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X-AFm stabilization as a mechanism of bypassing conversion phenomena in calcium aluminate cements

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ABSTRACT

Phase conversion phenomena are often observed in calcium aluminate cements (CACs), when the water-rich hydrates (e.g., CAH_{10}, C_2AH_8) formed at early ages, at temperatures ≤ 30 °C, expel water in time to form more compact, less water-rich structures (C_3AH_6). The phase conversions follow a path regulated by the thermodynamic stabilities (solubilities) of phases. Based on this premise, it is proposed that conversion phenomena in CACs can be bypassed by provoking the precipitation of phases more preferred than those typically encountered along the conversion pathway. Therefore, X-AFm formation (where in this case, $X = NO_3^-$) triggered by the sequential addition of calcium nitrate ($Ca(NO_3)_2 = CN$) additives is identified as a new means of bypassing conversion. A multi-method approach comprising X-ray diffraction (XRD), thermal analytics, and evaluations of the compressive strength is applied to correlate phase balances and properties of CAC systems cured at 25 °C and 45 °C. The results highlight the absence of the C_3AH_6 phase across all systems and the curing conditions considered, with enhanced strengths being noted, when sufficient quantities of CN are added. The experimental outcomes are supported by insights gained from thermodynamic calculations which highlight thermodynamic selectivity as a means of regulating and controlling the evolutions of solid phase balances using inorganic salts in CACs, and more generally in cementing material systems.

1. Introduction and background: conversion phenomena in calcium aluminate cements

Calcium aluminate cements (CACs) are an attractive class of binders which find use when rapid strength gain, high abrasion resistance and resistance to acid attack are desirable. These binders are utilized independently, and also in combination with ordinary Portland cement (OPC) and calcium sulfates when rapid setting and shrinkage control may be desired [1]. In spite of their attractive properties, on account of their cost (i.e., $\approx 5\times$ higher than OPC), and a susceptibility to phase conversion, they remain utilized only in specialty concreting applications. The conversion phenomenon in CACs is linked to their temperature dependent progress of chemical reactions and evolutions of phase balances [2,3]. More specifically, at short times and at lower temperatures,

often ≤ 30 °C, the initial hydrates formed, i.e., CAH_{10} and C_2AH_8 (and the amorphous AH_{3-x}, where "x" denotes a variable water content[1]), undergo phase conversion to form the stable hydrates C_3AH_6 and AH_{3-x}. This phase conversion mechanism is influenced by both kinetic and thermodynamic controls such that the eventual formation of C_3AH_6 at the expense of CAH_{10} and C_2AH_8 is assured [1–3].[2] The chemical reactions that result in such phase conversions are noted in Eqs. (1a)–(3). The impacts of the conversion phenomenon are substantial as they:

- *Result in a porosity increase*: as the stable hydrates, on account of a higher density, occupy a smaller solid volume than their metastable precursors, and thus the void space (porosity) in the microstructure increases, resulting in strength reductions, and

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[1] It should be noted that the crystallinity of the AH_x phase changes over time, with an eventual microcrystalline organization being formed. This results in correspondent changes in density, solubility etc. [29].

[2] Standard cement chemistry notation is used. As per this notation: $C = CaO$, $A = Al_2O_3$, $F = Fe_2O_3$, $S = SiO_2$, $CS = CaSO_4 \cdot 2H_2O$ and $H = H_2O$.

• *Result in the release of water from the metastable hydrates*: which upon being supplied to residual anhydrous clinker, if present in excess (anhydrous form), can continue to hydrate to somewhat offset the porosity increase(s) noted above.

$$CA + 10H \rightarrow CAH_{10} \tag{1a}$$

$$2CAH_{10} \rightarrow C_2AH_8 + AH_3 + 9H \tag{1b}$$

$$2CA + 11H \rightarrow C_2AH_8 + AH_3 \tag{2a}$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \tag{2b}$$

$$3CA + 12H \rightarrow C_3AH_6 + 2AH_3 \tag{3}$$

Understandably, the effects of conversion may exert a dramatic impact on the compressive strength of CAC binders, which increases initially and then decreases to a stable value [4]. As such, if the long-term, i.e., converted strength of these materials is not considered properly, the consequences can be disastrous. While conversion-related strength loss in CACs has been known and discussed in building codes dating back to at least the 1960s, the potential for conversion was thought to be minimized so long as the CAC specimen was not exposed to: (a) elevated temperatures during curing, or (b) prolonged exposure to temperatures above 27 °C and, high relative humidity over its service-life. The collapse of three CAC-binder containing buildings in the U.K. in the 1970s raised serious concerns about the use of CACs, with the consequence that CACs were banned from use in structural construction, until newer findings lifted the ban, more recently [1–3]. Although the collapse incidents were related to factors including: improper structural design, poor mixture proportioning, and chemical attack, these incidents resulted in a loss of confidence in the use of CACs, and especially in the futility of attempting to mitigate phase conversion phenomena — an initial cause of the ban on CAC use.

