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USE OF DIFFERENTIAL CALORIMETRY FOR CHARACTERIZATION OF HYDRATION PROCESSES IN THE SYSTEM $Ca_4(Al_6O_{12})(SO_4)$–$CaSO_4.2H_2O$–H_2O

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Differential calorimetry was used to determine the heat evolution and kinetics of hydration processes of the calciumsulphatealuminate phase $Ca_4(Al_6O_{12})(SO_4)$ with gypsum $CaSO_4 \cdot 2H_2O$ at room temperature with one mole of water added to the solid phase. An increasing content of sulphate ions in the sytem results in substitution of the monosulphate $Ca_4(Al_2O_6)(SO_4) \cdot 12H_2O$ in the reaction products by ettringite, $Ca_6(Al_2O_6)(SO_4)_3 \cdot 32H_2O$. Higher contents of ettringite influence the rates of hydration reactions and the values of the evolved heat.

The hydration of the pure calciumsulphatealuminate phase $Ca_4(Al_6O_{12})(SO_4)$ at room temperature was earlier investigated by means of differential calorimetry and direct quantitative X-ray phase analysis [1]. The comparison of the two methods showed the formation of a highly dispersive system, followed by crystallization of the monosulphate $Ca_4(Al_2O_6)(SO_4) \cdot 12H_2O$ and gibbsite, $Al(OH)_3$:

$$Ca_4(Al_6O_{12})(SO_4) + 18\,H_2O \rightarrow Ca_4(Al_2O_6)(SO_4) \cdot 12H_2O + 4\,Al(OH)_3 \quad (1)$$

A higher sulphate content in the system caused the formation of the trisulphate (ettringite), $Ca_6(Al_2O_6)(SO_4)_3 \cdot 32H_2O$ [2–5]:

$$\begin{aligned} &Ca_4(Al_6O_{12})(SO_4) + CaSO_4 \cdot 2H_2O + 26H_2O \rightarrow 4\,Al(OH)_3 + \\ &+ 1/2\,Ca_4(Al_2O_6)(SO_4) \cdot 12H_2O + 1/2\,Ca_6(Al_2O_6)(SO_4)_3 \cdot 32H_2O \end{aligned} \quad (2)$$

or

$$\begin{aligned} &Ca_4(Al_6O_{12})(SO_4) + 2(CaSO_4)2H_2O + 34H_2O \rightarrow 4\,Al(OH)_3 + \\ &+ Ca_6(Al_2O_6)(SO_4)_3 \cdot 32H_2O \end{aligned} \quad (3)$$

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The aim of this paper is to establish the influence of higher sulphate concentrations on the character of the heat evolution and the kinetics of the hydration process.

Experimental

The calciumsulphatealuminate phase $Ca_4(Al_6O_{12})(SO_4)$ was prepared by mixing an aqueous solution of $Ca(NO_3)_2$ with $CaSO_4 \cdot 2H_2O$ and $Al(OH)_3$, all of analytical reagent grade quality. The mixed suspension was evaporated, and the dry residue was heated to 870° to eliminate volatile components. After milling, the homogenized powder was heated at 1250° for 24 h. The phase composition of the products was controlled by quantitative X-ray phase analysis on a Philips 1540 powder diffractometer, applying CuK_α radiation. Heat evolution experiments were performed at room temperature, with the addition of one mole of water to the solid phase, in the differential calorimetry system ZIAC [6, 7]. The total heat evolved was evaluated by integration, using Simpson's method.

Results and discussion

The kinetics and thermodynamics of hydration processes in the system $Ca_4(Al_6O_{12})(SO_4)$–$CaSO_4 \cdot 2H_2O$ may compared by analyzing the time-dependences of the rate of the heat evolution dQ/dt in Fig. 1. In this diagram, the

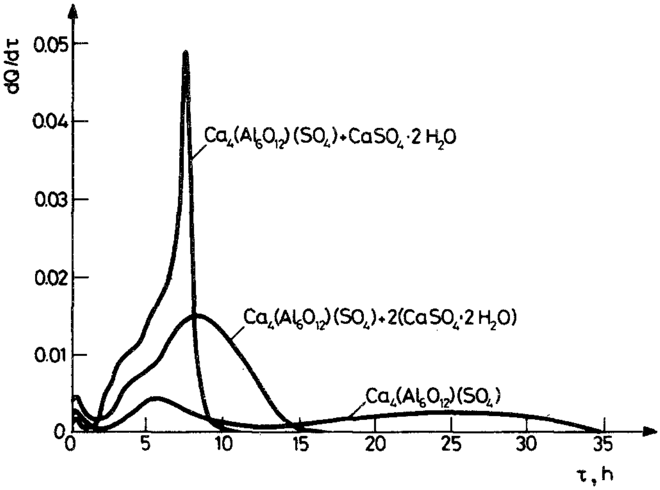

Fig. 1 Curves of heat evolution rate (dQ/dτ) vs. time τ for various content of gypsum

