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**Conference Paper****Author(s):**

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**Publication date:**

2022-07

**Permanent link:**

<https://doi.org/10.3929/ethz-b-000426814>

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# **BLENDED CALCIUM ALUMINATE CEMENTS FOR DIGITAL FABRICATION WITH CONCRETE**

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**SUMMARY:** Calcium Aluminate Cements (CACs) are often used as accelerators for Portland cement (PC). In addition to the construction applications for which CACs are normally used, digital fabrication could benefit from CACs as accelerators for achieving the desired strength build-up. In particular, a recent study showed that CACs can be effectively used as an accelerator for PC hydration for the purpose of layered extrusion. The present study attempts to determine if CAC blended with a calcium sulfate (C\$) source could be a better alternative than using CAC alone. For this, studies of the progress of hydration, the effect of acceleration and the associated microstructure development were performed on the binary CAC-C\$ mixes both in presence and absence of retarder. It was found that such systems can have considerably long induction periods when retarded with sodium gluconate. Also, similar rates of strength build-up can be obtained, irrespective of whether CAC-C\$ or CAC alone is used as the accelerator. However, the former offers an extra degree of freedom to vary the dosage, without running the risk of causing sulfate depletion.

**Keywords:** Accelerator, blended CAC, layered extrusion, microstructure.

## **INTRODUCTION**

Over recent years, concrete technology has seen the rapid advent of novel digital fabrication techniques. Such processes offer lots of advantages over conventional construction methods - reduced material waste and labour costs, and increased workspace safety to name a few <sup>[1]</sup>. 3D printing by layered extrusion with concrete is a subset of digital fabrication, and in recent years, this field has seen a rapid increase in interest for research, with a lot of groups around the world working on it <sup>[2,3,4,5]</sup>. 3D printing essentially means extruding layers of cement paste, mortar or concrete with the help of a mobile nozzle to facilitate construction without formworks, thereby greatly reducing costs <sup>[5]</sup>. This requires the material to have a long enough open time and thus be fluid enough initially to be processable. However, after the material is extruded out of the nozzle, hydration needs to take place, so that a particular extruded layer can withstand the load of the upper layers, in addition to its own weight <sup>[1,5]</sup>. With regard to achieving the desired strength build-up, the idea is to accelerate the hydration of Portland Cement (PC), and the reviews by Reiter et al. <sup>[1]</sup> and Marchon et al. <sup>[6]</sup> present various solutions, including accelerators and admixtures, as well as process related issues.

Calcium Aluminate Cements (CACs), owing to their rapid hardening properties, have enormous potential to be used as an accelerator for digital fabrication processes, especially for layered extrusion. CACs are already being widely used as an accelerator for PC for applications such as self-levelling compounds, tile adhesive and grouts <sup>[7,8]</sup>. The fact that CAC can be

effectively used as an accelerator for PC for the purpose of layered extrusion was substantiated in a recent study by the present authors [9]. That study involved using CAC paste as an accelerator for a binary PC-C\$ mix (anhydrite was used as the C\$ source and the ratio of CAC to C\$ was 2:1 by weight). The inclusion of additional C\$ is often necessary in such systems to avoid sulfate depletion and prevent any adverse effect on the hydration of silicates [10,11]. However, if redundant sulfates are introduced in the PC, it could lead to expansion and eventually result in cracking [12]. Additionally, tailoring the rate of strength build-up in 3D printing by varying the accelerator dosage is an important goal as this allows using similar mixes for different contour lengths and can provide robustness to compositional and environmental variability. Thus, the sulfates introduced for balancing of the CAC accelerator are ideally introduced as part of the accelerator.

Another requirement is that such accelerators which are used in the form of pastes also have long enough open times along with the base mortar/concrete mix, thereby providing long open times for printing. Long open times can be achieved by using retarders. The literature mentions that gluconic, phosphoric, citric and tartaric acids, and their alkaline salts are effective retarders for CAC based systems [13,14], while for CAC-C\$, citric, tartaric and phosphoric acids have been found to be effective [15].

