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Physico-chemical interaction between mineral admixtures and OPC–calcium sulfoaluminate (CSA) cements and its influence on early-age expansion

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ABSTRACT

The present study aims at examining the physico-chemical factors influencing the expansion characteristics of OPC–CSA blend in the presence of mineral admixtures. Three different admixtures: Class 'F' fly ash ('F'FA), Class 'C' fly ash ('C'FA) and silica fume (SF) were used as 15%, 15% and 5% replacement of total cementitious binder. Longitudinal expansion of cement pastes prepared at w/cm – 0.44 showed that the Class 'F'FA increased the expansion whereas the Class 'C'FA and SF reduced the expansion. The pore solution of the OPC–CSA cement pastes was extracted at different ages to monitor the concentration of various ionic species. The saturation level of ettringite was determined using a geochemical modeling program (GEMS). Furthermore, an upper bound of crystallization stress was estimated. The expansion behavior in the presence of Class 'F'FA and SF was found to be influenced by the changes in the stiffness, whereas the expansion of the Class 'C'FA-based mixture was governed by faster hydration of ye'elimite.

1. Introduction

Calcium sulfoaluminate (CSA) cements were originally developed and promoted as shrinkage-compensating cements [1]. Different combinations of CSA cements with ordinary Portland cement (OPC) have been used for various structural applications [2]. In structural concrete, the presence of restraint can fully or partially prevent the expansion of OPC–CSA concrete, which leads to the development of compressive stress that can be utilized to counteract the tensile stress developed due to drying shrinkage. Recently, there has been a tremendous increase in the research of CSA cements as its manufacturing is supposed to be more sustainable than that of the Portland cement. CSA clinkers can be produced at lower kiln temperature (~1250 °C) which reduces energy consumption considerably [3–6]. The limestone requirement is lower for producing CSA clinkers, which reduces the associated CO_2 emission. Additionally, CSA clinkers require less energy for grinding as they are more porous than the Portland cement clinker [7,8]. These factors contribute toward reducing the energy demand and carbon footprint of CSA cements. Ye'elimite ($C_4A_3\hat{S}$) is the main phase present in CSA cements along with other phases such as belite (C_2S), calcium sulfate ($C\hat{S}$) and ferrite (C_4AF) in $CaO–Al_2O_3–SiO_2–Fe_2O_3–SO_3$ system [7,8]. Based on the amount of added gypsum, various kinds of cements, ranging from rapid-hardening to expansive, can be produced [9]. The main hydration reactions associated with ye'elimite hydration are shown below [10]:

$$C_4A_3\hat{S} + 18H \rightarrow C_3A.C\hat{S}.12H + 2AH_3 \quad (1)$$

$$C_4A_3\hat{S} + 2C\hat{S}H_2 + 34H \rightarrow C_3A.3C\hat{S}.32H + 2AH_3 \quad (2)$$

$$C_4A_3\hat{S} + 6CH + 8C\hat{S}H_2 + 74H \rightarrow 3C_3A.3C\hat{S}.32H + 2AH_3 \quad (3)$$

where $C = CaO$, $A = Al_2O_3$, $S = SiO_2$, $\hat{S} = SO_3$, $H = H_2O$ according to the cement chemistry notation. According to reaction (1), it is evident that the hydration of ye'elimite in pure water forms AFm (monosulfate) and amorphous aluminum hydroxide. When there is sufficient sulfate in form of gypsum or anhydrite, ettringite (AFt) will be formed instead of monosulfate, according to reaction (2) [8,11]. However, a few studies have reported the formation of ettringite even in the absence of a sulfate source [12,13]. Furthermore, reaction (3) is favored over reaction (2) in the presence of portlandite. An increase in portlandite amount has been found to increase the rate of ye'elimite hydration at very early-age and decrease the induction period [14]. According to Mehta [15], the presence of portlandite results in the precipitation of smaller ettringite crystals which tend to be expansive due to their swelling characteristics. Among various proposed mechanisms of expansion, crystallization stress theory is a widely accepted mechanism according to which crystals grow from a supersaturated solution [16–18]. The upper bound of

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crystallization pressure, as set by supersaturation, can be expressed as [19]:

$$\sigma_C = \frac{RT}{\nu_m} \ln\left(\frac{K}{K_{sp}}\right) \quad (1)$$

where R, T, ν_m, K and K_{sp} are ideal gas constant (8.314 J/K/mol), absolute temperature (°K), molar volume, ion activity product and solubility product of a given crystal, respectively. Supersaturation governs the size of pores where crystals can precipitate [17]. For example, smaller crystals have higher surface energy which increases their solubility. Therefore, smaller crystals can only achieve equilibrium with a solution of higher concentration. Hence, supersaturation can be related to the pore sizes where precipitation of crystal occurs according to Freundlich equation [20]:

$$\gamma_{CL}\kappa_{CL} = \frac{RT}{\nu_m} \ln\left(\frac{K}{K_{sp}}\right) \quad (2)$$

where γ_{CL} and κ_{CL} are the interfacial free energy and the curvature of crystal, respectively. The expression shows that crystals will precipitate in pores with higher curvature (i.e. smaller pore size) if the supersaturation is high. In fact, in a related study on delayed ettringite formation (DEF), it has been argued that the initial expansion takes place due to crystallization in nanometric pores under high supersaturation [18].

