

HEAT EVOLUTION DURING HYDRATION OF $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$

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The hydration of the sulphatealuminate phase $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ at room temperature was observed by means of differential calorimetry and quantitative X-ray diffraction phase analysis in situ. The results were used to evaluate the kinetics of the hydration process and to explain the causes of the exothermic effects: an initial surface reaction, the formation of a highly dispersed system, and the crystallization of monosulphate, $\text{Ca}_4(\text{Al}_2\text{O}_6)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$, and gibbsite, $\text{Al}(\text{OH})_3$. The experiments showed an increase in efficiency of hydration with a higher mass ratio of water to solid phase (from 143.8 kJ/mol at $w/s = 1$ to 170.0 kJ/mol at $w/s = 10$).

The phase $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ is one of the important components of sulphatealuminate cement. The presence of this phase has fundamental influences on the reactivity of this system and the mechanical properties of the products in the initial period of the hardening process. Utilization of this phase in cement clinker production gives the possibility to substitute the alite and hence to decrease the annealing temperature and total energy consumption for cement manufacturing [1–3].

Monitoring the hydration by means of differential calorimetry and quantitative X-ray phase analysis is useful for practical purposes, mainly for the evaluation of the kinetics of the reaction



and for the calculation of the heat Q released during this process.

Experimental

The phase $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ was synthesized by mixing standard aqueous solutions of $\text{Ca}(\text{NO}_3)_2$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$, all of analytical reagent grade quality. The mixed suspension was evaporated to dryness, and the residue was

heated to 870° to eliminate the volatile components and to decompose the nitrates. After cooling, the mixture was homogenized in a laboratory vibrating mill for 20 min, and then heated at 1250° for 24 h. The phase composition of the homogenized powder product was controlled by quantitative X-ray phase analysis on a Philips 1540 powder diffractometer, applying CuK_α radiation at room temperature. Heat evolution measurements were performed with the ZIAC differential calorimetry system [4–6] at room temperature. Changes in the phase composition during hydration process were followed by direct X-ray phase analysis in situ on a DRON-1 diffractometer.

Results and discussion

The heat evolution during the hydration of $\text{Ca}_4(\text{Al}_2\text{O}_{12})(\text{SO}_4)$ was studied to determine the character of the reaction and to evaluate the hydration heat Q .

The kinetics of reaction are represented by curves of the heat evolution rate dQ/dt vs. time τ for various values of the mass ratio of water to solid phase w/s in Fig. 1.

The hydration process at $w/s = 1$ is characterized by three exothermic effects. A comparison of the results of differential calorimetry analysis (DCA) and direct quantitative X-ray phase analysis in situ (Fig. 2) allowed establishment of the type of the reaction. In the first hour, the adsorption and initial chemical reaction occur on the surface of the original solid phase. In this time interval, a drop in $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ concentration was observed. The heat of this reaction step, Q_1 ,

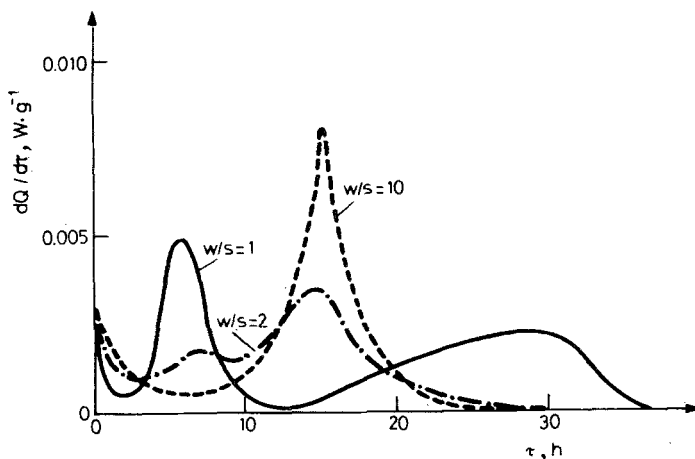


Fig. 1 Curves of heat evolution rate dQ/dt vs. time τ for various values of the water to solid phase mass ratio $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$

