 (XEA 5036) is used in the further study for mortar tests and investigations on the working mechanism. According to the results from heat flow calorimetry, addition of 0.1 wt.% of sodium alginates can reduce the time until maximum heat release is recorded by up to 50 % (Table 2), suggesting that the dormant period is reduced significantly.

For Secar 51, as an example, the point of maximum heat release was detected about 4 h earlier when alginate was added. This corresponds to an acceleration of 45 % of hydration time for sodium alginate XEA 5036 (9.2 h for the reference as compared to 4.9 h upon addition of 0.1 wt.% alginate). To probe whether the effect of the alginate is dependent on the w/b ratio, CAC pastes with w/b ratios of between 0.4 and 0.7 were prepared. No difference between them relative to the general trend was found.

Extensive testing employing CACs of different phase compositions revealed that the accelerating effect occurred in all CAC pastes, but

Table 2

Acceleration of cement hydration in percent measured for different CAC samples (w/b = 0.62) upon addition of alginate sample XEA 5036, calculated from the time periods to reach peak heat release in heat flow calorimetry (see Table S-3 in supporting information).

CAC	+ 0.1 wt.% Alginate	+ 0.2 wt.% Alginate
Fondu	≈ 20 %	≈ 20 %
Secar 41	≈ 20 %	≈ 25 %
Secar 51	≈ 45 %	≈ 50 %
Secar 71	≈ 45 %	≈ 50 %
Secar 712	≈ 50 %	≈ 60 %
Secar 80	≈ 5 %	≈ 15 %
Ternal EP	≈ 15 %	≈ 30 %
Ternal SE	≈ 20 %	≈ 25 %
Ternal LC	≈ 45 %	≈ 50 %

significantly differed with phase composition and particle size of the CAC sample (Table 1 and Table S-1 in supporting information). This can be explained by the clinker phase composition of the cements. Ternal EP (mainly C_{12}A_7), Ciment Fondu and Ternal SE (both with a high amount of C_4AF and traces of C_{12}A_7) have an inherent high reactivity because of the calcium rich clinker composition and are thus less influenced by alginate. Especially Secar 80 shows a minor acceleration by alginate, which can be attributed to an extremely high fineness which already provides fast hydration (*Blaine* value of Secar 80 is 10,600 cm^2/g as compared to 3,000–4,000 cm^2/g for the other cements).

Furthermore, the effect of this specific alginate sample XEA 5036 on the hydration of other binders including Portland cement, calcium sulfoaluminate (CSA) cement, anhydrite or a ternary binder system (OPC / CAC / AH) was probed. There no acceleration was detected, instead consistently no effect or a minor retardation occurred. This allows to conclude that the alginate specifically promotes the hydration of alumina cement only.

3.2. Influence of molecular properties of the alginates on acceleration

In the next step, the impact of the molecular properties of alginate samples on their accelerating effect was studied. Three key molecular parameters were considered: (1) the cation (e.g. Na^+ , K^+ and NH_4^+) balancing the anionic charge; (2) the M/G ratio which impacts viscosity and strength gel; and (3) the degree of polymerisation which directly correlates to viscosity and molecular weight, respectively.

(1) When comparing the accelerating effectiveness of for example a sodium and an ammonium alginate, no specific effect of the cation was found (see Figure S-2 in supporting information), thus indicating that the cation plays no role here.

(2) The monomeric composition of alginates which is expressed by the ratio of mannuronic to guluronic acid incorporated, was also found

