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Formation of ettringite in Portland cement/calcium aluminate cement/calcium sulfate ternary system hydrates at lower temperatures

Linglin Xu [a], Peiming Wang [a,b,*], Guofang Zhang [a,b]

[a] School of Materials Science and Engineering, Tongji University, Shanghai 201804, China
[b] Key Laboratory of Advanced Civil Engineering Materials, Ministry of Education, Shanghai 201804, China

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ABSTRACT

To explore the formation of ettringite at lower temperatures in the Portland cement/calcium aluminate cement/calcium sulfate ternary system hydrates, the effect of calcium sulfate variety on the setting time of the ternary system and the strength development of its mortars at 0, 5, 10 and 20 °C were investigated. The formation of ettringite was further analyzed using XRD and ESEM. The results show that, as temperature increases, both initial and final setting time are shortened and that compressive and flexural strength are enhanced. In particular, mortars with anhydrite develop higher strength between 0 and 10 °C but lower strength at 20 °C than those with hemihydrate. Further, pastes with anhydrite set faster than those with hemihydrate. It is also found that both the formation rate and amount of ettringite are sensitive to temperature and calcium sulfate variety.

1. Introduction

Formulations based on mixtures of calcium aluminate cement (CAC) and calcium sulfate (CS) are used extensively in the field of building chemistry [1]. In these systems, the initial hydrated product is ettringite which has high water content.

The formation of ettringite is associated with many factors, such as temperature [2,3], humidity [4] and CS variety [5–8]. With the correct formulation, this tendency of the ettringite to bind high capacity water can be used to produce products which are rapid drying and rapid hardening [1,9] as well as expansive or shrinkage compensating [6,8,10,11].

In practice, rapid hardening mortars are increasingly used in many applications [9,12–17] and even at temperatures below 20 °C, such as night repairs or winter constructions. However, relative to ambient temperature curing, rather less effort [7,13] has been expended in the quantification of the hydration of the Portland cement (PC)/CAC/CS ternary system and its behavior at low temperatures regimes.

Therefore, it is important and useful from the hydration behavior and microstructure development viewpoints to understand and clarify the effect of CS variety and temperature (particularly below 20 °C) on the hydration of the ternary system.

The present investigation is concerned with the hydration of the ternary system at 0, 5, 10 and 20 °C, respectively. Both setting time and compressive and flexural strength development of the mortars have been measured. In addition, XRD and ESEM were employed to identify the formation amount and morphology of ettringite.

2. Experimental

2.1. Raw materials

The PC (CEM I 42.5) and CAC (Ternal White) materials used in this study were supplied by Xinfa Cement Co. and Kerneos Cement Co. respectively. Two types of CS materials were used; natural anhydrite (labeled A) and α-hemihydrate (labeled H). The chemical composition of the raw materials used was determined by X-ray fluorescence (XRF) and is shown in Table 1 and the Rietveld quantitative phases analyses of the PC and CAC is shown as below: the content of C_3S, C_2S, C_3A, C_4AF and gypsum in PC was 64.4(1)%, 13.1(8)%, 4.7(1)%, 10.4(2)% and 4.3(7)%, respectively; the content of CA and CA_2 was 60.7(8)% and 39.2(2)%. In addition, the Blaine values of the PC, CAC, A and H was 344, 400, 387 and 412, respectively.

2.2. Mix proportions

When the CS in the binders is excessive and calcite is also present, thaumasite easily forms particularly at temperatures lower than 15 °C [18,19]. To avoid the formation of thaumasite, the content of CS added was lower than the stoichiometric amount to form ettringite. All the samples had fixed mix proportion, the PC:CAC:CS mass ratio was 77.5:15:7.5. The water/binder ratio was 0.5 by

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* Corresponding author at: School of Materials Science and Engineering, Tongji University, Shanghai 201804, China. Tel./fax: +86 21 69582140.

E-mail addresses: xulinglinok@hotmail.com (L. Xu), jwpm@126.com (P. Wang).

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Table 1
Chemical composition of raw materials determined by XRF (%).

Oxide	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	TiO_2	Loss of ignition
PC	21.50	64.20	4.14	2.40	2.57	2.89	0.84	0.67	0.32	1.67
CAC	0.34	31.20	67.10	0.10	–	0.06	–	0.34	–	0.9
A	1.72	39.44	0.35	0.16	1.80	51.96	–	–	0.02	4.15
H	1.03	38.50	0.17	0.04	0.10	53.40	0.14		0.01	6.08

mass. According to the variety of CS used, as well as the curing temperature (0, 5, 10 and 20 °C), the samples were labeled as follows: A0, A5, A10, A20 and H0, H5, H10 and H20.

