



Expansion mechanisms in calcium aluminate and sulfoaluminate systems with calcium sulfate



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ABSTRACT

The long-term expansion of calcium aluminate cement and calcium sulfoaluminate cement in the presence of added gypsum has been studied for samples cured under water. Progressively higher amounts of gypsum were added to the CAC or CSA and it was found that there is a critical amount of gypsum leading to unstable expansion and failure of the samples. The microstructures of systems with gypsum additions just below and above the threshold were similar. Pore solution analyses showed that supersaturation with respect to ettringite increases with the calcium sulfate content, which results in an increase of the crystallization pressure. The supersaturation determines the minimum pore size in which crystals can grow. Therefore with higher supersaturation a larger pore volume is accessible to growing ettringite crystals exerting pressure in the porous skeleton. This could explain the critical amount of gypsum leading to high unstable expansion.

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1. Introduction

Alternative cements such as calcium aluminate cement (CAC) and calcium sulfoaluminate cement (CSA) have useful properties when developing concretes and formulated binders with tailored behaviour, for example with fast setting and hardening, or shrinkage compensation. These cements are also interesting from the perspective of lowering CO₂ emissions associated with cement production [1,2]. In particular tailored behaviour requires understanding the microstructural development to predict the properties (e.g. strength and dimensional stability).

Cementitious materials undergo volumetric changes during their hydration. The porosity is initially saturated with water but when the hydration proceeds, there is self-desiccation due to it being consumed and there can be external evaporation. This leads to capillary stresses causing macroscopic shrinkage and possibly cracking [3,4]. To overcome this, expansive cements which can compensate shrinkage are used.

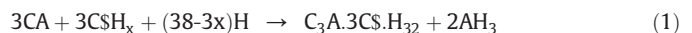
CSA and CAC blended with calcium sulfate are chemically similar. It can be considered that the reactive phase in CSAs, C₄A₃\$¹, is chemically equivalent to C\$ + 3CA (which is the reactive phase in CAC). Therefore the hydration of CAC blended with calcium sulfate and CSA is similar and both cements can be used as expansive or shrinkage compensating cements [5,6]. The kinetics of hydration and development of mechanical properties depend on the CAC:C\$ or CSA:C\$ ratio and the type of

calcium sulfate (anhydrite, hemihydrate or gypsum) [5,7]. The effect of gypsum content in CSA [8–10] and CAC [11] has already been reported, showing that the expansion increases with the gypsum content. Expansion is generally attributed to the formation of ettringite. However, there is a lack of understanding of the exact link between ettringite formation and expansion.

In this study we looked at the progressive addition of gypsum to both CAC and CSA, linking the expansive behaviour to microstructural changes, in order to better understand the underlying mechanisms of expansion.

1.1. Hydration in CAC + C\$ systems and CSA + C\$ systems

The hydration of CAC and CSA systems blended with calcium sulfate is comparable. The main phases of CAC and CSA are monocalcium aluminate (CA) and ye'elimite (C₄A₃\$), respectively. The hydration of these phases with calcium sulfate leads to the formation of ettringite and aluminium hydroxide (often poorly crystalline or amorphous), according to reactions (1) and (2).



with $x = 0$ for anhydrite, $x = 0.5$ for hemihydrate or plaster and $x = 2$ for gypsum.

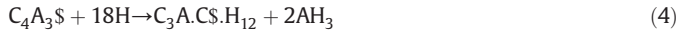
If the amount of calcium sulfate is less than that needed for all the CA or C₄A₃\$ to react according to Eqs. (1) and (2), calcium

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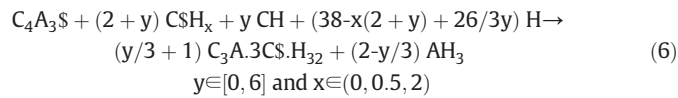
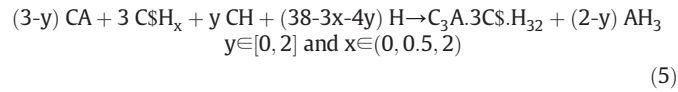
¹ \$: SO₃.

monosulfoaluminate will form after the depletion of the calcium sulfate [6]:



Rapid strength development is related to the fast hydration of monocalcium aluminate and ye'elimite. The complete reaction of ye'elimite, gypsum and water to form ettringite and aluminium hydroxide requires a high water/binder ratio (about 0.6 for 30 wt.% of calcium sulfate) [8]. In the present study the water/binder ratio of 0.4 is insufficient for complete hydration.

If calcium hydroxide is present, more ettringite can form relative to aluminium hydroxide, according to the reactions (5) and (6).



1.2. Theories of expansion

The expansive behaviour associated with ettringite formation in cement systems has been widely studied [12–17] but the mechanisms of expansion are still not fully understood. Various mechanisms implicated in external sulfate attack of cementitious materials were well reviewed by Brown and Taylor [18]. Most of their arguments have a general validity to systems in which expansion is related to ettringite formation: the main points are summarised here.

