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HYDRATION IN THE SYSTEM $C_4A_3\bar{S}$–$C\bar{S}H_2$–CH–H*

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Abstract

The system $C_4A_3\bar{S}$–$C\bar{S}H_2$–CH–H was investigated at room temperature by means of conduction calorimetry to illustrate the role played by the size of the $C_4A_3\bar{S}$ particles (aggregates) and the balance ratio $C\bar{S}H_2$/CH. These two factors greatly affect the hydration kinetics in the system $C_4A_3\bar{S}$–$C\bar{S}H_2$–CH–H and determine the hydrated phases formed. The amount of ettringite formed in the system depends on the $C_4A_3\bar{S}$ fineness, as determined by calorimetry. Ettringite and monosulphate are the main hydrated products, as identified by X-ray diffraction. The balance ratio $C\bar{S}H_2$/CH determines the mechanism of hydration and the nature of the calcium-aluminium sulphate hydrates.

Keywords: hydration calorimetry, particle size, sulphoaluminate cement

Introduction

The hydration of calcium sulphoaluminate in combination with gypsum and calcium hydroxide results in the generation of ettringite during the early stage of hydration [1]. The mechanism of ettringite formation is appreciably influenced by the grain sizes of the individual starting phases taking part in the reaction, the homogeneity of the mixture, the total ratio $C_4A_3\bar{S}/(C\bar{S}H_2 + CH)$ and the void available, allowing the formation and growth of ettringite between the particles. Many investigators have focused on the explanation of the mechanism of ettringite formation, the expansive phenomena during its formation, and the morphology of the resulting crystals [2–4, 9]. Two main theories have been deduced. The topochemical mechanism leads to blockage of the hydration on the surface of the $C_4A_3\bar{S}$ particles. The ettringite structure formed is gel-like and contributes to the expansion [7, 8]. The through-solution mechanism, on the other hand, results from supersaturation of the liquid interlayer. The pseudo-equilibrium of the supersaturated solution causes blockage of the dissolution of

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* Cement chemistry notation is used, where C = CaO, A = Al_2O_3, H = H_2O, $\bar{S}$ = SO_3, *AFt* = ettringite and *Afm* = monosulphate.

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the reacting phases, and in this case ettringite will precipitate far from the surface of $C_4A_3\overline{S}$.

The stability region of solid hydrated phases in the quaternary system $C_4A_3\overline{S}$–$C\overline{S}H_2$–CH–H and their relationship were determined some time ago [5]. The quaternary hydrates formed in this system are monosulphate $C_4A_3\overline{S}H_{12}$ and trisulphate $C_6A\overline{S}_3H_{32}$, which coexist with portlandite ($Ca(OH)_2$), gypsum ($C\overline{S}H_2$), gibbsite ($Al(OH)_3$) and hydrogarnet C_3AH_{16} [5].

It has been reported [2] that the *pH* strongly influences the formation of hydrated sulphates and their stability. Measurements under nonequilibrium conditions show that the boundary for the disappearance of monosulphate is $pH = 11.6$, while that for ettringite is $pH = 10.7$. At lower *pH*, gypsum and aluminium sulphate were the only stable phases present [2]. The presence of gypsum decreases the *pH*, whereas the presence of $Ca(OH)_2$ increases it. The final *pH* will depend on the balance ratio $C_4A_3\overline{S}/CH_2$. Generally, ettringite is formed when $1.0 < C/\overline{S} < 4.0$ and/or $0.25 < A/\overline{S} < 1$, while monosulphate is formed in the ranges, $C/\overline{S} > 2.5$ and $A/\overline{S} > 0.33$ [7]. The lack of sulphate ions leads to the formation of monosulphate at higher *pH*, due to the presence of calcium hydroxide.

The hydrates in the system $C_4A_3\overline{S}$–$C\overline{S}H_2$–CH_2–H_2O are produced by hydration according to the following equations [1]:

$$C_4A_3\overline{S} + 18H_2O \rightarrow C_3A{\cdot}C\overline{S}H_{12} + 2AH_3 \qquad (1)$$

$$C_4A_3\overline{S} + 8CH + 30H_2O \rightarrow C_3A{\cdot}C\overline{S}H_{12} + 2C_4AH_{13} \qquad (2)$$

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + 34H_2O \rightarrow C_3A{\cdot}3C\overline{S}H_{32} + 2AH_3 \qquad (3)$$