Understanding the expansion characteristics of CSA cements is important for achieving shrinkage-compensation successfully. A number of factors have been shown to affect the early-age expansion behavior of CSA cements including the degree of hydration of $C_4A_3\hat{S}$ [21], $C\hat{S}/C_4A_3\hat{S}$ ratio [22,23], presence of lime [15,24–27], particle size distribution of CSA cements [23,28], curing condition [29] and curing temperature [21]. As CSA cements can expand significantly on its own, the expansion can be controlled by blending it with the Portland cement. A blend of CSA cement and the Portland cement (OPC–CSA blend) is also called Type K cement [30]. In an OPC–CSA blend with low CSA cement content (less than 30%), hydration of ye'elimite occurs in the presence of lime (free lime and portlandite) and forms ettringite [31]. In a study by Le Saoût et al., a 10% CSA cement addition to OPC was reported not to affect the hydration mechanism of alite but retarded the C_3A reaction due to the presence of sulfates, and increased the amount of ettringite [32]. In a study by Mehta [15], ettringite was reported to have smaller size in the presence of lime, whereas Kurdoski and Thiel [25] did not observe any difference in the ettringite morphology.

Incorporating mineral admixtures with CSA cements is expected to have some economic and environmental benefits. Additionally, the use of mineral admixtures such as fly ash is expected to result in improved workability, reduced heat of hydration, higher ultimate strength and increased chemical resistance [33–35]. However, there have been very few studies toward understanding the expansion potential of Type K cement (OPC–CSA blend) in the presence of mineral admixtures and insufficient research is limiting practical application [36,37]. Lobo and Cohen [36] reported a decrease in expansion of Type K cement incorporating silica fume which was attributed to reduced pH of pore solution resulting in a slower reaction rate of ye'elimite. In a recent study by García-Maté et al. [33], no evidence of the interaction between fly ash and CSA cement hydration was found. This study examines the early-age unrestrained expansion of OPC–CSA cements in the presence of two types of fly ashes (Class 'C' and 'F') and silica fume. To better understand the influence of these admixtures while preventing the dilution of CSA cement, a fixed quantity of expansive component (15% by weight of total cementitious material) was used in this study. Physical changes, such as evolution of stiffness with time, and chemical changes, such as concentration of various ionic species in pore fluid, supersaturation levels of various phases such as ettringite and portlandite, and hydration of ye'elimite were monitored to understand the expansion characteristics. Furthermore, crystallization stresses in OPC–CSA cements were estimated using various models. It is believed that better understanding of expansion behavior in the presence of mineral admixtures is warranted as it can help the end user in making better predictions.

2. Materials and mixture proportions

The materials used in this study were a Type I ordinary Portland cement (OPC), a CSA-based expansive admixture manufactured by CTS company (trade name Komponent), Class 'C' fly ash ('C'FA), Class 'F' fly ash ('F'FA) and silica fume (SF). Table 1 shows the oxide composition of all raw materials. The phase composition of raw materials was determined using quantitative X-ray diffraction (QXRD) analysis, and is shown in Table 2.

Cement paste samples were prepared with a constant water-to-cementitious material ratio (w/cm) of 0.44 at 22 °C. A portion of the Portland cement was replaced by the CSA-based expansive admixture (Komponent) and one of the mineral admixtures ('C'FA or 'F'FA or SF). Komponent, Class 'C'FA, Class 'F'FA, and SF were used as 15%, 15%, 15% and 5% replacement (by mass) of the total cementitious material, respectively. Therefore, five different mixtures: 1) 100% Portland cement (OPC), 2) 85% Portland cement and 15% Komponent (OPC + K), 3) 70% Portland cement, 15% Komponent, and 15% Class 'C'FA (OPC + K + 'C'FA), 4) 70% Portland cement, 15% Komponent, 15% Class 'F'FA (OPC + K + 'F'FA), and 5) 80% Portland cement, 15% Komponent, and 5% silica fume (OPC + K + SF) were examined in this study.

3. Experimental methods

3.1. Unrestrained deformation at early-age

As the primary goal of this study was to examine the early-age expansion characteristics, it was important to select a test method which allows length measurements at the early-age (within 24 h). Considering the fact that ettringite starts forming immediately after mixing, but does not contribute to the stress build-up until a certain degree of rigidity is reached by the cement matrix [38], final setting time was chosen as the starting point for the expansion measurements. Final setting of cement pastes was determined using a Vicat needle apparatus in accordance to ASTM C191. Though primarily intended for determining autogenous shrinkage of cement paste, the corrugated tube test method, as per the ASTM C1698, was selected for expansion measurement in this study. The method is equally appropriate as the length measurements in the longitudinal direction can be made due to the least resistance offered by the corrugated tube in this direction. Also, the measurements can be started immediately after encapsulating paste in a corrugated tube. It is noted here that corrugated tube maintains a sealed curing condition inside the tube, and hence, were only used for measuring expansion occurring within the first 24 h.

In addition to the corrugated tube test, prismatic bars of size 1 in (25 mm) × 1 in (25 mm) × 11.25 in (285 mm) were prepared to determine the effects of lime water curing on the expansion measurements. Samples were demolded after 24 h, and kept in saturated lime water

Table 1
Chemical composition of raw materials.

	OPC	Komponent	'F' FA	'C' FA	SF
SiO_2	20.93	7.70	59.08	37.76	>93.0
Al_2O_3	4.45	7.00	22.43	19.43	–
Fe_2O_3	2.72	1.17	8.39	5.33	–
CaO	63.28	50.07	1.59	25.56	–
MgO	3.03	0.08	1.06	4.09	–
SO_3	2.44	26.04	0.20	2.23	–
Na_2O	0.13	0.18	0.64	1.07	–
K_2O	0.59	0.53	2.18	–	–
LOI	1.98	2.10	2.99	0.58	<6%