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HYDRATION STUDIES ON THE SYSTEM PULVERIZED FLY ASH—$Ca(OH)_2$–$CaCl_2$ USING DTA AND TG

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Differential thermal analysis and thermogravimetry were used to monitor the course of hydration in the system fly ash – $Ca(OH)_2$ – $CaCl_2$. It was shown that the $CaCl_2$ admixture is an activating agent in this system. The results should be used for the correction of the mixture ratio of binders and builiding materials based on fly ash.

Fly ash is a mineral by-product available in huge quantities; it is formed in power stations as a results of solid-fuel combustion processes, and it is utilized in concrete production as a cement replacement. As concerns their chemical properties, fly ashes are classified as acidic materials, containing predominantly SiO_2 and Al_2O_3. Part of the SiO_2 and Al_2O_3 is in active form, and this decides the pozzolanic properties of fly ashes, i.e. their ability to react with $Ca(OH)_2$ in aqueous medium, with the formation primarily of hydrated compounds such as the phases $CaO \cdot SiO_2 \cdot nH_2O$ and $4CaO \cdot Al_2O_3 \cdot nH_2O$ [1, 2]. This reaction occurs very slowly at room temperature, but there is a possibility of acceleration of the process by the addition of chemical activators.

This work presents results of investigations obtained by using differential thermal analysis (DTA) and thermogravimetry (TG). Studies were carried out on the systems fly ash —$Ca(OH)_2$ and fly ash —$Ca(OH)_2$—$CaCl_2$.

Experimental

The following materials and reagents were used: $Ca(OH)_2$ p.a.; $CaCl_2$ p.a.; and fly ash with the chemical composition: SiO_2 50.8%, Al_2O_3 23.9%, Fe_2O_3 8.6%, CaO 3.6%, MgO 2.8%, SO_3 0.8%, Na_2O 0.8%, K_2O 2.9%, loss on ignition 2.9%, density $d = 2.03$ g cm^{-3}, specific surface area 295 m^2 kg^{-1}.

Hydration was carried out on two mixtures:

Mixture I: 70 wt% of fly ash +30 wt% of $Ca(OH)_2$.
Mixture II: a mixture of 10 g of $CaCl_2$ per 100 g of mixture I.

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The samples were mixed witj distilled water in a mass ratio w/s equal to 0.6, and were then stored at 20 ± 2°. The hydration process was stopped after 1, 3, 7, 28, 90 or 180 days by washing the samples in acetone, then ether, and drying in vacuum at room temperature for 24 h.

All the samples were examined in an inert argon atmosphere, using a Mettler thermo-analyser.

Al_2O_3 was used as an internal standard. Samples were heated from room temperature to 800° at a heating rate of 10 deg min^{-1}. Quantitative determination of $Ca(OH)_2$ at 474–510° was carried out by means of thermogravimetry.

The amount of $Ca(OH)_2$ in the hydrated samples was calculated via the formula:

$$W_{Ca(OH)_2} = \frac{4.11\, \Delta Ca(OH)_2 + 1.68\, \Delta\, CaCO_3}{m} \tag{1}$$

where $W_{Ca(OH)_2}$ = total quantity of $Ca(OH)_2$ in sample,
$\Delta Ca(OH)_2$ = loss of mass as a result of $Ca(OH)_2$ decomposition at 470–510°, mg;
$\Delta CaCO_3$ = loss of mas as a result of $CaCO_3$ decomposition, mg;
m = mass of examined sample, mg.

X-ray diffraction phase characterization was carried out on all of the samples.

Results and discussion

Figures 1 and 2 illustrate DTA curves of hydrated sampls of mixture I and mixture II, respectively. It can be seen from Fig. 1 that there are three groups of thermal effects;

(a) Endothermic effects in the temperature range 100–400°, resulting from the decomposition of hydrated calcium silicates [3].

These effects were already distinct after 7 days of hydration, and they became more intense with increase of the hydration time.

(b) Endothermic effects at 470–510°, due to $Ca(OH)_2$ decomposition: with increase of the hydration time, the intensity of these effects decreased. This suggests that the components of fly ash react with $Ca(OH)_2$.

(c) Endothermic effects at 700–720°, due to $CaCO_3$ decomposition.

X-ray diffraction investigations of hydrated samples suggest the formation of poorly-crystallized hydrated calcium silicates, $CaO \cdot SiO_2 \cdot nH_2O$, and hydrated calcium aluminate, C_4AH_{13}.

DTA curves of mixture II are shown in Fig. 2. In the first stage of hydration (1, 3 and 7 days), there were endothermic effects not observed for samples hydrated