The goal of the present work is to achieve similar performance (long induction period of accelerator and rapid strength build-up after acceleration) using a sulfate balanced CAC accelerator for layered extrusion with a PC mortar, by comparing CAC-C\$ paste to pure CAC paste, both retarded with sodium gluconate.

## **MATERIALS AND METHODS**

The CAC used in this study was Ciment Fondu (Kerneos) with a CA content of about 40%, while anhydrite (Francis Flower) was used as the C\$ source. The accelerator mixes (in the form of pastes) were added to a PC paste prepared with CEM I 52.5R (Holcim Normo 5R, Switzerland). Sodium gluconate, indicated as SG obtained from Sigma Aldrich was used as retarder for the accelerator pastes (0.1% by weight of CAC or CAC-C\$ combination). In this way, these pastes do not react (much) before being brought into contact with the PC pastes.

The accelerator mixes with sodium gluconate were named as CAC\_0.1SG and CAC-C\$\_0.1SG while the non-retarded ones were simply called CAC and CAC-C\$. The effect of acceleration was studied on mix TR95 (95%PC+3.4%CAC+1.6%C\$ by weight). The possibility of including the C\$ either in the PC paste or in the accelerator paste (CAC-C\$ case) was also investigated, keeping the ratios between all components constant. The water to solids ratio for all the mixes was 0.38.

### **Mixing Procedure**

The cement pastes were mixed using an IKA mixer equipped with a 4-bladed propeller stirrer. The dry powder was added to the water and mixed at 500 rpm for 3 minutes. 1 hour after mixing of the PC, the accelerator mix was added to it as a paste. The relevant amount of CAC/CAC-C\$ paste was added and mixed at 500 rpm for a minute.

### **Isothermal Calorimetry**

The progress of hydration of the various accelerator mixes was studied using isothermal calorimetry, using a TAMAir calorimeter set at 23°C.

### **Hydration Stoppage**

The hydration of the accelerator mixes was stopped at different times for microstructural analysis, using the procedure by Mantellato et al. [16]. This method involved a solvent exchange with cold isopropanol (stored at -18°C). 100 mL isopropanol was used for 7-8 g cement paste. The samples were then dried with anhydrous calcium chloride (32% RH) as desiccant until further analysis.

### **XRD and SEM**

XRD and SEM analyses were carried out on hydration stopped samples for the accelerator mixes. For XRD, the samples were first ground and sieved below 20 µm size and then mounted on the sample holder using a method called Razor tamped surface [17]. The method of internal standard was followed to detect presence of amorphous phases. The internal standard used was corundum having particle size of 10 µm and it constituted 20% (w/w) of the measured powder. The amounts of amorphous phases were calculated based on the overestimated corundum amount obtained from Rietveld refinement. The measurement was done using a Bruker D8 Advance diffractometer which uses a cobalt anode for generation of X-rays. The measurement was done for 2θ values ranging from 5-80°. The software Diffrac.Eva V4.3 and Profex 3.13.0 were used for the qualitative and quantitative analyses, respectively.

The electron microscope FEI Magellan 400 was used to acquire the images, but prior to that the samples were made conductive using a Safematic CCU-010 Metal Sputter. This coated the samples with a Pt-Pd alloy having thickness of 4 nm.

### **Pore solution extraction**

The pore solution of the retarded and non-retarded CAC-C\$ mixes was extracted using centrifugation. An Allegra25R Centrifuge (Beckman Coulter) was used for this purpose and it was operated at 10000 rpm for 5 minutes at 23°C.

### **ICP-OES**

After centrifugation, pore solutions were filtered through a 0.45 µm Nylon filter (Millipore). They were then immediately diluted 10 times with 2% (w/w) nitric acid in ultrapure water (UPW) for the quantification of sulfur, potassium, magnesium, iron, sodium and silicon which were present in low concentrations. A portion of that solution was used for a further 20 times dilution, resulting in a final dilution of 1:200. This was used for quantifying the high concentration elements, namely calcium and aluminium and investigate possible high concentrations of iron and silicon. For the ICP-OES measurement, a Thermo Scientific iCAP6300 Dual View (Thermo Fisher Scientific Inc., Waltham, MA, USA) with a CETAC ASX-260 autosampler was used.

