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CONVERSION AND HEAT EVOLUTION DURING HYDRATION OF ALUMINIUM AND IRON-CONTAINING CLINKER PHASES IN PRESENCE OF SULPHATES

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(Dedicated to F. Hanic, D. Sc. on the occasion of his 60th birthday)

The progress of the reactions of water with brownmillerite (C_4AF^+) and its mixtures with gypsum ($C\bar{S}H_2$) and calcium sulphoaluminate ($C_4A_3\bar{S}$) was investigated by means of calorimetric measurements in situ and X-ray diffractometry to determine the reaction heat and the conversion of the solid reactants as functions of time up to 50 h. The rapid reaction of C_4AF with water and the modifying effect of sulphates on the composition of the hydrated phases were confirmed. The presence of sulphates causes the induction period during the reactions of aluminium and iron-containing clinker phases with water. These phenomena are important technologically too, especially in cements with increased contents of C_4AF and of sulphate-yielding phases ($C\bar{S}H_2$ and $C_4A_3\bar{S}$).

Researchers working on cement chemistry focus their attention on various modifications of the composition of cement clinkers, leading to energy-saving in cement production. The phases C_4AF and $C_4A_3\bar{S}$ synthesized at 1473–1573 K comprise the basis of one [1, 2] of many such ideas. Papers [1–3] suggest that clinkers containing these phases as main constituents' have hydration activity and technological parameters comparable to those of the Portland cement produced at 1673–1773 K.

The aim of this work was to compare the progress of the reaction in the systems C_4AF–H, C_4AF–$C\bar{S}H_2$–H and C_4AF–$C_4A_3\bar{S}$–H, using the time-dependences of the heat evolution and the conversion of the reactants up to 50 h. Such data do not appear to have been published previously.

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* Cement chemistry notation used:
c — Cao, A — Al_2O_3, F — Fe_2O_3,
$\bar{S}$ — SO_3 and H — H_2O

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Experimental and results

Solid reactants were prepared by blending the corresponding sieved fractions of the phases C_4AF and $C_4A_3\bar{S}$ synthesized at 1473 K [4, 5] and of $C\bar{S}H_2$ (analytical grade). The progress of the hydration reactions was studied in distilled water according to the following methodological design:

(i) Reaction conditions: $T = 293 \pm 5$ K, reaction time: $0 < t \leqq 50$ h, grain size ($\varnothing$) of C_4AF, $C_4A_3\bar{S}$ and $C\bar{S}H_2$: $0 < \varnothing \leqq 60$ μm, molar ratios:

$$\frac{n(C\bar{S}H_2)}{n(C_4AF)} = 4/3 \text{ or } 4, \ \frac{n(C_4A_3\bar{S})}{n(C_4AF)} = 1,$$

weight ratio:

$$\frac{\text{water}}{\text{solidus}} = 1.$$

For X-ray phase analysis the hydration was stopped after selected times t_i, with acetone and vacuum drying.

(ii) Heat characteristics were measured in situ in each system, using the method of differential calorimetric analysis (DCA) [6] on DC–J3/JN and DC–N3 ZIAC differential calorimeters, and gave $Q = f(t)$, $Q(t_\infty)$ and dQ/dt, the latter characterizing the periods with different reaction rates.

(iii) Phase analysis and time-dependences of the conversion (α) of the reactants: Powder diffraction patterns (step-scanned on an HZG 4 diffractometer) gave $d_1$nm, and $I(r)$ indicating the presence of the crystalline phases, p, and their semiquantitative characteristics $\bar{Y}(p)$ at t_i; more details can be found in [7].

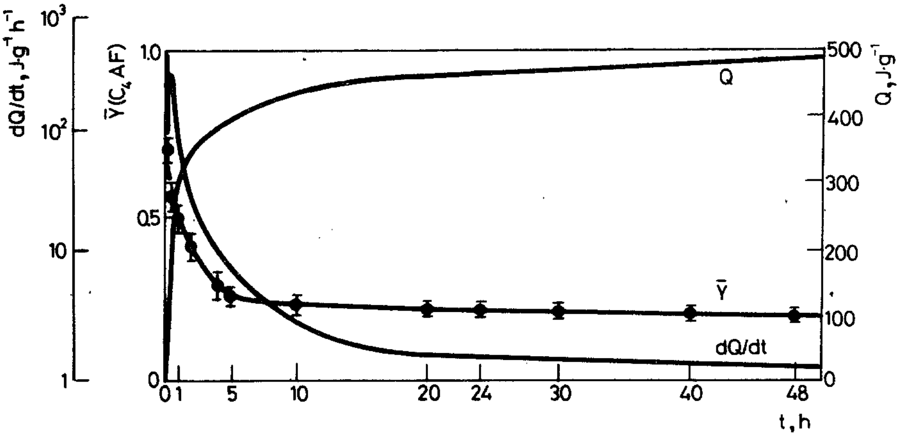

Fig. 1 Changes of Q, dQ/dt and $\bar{Y}(C_4AF)$ parameters of the C_4AF–$\bar{H}$ system up to 50 hours reaction time. Results: $Q(t_\infty) = 500$ Jg^{-1}, $t_{0.5}$ of $C_4AF = 1$ hour, $\bar{Y}(C_4AF)$ at $t_i = 50$ hours is 0.20 ± 0.05