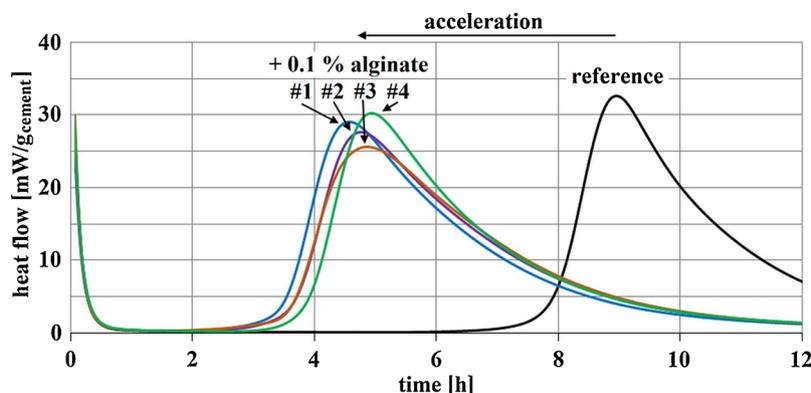


Fig. 2. Accelerating effect of four different alginate samples on CAC added at a dosage of 0.1 wt.%, as determined via heat-flow calorimetry (Secar 51, w/b = 0.5 ; #1 XEA 5036, #2 FD 170, #3 Manucol DH, #4 Protanal LF 200 FTS).

Table 3

Properties of four sodium alginate samples of different M/G-ratio (top) and properties of three sodium alginates of different viscosity grade (bottom), according to suppliers' specifications (viscosity, particle size) and own analysis (M/G ratio).

Alginate sample	Viscosity of a 1 % solution (20 °C)	Particle size	M/G ratio measured
Protanal LF 200 FTS	200–400 mPa s	< 200 μm	0.46 \pm 0.04
XEA 5036	300–600 mPa s	< 180 μm	0.82 \pm 0.04
FD 170	20–50 mPa s	< 100 μm	1.08 \pm 0.05
Satialgine S 900 NS	350–550 mPa s	< 125 μm	1.46 \pm 0.05

Alginate sample	Viscosity of a 1 % solution (20 °C)	Viscosity of a 10 % solution (20 °C)	Particle size	M/G ratio measured
ALGIN IL-2	20–50 mPa s	–	< 180 μm	1.49 \pm 0.06
ALGIN ULV-1	< 1 mPa s	100–200 mPa s	< 180 μm	1.31 \pm 0.05
ALGIN ULV-L3	–	20–50 mPa s	< 180 μm	1.16 \pm 0.08

to be of no significant impact on the acceleration. To demonstrate, the accelerating effect of four alginates exhibiting very different M/G ratios, as shown in Table 3 (top), was assessed by heat-flow calorimetry (results displayed in Fig. 2). There, no noticeable difference related to the specific composition (M/G ratio) could be observed. The product samples tested exhibited M/G ratios between 0.4 and 1.6.

(3) Opposite to this, the viscosity grade of the alginate samples was found to be most critical for their accelerating effect. Using three samples of different viscosity grade, but of similar particle size and M/G ratio (Table 3, bottom), a comparison was performed. At decreasing viscosity, the acceleration observed via heat-flow calorimetry (Fig. 3) became less and even changed to retardation for ultra-low viscosity grades. Whereas for all alginate samples of high or very-high viscosity grade, no adverse effect could be observed.

Generally, the viscosity of an alginate solution is strongly influenced by the molecular weight of the polymer. This relationship is used in the Mark–Houwink equation to calculate the viscosity average molar mass from the intrinsic viscosity of a solution.

The correlation between the molecular weight and the viscosity grade of different sodium alginate samples was established based on existing literature (see Figure S-3 and S-4 in supporting information). There, for ultra-low viscosity grade alginate samples molecular weights (M_w) in the order of 10^4 Da are reported. It has to be noted that because of their natural origin, alginates exhibit a broad molecular weight distribution. The PDIs (determined by the ratio of M_w/M_n) of commercial products are reported to be as high as four (Fu et al., 2010). Accordingly, even sodium alginates with a higher molecular weight of e.g. 200 kDa ($DP > 1000$) can contain a noticeable fraction of low molecular ($DP \approx 250$ at 50 kDa) alginate polymer. Moreover, low molecular weight samples may contain fractions with M_w as low as 10^3 Da. Those short-chain polysaccharides or even oligomeric components which

often originate from the isolation process of the alginate (alkaline extraction and to some extent heat treatment for depolymerisation) seem to cause the retarding effect commonly observed for polysaccharides.

According to this analysis, it is recommendable to use alginates with a M_w of at least 10^5 Da or even higher molecular weight to achieve an accelerating effect.