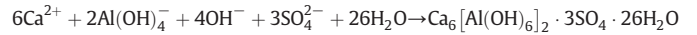
- One of the simplest ways used to explain expansion is that the precipitation of ettringite leads to an increase of solid volume [19]. However, there is a lack of evidence to link expansion directly to the amount of ettringite [20,21]. Furthermore, the formation of other hydrates, such as C–S–H, also gives an increase in solid volume, but their formation is not generally considered to be expansive.
- Mehta [14] linked expansion to the adsorption of water by colloidal sized ettringite crystals. However, he gave little theoretical support for this hypothesis. It is unlikely that crystalline ettringite would show gel-like swelling behaviour and such behaviour has never been reported for synthetic preparations of this phase. A crystalline structure cannot adsorb water molecules within the crystal lattice and therefore it cannot swell by water adsorption. Furthermore he suggested that the “colloidal” ettringite formed only in the presence of lime or calcium hydroxide, whereas expansion also occurs when lime is absent, as in the present study.
- Several authors have proposed that expansion is due to the solid state formation of ettringite around the cement grains, but the totally different crystal structure of ettringite from any of its precursors make such theories invalid [18,22].

These arguments leave the theory of crystallization pressure as the most plausible mechanism of expansion. This theory was developed and experimentally validated more than a century ago [23,24]. The first important aspect is that the crystal must grow from a supersaturated solution. The saturation index (SI) is defined by Eq. (7), if $SI = 0$ the solution is at equilibrium, if $SI < 0$ the solution is undersaturated and if $SI > 0$ the solution is supersaturated with respect to a given crystal.

$$SI = \log_{10} \left(\frac{K}{K_{sp}} \right) \quad (7)$$

Where K is the ion activity product and K_{sp} is the solubility product of a given phase.

The species forming ettringite are:



The resulting K for this phase is:

$$K = (\alpha_{\text{Ca}^{2+}})^6 \cdot (\alpha_{\text{Al}(\text{OH})_4^-})^2 \cdot (\alpha_{\text{OH}^-})^4 \cdot (\alpha_{\text{SO}_4^{2-}})^3 \cdot (\alpha_{\text{H}_2\text{O}})^{26} \quad (8)$$

and the solubility product of ettringite at 20 °C is $K_{sp} = 10^{-45.45}$ [25].

Supersaturation provides the driving force for the development of crystallization pressure (P_c) and expansion according to Eq. (9) (valid for large pores above 0.1–1 μm where size effects are negligible [26]). P_c is the maximum pressure that can be achieved with a given supersaturation.

$$P_c = \frac{RT}{v_m} \ln \left(\frac{K}{K_{sp}} \right) \quad (9)$$

Where: $R = 8.314$ J/K/mol is the gas constant, T is the absolute temperature and v_m is the molar volume of the crystal (for ettringite $v_m = 705.8$ cm³/mol using a density of 1.78 g/cm³ [27] and a molar mass of 1255 g/mol).

In the case of crystals growing in small pores, where size effects are relevant, it is important to consider the interfacial free energy of the crystal–liquid interface which is described by Eq. (10) assuming spherical pores [16]. This pressure opposes the pressure generated by the salt supersaturation. There is a film of solution of thickness δ between the crystal and the pore wall that brings ions for the crystal growth. The radius r_c of the crystal is given by $r_c = r_p - \delta$, r_p is the radius of the pore and δ is estimated to be 1–2 nm [16].

$$P_w = \gamma_{cl} K_{cl} = \gamma_{cl} \frac{2}{r_c} = \gamma_{cl} \frac{2}{r_p - \delta} \quad (10)$$

Where K_{cl} is the curvature of the crystal and γ_{cl} is the interfacial free energy between the crystal and the liquid. The interfacial free energy of salts present in cementitious materials is expected to be highly anisotropic, moreover there are no reliable data for these values. The value used in this study ($\gamma_{cl} = 0.1$ J/m²) is just an estimate previously used by other authors [17,28]. The pressure P_w which is relevant in the case of crystals or pores below 0.1–1 μm [28] and which has to be taken into account in the determination of the net crystallization pressure exerted by the crystal on the pore wall is given by Eq. (11).

$$\Delta P = P_c - P_w = \frac{RT}{v_m} \ln \left(\frac{K}{K_{sp}} \right) - \gamma_{cl} \frac{2}{r_p - \delta} \quad (11)$$

Eq. (11) combines the effects of a supersaturated crystal growing in a small pore and exerting positive pressure on it and of the curvature of the crystal–liquid interface generating a negative pressure opposing its growth resulting in a net crystallization pressure ΔP .

The equilibrium condition is described by Eq. (12) when the overall pressure is equal to 0 (valid for a spherical pore/crystal) (adapted from [29]).

$$\Delta P - P_c - P_w = 0 \quad (12)$$

From Eq. (12) the Freundlich Eq. (13) is derived [30]:

$$\frac{RT}{v_m} \ln \left(\frac{IAP}{K_{sp}} \right) = \gamma_{cl} \frac{2}{r_p - \delta} \quad (13)$$

For a given supersaturation there is a corresponding pore radius (r_p) where equilibrium conditions are met. To have crystallization pressure,

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