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EFFECT OF SOME ADDITIVES ON THE REACTIONS IN FLY ASH–$Ca(OH)_2$ SYSTEM

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Abstract

Differential thermal analysis and thermogravimetry were used to evaluate the effect of some additives, such as $CaSO_4$, $CaCl_2$ and silica fume amorphous silica from ferrosilicon synthesis on the mechanism and kinetics of reactions occurring in fly ash–$Ca(OH)_2$ system. The accelerating role of these additives was demonstrated from the data relating to $Ca(OH)_2$ consumption in hydrated pastes, determined by TG measurements.

Keywords: additives, fly ash–$Ca(OH)_2$ system, lime, pozzolanic reaction

Introduction

Fly ash is generated as a by-product of the combustion of pulverized coal in power plants, removed as a residue by the dust collection systems from the combustion gases. For many years it has been used as cement mineral admixture or as a component in concrete production [1, 2]. The potential use of fly ash in concrete is determined by the so-called pozzolanic activity. By definition fly ash is a pozzolan [3, 4].

The pozzolanic reaction goes very slowly at room temperature and the positive effect of the products thus formed on the properties of concrete composite can be observed after a long time. The rate of pozzolanic reaction is determined by chemical and mineral composition of fly ash. The main active constituent of fly ash–vitreous aluminosilicate substance dissolves in liquid phase of hydrating systems and the silicate and aluminate ions enter the solution. This process occurs very slowly and it is a 'rate determining' step in pozzolanic reaction. It has been pointed out in many reports that at high pH the migration of aluminate and silicate anions to the liquid is significantly accelerated [5–7]. The other factors improving the fly ash reactivity are as follows: fineness, microstructure (morphology) of fly ash particles and additional activating treatment, such as grinding, thermal processing and use of chemical additives [8, 9]. DTA and calorimetric methods were widely used in the studies of cement hydration [10–17].

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In this work the effect of chemical additives in the fly ash–$Ca(OH)_2$ reaction was investigated. The role of calcium sulphate $CaSO_4$, calcium chloride $CaCl_2$ and silica fume was discussed. The hydrated pastes were subjected to DTA-TG measurements to characterize quantitatively the formation of hydration products *vs*. time.

Silica fume is formed as a result of quartz reduction in electric arc furnace, during the silicon metal or ferrosilicon alloys production. It is separated from gaseous phase in the form of very fine grained particles of spherical shape. Silica fume exhibits amorphous character. With the mean particle size of 0.03–0.3 μm and specific surface of 20 000 $m^2 kg^{-1}$ it belongs to the materials of the highest pozzolanic activity.

Experimental

Fly ash from bituminous coal combustion was used in this work. Chemical composition of slag is given in Table 1. The Blaine specific surface and the density of fly ash were 295 $m^2 kg^{-1}$ and 2.03 g cm^{-3}, respectively. Chemical composition of silica fume used as an additive is given in Table 1. The other additives, such as $Ca(OH)_2$, $CaCl_2$ and $CaSO_4$ – were commercially available, analytically pure materials.

Table 1 Chemical composition of fly ash and silica fume

Material	Content/mass%								
	L.o.i.	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	Na_2O	K_2O
Fly ash	2.9	50.8	23.9	8.6	3.6	0.8	2.8	0.8	2.9
Silica fume	2.2	90.4	1.04	2.8	0.2	–	–	0.63	1.6

Chemical composition was determined using standard procedures for cement; the rest up to 100% – the other minor components; not determined.

The following mixtures were produced (proportions given in % by mass):

- mixture I: 70% fly ash+30% $Ca(OH)_2$,
- mixture II: (70% fly ash+30% $Ca(OH)_2$)+10.0 g $CaCl_2$/100 g mixture I
- mixture III: (70% fly ash+30% $Ca(OH)_2$)+10.0 g $CaSO_4$/100 g mixture I
- mixture IV: (70% fly ash+30% $Ca(OH)_2$)+10.0 g silica fume/100 g mixture I

Mixtures I–IV were thoroughly homogenized and used in paste preparation by mixing with distilled water. The water to mixture (*w*/*m*) ratio was 0.6.

The portions of hydrating pastes were collected after 1, 3, 7, 14, 28, 90 and 180 days and subjected to the 'stopping of hydration' procedure, by removal of excess, unbound water (grinding and washing with acetone, followed by drying at 60°C for 2 h). The dried 180 mg samples thus produced were heated in TA-1 Mettler thermoanalyser in argon atmosphere, Pt crucibles, at heating rate 10°C min^{-1}.

Amount of $Ca(OH)_2$ consumed by reactive components of fly ash in pozzolanic reaction (A) was calculated from TG data using the following formulae:

$$A=A_0-A_n \tag{1}$$

where A_0 – calcium hydroxide content in the mixture before hydration, as measured by TG before hydration, [%]; A_n – calcium hydroxide content in the hydrated sample cured within n=1, 3, 7, 14, 28, 90, 180 days, [%].