3.3. Comparison of acceleration from alginates and lithium salts

As mentioned in the introduction, lithium salts are generally used to accelerate alumina cements. In order to check on the substitution potential of lithium via addition of alginates, respective systems and combinations were tested. The results of these experiments are displayed in Fig. 4.

First, it becomes clear that the alginate can achieve a comparable acceleration than lithium carbonate, albeit at a significantly higher dosage only. Furthermore, a combination of Li_2CO_3 and alginate produces an even stronger acceleration, thus demonstrating that both products can be combined well. Accordingly alginate can be used to save the precious lithium compound while keeping the same performance with respect to setting and hardening behavior of this cement. Similar results were obtained in other CAC samples.

3.4. Strength development of alginate treated CAC mortar

To probe further into the accelerating effect of the alginate, mortar testing was conducted using three different CAC samples of distinctly different composition and reactivity. The aim was to affirm the previous results from heat flow calorimetry.

In Ciment Fondu ($\approx 38\% \text{ Al}_2\text{O}_3$), which exhibits a relatively fast setting, addition of the alginate XEA 5036 at a dosage of 0.1 wt.%

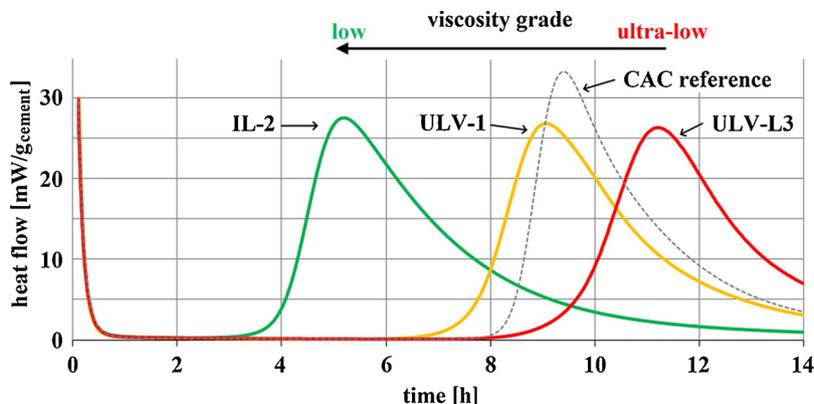


Fig. 3. Accelerating effect of three alginate samples of different viscosity on CAC added at a dosage of 0.1 wt.%, as determined via heat-flow calorimetry (Secar 51, w/b = 0.5).

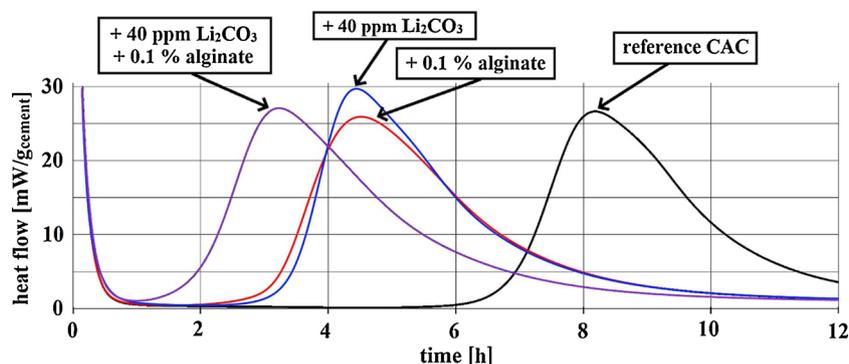


Fig. 4. Accelerating properties of a lithium salt, alginate XEA 5036 and a combination of both on CAC (Secar 71), as determined via heat-flow calorimetry ($w/b = 0.62$).

accelerates compressive strength development by $\approx \frac{1}{2}$ hour. Demolding of the specimens (at a compressive strength $> 1 \text{ N/mm}^2$) in the presence of alginates was possible earlier compared to the reference.

