

Effect of sulfate content on cement mixtures



D. Torréns-Martín, Lucia Fernández-Carrasco*

Department of Architectural Technology I and Center for Research in Nanoengineering, Universitat Politècnica de Catalunya, Spain

HIGHLIGHTS

- Portland cement, calcium aluminate cement and calcium sulfate mixtures were hydrated.
- We examine changes in the microstructure and dimensional variations.
- We submitted the samples at the ambient to analyze durability.
- The longitudinal change of samples was depending on the initial sulfate.
- Amorphous ettringite formation but also a later developed C-S-H gel was detected.

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ABSTRACT

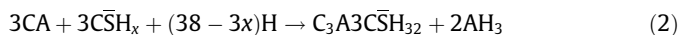
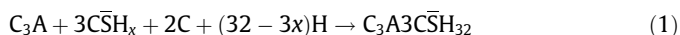
Portland cement, calcium aluminate cement and calcium sulfate mixtures were investigated to determine the influence of sulfates and the effect of curing conditions on durability. This study focused on the richest mix of Portland cement. The PC/CAC ratio was kept constant at 5.67, and different proportions of calcium sulfate were added (0%, 1%, 3%, 5% and 10%). Samples were kept at 20 °C and 97% relative humidity or immersed in water. The dimensional change and mineralogical composition of samples were evaluated. The results showed that the dimensional change of samples in the PC/CAC and PC/CAC/C \bar{S} systems depended on the amount of sulfate added and on the curing conditions. The dimensional change was associated not only with amorphous ettringite formation, but also with the subsequent formation of a C-S-H gel.

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1. Introduction

Mixtures of Portland cement (PC), calcium aluminate cement (CAC) and calcium sulfate (C \bar{S}) are used as tile adhesives and self-leveling building materials. They must be fast setting and develop early strength as well as shrinkage compensation [1]. The microstructure of these systems has been reported as very complex. However, some studies have suggested that PC/CAC and CAC/C \bar{S} ratios may be dependent on the hydration processes [2–4].

Fast setting in PC/CAC systems is produced by the reaction between aluminates from PC and sulfates (Eq. (1)), but also by the reaction with CAC aluminates (Eq. (2)).



The complexities of the mechanisms involved in these systems have been revealed by various studies [5–8], and it has been stated that these processes can be radically modified by changing the proportions of CAC or calcium sulfate. The early age hydration of these

systems would be dominated by ettringite formation. The initial proportions of PC and CAC also influence the final hydration products: it has been reported that when CAC is less than 20%, the main product that is developed is C-S-H and the alumina is as ettringite, monosulfoaluminate and/or C $_4$ AH $_x$. However, when there is less than 20% of PC, the final products are close to those of pure CAC. Outside these proportion limits, the mechanisms are not yet well defined, and C $_2$ ASH $_8$ aluminosilicates have been reported [9].

Systems comprised of CAC and C \bar{S} mixtures are used to develop dried products and fast-hardening materials [9]. The principal products are ettringite and aluminum hydroxide (Eq. (2)). When C \bar{S} has been totally consumed, CA may react with the previously formed ettringite, and monosulfate is then formed (Eq. (3)) [2].



Some papers have indicated that the type of sulfate used in the mixtures may influence the products that initially develop, since dissolution rate could be a key parameter in the morphology or spatial distribution of the hydrates: hemihydrate < gypsum < anhydrite. When sulfates, hemihydrate and gypsum (9.0 g/l and 2.4 g/l respectively) dissolve rapidly, Al $^{3+}$ ions will not dissolve well and short crystals of ettringite will form on the surface of CAC grains. In the slow dissolution scenario with anhydrite

* Corresponding author. Tel.: +34 93 401 6390; fax: +34 93 401 6426.

E-mail address: lucia.fernandez@upc.edu (L. Fernández-Carrasco).

(2.7 g/l), calcium sulfate is less soluble than calcium aluminate. The solution is poor in SO_4^{2-} and leads to the growth of long thin needles of ettringite [10].

In PC/CAC/ $\text{C}\bar{\text{S}}$ ternary systems, two mixes can be distinguished.

- A CAC/ $\text{C}\bar{\text{S}}$ richer mix with fast-hardening kinetics, self-drying capacity and volume variation control. Most self-leveling floors, high-tech tile adhesives and rapid repair mortars are based on this technology.
- A PC richer mix with a better hardening profile and shrinkage compensation. This mix can be used to repair concrete and to protect [11].

This research focused on the richer mix of Portland cement in the PC/CAC/ $\text{C}\bar{\text{S}}$ ternary system. To evaluate the dimensional change and mineralogical composition of samples, the PC/CAC ratio was kept constant at 5.67 (from previous results) and the calcium sulfate concentration was varied (0, 1, 3, 5 and 10 wt.%). Two curing conditions were selected: *wet* for samples immersed in water and *dry* for samples submitted to curing chamber conditions.

2. Materials and methodology

2.1. Materials

The materials used in this research were Portland cement type I 52.5R, Electro-land calcium aluminate cement and a commercial calcium sulfate from Algiss. The X-ray fluorescence technique (XRF) was used to determine the chemical composition of the cements (Table 1). Both cements and the calcium sulfate were analyzed by X-ray diffraction and infrared spectroscopy techniques (XRD and FTIR, respectively) to verify their mineralogical composition.

Fig. 1 shows the granulometric analysis of raw materials carried out by laser diffraction spectroscopy.