The Ca(OH)$_2$ content in hydrated samples was calculated using the following formula:

$$A_n = \frac{4.11\Delta \mathrm{Ca(OH)_2} + 1.68\Delta \mathrm{CaCO_3}}{M} 100\% \tag{2}$$

where ΔCa(OH)$_2$ – mass loss (calculated from TG curve) attributed to the Ca(OH)$_2$ decomposition in the temperature range 470–510°C, [mg]; ΔCaCO$_3$ – mass loss attributed to the CaCO$_3$ decarbonisation in the temperature range 700–750°C, [mg]; M – sample mass, [mg].

The series of samples subjected to 28 days hydration process was analysed by XRD using a Philips diffractometer.

Results and discussion

In Fig. 1 the DTA curves for hydrated samples produced using mixture I [fly ash–Ca(OH)$_2$] are shown. The following three peaks can be distinguished:

- endothermic peak in temperature range 100–300°C relating to the dehydration of calcium silicate and calcium aluminate hydrates; in mixture I this peak becomes clearly visible after 7 days reaction with water,
- endothermic peak at temperature range 470–510°C attributed to the Ca(OH)$_2$ decomposition. This peak reduces for samples with longer hydration time; thus proving the progress of pozzolanic reaction (consumption of Ca(OH)$_2$ by active fly ash components),
- endothermic peak at temperature 700–750°C attributed to the CaCO$_3$ decomposition.

The formation of poorly crystallized calcium silicate hydrates (so-called C–S–H) as well as hydrated calcium aluminate $3\mathrm{CaO}\cdot\mathrm{Al_2O_3}\cdot 13\mathrm{H_2O}$ (Fig. 3), was found in XRD studies; this also proves the progress of pozzolanic reaction in the fly ash–Ca(OH)$_2$ system.

The course of DTA curves for mixture II (fly ash–Ca(OH)$_2$–CaCl$_2$) is quite different (Fig. 2). At early hydration time (1–3 days) DTA plots reveal the presence of endothermic peak at temperature range 537–545°C. This peak may be attributed to the formation of calcium chlorosilicate $\mathrm{Ca_3(SiO_4)Cl_2}$ on heating [18]. For longer hydration time (7 days or more) an endothermic peak with maximum at temperature 313–319°C appears on DTA curves. This peak could be attributed to the presence of hydrated calcium chloroaluminate $3\mathrm{CaO}\cdot\mathrm{Al_2O_3}\cdot\mathrm{CaCl_2}\cdot 10\mathrm{H_2O}$ (Fig. 3); dehydration of this compound takes place at the temperature range 300–320°C [19].

In case of hydrated samples based on mixture II the endothermic peak of Ca(OH)$_2$ decomposition is significantly diminished with time of hydration. In 90 days hydrated sample calcium hydroxide is totally bound to form hydrated calcium aluminates, chloroaluminates and silicates.