For Ternal LC cement ($\approx 52\% \text{ Al}_2\text{O}_3$) similarly an increase in early strength was observed upon addition of alginate. Here the strength increase after 6 hours of curing was 75% ($9.7 \text{ N/mm}^2 \rightarrow 17.2 \text{ N/mm}^2$; see Table S-3 in supporting information). Like in Ciment Fondu, addition of the biopolymer (dosage 0.1 wt.% XEA 5036) decreased the workability of the mortar because of its viscosifying property, resulting from a strong gelation in the presence of Ca^{2+} ions as was mentioned in the introduction. This undesired effect necessitates additional treatment with a PCE superplasticizer to achieve good workability. When Li_2CO_3 is used, no such extra treatment with a superplasticizer is required.

In the CA_2 rich Secar 712 ($\approx 69\% \text{ Al}_2\text{O}_3$), which shows a long dormant period because of a surface modification of the clinker, the improvement in early strength was more pronounced. For example, after 16 hours of curing the compressive strength of the mortar was increased by 110% upon addition of 0.1 wt.% XEA 5036 alginate ($15.8 \text{ N/mm}^2 \rightarrow 33.4 \text{ N/mm}^2$; see Table 4). Moreover, after 12 hours of ageing the mortar from neat Secar 712 still had not hardened, whereas the sample containing alginate already had developed 11.5 N/mm^2 of compressive strength. This value is comparable to the strength of the neat cement after 16 h of curing, thus indicating an acceleration of about four hours.

3.5. Combination of alginate with PCE superplasticizers

Combination of alginate with PCE superplasticizer can effectively compensate the observed loss of workability owed to the water-binding and viscosifying properties of alginate. However, for PCEs has been shown before that they can induce severe retardation on calcium

aluminate cements. Though this effect is much dependent on the specific molecular structure, particularly the side chain length and charge density of the PCE. Moreover, PCEs possessing short side chains and high anionic charge have proven to be almost ineffective in CAC because of chemical absorption (intercalation) into the structure of the C-A-H phases (Plank, Keller, Andres, & Dai, 2006; Ng, Metwalli, Müller-Buschbaum, & Plank, 2013; Assis, Parr, & Hu, 2008).

Here, a PCE possessing long side chains and a low anionic charge was selected for combination with alginate XEA 5036, to offset the viscosifying effect of the biopolymer. As can be seen from Table 4 this PCE effectively restores the fluidity of CAC pastes treated with alginate. Moreover, the retarding effect of the PCE is well compensated by the alginate. Similar results were obtained in other CAC samples.

Thus, this series of tests allows to conclude that CAC paste of high fluidity can be obtained even when alginate is used as accelerator.

4. Mechanistic study

The unexpected accelerating behaviour of alginate which moreover seems to be specific for CAC cements prompted an investigation into the mechanism underlying this effect. As a first step, a study was conducted by analysing the pore solution of the CAC in order to examine the influence of alginates on the ion concentrations shortly after preparing the cement paste.

4.1. Interaction of alginate with ions present in CAC pore solution

As mentioned in the introduction, alginates can interact with a variety of cations. Especially divalent cations such as Ca^{2+} are strongly complexed by the GG blocks of the alginate, leading to an ionotropic gelation. Alginate also shows a strong complexation with Sr^{2+} and Ba^{2+} , while on the other hand Mg^{2+} produces a weak gelation because

Table 4

Mortar properties for Secar 712 ($w/b = 0.5$) after 16 h of hydration, with and without addition of alginate XEA 5036 and in combination with PCE superplasticizer 114PC6.

Secar 712 16 h of curing	Reference	+ Alginate 0.1 %	+ PCE 0.02 % + Alginate 0.1 %	+ PCE 0.02 %
compressive strength (N/mm^2)	15.8 ± 1.5	33.4 ± 1.6 → 110 % increase	36.9 ± 1.3 → 135 % increase	5.2 ± 1.1 → 70 % decrease
tensile strength (N/mm^2)	2.1 ± 0.3	4.4 ± 0.4 → 110 % increase	4.4 ± 0.4 → 110 % increase	0.8 ± 0.2 → 65 % decrease
mortar density (g/L)	2240 ± 10	$2,230 \pm 5$	$2,290 \pm 10$	$2,300 \pm 5$
spread flow (cm)	19.7 ± 0.1	17.8 ± 0.2	21.3 ± 0.1	24.0 ± 0.1

