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Formation and hydraulic behavior of chromium–phosphorus doped calcium sulfoaluminate cement

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Abstract

The formation and the hydration processes of solid solutions based on calcium sulfoaluminate with chromium and phosphorus additions are studied. The synthesized solid solutions are analyzed with X-ray diffraction and infrared spectroscopy. The high concentrations of additives slow the formation of the calcium sulfoaluminate phase. The early hydration behavior is followed by Tian–Calvet calorimetry. The results show that incorporation of chromium and phosphorus in the crystal lattice of calcium sulfoaluminate induces a long induction period. The setting period in the doped sample has a higher heat output than the pure phase. Identification of the hydration products is done by differential thermal analysis (DTA). The degree of transformation of ettringite into the monosulfate is lower in the modified calcium sulfoaluminate than in the additives-free cement.

Keywords: Sulfoaluminate cement; Hydration; Ettringite; Thermal analysis; Calorimetry

1. Introduction

Cement chemistry notations are used in this paper: C = CaO, A = Al_2O_3, $\bar{S}$ = SO_3 and H = H_2O. Calcium sulfoaluminate $Ca_4Al_6SO_{16}$ ($C_4A_3\bar{S}$) is the main phase of calcium sulfoaluminate (CSA) cement. It can be synthesized at temperatures about 200 °C lower than that required for the formation of ordinary Portland cement, entails a lower grinding energy and leads to a high early strength. The $C_4A_3\bar{S}$ phase can replace tricalcium silicate C_3S, the main component of classic Portland cement, in the development of early strength [1,2]. The sulfoaluminate cement boasts a 25% energy saving and can give early strengths, as high as 35 and 60 MPa, respectively, after 1 and 28 days. It has good durability, especially in sulfate environment [3,4]. Hydration of the $C_4A_3\bar{S}$ phase is a rapid reaction, inducing formation of needle-like ettringite, $C_6A\bar{S}_3H_{32}$ crystals, which are responsible for the quick setting of the sulfoaluminate cement during the initial period of the hydration reaction.

One solution to the problem caused by toxic elements such as chromium is incorporation of these elements into cements, especially calcium aluminates, because they will be indefinitely trapped [5]. Chromium, derived from raw materials, refractories and grinding media, can affect the reactions of the clinker formation and the properties of the product. Moreover, it has been reported to lead to high early strength in Portland cement [6–9]. Murat and Sorrentino [5] showed that calcium aluminate cements easily trap large amounts of chromium with delayed setting and good strength development. It was also shown that ettringite can reduce solution concentrations of potentially hazardous elements by fixation in the crystal lattice [10].

The effect of Cr_2O_3 on the CaO–Al_2O_3–SO_3 system was investigated by Ivashchenko [11], showing that the solubility limit of chromium in calcium sulfoaluminate is 5 wt.%,

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and the formation reactions of $C_4A_3\bar{S}$ are intensified and the thermal stability at high temperature is raised. The hydration study of the modified calcium sulfoaluminate with chromium indicated an improvement of the strength properties compared to that of chromium-free $C_4A_3\bar{S}$. Chae et al. [12] studied the formation of calcium sulfoaluminate by adding calcium phosphate as $CaHPO_4 \cdot 2H_2O$ (3 wt.%). They indicated that phosphorus hinders $C_4A_3\bar{S}$ formation. In that study, 0.20 wt.% of P_2O_5 oxide was incorporated in the pure calcium sulfoaluminate phase.

The aim of the present work is to determine the effect of simultaneous additions of Cr_2O_3 and P_2O_5 on the formation and hydration of $C_4A_3\bar{S}$ by X-ray diffraction, infrared spectroscopy, isothermal heat-conduction calorimetry, and differential thermal analysis (DTA).

2. Experimental

Samples were synthesized from stoichiometric amounts of reagent grade $CaCO_3$, Al_2O_3, $CaSO_4$, Cr_2O_3 and $(NH_4)_2HPO_4$. The mixtures were ground in an agate mortar with ethanol as dispersive and homogeneity medium. The corresponding chemical compositions (wt.% oxide) are reported in Table 1. The samples were treated in a laboratory furnace at 300, 500, 800 and 1000 °C with intermediate grindings, then compacted in pellets and fired at 1100 and 1250 °C for 12 h and finally rapidly quenched in air.

Identification of the crystalline phases in the solid solutions formed at 1250 °C was performed by X-ray diffraction at room temperature with a Siemens D-5000 diffractometer with Cu Kα radiation. The sintered solid solutions were analyzed by infrared spectroscopy with a Bruker spectrometer from 400 to 3800 cm^{-1}. The powder samples (3 mg) were mixed in an agate mortar with potassium bromide KBr (300 mg) prior to pellet formation.

