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Accelerating early age properties of ultra-low clinker cements for extrusion-based 3D printing

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Abstract. In this study, we investigated the influence of commercial sodium nitrate/thiocyanate accelerator compared to calcium sulfoaluminate cement addition on setting time, rheology and reaction kinetics of ultra-low clinker composite cement for extrusion-based 3D printing application. CEM I 52.5 N and a ternary composite cement with 70% clinker replaced by slag and limestone were evaluated. Results indicate that final setting time of 30 minutes and buildable yield stresses can be attained with less than 5% addition of calcium sulfoaluminate, with ettringite and C-(A)-S-H as main reaction products. This demonstrates the synergy between slag and calcium sulfoaluminate cements can be harnessed to control rheology and hardening. This is significance for evidencing suitability of ultra-low clinker composite cements for extrusion-based 3DCP, thus helping to fulfil its wider potential as a low-carbon concrete technology.

Keywords: 3D printing, low-carbon cements, admixtures, setting time, early age properties.

1   Introduction

The potential of 3DCP to revolutionize the construction industry is enormous. Despite this, application of the 3DCP by the construction industry is limited [1, 2]. Fabrication by extruding fast setting cementitious formulations is one of the most investigated 3DCP techniques [1, 3]. The technique successively deposits layers of fresh cementitious material, often mortars. These mixtures must be sufficiently workable for extrusion, and retain its shape upon deposition whilst undergoing rapid structuration and strength development to support subsequent layers without weakening the inter-layer bond strength [2, 3]. Such demanding characteristics of 3DCP cannot be achieved with conventional concrete mix design.

Mix design is a critical consideration of extrusion-based 3DCP. It controls the rheological properties which in turn determine extrudability, buildability and structu-

2

ration [4]. These are characterized in terms of static and dynamic yield stresses, thixotropy, setting time and strength evolution in the extruded material. Several parametric studies exploring relationships between constituent materials, proportioning and rheology have been reported [4-6] and reviewed in [7]. For example, Rahul *et al.* [5] investigated the effect of plasticizer dosage and viscosity modifying agents (VMA) on Portland composite cements and found that printable mixes had yield stresses ranging between 1.5 – 2.5kPa. Chaves *et al.* [8] evaluated similar parameters on limestone ternary GGBS or PFA cements. Yield stresses comparable to [5] were reported for printable mixes, but these increased proportionately as the VMA and inversely as plasticizer and SCM content. Yuan *et al.* [9] found significantly lower static yield stresses and structuration in mixes containing GGBS and PFA compared to VMAs such as nanoclay, carbonate or silica. These highlight fundamental challenges around mix design for 3DCP, i.e. overreliance on Portland cement and high cement content in mortars (typically>800 kg/m^3). One way to reduce the clinker factor is to use SCMs. However, these hydrate slowly, requiring some of acceleration to be suitable for 3D printing. The potential use of calcium aluminate and calcium sulfoaluminate cements as accelerators for regulating setting have been suggested elsewhere [10, 11] but have received limited attention in the literature.

In this study, it is investigated the feasibility of using calcium sulfoaluminate cement as an accelerator in high SCM composite cement designed for digital fabrication applications. Results are compared to those of systems produced with commercial sodium nitrate/thiocyanate accelerators.

2   Materials and Methods

2.1   Materials

Two cementitious systems, CEM I 52.5 N and ternary limestone-slag composite cement containing 70% OPC replacement, designated as C and CSL were used in this study. Commercial sodium nitrate/thiocyanate (designated Rp) or calcium sulfoaluminate cement was used as accelerator. Composition and particle size distribution (PSD) of the cementitious materials as determined by X-ray fluorescence (XRF) and laser difractometry are shown in Table 1 and Fig 1 respectively.

Table 1. Oxides composition of cement constituent materials as determined by XRF.