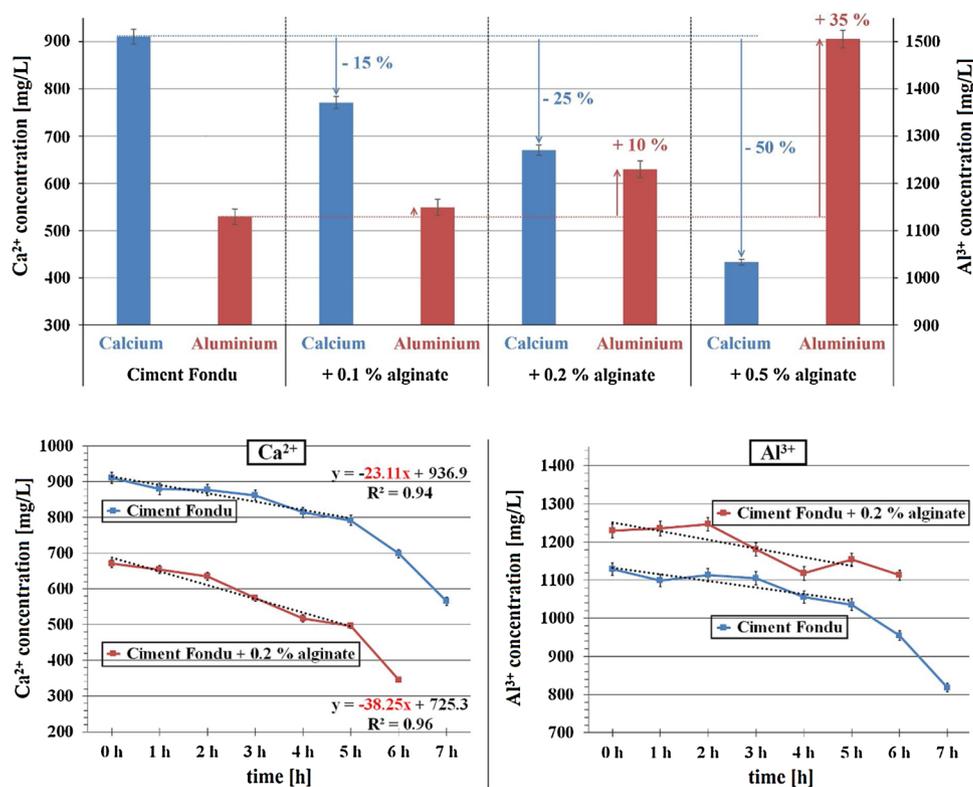


Fig. 5. Top: Ion concentrations of Ca^{2+} and Al^{3+} dissolved in the pore solution of Ciment Fondu ($w/b = 0.5$), treated without and with increasing dosages of alginate XEA 5036, as determined by ICP-OES; Bottom: Time dependent ion concentrations of Ca^{2+} (left) and Al^{3+} (right) in the pore solution of Ciment Fondu ($w/b = 0.5$), in the absence and presence of 0.2 wt.% alginate XEA 5036, determined via ICP-OES.

only a diffuse bonding takes place between magnesium and the alginate (Topuz, Henke, Richtering, & Groll, 2012).

According to Mignon et al. (2016), when sodium alginates are dissolved in ordinary portland cement paste, about 85 % of the sodium will be exchanged against calcium, leading to the formation of a viscous hydrogel. In our study, likewise an uptake of Ca^{2+} from pore solution of CAC (Ciment Fondu) upon addition of 0.1 wt.% alginate XEA 5036 was detected, whereby the concentration of Ca^{2+} in the CAC pore solution is decreased by 15 % compared to the neat cement paste (Fig. 5, top). At higher alginate dosages the Ca^{2+} binding capacity becomes even more pronounced and increases to 50 % of the free calcium which is removed from the solution. Such a strong reduction and complexation of the Ca^{2+} ion concentration normally comes with a strong retardation, such as is well-known from trisodium citrate or Rochelle salt. Hence it is most surprising that alginate, inspite of its pronounced calcium complexation ability as is demonstrated here, acts as an accelerator, and not as a retarder.