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + 6CH + 22H_2O \rightarrow C_3A{\cdot}3C\overline{S}H_{32} \qquad (4)$$

$$C_4A_3\overline{S} + 8C\overline{S}H_2 + 34H_2O \rightarrow C_3A{\cdot}3C\overline{S}H_{32} + 2AH_3 + 6C\overline{S}H_2 \qquad (5)$$

These equations typically represent the hydration in the system $C_4A_3\overline{S}$–$C\overline{S}H_2$–CH_2–H_2O, but variation of the molar ratio $C\overline{S}H_2/CH_2$ leads to changes in the *pH* of the liquid interlayer surrounding the $C_4A_3\overline{S}$ phase and in the diffusional gradient of Al^{3+}. The dissolution blocking effect due to the formation of an impervious layer of hydrates and the lack of Ca^{2+} and SO_4^{2-} influences the mechanism of hydration and the nature of the sulphate hydrates. This phenomenon has an important effect on the structure of the hydrated material and greatly influences its strength development.

The goal of the present investigations was to elucidate the conditions under which the different hydrated sulphates are formed with respect to the ratio $C\overline{S}H_2/CH$ and the particle size of $C_4A_3\overline{S}$.

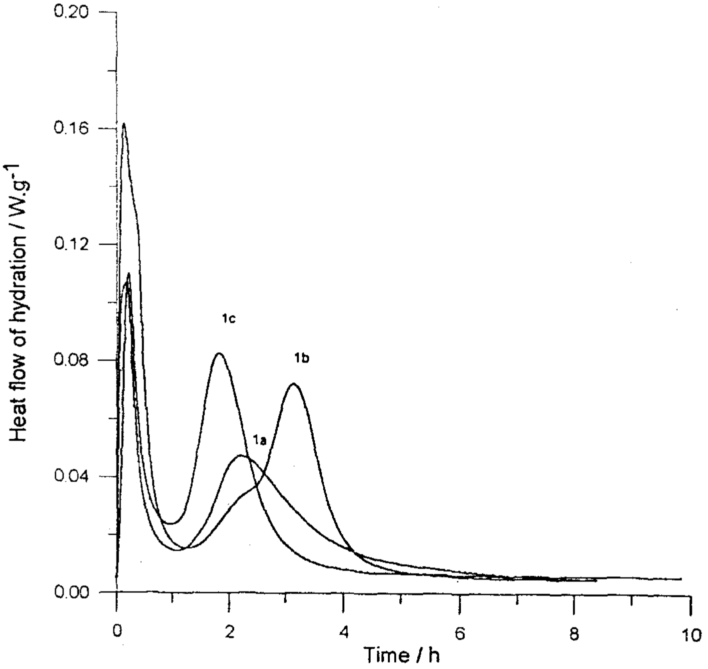

Fig. 1 Sample 1 with different particle size of $C_4A_3\bar{S}$; 1a – coarse, 1b – middle and 1c – fine particles

Experimental

$C_4A_3\bar{S}$ was synthesized by heating a homogenized stoichiometric mixture of analytical grade $CaCO_3$, $CaSO_4 \cdot 2H_2O$ and $Al(OH)_3$ at 1300°C for 3 h. The sample thus synthesized was ground and the fractions 40–56, 20–40, 5–20 and 0–5 μm were collected by sieving and air separation. In this study, we chose the $C_4A_3\bar{S}$ fractions 40–56, 20–40 and 5–20 μm. To avoid the evolution of hydration heat during the hydration reaction, $Ca(OH)_2$ was used instead of CaO. The gypsum fraction 0–10 μm was used in all experiments. Four mixtures of $C\bar{S}H_2$ and CH were prepared (Table 1). The final mixtures contained 70 wt.% of $C_4A_3\bar{S}$ and 30 wt.% of ($C\bar{S}H_2$ + CH). Hydration experiments were performed with a ZIAC conduction calorimeter. The equipment easily lends itself to a computer link for the purpose of continuous monitoring of the heat generation rate. In each experiment, 2 g of a fresh sample of the above mixtures was taken, placed in the calorimeter and tempered for 1 h, together with water for hydration corresponding to the standard water/cement ratio set to 0.5. The phase composition and the hydration products were determined by means of X-ray diffraction phase analysis and thermal analysis using a derivatograph (MOM, Budapest).