Constituent	SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	MgO	Na$_2$O	K$_2$O	SO$_3$	LOI*
CEM I (C)	19.4	5.1	64.9	3.1	1.1	0.1	0.6	3.1	1.9
Slag (S)	34.9	11.6	41.8	0.5	5.8	0.1	0.5	3.1	1.5
Limestone (L)	2.0	0.8	53.1	0.3	0.6	-	0.1	0.1	42.3
Anhydrite (Anhy)	2.1	0.6	38.2	0.2	1.5	-	0.2	52.3	3.7

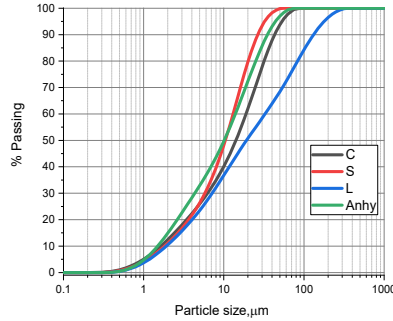*Loss on ignition (LOI) obtained as mass loss up to 950°C.

Figure1. PSD of constituent materials by laser diffraction.

2.2   Methods

Flow table and rheology measurements were used to evaluate printability of the mortar samples whilst isothermal calorimetry and setting time provided an evaluation of structuration and the microstructure. Table 2 shows the investigated mixes. In preparing the ternary cement, the slag to limestone ratio was kept at 3.8:1 and the sulfate content adjusted to 3% using natural anhydrite.

Pastes and mortar samples were made at 0.4 water to binder (w/b) ratio and 0.3% plasticizer content. A vortex mixer was used to prepare 9g paste samples for calorimetry. A planetary mixer was used to mix samples for setting, rheology and strength testing based on modified EN 196-1 procedure. The mortar samples were made with 1:2 binder:sand ratio. The plasticizer was added to the mixing water about 5 minutes before preparing the paste or mortar mix.

Table 2. Composition of investigated mixes per 100g of paste.

Mix ID	CEM I	GGBS	Anhydrite	Accelerator	Plasticizer	w/b
C	100	-	-	-	0.3	0.4
C-Rp	100	-	-	3.5[*]	0.3	0.4
CSL	30	53.5	3.5	-	0.3	0.4
CSL-Rp	30	53.5	3.5	3.5[*]	0.3	0.4
CSL-Es	30	53.5	3.5	3.5[†]	0.3	0.4

Note: [*] is SikaRapid-1 accelerator and [†] is calcium sulfoaluminate cement

The liquid accelerator or calcium sulfoaluminate powder was added to the plain mortar and mixed at high shear for 30s before the measurements. Flow table and viscometry were measured on independently prepared samples; the measurement performed within 5 minutes after the high shear mixing. Flow table was measured using an automatic jolter conforming to EN1015-3. Photographs were taken after removing the mould and after 15 jolts. A HAAKE viscometer IQ apparatus was used for rheology measurement. After placing into the 60mm diameter test container, the shear rate was linearly increased from 0.1 to 100s^{-1} in 100s and held for 5 seconds. Subsequently, the rate was decreased to 0.1s^{-1} in 100s. Static yield stress was taken as the peak stress in the shear stress versus shear rate plot whilst the Bingham model was fitted to the stabilized portion of the curve, the intercept taken as dynamic yield stress [9, 12].

Setting time was measured with an Automatic Vicat apparatus according to a modified EN 196-3 procedure but at 0.4 W/b ratio from the point of adding the accelerator.

4

3   Results and discussion

Flowability and shape retention are important parameters that govern printability of cementitious materials. The flow table test indirectly evaluates these and have been used elsewhere to assess buildability [7]. Fig 2 shows representative photographs of the fresh mortars immediately after removing the conical moulds (i.e. 0 jolts) and after 15 jolts. With the commercial accelerator, the CEM I mortar (C-Rp) retained its shape upon removal of the cone and deformed minimally after 15 jolts. For the limestone ternary blend (CSL), addition of both accelerators improved the initial shape retention compared to the plain ternary cement mortar i.e. without the added accelerator. Despite improved shape retention, significant spread was noticed upon jolting when the commercial accelerator was added (i.e. CSL-Rp).

Conversely, with the sulfoaluminate cement addition, shape retention before and after jolting was comparable to the reference C-Rp mortar.