Theoretically, complexation of Fe^{3+} or Al^{3+} ions by the carboxylate groups present in the alginate is also possible, but because of the alkaline pH (≈ 12) in CAC pore solution those ions will form either $[\text{Al}(\text{OH})_4]$ or insoluble hydroxides (e.g. $\text{Fe}(\text{OH})_3$). As such, an interaction with the negatively charged carboxylate groups is unlikely. Interestingly, the Ca^{2+} chelating effect of the alginate fosters an increase in the concentration of Al^{3+} in the pore solution. The increased solubility of Al^{3+} can be explained by the decreased Ca^{2+} concentration, which promotes the dissolution of the aluminate from the clinker and might this way promote favourable conditions for the earlier formation of CAH phases.

This analysis signifies that if the accelerating effect of the alginate would increase with higher dosage, then its strong calcium complexing ability which favours the dissolution of the aluminate phases would be the key property responsible for its accelerating effect. However, the accelerating effect reaches a plateau at about 0.1 wt.% dosage and increases only marginally at higher dosages. Hence, an influence of the alginate on the solubility and dissolution of the clinker as it is proposed for lithium compounds can be excluded and does not present the

mechanism behind its unusual accelerating effect. Furthermore, lithium carbonate, the classical CAC accelerator, was found to increase the concentration of both calcium and aluminium ions in the pore solution of CAC paste simultaneously by 5–10 % (Li_2CO_3 dosage of 25–100 ppm), thus signifying that lithium compounds work according to a completely different mechanism of acceleration, compared to alginate.

To further study the ion binding capability of alginate, the time dependent evolution of the Ca^{2+} concentration in cement paste with and without 0.2 wt.% of alginate was assessed (Fig. 5, bottom). Here, a gradual decrease of Ca^{2+} concentration with time was observed for both systems, but the decline was much more pronounced when alginate was present. In the presence of the biopolymer, the amount of free calcium in solution decreases considerably faster than in the neat cement. This implies an earlier formation of C-A-H phases which is consistent with the calorimetric tests (Fig. 2) and the results on strength development (Table 4). On the other hand, in the presence of alginate the concentration of aluminium ions is substantially higher than in the neat cement, thus confirming its increased solubility in the presence of alginate.

4.2. Interaction of alginate with common retarders

This reduction in Ca^{2+} ion concentration in pore solution as described above is most surprising for an accelerator, as this behaviour is characteristic for retardation. Therefore, the question arose how alginate would behave in combination with known retarders. Here, it would be expected to find an increased retardation as the amount of free calcium would be reduced severely by the combined calcium complexing ability. To investigate, combinations of alginate with Na_3 -citrate and KNa -tartrate were tested. The calorimetric results are displayed in Fig. 6 (top).

At first it becomes obvious that in CAC citrate and tartrate develop their well-known retarding effect. However, when combined with them, alginate still accelerates and is able to not only compensate their retarding effect, but even produce a significant acceleration, inspite of the