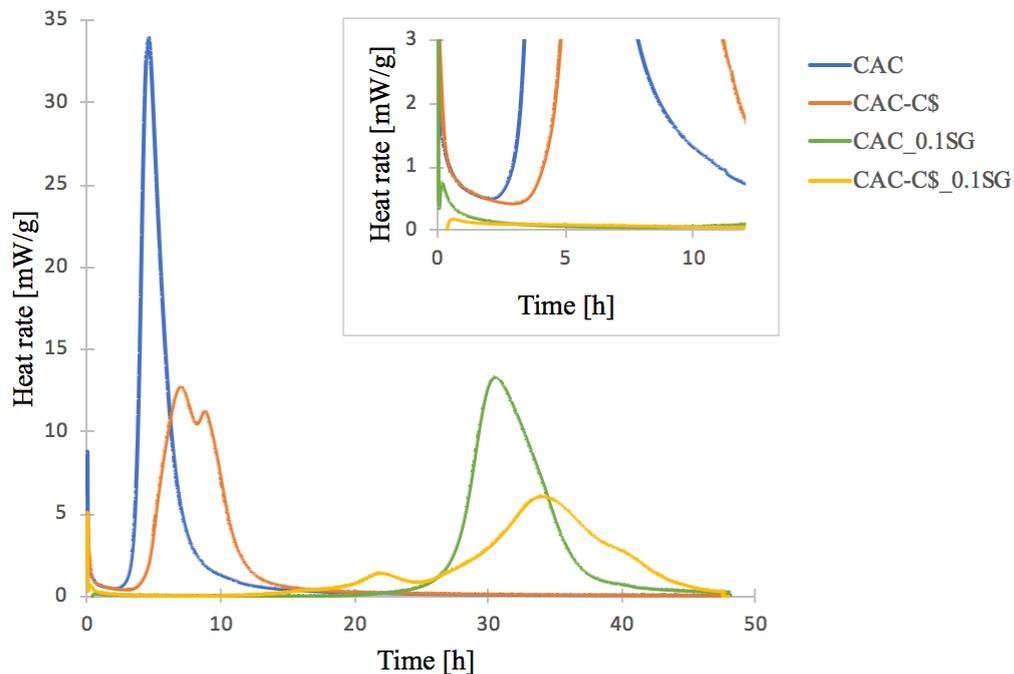
### **Rotational rheometry**

The rate of strength build-up of the two TR95 mixes was studied using a rotational rheometer Anton Paar MCR 501. A parallel serrated plate geometry was used whereby the gap between the upper and lower plates was 1 mm and their diameters being 25 mm and 50 mm, respectively. The test protocol consisted of two phases and were the same as proposed by Reiter et al. [19]. The test was started immediately after mixing the accelerator with the PC mix. First, the sample was subjected to a constant shear rate of 50 s<sup>-1</sup> (simulating processing and printing) and in the second phase, it was subjected to a shear strain oscillation of 0.0005% at a frequency of 1 Hz for 20 minutes (probing structural build-up after placing).

## RESULTS AND DISCUSSION

### Isothermal Calorimetry

Fig.1 shows the isothermal calorimetry results of the CAC and CAC-C\$ mixes both with and without sodium gluconate. It can be seen that the CAC-C\$ mixes have a longer induction period and lower peak of heat rate compared to the corresponding CAC mixes whether a retarder is present or not. Also, it can be seen that the retarded mixes have considerably longer induction periods (over 15 hours). A zoom-in image of the figure also shows that the heat rate in the induction period for the retarded mixes is significantly lower than the non-retarded ones. A lower heat rate qualitatively implies a small change of rheological properties within the induction period.



**Fig 1.** Isothermal calorimetry results of the CAC and CAC-C\$ mixes both with and without sodium gluconate

### XRD

The XRD measurements of the CAC mixes at 1 hour did not reveal the presence of any crystalline hydration product but it did show the presence of amorphous phases based on the method of internal standard followed. Table 1 shows the quantities of phases obtained from XRD measurements and Rietveld refinement of the CAC-C\$ mix at 1 hour and 4.5 hours, the latter being the time of onset of acceleration period. It also shows the quantities of phases for the CAC-C\$ mix with sodium gluconate at two different times in the induction period (1 and 7 hours). The calculated amount of the amorphous phases based on the overestimated corundum amount is also shown.