The hydration of the product fired at 1250 °C was followed with an isothermal Tian–Calvet calorimeter of original design, built several years ago in the Centre de Thermodynamique et de Microcalorimétrie du CNRS à Marseille. The thermopiles constituted by hundreds of chromel–alumel thermocouples are inserted in an isothermal aluminum block. The great stability of the apparatus allows very long experiments. Experimental conditions were identical for all samples. The measurements were carried out at 26 °C using a sample weight of 0.1 g. A syringe containing deionized water corresponding to the water/solid ratio (w/s) of 10 was placed in the calorimetric cell 1 h before the beginning of the hydration reaction. After 1 day, as the rate of heat output decreased significantly, the hydrated sample was removed from the calorimeter, washed with acetone, and heated at 60 °C for 3 h. The dried pastes were analyzed by a DTA of original design which allows very slow scannings in temperature up to 1800 K. The reference was an empty alumina crucible. The samples (100–200 mg) were heated at constant heating rate of 2 °C/min under air atmosphere.

Table 1
Chemical compositions (wt.% oxide) of studied starting mixtures

Samples	CaO	Al_2O_3	$CaSO_4$	Cr_2O_3	P_2O_5
S1	27.56	50.12	22.31	0.00	0.00
S2	27.49	50.06	22.09	0.12	0.23
S3	27.36	49.97	21.77	0.31	0.58
S4	27.16	49.81	21.23	0.62	1.17
S5	26.96	49.65	20.69	0.94	1.75

3. Results and discussion

3.1. High temperature mineralogy

X-ray diffraction patterns of the samples heated at 1250 °C all show the same diffraction pattern. The only identified crystalline phase is the $C_4A_3\bar{S}$ cubic polymorph. This phase is characterized by XRD peaks at $d = 3.74$, 2.65 and 2.17 Å corresponding to 2θ values at 23.8, 33.8 and 41.7 [13]. The intensities of the diffraction peaks for chromium–phosphorus doped $C_4A_3\bar{S}$ phase are higher than in the pure sample. Samples S1–S4 heated at 1100 °C showed the same mineralogical composition, essentially $C_4A_3\bar{S}$, CA and $C\bar{S}$. A decrease of the CA and $C\bar{S}$ content was observed with an increase of the concentration of Cr_2O_3 and P_2O_5. Thus, the crystalline phase $C_4A_3\bar{S}$ in the doped samples became more abundant compared to the pure sample, indicating that Cr_2O_3 and P_2O_5 oxides promote formation of the calcium sulfoaluminate mineral at 1100–1250 °C. At higher Cr_2O_3 and P_2O_5, the S5 sample shows that complete formation of calcium sulfoaluminate phase is not achieved and a small amount of the CA phase is also identified.

Formation of the cubic polymorph of calcium sulfoaluminate occurs at chromium and phosphorus contents less than 0.62 wt.% Cr_2O_3 and 1.17 wt.% P_2O_5. Beyond these concentrations, the formation of the $C_4A_3\bar{S}$ phase is delayed, and the CA phase persists. This phenomenon is mainly due to the presence of the phosphorus that hinders the chemical transformation $3CA + CaSO_4 \rightarrow C_4A_3\bar{S}$ at high temperature. By formation of solid solutions, the phosphorus enlarges the field stability of CA phase at the expense of the $C_4A_3\bar{S}$ field. This process can be compared to that shown by Chae et al. [12] who noted that additives like calcium phosphate hinder calcium sulfoaluminate crystallization at 1250 °C. On the other hand, in solid solutions of doped $C_4A_3\bar{S}$ at a high amount of additive, the presence of chromium does not influence the effect of phosphorus. In the XRD pattern, the peaks of the doped calcium sulfoaluminate occur at lower 2θ values than for the pure $C_4A_3\bar{S}$. Thus, the incorporation of the chromium and phosphorus ions in the cubic structure of calcium sulfoaluminate induces an expansion of the crystal lattice.