course of hydration of the sulphatealuminate phase is plotted for various contents of gypsum. The first period is practically identical in all reaction systems. On the other hand, the reactions in the second and third time periods are different. In the case of pure sulphatealuminate phase, the slow hydration process is clearly divided into (i) formation of a highly dispers system and (ii) crystallization of monosulphate and gibbsite. Higher concentrations of sulphate ions in aqueous solution cause an acceleration of both processes. The formation of crystals is influenced by the changes in the concentration and the diffusion conditions. The accelerating effect of sulphate ions is most marked for the mixture with the molar ratio

$$r = \frac{x_{CaSO_4 \cdot 2H_2O}}{x_{Ca_4(Al_{12})(SO_4)}} = 1 \qquad (4)$$

Reaction scheme (2) shows that the hydration process includes two simultaneous reactions, (1) and (3). The products of this process (ettringite, monosulphate and gibbsite) are created by crystallization from saturated solution and the optimum local concentration conditions give the possibility for their formation. These conditions are more advantageous than those for process (3). The competition between the two reactions results in the sudden completion of the hydration process, and in the asymmetry of the exothermic peak.

In Fig. 2, the total evolved heat Q is plotted against time t for various values of r. The diagram demonstrates the increase of the hydration efficiency in the presence of sulphate ions. In the case $r = 1$, the hydration process is completed after 8 h and $Q = 300.0$, ± 8.7 kJ mol^{-1} for the sulphatealuminate phase (384.7 J g^{-1} for the hydrated solid mixture). Hydration at $r = 2$ takes about 15 h and gives

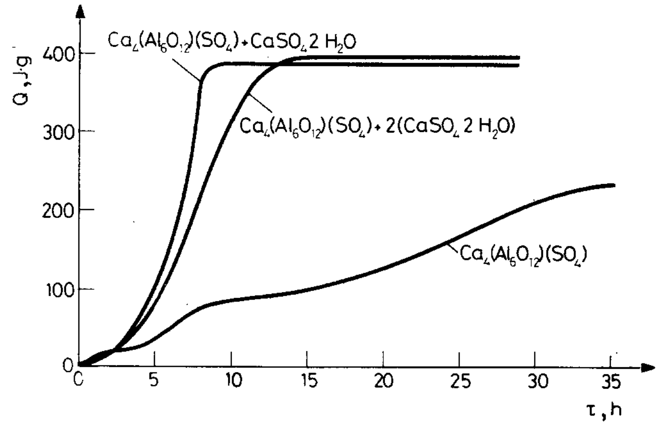

Fig. 2 Time dependence of Q released during the hydration of $Ca_4(Al_6O_{12})(SO_4)$ and its mixtures with gypsum

$Q = 381.3 \pm 6.3$ kJ mol^{-1} (396.6 kJ g^{-1}). For pure $Ca_4(Al_6O_{12})(SO_4)$, $Q = 143.8 \pm 7.2$ kJ mol^{-1} (247.0 J g^{-1}) [1], but after 35 h of hydration quantitative X-ray phase analysis demonstrates that about 20 mass % of the original solid phase is still present.

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Zusammenfassung — Die Wärmeentwicklung und ihr zeitlicher Ablauf bei der Hydratation des Calciumsulfat-aluminats $Ca_4(Al_6O_{12})SO_4$ mit Gips $CaSO_4 \cdot 2H_2O$ bei Zimmertemperatur und einem Wasser/Feststoff-Massenverhältnis $w/s = 1$ wurde durch isotherme Differenzkalorimetrie untersucht. Bei erhöhtem Sulfatgehalt wird das Monosulfat $Ca_4(Al_2O_6)SO_4 \cdot 12H_2O$ im Reaktionsprodukt durch Ettringit $Ca_6(Al_2O_6)(SO_4)_3 \cdot 32H_2O$ ersetzt. Der erhöhte Ettringitgehalt beeinflusst die Beschleunigung der Hydration und die abgegebene Wärmemenge.

Резюме — Метод дифференциальной калориметрии был использован для определения теплоты выделения и кинетики процессов гидратации сульфоалюмината $Ca_3(Al_6O_{12})(SO_4)$ с гипсом при комнатной температуре и при одинаковом соотношении воды и твердой фазы. Увеличение в системе содержания сульфат-ионов вызывает появление в продуктах реакции эттрингита $Ca_6(Al_2O_6)(SO_4)_3 \cdot 32H_2O$, более высокое содержание которого вызывает ускорение реакций гидратации и увеличение значений теплот выделения.