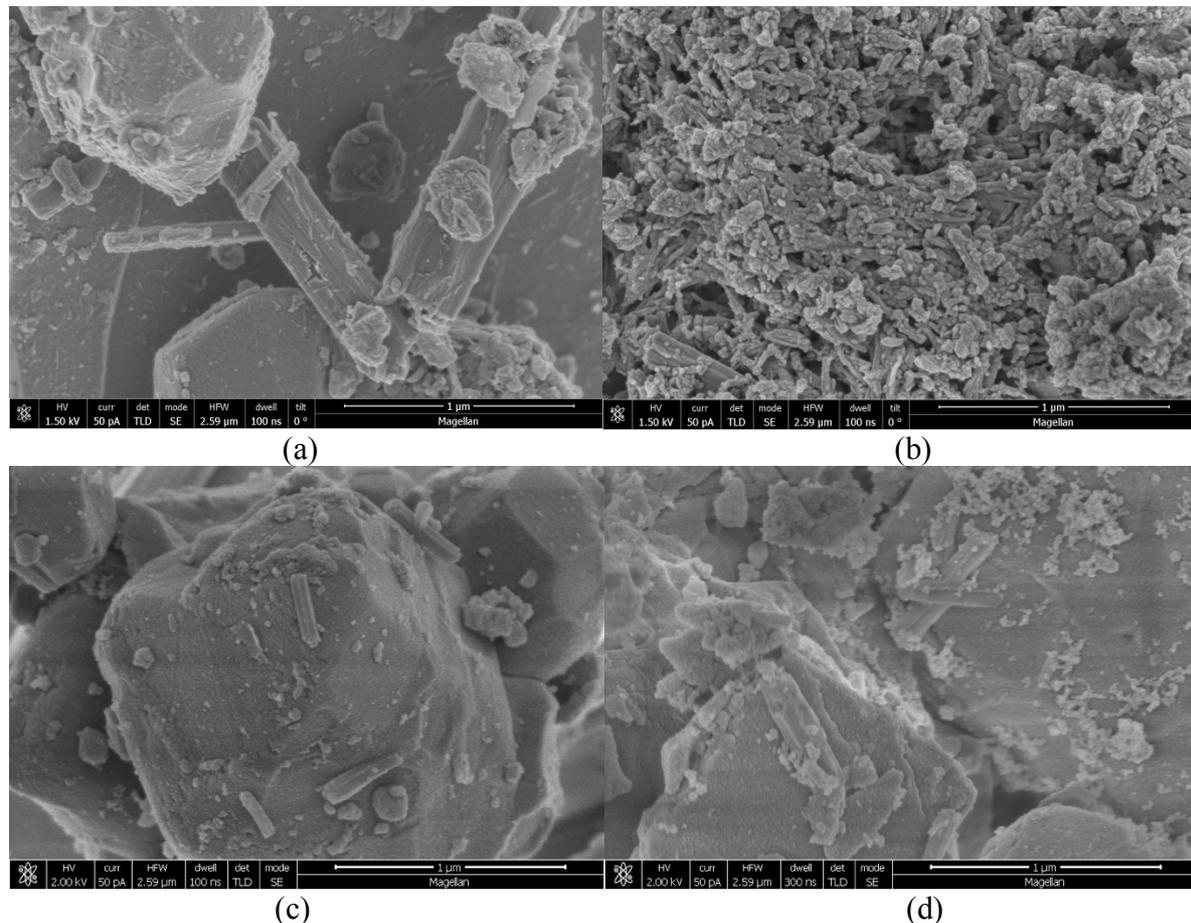
It can be seen that the amount of corundum increases for both the mixes which also implies that the amorphous content increases. The increase in amorphous content would suggest that it could be either  $CAH_{10}$  or  $AH_3$  or both precipitate during the induction period. The qualitative analysis of CAC-C\$ at 1 and 4.5 hours barely shows an increase in the ettringite (AFt) content. For CAC-C\$\_0.1SG, Rietveld refinement does not show the presence of any ettringite. However, the qualitative analysis shows the presence of ‘little’ peaks around  $2\theta$  values of 10 and 18 degrees, which are characteristic values for ettringite. The fact that the Rietveld refinement does not identify it probably is because it lies below the detection limit of 0.1%.