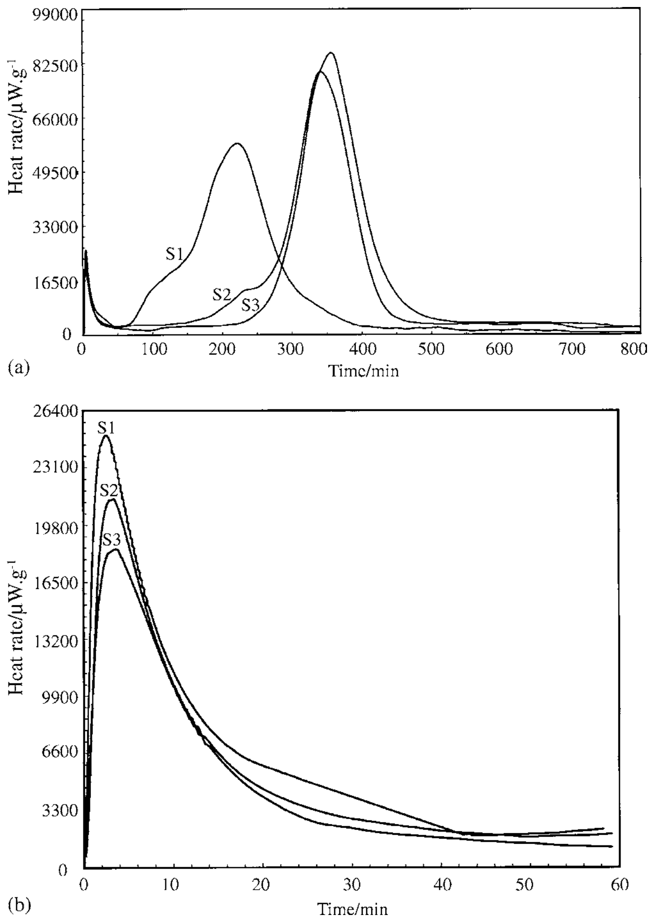

Fig. 1. (a) Hydration calorimetric curves at 26 °C with water/solid ratio = 10 of the S1–S3 samples, (b) expanded portions of the early hydration stage of the S1–S3 samples.

3.2. Infrared spectroscopy

The infrared absorption spectra of the S1–S4 products synthesized at 1250 °C show the vibration frequency of entities of pure and doped $C_4A_3\bar{S}$ that appear in the range 400–1300 cm^{-1}. [AlO$_4$] groups are identified at 411, 644, 690, 821 and 875 cm^{-1} [14,15]. Absorption bands located at 615, 663, 987, 1100, 1149 and 1195 cm^{-1} are assigned to the [SO$_4$] groups [14,15]. Shoulder absorption bands around 1025 cm^{-1}, observed only in the spectrum for the doped calcium sulfoaluminate, are attributed to P–O vibrations [16–18]. Cr_2O_3 and P_2O_5 influence the wave number and shape of the absorption bands of the [AlO$_4$] and [SO$_4$] groups in the $C_4A_3\bar{S}$ phase, indicating that chromium and phosphorus incorporation distorts the calcium sulfoaluminate lattice.

3.3. Calorimetric behavior of hydration

Hydration of the S1, S2 and S3 samples followed by heat-conduction calorimetry during 12 h following the injection of distilled water onto the anhydrous sample is shown in Fig. 1a. The early hydration stage, up to 60 min, is shown in Fig. 1b. All three samples exhibit a similar behavior, with an initial exothermic peak lasting about 1 h, a slow reaction period (from 1 to 4 h) defined as the induction period, followed by a second exothermic peak.

The sample S1 without additives shows an hydration process of pure calcium sulfoaluminate with the highest heat rate during the first minutes followed by a very short induction period which goes up to 12 min. The observed second peak due to the setting period with rising heat output exhibits a magnitude much higher than the first peak and the maximum is reached after approximately 4 h. After begins the deceleration period controlled by progressive diffusion of water into the interior of the grains.

Analysis of the calorimetric curves of chromium and phosphorus doped $C_4A_3\bar{S}$ (S2 and S3 samples) reveals that the initial heat rate is less compared with the pure $C_4A_3\bar{S}$. The maximum heat rate at 200 s decreases with increasing concentrations of the Cr_2O_3 and P_2O_5 oxides. The induction period has a very low heat rate and is longer in the case of S2 and S3. This observation agrees with previous studies which show that the addition of modifying agents to the raw calcium sulfoaluminate mixes induce an increasing induction period and thus setting time of the rapid hardening cements based on $C_4A_3\bar{S}$ [11]. This behavior is typical of an addition that is commonly described as a retarder in cement chemistry.

It has been claimed [19] that the very short induction period in the pure $C_4A_3\bar{S}$ phase is due to the very rapid reaction with water, resulting in the formation of needle-like ettringite crystals that do not cover the whole surface of the sulfoaluminate particles. The presence of impurities causes a rapid increase in the number of ions in the liquid phase and thus intensifies the ettringite formation that then covers the whole $C_4A_3\bar{S}$ surface. As a consequence, transport of Ca^{2+} and $SO_4{}^{2-}$ ions to the surface is hindered and hydration is delayed. Tashiro et al. [20] have studied the effect of Cr_2O_3 on ettringite formation; the chromium improves the crystal growth of ettringite. On the other hand, it is well known that impurities such as P_2O_5 delay the setting time of Portland cement clinker [21].