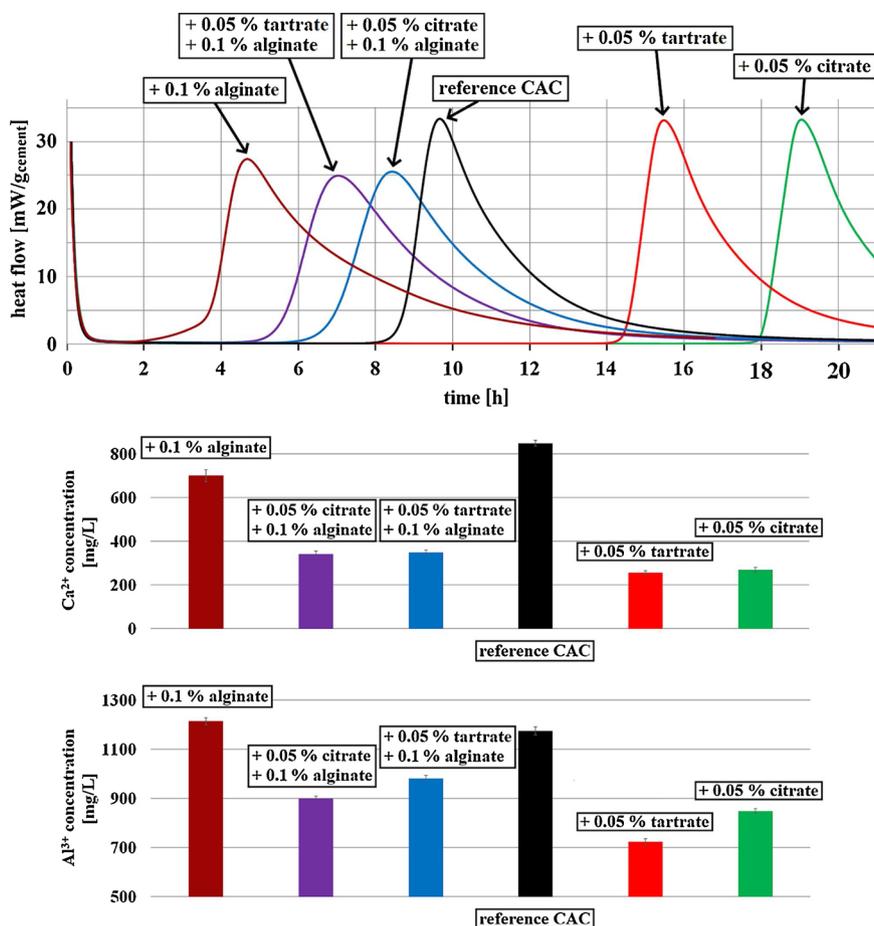


Fig. 6. Comparison of heat release and development of Ca^{2+} and Al^{3+} ion concentrations in CAC pore solution (Secar 51, w/b = 0.5, in the presence of the citrate and tartrate retarders, alginate XEA 5036 and combinations thereof), as determined by ICP-OES.

free calcium concentration in the pore solution being even substantially lower ($\approx 40\%$ of the amount present in the neat cement paste) than in the presence of the alginate only (Fig. 6, bottom). Furthermore, the amount of aluminium ions in the pore solution was also reduced upon presence of the retarders in the CAC paste. Therefore should be expected that for the observed free ion concentrations of Ca^{2+} and Al^{3+} , the crystallisation of the CAH phases from the pore solution to be less favourable and result in a retardation.

Based upon these findings the question arises whether the decreased Ca^{2+} and Al^{3+} concentrations in fact accelerate the formation of C-A-H phases.

5. Conclusion

Our study demonstrates that alginates present a novel accelerator for aluminate cements, as is evidenced by heat-flow calorimetry and strength tests of mortar samples. Addition of this biopolymer seems to shorten the dormant period and therefore shifts the beginning of the hydration reaction to earlier times and results in noticeably higher early strengths. In comparison to lithium salts such as Li_2CO_3 , alginate requires higher dosages and the addition of a superplasticizer to counteract its viscousifying effect. Moreover, a combination of alginate with lithium salts presents a viable option to reduce the consumption of precious lithium compounds in construction.

A first mechanistic study revealed that alginates reduce the concentration of free calcium ions present in the pore solution up to 50%. This effect is owed to the well-known high calcium complexing ability of alginates as described by the “egg box” model. This result is most remarkable, because a chelation of Ca^{2+} is characteristic for common cement retarders. On the other hand, lithium compounds were found to

increase the calcium as well as the aluminium ion concentrations which is caused by increased dissolution of the clinker. The experiments on alginates however clearly suggest, that the accelerating mechanism of lithium compounds does not apply to alginates. Consequently, a completely different mechanism is at work when alginates are added to CAC.

In future studies, further investigations on the accelerating mechanism involving XRD and solid state ^{27}Al MAS NMR spectroscopy are planned in order to observe the formation of the hydrate phases under these unusual conditions.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: <https://doi.org/10.1016/j.carbpol.2020.116038>.

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