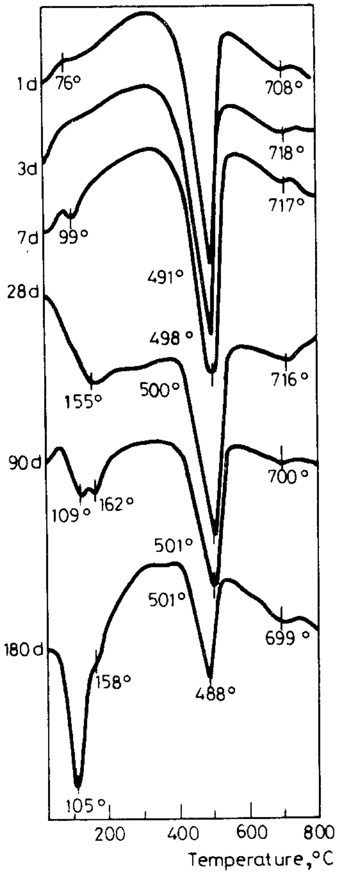

Fig. 1 DTA curves of mixture I: fly ash–$Ca(OH)_2$

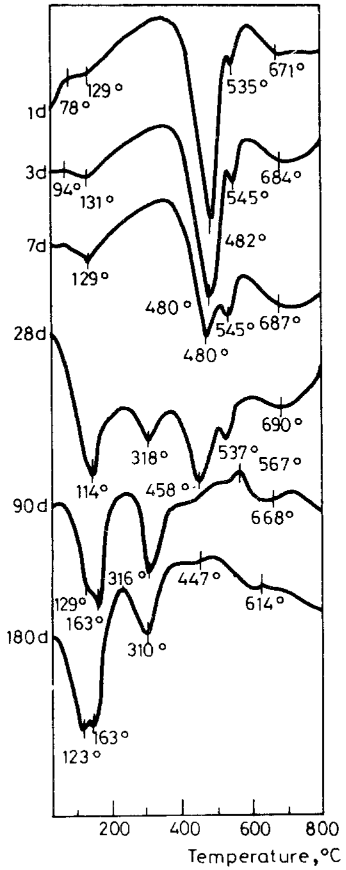

Fig. 2 DTA curves of mixture II: fly ash–$Ca(OH)_2$–$CaCl_2$

without $CaCl_2$ (Fig. 1). Another new phenomenon in the DTA curves in Fig. 2 was an endothermic effect at 537–545°, probably due to the formation of calcium silicate chloride, $Ca_3(SO)_4Cl_2$ [4]. The endothermic effect at 313–319° was characteristic of the latter stage of hydration. The occurrence of this effect agrees with results obtained by X-ray diffraction, and it was confirmed that the new phase was $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$.

The intensity of the endothermic effect due to $Ca(OH)_2$ decomposition decreased faster than in the case of mixture I. The total disappearance of this effect was noticed after 90 days of hydration. This result proves that after 90 days of hydration in the presence of $CaCl_2$ the whole amount of $Ca(OH)_2$ had reacted with the compounds of fly-ash. From the results of thermogravimetry, we calculated the quantity of $Ca(OH)_2$ which reacted with the components of fly ash.

The amount of reacted $Ca(OH)_2$ was calculated via the formula:

$$C = C_0 - C_n \tag{2}$$

where C_0 = amount of $Ca(OH)_2$ in dried sample before hydration, wt%;
C_n = amount of $Ca(OH)_2$ in sample after hydration (n = 1, 3, 7, 28, 90 or 180 days), wt%;
C = amount of reacted $Ca(OH)_2$, wt%.

Finally the results presented here from the thermogravimetric determinations (Fig. 3) show that the $CaCl_2$ admixture accelerated the reaction of fly ash with $Ca(OH)_2$.

The results should be used for the correction of the mixture ratio of binders and building materials based on fly ash.

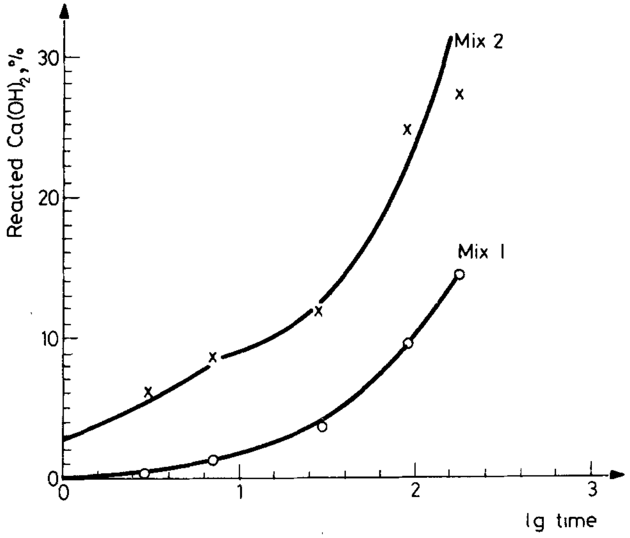

Fig. 3 Amount of reacted $Ca(OH)_2$ with fly ash in dependence on time of hydration

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Zusammenfassung — Mittels DTA und Thermogravimetrie wurde die Hydratation im System Flugasche-$Ca(OH)_2$–$CaCl_2$ verfolgt. Dabei wurde gefunden, dass $CaCl_2$ in diesem System als Aktivator wirkt. Die Ergebnisse sollen zur Korrektur des Mischungsverhältnisses von Bindemitteln und Baumaterialien auf Basis Flugasche verwendet werden.

Резюме — Дифференциальный термический анализ и термогравиметрия были использованы для контроля процесса гидратации в системе зольная пыль–$Ca(OH)_2$–$CaCl_2$, оказано, что в такой системе примесь хлористого кальция является активирующим агентом. Результаты могут быть использованы для правильного установления соотношения цементирующих присадок и стройматериалов на основе летучей золы.