**Table 1:** Quantification of phases obtained from XRD measurements/Rietveld refinement

Phase	Weight [%]			
	CAC-C\$		CAC-C\$_{0.1SG}\$	
	1 hour	4.5 hours	1 hour	7 hours
CA	29.8	21.5	32.2	30.2
C <sub>12</sub> A <sub>7</sub>	1.7	1.2	2.1	1.9
C <sub>2</sub> S	3.2	5.8	3.6	3.3
C <sub>2</sub> AS	0.9	1.0	1.1	1.0
C <sub>4</sub> AF	11.0	13.6	11.5	11.1
Anhydrite	26.4	24.5	27.3	29.0
Ettringite	1.4	0.1	0.0	0.0
Corundum	25.6	32.2	22.3	23.6
Amorphous	27.4	47.4	12.6	18.9

### SEM

Fig 2. shows the SEM images of the CAC-C\$ mixes without retarder (at 1 and 4.5 hours) and with sodium gluconate (at 1 and 7 hours). Fig. 2 (a) shows the presence of ettringite crystals at 1 h, while in Fig. 2(b), such crystals are barely visible and the image is dominated by the presence of seemingly amorphous hydration products. Similar observations can be made when sodium gluconate is used as shown in Fig. (c) and (d).



**Fig 2.** SEM images with horizontal field width of 2.59  $\mu\text{m}$ . (a) CAC-C\$ at 1h; (b) CAC-C\$ at 4.5h; (c) CAC-C\$\_{0.1SG}\$ at 1h; (d) CAC-C\$\_{0.1SG}\$ at 7h

### Pore solution analysis using ICP-OES

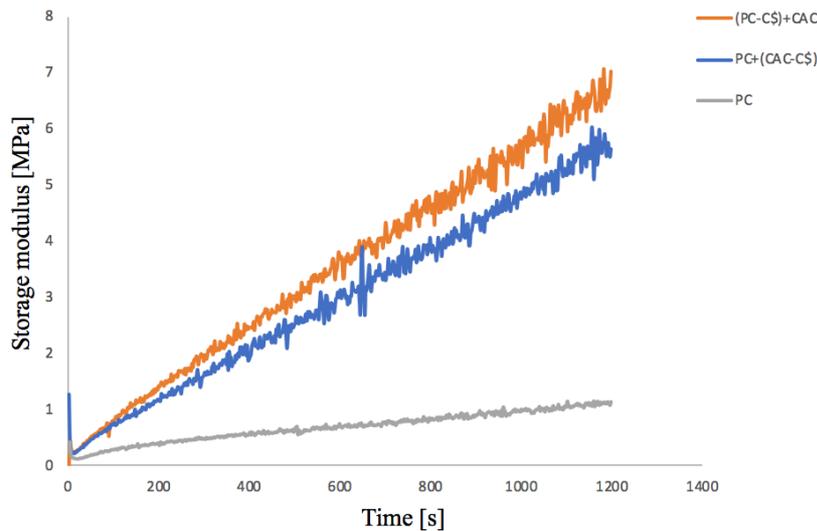
Table 2 shows the pore solution composition of the various elements for the mixes CAC-C\$ and CAC-C\$\_{0.1SG}\$ at two different times within the induction period. As can be seen, there is very little change in the composition for the various elements over time. The CAC-C\$ reaches similar pore solution composition as measured in the induction period of pure CA system (reaching curve of superficially hydroxylated CA)<sup>[20]</sup>. The pH of these systems was measured using the strips and pH meter and they either showed a value of 9 or 11, indicating respectively under and oversaturation with respect to ettringite in a GEMS thermodynamic model. Hence, the stability of ettringite at these times cannot be confirmed as it is stable only above pH of 10.5<sup>[21]</sup>.

