Retardation effect of elevated temperature on the setting of calcium sulfoaluminate cement clinker

Linglin Xu [a,b], Siyu Liu [a], Nan Li [a], Yu Peng [c], Kai Wu [a,b,*], Peiming Wang [a,b]

[a] *School of Materials Science and Engineering, Tongji University, Shanghai 201804, China*
[b] *Key Laboratory of Advanced Civil Engineering Materials (Tongji University), Ministry of Education, Shanghai 201804, China*
[c] *College of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310058, China*

HIGHLIGHTS

- The hydration of CSA clinker at 5, 20, 40 °C was characterized.
- Different from AFt, the formation amount of AH_3 increases prominently at 40 °C.
- Massive AH_3 could account for the retardation of elevated temperature on setting.

ARTICLE INFO

ABSTRACT

The hydration of calcium sulfoaluminate (CSA) clinker at 5, 20 and 40 °C was characterized by a combination of XRD, DTA-TG and ESEM analysis (also with backscattered electron imaging, BEI). Meanwhile, the setting times and compressive strength development were studied. It was interesting to notice that elevated temperature retards the setting of CSA clinker and decreases compressive strength prominently, while it promotes the hydration heat releasement and hydration degree. With the temperature rising from 5 °C to 40 °C, the amount of ettringite formed after 1 d decreases by half, but alumina gel increases by more than 4 times, accompanying with a more inhomogeneous microstructure and higher porosity. ESEM observations indicate that such massive alumina gel covers on the unreacted particles and other hydrates, which could account for the retardation of elevated temperature on the setting of CSA clinker.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Calcium sulfoaluminate (CSA) cement, which was invented by the Chinese Building Materials Academy in the 1970s, attracts a renewal in interest from both researchers and industry worldwide. It has become a potential and commercial alternative to Portland cement (PC) from aspect of their considerably environmental benefits. The fabrication of CSA cement requires less limestone [1], 150–200 °C lower calcining temperature and less electricity energy for milling than PC [2–4]. It can even fully utilize large volumes of by-products as raw materials, such as slag, phosphogypsum, red mud and even municipal solid waste incineration fly ash [5–11], and thus realizes up to 35% lower CO_2 footprint than PC. Additionally, CSA clinker can be manufactured in conventional rotary kiln systems as used for PC clinkers, and it can use bauxite with low quality, which significantly reduces the manufacturing costs relative to calcium aluminate cement [4,12]. The recent prominent progress which made in the development of CSA cement provides a way to realize a sustainable cement industry [13].

Different from Portland cement, CSA clinker principally utilizes ye'elimite ($C_4A_3\bar{S}$, also known as Klein's compound) as the primary early-age strength gaining phase and utilizes dicalcium silicate (belite, C_2S) to develop additional long-term strength [4] (cement notation is used in the text with A = Al_2O_3, C = CaO, F = Fe_2O_3, H = H_2O, S = SiO_2, $\bar{S}$ = SO_3, T = TiO_2). Typically, ye'elimite accounts for 30–70% of the total mass in commercial CSA cement [14]. Once it is contacted with water, ettringite (AFt) and alumina hydroxide (AH_3) form as hydration products, while monosulfate (AFm) forms instead once when the sulfate in the pore solution is depleted [15–19]. However, few authors state that ye'elimite can directly generate AFt at early hydration stage [20,21]. Anyway, it is well accepted that AFt contributes much to the outstanding performance of CSA cement, such as rapid strength development,

high early strength, low basicity, and good corrosion resistance to seawater and saline environments [5,22–26], enabling CSA cements successfully applied in different circumstances with variable ambient temperatures.

Besides the temperature changes from external environment (at different sites and in different seasons), the exothermic chemical reaction between cement and water also generates massive heat at early hydration stage. For instance, the inner temperature of 1.7 L of CSA cement paste which cured at 22 °C would increase by 5 °C within 1 day [27]. And such elevated temperature would exert prominent impacts on the hydration of CSA cements. Most importantly, the formed AFt would dehydrate or convert to other phase at elevated temperature. It starts to dehydrate at quite low temperatures (≈30 °C, about 50–150 °C for practical application as some water molecules are removed from its structure to form metaettringite [28]. And it converts to AFm at certain temperature, depending on the calcium sulfate/ye'elimite molar ratio (M value). It started to dehydrate at 70 °C at low M value (0.6 or 1.0), while stayed stable under the same temperature when M is 1.4 or 3.9 [29]. Our previous investigation showed that elevated curing temperature promoted the hydration of CSA cement ($M = 0.84$) at early hydration stage and decreased the proportion of AFt/AFm, especially at 40 and 80 °C, accompanying with an inhomogeneous microstructure [30].