Table 1 Phase compositions of the experimental cement mixtures (wt.%)

Sample	$C_4A_3\bar{S}$ /%	$C\bar{S}H_2$ /%	CH /%
1	70	24	6
2	70	18	12
3	70	12	18
4	70	6	24

Results and discussion

The calorimetric curves of hydration (Figs 1–4) clearly reveal that the kinetics of reaction in the system $C_4A_3\bar{S}$–$C\bar{S}H_2$–CH is governed by the size of $C_4A_3\bar{S}$ and by the ratio $C\bar{S}H_2$/CH at constant $C_4A_3\bar{S}$ content. The stable hydrated products determined by thermal analysis and X-ray diffraction were ettringite and monosulphate (Table 2). The X-ray diffraction results showed the coexistence of monosulphate and ettringite for the ratio $C\bar{S}H_2/CH \geq 2/3$. Indeed, when ettringite is formed at a high lime concentration, expansion is observed and the mechanism is topochemical [3]. The features of the calorimetric curves suggest that the kinetics of ettringite formation differs for the same ratio of

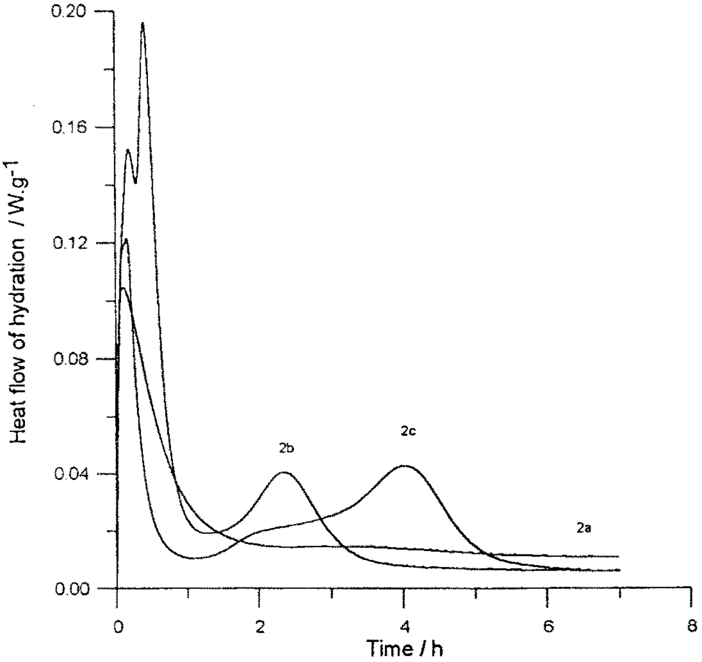

Fig. 2 Sample 2 with different particle size of $C_4A_3\bar{S}$; 2a – coarse, 2b – middle and 2c – fine particles

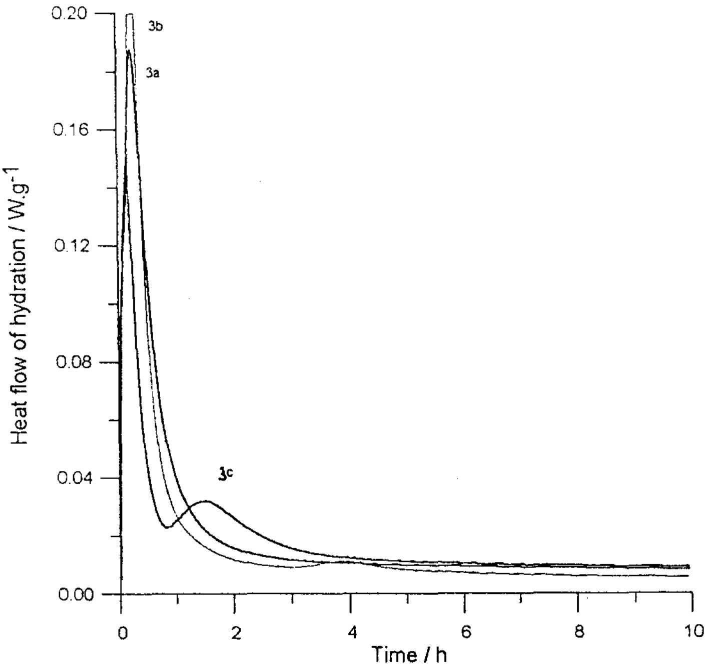

Fig. 3 Sample 3 with different particle size of $C_4A_3\bar{S}$; 3a – coarse, 3b – middle and 3c – fine particles

phases. This phenomenon is due to the formation of aluminium anions in solution by the fine particles of $C_4A_3\bar{S}$, the only phase containing Al^{3+} necessary for the formation of ettringite. Although the mobility of $Al(OH)_4^-$ is low, fine particles of calcium–aluminium sulphate saturate the solution and cause the formation of ettringite apart from the $C_4A_3\bar{S}$ surface. Because of the low mobility of Ca^{2+} and SO_4^{2-}, $Al(OH)_4^-$ at higher concentration might diffuse into the solution before the nuclei of ettringite crystals can be formed.