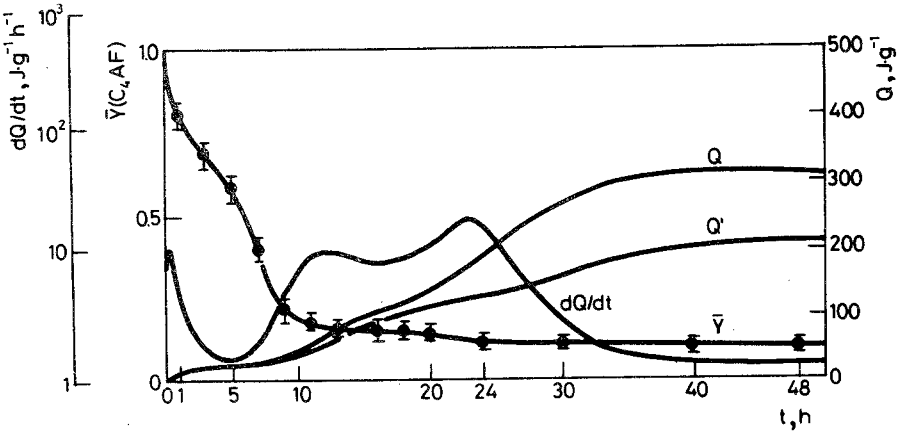

Fig 2 Changes of Q, dQ/dt and $\bar{Y}(C_4AF)$ parameters of the C_4AF–$C\bar{S}H_2$–H system up to 50 hours reaction time. Results: $220 \leq Q(t_\infty)/Jg^{-1} \leq 320$ depending on the amount of $C\bar{S}H_2$, Q — for ratio $n(C\bar{S}H_2)/n(C_4AF) = 4/3$, Q'—for ratio $n(C\bar{S}H_2)/n(C_4AF) = 4$. $t_{0.5}$ of C_4AF = 7 hours, $\bar{X}(C_4AF)$ at t_i = 50 hours is 0.10 ± 0.05

The heat evolved Q, the rate of heat evolution dQ/dt and the quantity $\bar{Y}(p)$ plotted *vs.* the reaction time in the systems C_4AF–H (Fig. 1), C_4AF–$C\bar{S}H_2$–H (Fig. 2) and C_4AF–$C_4A_3\bar{S}$–H (Fig. 3) permit comparisons of the progress of the hydration reactions in the individual systems up to 50 h. The quantity $\bar{Y}(p)$ originated from the series of ratios of $I(r)$ of the pure phase p, and that at t_i is proportional to $(1-\alpha)$ for C_4AF and $C_4A_3\bar{S}$ and is related to their reactivites. The values $Q(t_\infty)$, the times at which the conversions of C_4AF and $C_4A_3\bar{S}$ reach 50%, $t_{0.5}$, and the values $\bar{Y}(p)$ at t_i = 50 h gave supplementary information on each system.

Discussion

The maximum rate of heat evolution dQ/dt in the system C_4AF–H was recorded with the first hour, and the $t_{0.5}$ for C_4AF in this system was 1 h too (Fig. 1). The measured characteristics become monotonously settled in the subsequent course of the hydration. The value of $Q(t_\infty) = 500$ J g^{-1} established by extrapolation is significantly higher than that for C_4AF synthesized from the melt (419 J g^{-1}) [8]. The difference has been discussed as a consequence of the different grain size distribution [7].

The modifying effects of $C\bar{S}H_2$ and $C_4A_3\bar{S}$ on the composition of the hydrates of aluminium and iron-containing clinker phases are well known [3, 7, 9, 10]. Our

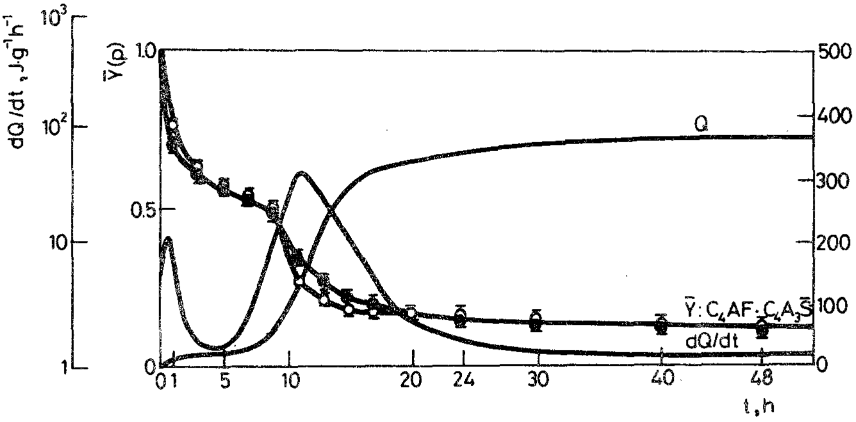

Fig. 3 Changes of Q, dQ/dt, $\bar{Y}(C_4AF)$ and $\bar{Y}(C_4A_3\bar{S})$ parameters of the C_4AF–$C_4A_3\bar{S}$–H system up to 50 hours reaction time. Results: $Q(t_\infty)=370$ Jg^{-1}, $t_{0.5}$ of $C_4AF = t_{0.5}$ of $C_4A_3\bar{S} = 9$ hours, $\bar{Y}(C_4AF)$ and $\bar{Y}(C_4A_3\bar{S})$ at $t_i = 50$ hours are 0.10 ± 0.05