While numerous efforts to bypass conversion have been attempted, success has been limited. The addition of siliceous substances (i.e., silica fume, with supporting alkali ions) resulting in the formation of strätlingite (i.e., C_2ASH_8, which also forms to a limited extent when phases such as gehlenite, C_2AS, or belite, C_2S, may be present in the anhydrous CAC) and phosphate additions have been shown to be somewhat capable of inhibiting the conversion process [5–7]. To mitigate the effects of conversion, nowadays, CACs are often proportioned at low w/c (water-to-cement ratio, mass basis), i.e., w/c ≤ 0.40 — resulting in CAC use at levels higher than would otherwise be necessary from a strength perspective — as some of the CAC remains unreacted, serving only as a *hard inclusion* in the composite. Furthermore, the design of CAC mixtures and of structural elements based on their converted strength (i.e., as approximated by testing of samples cured at 38 °C for 5 days [8]) does not exploit the attractive early-strength gain of CACs, as rather than early strength, the converted strength is used as a design parameter. Moreover, the need to design on the basis of converted strength results in inefficient cement use, due to the use (and prescription) of a lower than necessary w/c — at least from a strength perspective.

The discussion above is significant in that, while cost is certainly a crucial factor in limiting the use of CACs, the risks of conversion and the complications therein, are critical factors which have contributed to the limited usage of such materials. It is conjectured that solving the conversion problem could unlock numerous applications of CAC systems, where their other advantages may be
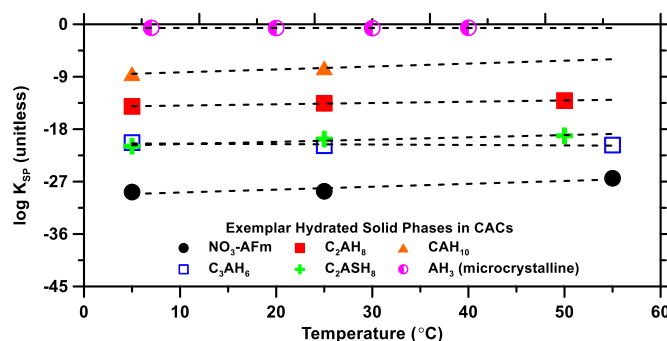

Fig. 1. The solubility constants (K_{SP}[3]) of a variety of phases relevant to hydrated CACs and for comparison, the NO_3-AFm phase, as a function of temperature [12–14]. Simple linear fittings of measured solubility data are shown as dashed lines.

beneficial. This may be especially so in a CO_2-penalized economy, where the reduced CO_2 impact of CAC production (i.e., as compared to OPC production) may offer cost efficiencies, and environmental benefits.

2. Thermodynamic selectivity: a means for bypassing phase conversions in CACs

The phase conversion process in CACs is ensured by thermodynamic considerations. Thus, while kinetic factors describe the evolution(s) of phases and their balances at short time scales, and at lower temperatures, in the limit of long time scales and at temperatures in excess of 30 °C [9], the stable (preferred) phases dominate. The phase conversion process is driven by the system's inclination to minimize its (Gibbs) free energy and achieve the most stable state. This desire to minimize free energy can be applied to discriminate preferred (and hence stable) phases from those susceptible to conversions. This suggests that manipulation of the CAC system's chemical composition to form preferred phases (i.e., as indicated by the Gibbs free energy [10,11]) whose formation is fast, i.e., not subject to kinetic restraint, would be an effective means of bypassing phase conversion phenomena in CAC systems. Fig. 1 shows solubility products (K_{sp}) of the different hydrates that may form in CAC systems.[3] Solubility data of the form noted in Figure 1 can be applied to estimate the preference for the formation of one phase, as compared to another.

Based on the reasoning above, the general mechanism of bypassing conversion as proposed and demonstrated herein is as follows. When CN is added to a CAC system, it makes available mobile NO_3^- ions to participate in chemical reactions. The presence of NO_3^- ions ensures that, in relation to the added CN dosage, a NO_3-AFm phase (but with additional AH_{3-x} and C_2ASH_8, if gehlenite

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[3] It is difficult to equitably compare K_{sp} data of the different phases as an indicator of *phase stability*, due to the different numbers of participating species involved in their formation. While one option would be to normalize the K_{sp} of a given phase by the number of ions participating in its formative reactions (as an indicator of phase stability), this choice is imperfect. However, K_{sp} data can be related to the preference, or potential for phase formation, absent any kinetic restraint, via the Gibbs free energy of reaction (ΔG_R, kJ/mol), which for a given (p,T) can be written as: $\Delta G_R = \Delta G_{PR} - \Delta G_{RE} = -RT\ln(K_{sp})$ where the subscripts PR and RE designate the product and reactant components respectively, R is the gas constant (8.314 J/K·mol), T is the thermodynamic temperature (K) and K_{sp} is the thermodynamic solubility product (unitless). Therefore, pending the presence (i.e., both abundance and activity) of suitable ion species, preferred product phases (e.g., NO_3-AFm) will form in a manner designed to minimize the overall free energy of the system, and so as to maximize the difference in free energies between the reactants and products involved in a given chemical reaction.