Observation of the calorimetric curves indicates that the $C_4A_3\bar{S}$ fineness (even at the same chemical ratio in the mixtures) affects not only the intensities of the main peaks, but also the duration of the induction period. The simultaneous action of the chemical composition does not allow a mathematical quantification of the real influence of the $C_4A_3\bar{S}$ particle size, but in all studied cases the 20–40 μm fraction has the greatest influence on the intensities of the first peaks, and a diversified influence on the second main peaks. If it is considered that the induction period is caused by a protective layer due to the formation of primary hydration products, and that the mechanism for the next reaction is controlled either by the rate at which the reactant ions diffuse through a barrier that surrounds the unreacted phase or by the rate at which nuclei of the stable product form and grow, it can be stated that the rate of diffusion of $Al(OH)_4^-$

Table 2 Hydrated phases in the system $C_4A_3\bar{S}$–$C\bar{S}H_2$–CH–H

Time	Sample			
	1	2	3	4
30 min	Aft	Aft	Afm	Afm
1 h	Aft	Aft	Aft + Afm	Afm
2 h	Aft	Aft	Aft + Afm	Aft + Afm
4 h	Aft	Aft	Aft + Afm	Aft + Afm
24 h	Aft	Aft	Aft + Afm	Aft + Afm

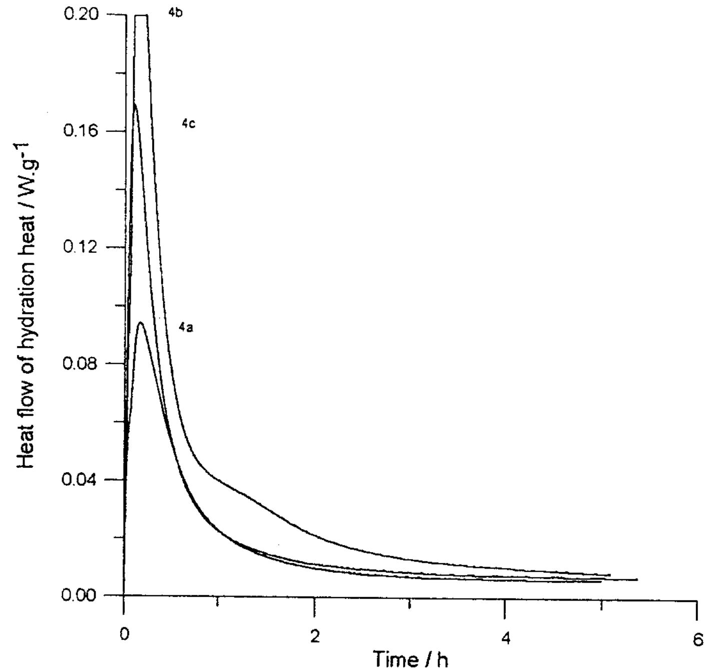

Fig. 4 Sample 4 with different particle size of $C_4A_3\bar{S}$; 4a – coarse, 4b – middle and 4c – fine particles

governs the kinetics of formation of the hydrated sulphate products (ettringite and monosulphate) in the system. Indeed, the formation of ettringite besides monosulphate after hydration for 30 min in sample 3 and after 1 h in sample 4 is due to the change in *pH*. The $C_4A_3\bar{S}$ fineness exerts a great influence on the amount of hydrates, but less so on their nature.

Conclusions

The transfer of $Al(OH)_4^-$ into solution determines the kinetics of ettringite and monosulphate formation in the case of the through-solution mechanism.

The particle size influences the rate of dissolution of the calcium sulphate phase. The rate of $Al(OH)_4^-$ transfer depends on the surrounding *pH*, which is correlated with the balance ratio $C_4A_3\bar{S}/C\bar{S}H_2$. When the molar concentration of lime is higher than that of gypsum, monosulphate appears besides ettringite; its amount increases with the lime concentration, whereas the quantity of ettringite decreases.

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