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HYDRAULIC ACTIVITY OF C_4A_3Cr IN PRESENCE OF $C_4A_3\overline{S}$

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Abstract

This paper deals with synthesis and assessment of the hydraulicity of C_4A_3Cr[**], analog phase to $C_4A_3\overline{S}$, relevant to the phase chemistry and properties of sulfoaluminate cements. C_4A_3Cr, synthesized at 1250°C is well crystallized phase, latently hydraulic, with hydration accelerated in the presence of $C_4A_3\overline{S}$, or $C\overline{S}$. Calorimetric curves show reciprocal influence of sulfate and chromate phase in hydration of $C_4A_3\overline{S}$– C_4A_3Cr system. The total heat expressed at hydration is nearly the same for all specimens, but the rate of heat evolution depends on the ratio of $C_4A_3\overline{S}$/C_4A_3Cr phases. X-ray diffraction pattern and DTA curves showed that, increasing content of C_4A_3Cr in hydrating mixture results in a coexistence of two types of ettringite (chromate and sulfate ettringite) hydrogarnet, gibbsite and monosulfate.

Keywords: calcium chromoaluminate, chromate and sulfate ettringite, hydration reactions, TA

Introduction

$CaO–Al_2O_3–SO_3–(CrO_3)$ system is of importance from two points. One is concerned with production of the low-energy calcium sulfoaluminate cements [1–5], the second one with possibility to immobilize hexavalent chromium [6] in a hydration course of these cements. Chromium potentially present in the raw meal can readily substitute either (Al(III), or S(VI) atoms in the crystal structure of the clinker phase calcium sulfoaluminate ($C_4A_3\overline{S}$) [6, 8]. Even the full substitution of the SO_3 by CrO_3 can take place [8, 9], forming thus the phase analogous to $C_4A_3\overline{S}$.

It is well known that $C_4A_3\overline{S}$, as a decisive phase of calcium sulfoaluminate cements hydrates in the presence of gypsum to form, next to gibbsite ettringite (Eq. (1)). Full ettringite formation can be achieved when also calcium hydroxide is present (Eq. (2)) [10].

$$C_4A_3\overline{S}+2C\overline{S}H_2+34H\rightarrow C_6A\overline{S}_3H_{32}+2AH_3 \qquad (1)$$

$$C_4A_3\overline{S}+8C\overline{S}H_2+6CH+74H\rightarrow 3C_6A\overline{S}_3H_{32} \qquad (2)$$

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[**] Cement chemistry notation is used C=CaO, A=Al_2O_3, $\overline{S}$=SO_3, Cr=CrO_3, H=H_2O

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With regard to the ettringite structure, sulfate ions can be partially or totally replaced by CrO_4^{2-}, BO_4^{2-} forming thus the derivative ettringites [11, 13–15]. The pure chromate ettringite has been synthesized in laboratory conditions too [19]. Also ionic substitution, including Fe^{3+} and Cr^{3+} for Al^{3+} was reported [16, 17].

It was of an interest to see what kind of crystallohydrates will be formed by hydration of the calcium chromoaluminate phase (C_4A_3Cr) associated with $C_4A_3\overline{S}$. On the other hand, a replacement of SO_4^{2-} by CrO_4^{2-} in ettringite structure may be an important means of immobilized Cr^{6+} ions contained in the environmentally prohibitive water solutions.

Experimental

Homogenized mixture of reagent grade $CaCO_3$, $Al(OH)_3$ and CrO_3 was burnt at 1250°C for 4 h to synthesize C_4A_3Cr. Likewise, the mixture of $CaCO_3$, $Al(OH)_3$ and $CaSO_4{\cdot}H_2O$ was used to synthesize $C_4A_3\overline{S}$. The obtained minerals were milled to specified fineness (to pass a 40 μm sieve). The sample phases were controlled by STOE Powder Diffraction System (STADI P) using CoK_α radiation, operating at 40 kV and 30 mA. Then, series of specimens were prepared by mixing both minerals in different proportion. The hydration of synthesized mineral mixes, accomplished at water/solid ratio (w/s)=0.5 was followed by using conduction calorimeter as described by [12]. Hydrate products were prepared also separately by mixing suspensions (w/c=10) at laboratory temperature for 7 days. Filtered samples were washed in acetone and ether to eliminate chemically non-bonded water. The thermal analysis were conducted using the T.A.I SDT 2960 equipment at a heating rate 10°C min^{-1} in static air atmosphere, using 20 mg of sample material.