**Table 2:** Quantification of calcium, aluminium, sulfur, iron, silicon, sodium, magnesium and potassium obtained from ICP-OES. The Limit of Detection (LOD) for magnesium is 0.9 ppb.

Element	Pore solution concentration [mM]			
	CAC-C\$		CAC-C\$ 0.1SG	
	1 hour	2 hours	1 hour	6 hours
Ca	19.71	19.61	14.11	15.20
Al	38.62	39.14	36.73	39.90
S	0.20	0.16	0.22	0.23
Fe	0.007	0.002	0.009	0.011
Si	0.007	0.022	0.016	0.007
Na	1.08	1.50	12.77	11.6
Mg	<LOD	<LOD	<LOD	0.0001
K	2.16	2.73	1.47	1.7

### Rotational Rheometry

The first phase of the testing resulted in a steady state shear stress value for both the mixes. This part of the testing essentially breaks down the structure of the material and represents the situation after the mixing and extrusion processes. The evolution of storage modulus for both the TR95 mixes and a pure PC paste without acceleration measured by small amplitude strain oscillation are shown in Fig. 3. This shows that similar rates of strength build-up are obtained, irrespective of whether CAC or CAC-C\$ is used as an accelerator. The benefit of using either of these accelerators is also evident when comparing to the PC paste in the same figure.



**Fig. 3** Evolution of storage modulus for both the TR95 mixes and pure PC paste.

The ensemble of the results presented indicates that the CAC-C\$ system can be well retarded and that its hydration path in the induction period is similar to a pure CAC system. Concerning retardation of the CAC-C\$ system, the sodium gluconate inhibits the precipitation of  $AH_3$  which is similar to what is observed in a pure CAC system<sup>[13]</sup>. The SEM and XRD results show that the amorphous hydration products precipitate during the induction period but the question whether ettringite precipitation continues or not cannot be known yet. A deeper investigation needs to be carried out concerning this. Independently from this, it can be noted that in presence of sodium gluconate, less ettringite appears to precipitate based on SEM images. This, in addition to a slowed down formation of  $AH_3$  for the retarded systems are in line with the low heat of hydration measured by isothermal calorimetry during the induction period. In short, CAC-C\$ can be well retarded by sodium gluconate and can therefore be a good starting point to be used as an accelerator for PC.

An important conclusion is that the combination of CAC-C\$ paste could be a better alternative than including the C\$ with the PC and using CAC alone as accelerator. Indeed, the calorimetry results show that such the CAC-C\$ combination can be better retarded than CAC alone. However, in terms of performance in the accelerated PC paste, both options lead to very similar rates of strength build-up. Also, it should be noted that, using CAC-C\$ as an accelerator makes it possible to vary the dosage as per process requirement without having to worry about sulfate depletion. Moreover, it also eliminates any risk of causing expansion issues due to excess sulfates in the system.

## CONCLUSIONS

This study investigated the potential of using a CAC blended with a C\$ source as an accelerator for PC. Results show that combining CAC and C\$ is a better alternative. While the rates of structural build-up are similar, the CAC-C\$ option provides for an accelerator that can better be stabilized against hydration before. Additionally, by combining CAC and C\$ together, the accelerator dosage can be varied without the risk of having an undersulfated system in which the PC hydration would be seriously compromised. The microstructural analysis shows that for CAC-C\$ systems, amorphous hydrate phases, such as  $CAH_{10}$  and/or  $AH_3$  can form during the induction period, while the stability of AFt during this time is uncertain. For the retarded CAC-C\$ systems, the slowed down precipitation of  $AH_3$  implies long induction periods with very little change in rheological properties.

## ACKNOWLEDGEMENTS

This research was supported by the NCCR Digital Fabrication, funded by the Swiss National Science Foundation. (NCCR Digital Fabrication, Agreement # 51NF40-141853). The authors would also like to thank Dr. Giulia Gelardi (PCBM, ETH Zurich) for helping in the ICP-OES measurements and the staff at the Scientific Center for Optical and Electron Microscopy (ScopeM), ETH Zurich for the help in acquiring the SEM images.

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