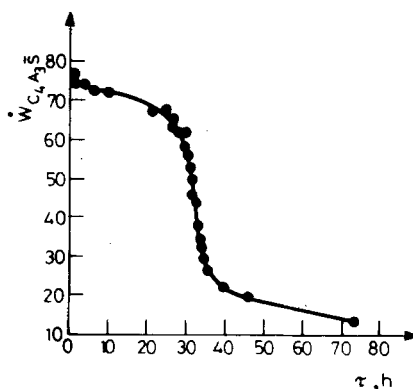


Fig. 2 Time-dependence of mass fraction of $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ achieved, observed via direct quantitative X-ray phase analysis in situ. $w/s = 1$

was 6.2 kJ/mol. The next 7 hours was characterized by an exothermic effect with $Q = 65$ kJ/mol and practically no changes in phase composition. We assume the formation of a highly dispersed system, which gave the opportunity for the next step to proceed in the whole volume of the reaction system. The third effect represented the crystallization of monosulphate, $\text{Ca}_4(\text{Al}_2\text{O}_6)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$, and gibbsite, $\text{Al}(\text{OH})_3$, and a drop in the $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ content. The changes in time of the concentrations of hydrated phases with respect to the possibility of amorphous phase formation in standard samples were not plotted in Fig. 2.

The asymmetrical shape of the last peak of Fig. 1 indicated that the formation of larger crystals suddenly brought the hydration process to an end after 37 hours. On the other hand, the time-dependence of the mass fraction of $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ in Fig. 2 demonstrated that about 20 mass% of this phase remained in the reaction system after 40 hours.

Higher w/s ratios led to lower values of Q_2 (heat evolution during the reaction in a highly dispersed system) and acceleration of the crystallization process. The total released heat Q increased with increasing ratio w/s , as shown in Table 1. These results revealed an intensification of the hydration process at higher ratios w/s .

Table 1 Values of total released heat for various mass ratio of water to solid phase

w/s	Q , kJ/mol
1	143.8
2	153.1
10	170.2

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Zusammenfassung — Die Hydratation der Sulfat-aluminat-Phase $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$ bei Zimmertemperatur wurde mittels Differentialkalorimetrie und quantitativer in-situ-Röntgenbeugungs-Phasenanalyse verfolgt. Ein Vergleich der Ergebnisse erlaubte die Kinetik des Hydratationsprozesses abzuschätzen und die Ursache der exothermen Effekte zu klären: Anfängliche Oberflächenreaktion, Bildung eines hochdispersen Systems, Kristallisation von Monosulfathydrat $\text{Ca}_4(\text{Al}_2\text{O}_6)\text{SO}_4 \cdot 12\text{H}_2\text{O}$ und Hydrargillit $\text{Al}(\text{OH})_3$. Die Versuche zeigten eine Zunahme der Hydratationseffektivität mit steigendem Verhältnis Wasser : Feststoff (w/s) von $143,8 \text{ kJ mol}^{-1}$ bei $w/s = 1$ auf $170,0 \text{ kJ mol}^{-1}$ bei $w/s = 10$.

Резюме — С помощью дифференциальной calorиметрии и количественного рентгенофазового анализа изучена при комнатной температуре in situ гидратация сульфаталюмината $\text{Ca}_4(\text{Al}_6\text{O}_{12})(\text{SO}_4)$. Полученные данные были использованы для оценки кинетики процесса гидратации и для объяснения таких экзотермических эффектов, как начальная реакция на поверхности, образование высокодисперсной системы и кристаллизация моносульфата $\text{Ca}_4(\text{Al}_2\text{O}_6)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$ и гидбсита $\text{Al}(\text{OH})_3$. Экспериментальные результаты показали увеличение эффективности гидратации при более высоком весовом соотношении воды и твердой фазы: от $143,8 \text{ кдж} \cdot \text{моль}^{-1}$ при соотношении равным 1 до $170,0 \text{ кдж} \cdot \text{моль}^{-1}$ при соотношении равным 10.