Results and discussion

According to the XRD pattern of the prepared C_4A_3Cr (Fig. 1) is a phase of pure product. Its diffraction has been indexed by analogy to the $C_4A_3\overline{S}$ phase powder diffraction pattern. The refined unit cell dimension of C_4A_3Cr (a_0=18.489(1) Å) is very close to the cell dimension of $C_4A_3\overline{S}$ (a_0=18.392 Å) [11].

Figure 2 shows the hydration behaviour of C_4A_3Cr, with (2) and without $C\overline{S}$ (1). Molar ratio C_4A_3Cr to $C\overline{S}$ was kept at 2:1 to form ettringite (Eq. (1)). C_4A_3Cr phase alone hydrates and sets very slowly, but addition of gypsum (sulfate ions) accelerates hydration process. In the presence of sulfate ions, reaction occurs in two periods, separated by induction period. Calorimetric curves present two peaks. While the first peak is due to dissolving and wetting process, the second one characterize the exothermic hydration of ettringite formation. The very slow hydration of single C_4A_3Cr was a reason to systematically study its co-hydration with the paternal phase $C_4A_3\overline{S}$. The composition of mixes is given in Table 1. The hydration curves are shown in Fig. 3. Table 1 contains also the total heat as obtained by integration of hydration curves.

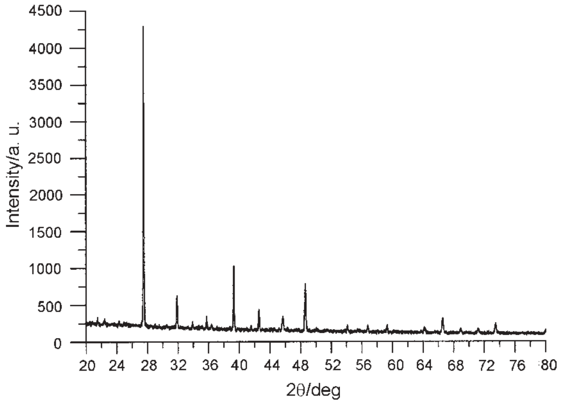

Fig. 1 XRD pattern of C_4A_3Cr

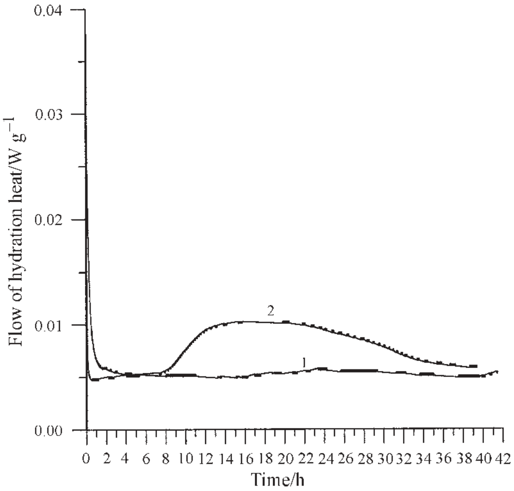

Fig. 2 Calorimetric curves of C_4A_3Cr hydration without (1) and with (2) $C\overline{S}$

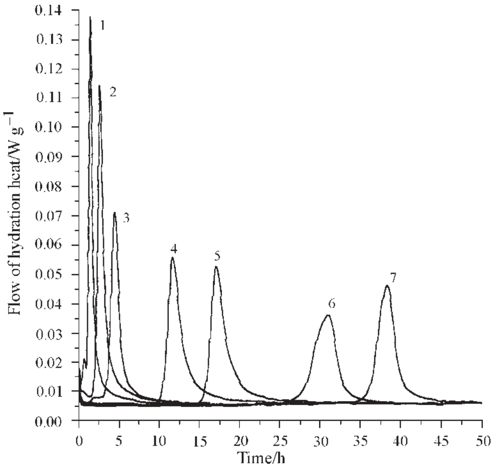

Fig. 3 Calorimetric curves of specimens 1–7

Calorimetric curves clearly prove the influence of sulfate phase on the hydration of C_4A_3Cr. As seen from Table 1 the total heat expressed at hydration is nearly the same for all samples, but the rate of heat evolution seem to be dependent on the ratio of phases. The latent hydraulicity of C_4A_3Cr is fully evoked by a 10% presence of $C_4A_3\overline{S}$ (specimen 7). The length of induction period can be considered as exponential function of the ratio of hydrating phases (Fig. 4). $C_4A_3\overline{S}$ is therefore a pronounced accelerator of C_4A_3Cr hydration, and reciprocally, C_4A_3Cr a pronounced retarder of $C_4A_3\overline{S}$ hydration.