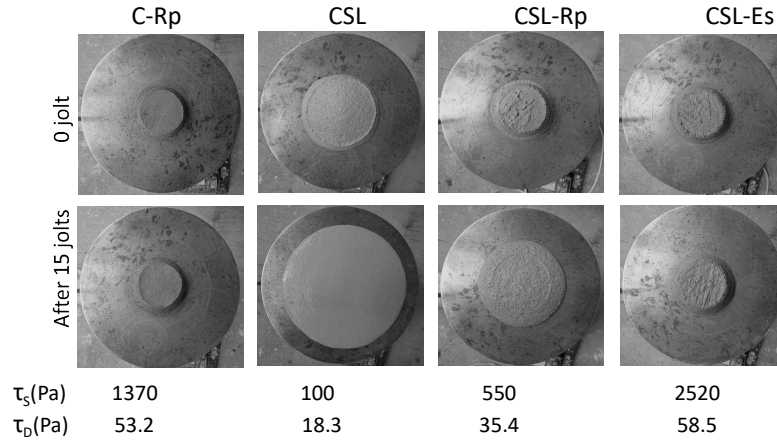|	C-Rp	CSL	CSL-Rp	CSL-Es
τ_S(Pa)	1370	100	550	2520
τ_D(Pa)	53.2	18.3	35.4	58.5

Figure 2. Photograph of flow table test showing the influence of cement and accelerator types on flowability; and yield stresses of investigated mortars.

Also summarized in Fig 2 are the rheological parameters, characterized in terms of the static (τ_S) and dynamic (τ_D) yield stresses. One must note that lower dynamic yield stresses are requisite for extrudability, but higher static yield stresses facilitate buildability. Without the added accelerator, lower static and dynamic yield stresses were observed in the plain and ternary mortars, both of which increased with the commercial accelerator but to a lesser extent in the composite cement than CEM I. For the ternary cement, flow resistance was greater in the calcium sulfoaluminate mix than the commercial accelerator. An inverse relationship between yield stresses and flowability is well established. The observed dynamic yield stresses are within the ranges reported in Yuan *et al.* [9] but an order of magnitude lower than [5], potentially due to lower w/b ratios and fibre inclusions in the latter [10]. Meanwhile, the sulfoaluminate cement improved the dynamic yield stress to comparable level as the

reference (C-Rp) but the static yield stress was higher. Based on the static yield stress ranges for printability suggested in [5], mixes C-Rp and CSL-Es can be considered buildable through extrusion-based printing.

Isothermal calorimetry (Fig 3) gives insight into kinetic factors controlling structuration. Compared to the ternary cement, more heat was generated in the CEM I pastes, implying faster structuration. The commercial accelerator shortened the dormant period in the CEM I (i.e. C-Rp), but the silicate reaction rate was comparable to the plain cement mix, C. This suggests the accelerator did not modify the silicate reaction rate significantly. However, the aluminate reaction shoulder was not seen, suggesting that its reaction plausibly preceded the silicate reaction, thus explaining the shortened dormant period. Meanwhile, the commercial accelerator did not alter onset of the silicate peak in CSL-Rp, but accelerated aluminate reactions. The sulfoaluminate cement however accelerated silicate and aluminate peaks in CSL-Es profoundly to a comparable extent to that of calcium aluminate cement on OPC, as reported in [11]. Irrespective of the cement, accelerated hydration led to lower cumulative heat at 48 hours, suggesting that overall hydration would be lower in the accelerated mixes.
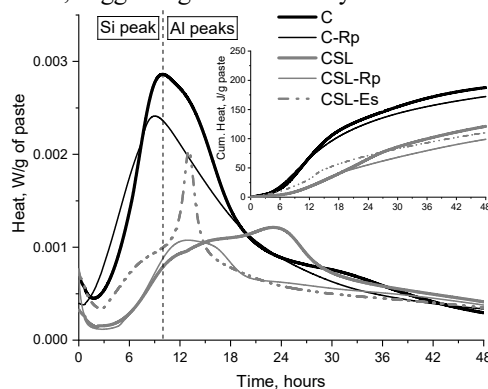