2.3. Curing and testing

Water, cements, and aggregates were stored for 2 days at the respective temperatures before mixing. All the specimens were cured at 0, 5, 10 and 20 °C with a variation of ±1 °C respectively and the relative humidity was 60 ± 10%. The setting times of pastes were determined according to ASTMC191 using a Vicat apparatus at 0, 5, 10 and 20 °C. Mortar specimens (40 mm × 40 mm × 160 mm) for flexural and compressive strength testing were prepared and measured according to ISO 679:1989 and were demolded after 24 h and were randomly selected for mechanical testing after periods of 1, 3 and 28 days.

Fresh fractured surfaces were examined under the ESEM (FEI, QUANTA 200) using the low vacuum mode (at 1 Torre H_2O). The solid fractions of the pastes were crushed and ground in acetone, dried at curing temperature and then used for XRD analysis.

The XRD data of ettringite were recorded using an Rigaku-D/max2550VB3+ and the scanning was performed between 8.5° and 9.5° with a 2θ increment 0.02° per min, a dwell time of 4 s and a Cu Kα radiation (λ = 1.541 Å). In addition, an accelerating voltage of 40 kV and a current of 100 mA were selected.

2.4. Quantitative analysis of ettringite

2.4.1. Synthesis

Ettringite was synthesized according to the method described by Taylor [20]. The mixed solution was stirred continuously at 20 °C for 8 h and then was stored for 14 days until an initially precipitated gel was replaced by a crystalline material.

The precipitates were filtered from the synthesis solution and washed several times with ultrapure water and then were dried over a saturated $CaCl_2$ solution (approximately 30% relative humidity) to equilibrium condition. The XRD pattern of synthetic ettringite is shown in Fig. 1.

Table 2
Setting times of ternary system at 0, 5, 10, and 20 °C.

Sample	Setting times (min)	
	Initial	Final
A0	28	77
A5	30	45
A10	17	32
A20	14	24
H0	32	151
H5	30	77
H10	25	56
H20	20	48

2.4.2. Quantitative analysis

The amount of ettringite produced during hydration was quantitatively determined by X-ray diffraction (XRD). A mass of 5%, 10%, 15% and 20% of synthetic ettringite was evenly milled with Portland cement that was used as the external standard. The ettringite peak area was first determined using the method of numerically integrating functions fitting the peak profile obtained by XRD and then the calibration curve was plotted. The amount of ettringite formed in hydrates (“x” axis values) was determined by comparing its peak area (“y” axis values) with that of the calibration curve.

3. Results and discussion

3.1. Setting times

Setting times are of great importance to the construction industry since they directly influence the workability of mortars and

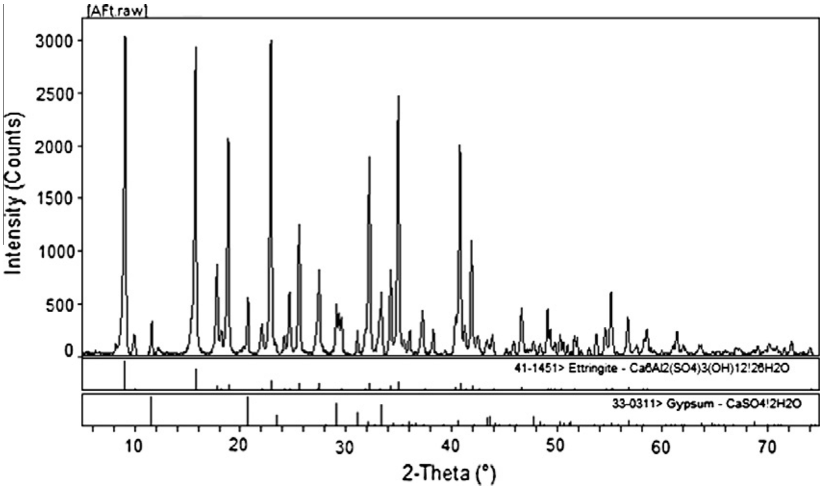

Fig. 1. XRD pattern of synthetic ettringite.