Table 1 Specimens made by mixing of $C_4A_3\overline{S}$ and C_4A_3Cr and heat of its hydration

Specimens	1	2	3	4	5	6	7
$C_4A_3\overline{S}$/%	100	90	80	60	50	20	10
C_4A_3Cr/%	0	10	20	40	50	80	90
Total heat/J g^{-1}	405	476	500	513	515	514	500

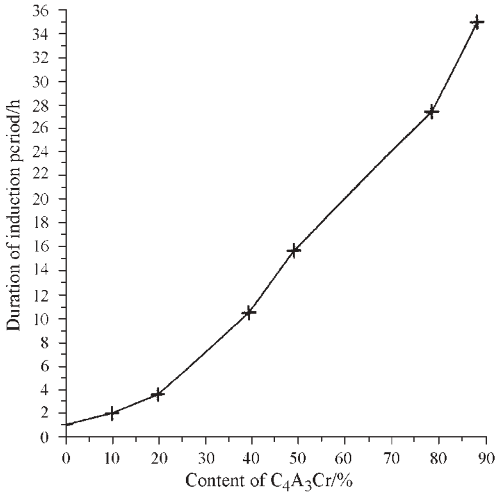

Fig. 4 Influence of C_4A_3Cr content upon the induction period at hydration of specimens 1–7

Figure 5 shows the results of X-ray patterns of hydration products of specimen 1, 4, 6 and 7 as illustrated in Table 1. The interpretation of XRD patterns in Fig. 5 supports the hypothesis that at hydration of pertinent mixes two types of ettringites are formed. The relative intensity of the {100} sulfate ettringite is at *d*-spacing 9.77 Å, while that of chromate ettringite is found at *d*-spacing 10.30 Å. This disproportion could be explained by the difference in molecule mass of SO_4^{2-} and CrO_4^{2-}. The peak at *d*-spacing {100} of sulfate ettringite diminishes with increasing C_4A_3Cr content (specimen 4, 6 and 7). X-ray patterns (specimens 6 and 7) show chromate and sulfate ettringite coexisting. Monosulfate is also found coexisting with sulfate ettringite (specimen 1) as it was already demonstrated by [20].

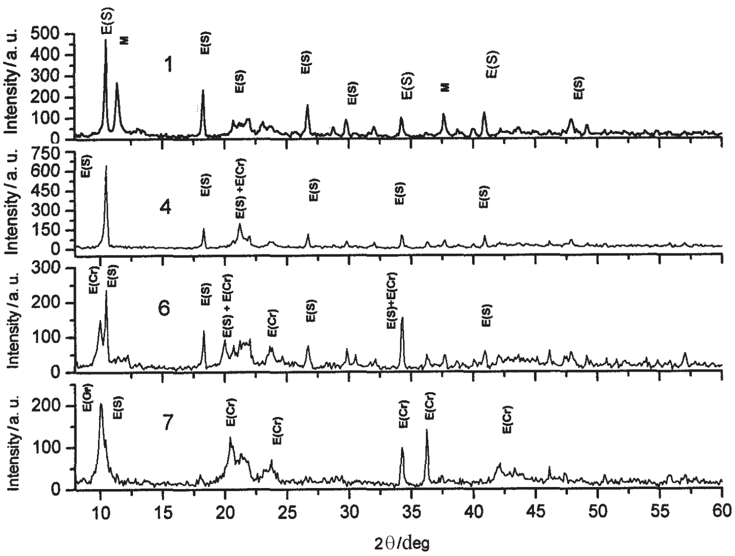

Fig. 5 XRD pattern of hydration products of specimens 1, 4, 6 and 7. *E*(*S*)=sulfate ettringite, *E*(*Cr*)=chromate ettringite, *M*=monosulfate

The resulting equation can be thus summarized:

$$4C_4A_3\bar{S}+80H \rightarrow C_6A\bar{S}_3H_{32}+C_4A\bar{S}H_{12}+2C_3AH_6+8AH_3 \quad (3)$$