Figure 3 Effect of cement and accelerator type on heat of reaction and cumulative heat (insert)
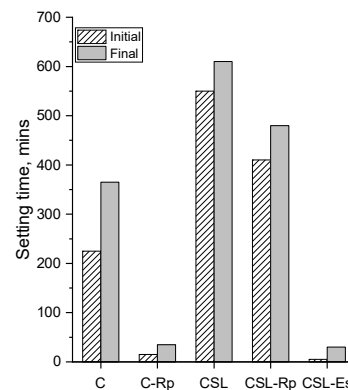

Figure 4 Effect of cement and accelerator type on setting time

Setting time provides further indication of microstructure development at early age and approximately defines the open-time during extrusion [3, 4]. The results in Fig 4 confirm faster structure build-up in both cements when an accelerator (e.g. commercial of sulfoaluminate cement) was added in the mix. The calcium sulfoaluminate-based accelerator enhanced structuration in the ternary cement more effectively than the commercial nitrate/thiocyanate accelerator.

Concluding remarks

The rheology, kinetics of hydration and setting time results showed that the commercial sodium nitrate/thiocyanate accelerator was effective in CEM I mortar, but less effective in the ternary cement mortar. In contrast, a calcium sulfoaluminate cement is a highly effective accelerator for the ternary cement mortar. These results imply that

6

small additions of calcium sulfoaluminate makes it possible to achieve printable mortars with ultra-low clinker composite cements. Further work on controlling setting time in the sulfoaluminate-ternary systems are ongoing.

References

[1] Bos F, Wolfs R, Ahmed Z, Salet T. Additive manufacturing of concrete in construction: potentials and challenges of 3D concrete printing. Virtual and Physical Prototyping. 2016;11(3):209-25.

[2] Wangler T, Lloret E, Reiter L, Hack N, Gramazio F, Kohler M, et al. Digital Concrete: Opportunities and Challenges. RILEM Technical Letters. 2016;1(0):67-75.

[3] Buswell RA, Leal de Silva WR, Jones SZ, Dirrenberger J. 3D printing using concrete extrusion: A roadmap for research. Cement and Concrete Research. 2018;112:37-49.

[4] Le TT, Austin SA, Lim S, Buswell RA, Gibb AGF, Thorpe T. Mix design and fresh properties for high-performance printing concrete. Materials and Structures. 2012;45(8):1221-32.

[5] Rahul AV, Santhanam M, Meena H, Ghani Z. 3D printable concrete: Mixture design and test methods. Cement and Concrete Composites. 2019;97:13-23.

[6] Kolawole JT, Combrinck R, Boshoff WP. Measuring the thixotropy of conventional concrete: The influence of viscosity modifying agent, superplasticiser and water. Construction and Building Materials. 2019;225:853-67.

[7] Zhang C, Nerella VN, Krishna A, Wang S, Zhang Y, Mechtcherine V, et al. Mix design concepts for 3D printable concrete: A review. Cement and Concrete Composites. 2021;122:104155.

[8] Chaves Figueiredo S, Romero Rodríguez C, Ahmed ZY, Bos DH, Xu Y, Salet TM, et al. An approach to develop printable strain hardening cementitious composites. Materials & Design. 2019;169:107651.

[9] Yuan Q, Zhou D, Li B, Huang H, Shi C. Effect of mineral admixtures on the structural build-up of cement paste. Construction and Building Materials. 2018;160:117-26.

[10] Marchon D, Kawashima S, Bessaies-Bey H, Mantellato S, Ng S. Hydration and rheology control of concrete for digital fabrication: Potential admixtures and cement chemistry. Cement and Concrete Research. 2018;112:96-110.

[11] Reiter L, Wangler T, Anton A, Flatt RJ. Setting on demand for digital concrete – Principles, measurements, chemistry, validation. Cement and Concrete Research. 2020;132:106047.

[12] Roussel N. Rheological requirements for printable concretes. Cement and Concrete Research. 2018;112:76-85.