results show that the influence of $C\bar{S}H_2$ and $C_4A_3\bar{S}$ on the progress of the hydration reactions of C_4AF up to 50 h consists in the appearance of an induction period (Figs 2 and 3). It is observed more expressively in the system C_4AF–$C_4A_3\bar{S}$–H (Fig. 3) than in the system C_4AF–$C\bar{S}H_2$–H (Fig. 2) between the 5th and 10th hours, and is manifested by a minimum in the rate of heat evolution dQ/dt, by the slower decline of $\bar{Y}(C_4AF)$ and $\bar{Y}(C_4A_3\bar{S})$ and by the existence of a plateau in the $Q = f(t)$ curves. The induction period is connected with $t_{0.5}$ too; $t_{0.5}$ for C_4AF in the systems C_4AF–$C\bar{S}H_2$–H and C_4AF–$C_4A_3\bar{S}$–H is equal to 7 and 9 h, respectively. The latter is valid for the $t_{0.5}$ for $C_4A_3\bar{S}$ too. The heat evolution and conversion increase after this period and from 30 to 50 h are quasi-settled. For the system C_4AF–$C\bar{S}H_2$–H, we extrapolated $220 \leq Q(t_\infty) = 320$ J g^{-1} for the dependence on the amount of $C\bar{S}H_2$. The extrapolated $Q(t_\infty) = 370$ J g^{-1} for the system C_4AF–$C_4A_3\bar{S}$–H corresponds with the arithmetic mean of $Q(t_\infty)$ for the C_4AF–H system (500 J g^{-1}) and the $C_4A_3\bar{S}$–H system (250 J g^{-1}) [11].

The values of $\bar{Y}(C_4AF)$ and $\bar{Y}(C_4A_3\bar{S})$ show that at $t_i = 50$ h the hydration reactions in the presence of sulphates are in a more advanced stage than the reactions of C_4AF alone (see the $\bar{Y}$ curves in Figs 1–3). No influence of the grain size of the reactants on the conversion up to 50 h was observed. The number of defects conditioned by the grain size [7] affects the rates of the studied reactions at low concentrations of the reactants (long reaction time, high water/solidus ratio).

Conclusions

1. The combination of the results of the independent methods used is suitable and profitable in the study of the hydration activities of prospective cementitious systems.

2. The interactions of the studied phases during hydration reactions cause changes in the compositions of hydrates, in the heat evolution characteristics of the reactions and in the conversions of the reactants.

3. The results demonstrate an induction period in the heat evolution and conversion during the hydration reactions of aluminium and iron-containing clinker phases in the presence of sulphates, a technologically typical and necessary phenomenon of the cementitious systems.

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Zusammenfassung — Der Verlauf der Hydratation von Brownmillerit Ca_4AF^* bzw. seinen Mischungen mit Gips ($C\bar{S}H_2$) und Calcium-sulfat-aluminat ($C_4A_3\bar{S}$) wurde durch kalorimetrische Messungen in situ und Röntgendiffraktometrie verfolgt, um die Abhängigkeit der Reaktionswärme und des Umsatzes der festen Reaktanden von der Zeit (bis 50 h) zu bestimmen. Die schnelle Reaktion von C_4AF mit Wasser und der modifizierende Effekt der Sulfate auf die Zusammensetzung der hydratisierten Phase wird bestätigt. Die Anwesenheit von Sulfat bewirkt eine Induktionsperiode bei der Reaktion von aluminium- und eisenhaltigen Klinkerphasen mit Wasser. Diese Erscheinungen sind von technischer Bedeutung, insbesondere für Zemente mit erhöhtem Gehalt an C_4AF und sulfatbildenden Phasen wie $C\bar{S}H_2$ und $C_4A_3\bar{S}$.

Резюме — Ход реакций черного миллерита ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) и его смесей с гипсом и кальцийсульфоалюминатом ($4CaO \cdot 3Al_2O_3 \cdot SO_3$) с водой был изучен с помощью калориметрии и рентгеновской диффрактометрии с целью определения теплоты реакции и степени превращения твердых реагентов в зависимости от времени (до 50 часов). Подтверждены быстрая реакция миллерита с водой и видоизмененное влияние сульфатов на состав гидратированных фаз. Присутствие сульфатов вызывает индукционный период реакций алюминий- и железосодержащих клинкерных фаз с водой. Установленные явления являются также технологически важными, особенно, для цементов с увеличенным содержанием миллерита и сульфат-содержащих фаз.