Likewise, C_4A_3Cr could hydrate according to reaction

$$4C_4A_3Cr+80H \rightarrow C_6ACr_3H_{32}+C_4ACrH_{12}+2C_3AH_6+8AH_3 \quad (4)$$

Co-hydration of mixes could potentially form either solid solution phases,

$$4C_4A_3\bar{S}+4C_4A_3Cr+80H \rightarrow$$
$$\rightarrow C_6A(\bar{S},Cr)_3H_{32}+C_6A(\bar{S},Cr)_3H_{12}+2C_3AH_6+8AH_3{}^{***} \quad (5)$$

DTA profiles of specimens 1–7 bring another demonstrations of existence of two ettringites. DTA curve of the hydration products of single phase $C_4A_3\bar{S}$ (specimen 1) shows an endotherm about 100°C that is attributed to the decomposition of ettringite, monosulfate is found decomposing at 170 and hydrogarnet at 260°C. The pure synthetic chromate ettringite decomposes at temperature range of 40 to 180°C [18].

Correspondingly, DTA curves for samples containing chromate ions show four or five significant endothermic peaks. Contrary to DTA curve of pure ettringite, one can observe a first peak due to release of water from hydrated samples containing C_4A_3Cr. The intensity of this peak and associated mass loss corresponds to increase of the calcium chromoaluminate content in mixes. The first peak is due to the release of water from chromate ettringite followed by sulfate ettringite decomposition. Spec-

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[***] Bull formulae give an approach to expression because $\bar{S}$/Cr ratio either in ettringite or monosulfate is not known.

imens 6 and 7 reflect cases where chromate ettringite is dominant. Due to the hydraulic activity of C_4A_3Cr, the formation of chromate ettringite is not so quick than that of sulfate ettringite. Another explanation of DTA/TG curves may rest on the two-stage decomposition of the ettringite solid solutions.

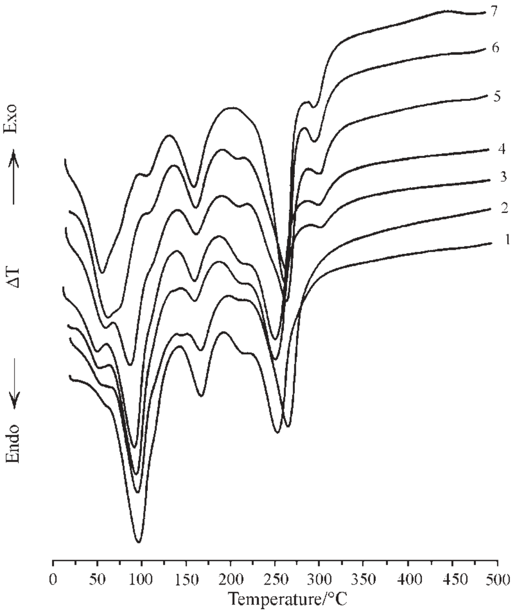

Fig. 6 DTA curve profiles of specimens 1–7

The endotherm at 165–170°C in all specimens proves the existence of monosulfate or chromate hydrocalumite [18], phase analogous to monosulfate, in which SO_4^{2-} are substituted by CrO_4^{2-}. Moreover chromate hydrocaluminate seems to form with monosulfate immiscible solid solutions (absence of peak doublet as in case of ettringite).

The endotherm in temperature range of 250–270°C is attributed to the decomposition of hydrogarnet. This phase is found in all hydrated specimens, confirming thus that hydration occurs according to Eqs ((4), (5)). Also, one can expect that C_4A_3Cr exhibits variable hydrating states, including probably formation of $CaCrO_4{\cdot}2H_2O$ or $Ca(OH)_2$. The appearance of an endotherm at 310°C is due to the presence of AH_3.

Conclusions

C_4A_3Cr is a mineral, which can be synthesized at same temperature than that of $C_4A_3\overline{S}$, with comparable crystallographic structure and with latent hydraulic properties. Its hydration reaction is accelerated in the presence of sulfate. The hydration products of $C_4A_3\overline{S}$–C_4A_3Cr system could be expected as a mixture of chromate and sulfate ettringite in the proportion depending, before all on the CrO_4^{2-} content. The kinetics of hydration of each phase is a main factor determining, at a given time, the mass ratio of both phases. Referring to the result of thermal analysis and X-ray diffraction patterns, one can observed a coexistence between ettringite, monosulfate, hydrogarnet and gibbsite.

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