The large exotherm in the S2 and S3 samples is higher in magnitude than that of the S1 sample. The maximum heat rate for pure $C_4A_3\bar{S}$ is 57.8 mW/g, whereas for S2 and S3 doped samples it reaches 80.2 and 84.8 mW/g, respectively, indicating that reaction of the setting process is intensified in the modified calcium sulfoaluminate. In the crystal lattice, chromium ions as Cr^{6+} (ionic radius = 0.26 Å) can be located in the tetrahedral sites of aluminum ions as Al^{3+} (ionic radius = 0.39 Å) [11], leading to the distortion of the crystal structure. The coordinated oxygen ions approach the central ions and reduce the size of the coordination tetrahedra, inducing a lower stability of the crystal lattice. Thus, during hydration the [CrO$_4$] groups are more easily broken up by water molecules. As the chromium concentrations increase, the $C_4A_3\bar{S}$ crystal lattice is distorted and the reactivity increases; thus, this can explain the observed increase in the hydrating heat released during the setting period.

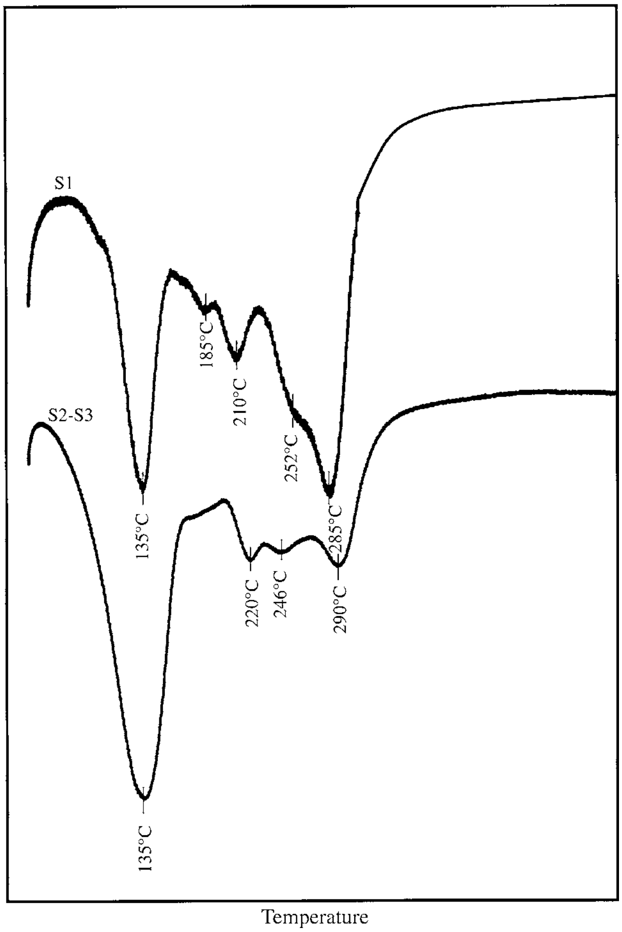

Fig. 2. DTA curves of hydrated S1–S3 samples.

3.4. *Differential thermal analysis*

The DTA patterns of selected hydrated samples are given in Fig. 2. The endothermic peak at 135 °C corresponds to the dehydration of ettringite ($C_6A\bar{S}_3H_{32}$). At 246–252 °C an endothermic effect due to the dehydration of AH_3 appears. The decomposition process of calcium monosulfate ($C_4A\bar{S}_3H_{12}$) is observed at 185, 210–220 and 285–290 °C [22]. In the chromium and phosphorus modified $C_4A_3\bar{S}$, the degree of transformation of ettringite into the monosulfate form is less compared to that of the pure sample. Thus, the presence of Cr_2O_3 and P_2O_5 oxides leads to a greater amount of ettringite which exhibits a greater resistance to transformation into the calcium monosulfate. This agrees with the results of Ivashchenko [11] who showed that additives forming solid solutions with calcium sulfoaluminate increase crystallization of ettringite and lower the degree of transformation into monosulfate, which is decisive for the improvement of strength properties of binders based on modified calcium sulfoaluminate.

4. Summary

The formation of solid solutions of $C_4A_3\bar{S}$ is hindered by rich concentrations of additives, mainly due to the phosphorus effect that enlarges the stability field of the CA phase at the expense of the calcium sulfoaluminate field. The maximum of the initial heat rate of the hydration process of $C_4A_3\bar{S}$ decreases with an increase in the concentration of the Cr_2O_3 and P_2O_5 oxides. The incorporation of chromium and phosphorus in the crystal lattice of $C_4A_3\bar{S}$ induces a long induction period during the hydration reaction. The setting period in the doped samples shows a higher heat rate than that of pure sample. The principal products of hydration are ettringite $C_6A\bar{S}_3H_{32}$, calcium monosulfate $C_4A\bar{S}_3H_{12}$ and AH_3. The extent of the transformation of ettringite into the monosulfate form is lower in the modified $C_4A_3\bar{S}$ than in the additives-free calcium sulfoaluminate phase.

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