2.2. Methodology

The PC/CAC/ $\text{C}\bar{\text{S}}$ compositions are depicted in Fig. 2. In this research, the PC/CAC ratio was kept constant at 5.67, to assess the influence of sulfate content on the mixtures. The proportion of raw materials used is shown in Table 2. For the prepared pastes, the w/c ratio was kept constant at 0.4.

The expansion measurements were carried out on $25 \times 25 \times 100$ mm sized specimens. First, the raw materials were homogenized in the appropriate proportions in a mixer for 1 h at 9 rpm speed. Then, the specimens were processed by adding distilled/deionized water to the homogenized raw material and mixing for 45 s at medium speed, followed by a 10 s pause and then mixing at medium speed for another 30 s. The paste was cured for 6 h in metal molds inside a curing chamber under the following conditions: 97% of relative humidity (RH) and 20 °C. After this period, unmolded samples were cured under two different conditions: (i) in the chamber at 20 °C and 97% RH (hereafter called dry curing) and (ii) immersed in distilled water at 20 °C (wet curing). The selected ratio for the immersion was 2 ml of water per 1 g of cement paste.

We performed mineralogical and microstructural studies on samples after 6, 7, 9 h and 7 days of hydration using XRD with a PANalytical X'Pert PRO MPD diffractometer (model DY 3197), and infrared spectroscopy analysis with a Fourier transform Bomem ABB FT/IR spectrophotometer. The spectrums of the samples were registered in the region of mid-infrared ($4000\text{--}400\text{ cm}^{-1}$) with a spectral resolution of 4 cm^{-1} . The samples for FTIR were prepared using the pellets procedure (1.3 mg sample/300 KBr). The acetone/ethanol method was used [11] to prevent hydration of the samples at different ages.

3. Results and discussion

3.1. Dimensional change

The magnitude of the dimensional change (Fig. 3) was markedly different for dry cured and wet cured samples. The dimensions of

Table 1

Chemical composition of raw materials (wt.%).

	Fe ₂ O ₃	MnO	TiO ₂	CaO	K ₂ O	P ₂ O ₅	SiO ₂	Al ₂ O ₃	MgO
PC	3.50	0.04	0.22	63.25	0.75	0.06	19.56	5.04	1.96
CAC	15.50	0.02	1.68	36.54	0.05	0.09	4.83	40.55	0.50

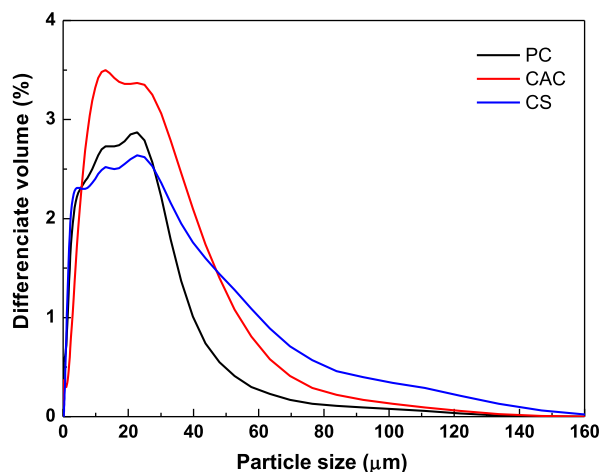


Fig. 1. Granulometric analysis of raw materials.

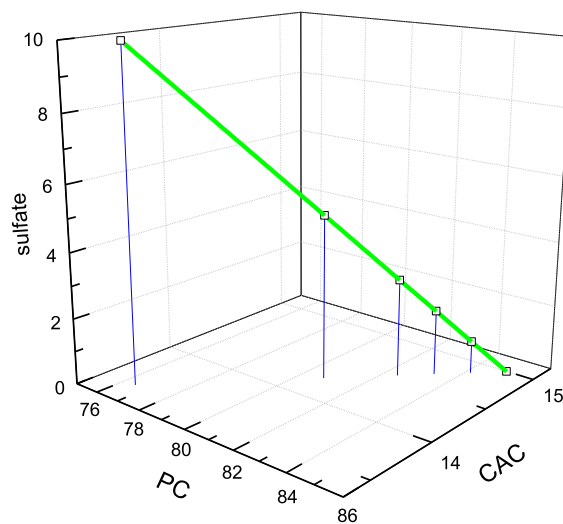


Fig. 2. Selected PC/CAC/CS compositions (%wt).

Table 2

Proportion of raw material (wt.%).

Composition	% PC	% CAC	% $\text{C}\bar{\text{S}}$
T0	85.00	15.00	0
T1	84.15	14.85	1
T2	83.30	14.70	2
T3	82.45	14.55	3
T5	80.75	14.25	5
T10	76.50	13.50	10

wet cured samples varied considerably over time. All wet samples expanded, whilst only dry cured samples with a high sulfate content (of 5% or 10%) expanded. However, the 5% sulfate dry cured sample only expanded at early ages, after which shrinkage compensation was observed. Due to the high expansion of wet samples with 10% of sulfates, measurements could not be taken after 200 h, as they were outside of the range.

Wet samples became stable, i.e. there were no further dimensional changes, earlier (almost 24 h) than dry cured samples. Dry cured samples became stable at around 72 h. This variation in behavior is a clear indication that different microstructures may be formed by the selected curing conditions (see Fig. 4).

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