Calcium sulfate ($C\bar{S}Hx$, x = 0, 0.5 or 2) is normally added in CSA cement clinker, aiming to stabilize the formed AFt in hydrates and to modify the mechanical properties of CSA cement. Therefore, the majority of literature focus on the impacts of calcium sulfate sources and its amount on the hydration of ye'elimite phase or CSA clinker [17,20,31–35]. It is revealed that the addition of calcium sulfate accelerates the hydration of ye'elimite and favors the formation of AFt [20], but it decreases the compressive strength prominently, especially at high dosage [17,35]. This may result from the descending of formed alumina gel, which fills empty spaces and thus improves the compaction degree of cement matrix [25]. However, as the main amorphous phase in CSA cement paste, alumina gel was given much less attention than AFt generally.

Our latest investigation indicates that the setting of CSA clinker was prominently retarded by elevated temperature, which seems difficult to be explained by the obtained knowledge from literatures. In order to address this question and fill the investigation gap, this paper works on the impacts of elevated temperature on the early hydration of CSA clinker, from aspects of both macro-properties and microstructure evolution. The setting times, compressive strength, heat evolution, hydrates assemblages and morphology of CSA clinker cured at 5 °C, 20 °C and 40 °C were systematically considered. The formation amount of AFt and alumina gel at different temperature was quantitatively determined by both DTA-TG and BEI.

2. Experimental

2.1. Raw materials

The CSA clinker was obtained from Beijixiong Special Cement Co. (China). Its chemical compositions were analyzed by X-ray fluorescence (XRF). Combined with XRD analysis, its main mineral compositions were carried out by stoichiometric calculations and the result was summarized in Table 1. The density of CSA clinker is 2.90 g/cm^3. CSA paste was prepared with a constant water to binder ratio of 0.5.

2.2. Methods

2.2.1. Sample preparation

To have a wide climate temperature coverage, 5 °C, 20 °C and 40 °C was chosen as curing temperatures. Before mixing, both CSA cement clinker and water used in this study were stored at the corresponding temperature for 2 days. Pastes were immediately cured at respective temperatures after casting, with a variation of ±1 °C and the relative humidity in each curing chamber was 60 ± 10%.

In parallel, a set of cylinders were firstly casted (Ø 35 mm × 50 mm) for XRD, DTA-TG and ESEM analysis and then broken to small pieces at the end of each aging period. Cement hydration was stopped by submerging the crushed pastes in ethanol for 7 days (the ethanol was changed every 3 days). Afterwards, the samples were dried at 40 °C and stored in a desiccator over silica gel to ensure protection against H$_2$O and CO$_2$. Prior to XRD and DTA-TG tests, the crushed pastes were grounded to a grain size of less than 70 μm.

Before backscattered electron imaging (BEI) analysis, the pre-mentioned small pieces were pre-lapped with 800# (# stands for mesh) emery papers to obtain fresh flats. Then they were impregnated with a low viscosity resin in a vacuum chamber at 0.1 bar. After the resin hardened at room temperature, the specimens were lapped by emery papers (with successively finer grit size of 240, 800, 1000, 1200, 1500 and 2000 #), and polished by water-free polycrystalline diamond suspension at grades of 9, 3, and 0.25 μm. Finally, the flat-polished specimens were ultrasonically cleaned in ethanol and carbon coated before examination in the microscope.

2.2.2. Setting time and compressive strength tests

The setting time of cement pastes were tested by Vicat apparatus under the same curing conditions as previously described. Cement pastes were casted with fixed w/c ratio (0.5). The initial setting time was determined when the Vicat needle penetrated 25 mm. The final setting time was the time when the needle made an impression on the surface of the pastes but did not penetrate.

Mortar prisms (40 mm × 40 mm × 160 mm) for compressive strengths test were prepared and measured at 1, 3 and 28 days according to ISO 679: 1989. Chinese standard sand was applied, and the cement to sand ratio was fixed at 1: 3. After 24 h of curing, samples were demoulded and wrapped with plastic film to avoid rapid water evaporation until designated ages. Finally, three specimens were tested for the calculation of average value of compressive strength. The tests were undertaken at a loading speed of 2.4 kN/s.

2.2.3. Hydration heat evolution

TAM-Air micro-calorimeter (Thermometric AB, Sweden) was employed to monitor the heat evolution during cement hydration.

Table 1
Chemical and mineralogical compositions of CSA clinker (wt.%).

Oxide	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	SO$_3$	Cl	K$_2$O	CaO	TiO$_2$	Gr$_2$O$_3$	Fe$_2$O$_3$	SrO	ZrO$_2$	MnO
Content	0.09	1.69	33.36	8.28	0.14	7.90	0.11	0.23	43.00	1.35	0.02	1.95	0.07	0.05	0.02
Minerals	C$_4$A$_3$$\bar{S}$			C$_2$S			C$_4$AF			C$_{12}$A$_7$			CT		
Content	60.28			23.67			5.93			3.65			2.30		