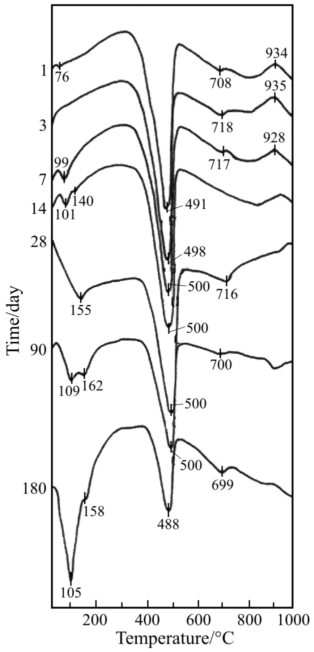

Fig. 1 DTA curves of samples produced from mixture I

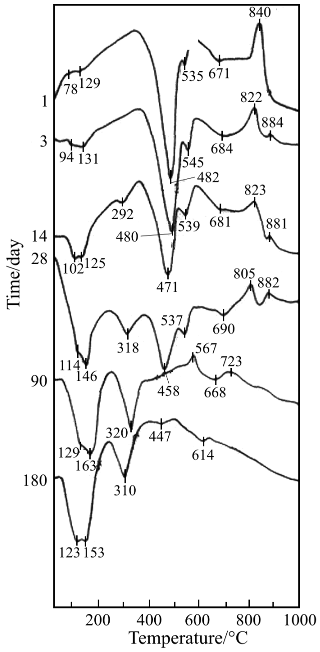

Fig. 2 DTA curves of samples produced from mixture II

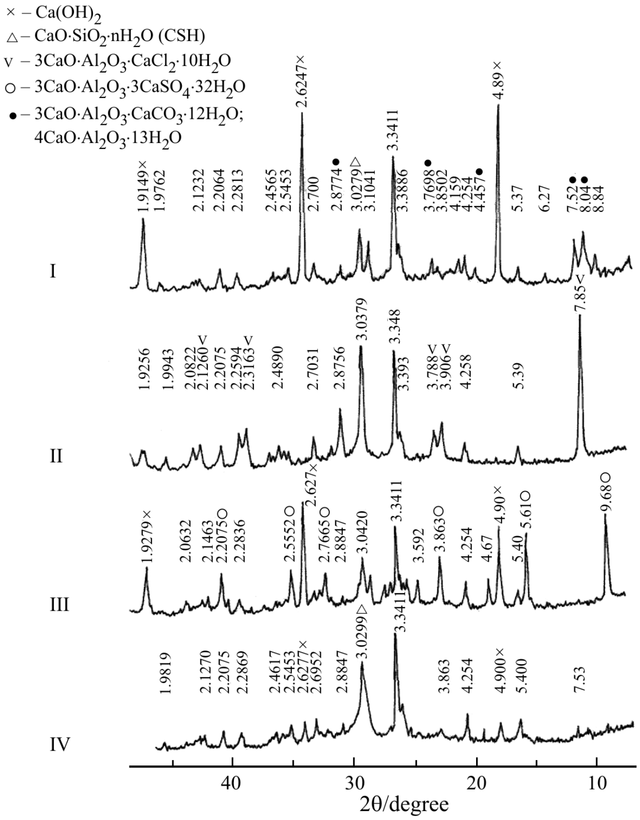

Fig. 3 XRD patterns of samples produced from 28 days hydrated mixture I– IV

DTA curves plotted for samples prepared from mixture III (fly ash–Ca(OH)$_2$–CaSO$_4$) exhibit the endothermic peak being the result of hydrated calcium aluminates and silicates decomposition (dehydration) with the maximum at temperature 130–150°C (Fig. 4). The decrease in Ca(OH)$_2$ content with hydration time is also observed. The XRD patterns reveal the formation of hydrated calcium sulphoaluminate – ettringite 3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O (Fig. 3).

In the presence of silica fume – mixture IV (fly ash–Ca(OH)$_2$–silica fume), the Ca(OH)$_2$ consumption begins early and the Ca(OH)$_2$ content decreases quickly with hydration time. (Fig. 5; endothermic peak at temperature 466– 492°C). The reaction of this mixture with water results in the formation of calcium silicate hydrate (C–S–H) of low CaO/SiO$_2$ ratio, as observed from the endothermic peak on DTA curve in the temperature range 115–130°C occurring together with the exothermic one in the temperature range 847–938°C. The latter is attributed to the wollastonite formation from the dehydrated C–S–H of CaO/SiO$_2$ ratio close to 1. On the XRD pattern (Fig. 3) the peaks derived from C–S–H can be observed.

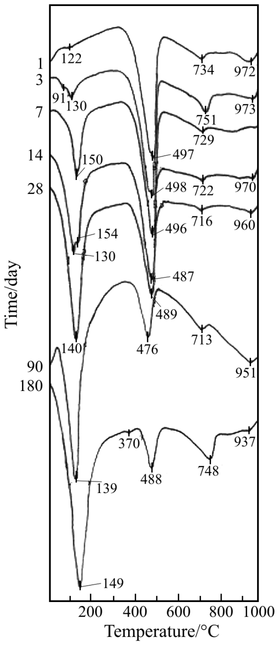

Fig. 4 DTA curves of samples produced from mixture III

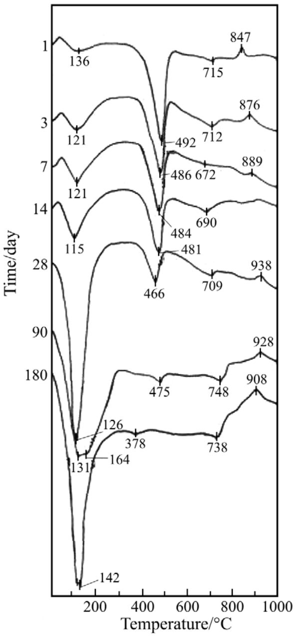

Fig. 5 DTA curves of samples produced from mixture IV

On the XRD pattern (Fig. 3) the peaks derived from C–S–H can be observed. The amount of $Ca(OH)_2$ consumed in pozzolanic reaction by reactive fly ash components *vs*. time of hydration, is plotted in Fig. 6. The calculations were done using the formula (1) and (2) given above.

The data presented above prove that the additives, such as $CaCl_2$, $CaSO_4$ and silica fume, play the role of an activator in fly ash–$Ca(OH)_2$ hydrating mixture, accelerating the transformation of fly ash substance into the hardened matter.

The silica fume additive seems to be the most efficient, particularly at early age. Such proportioning of two components having quite different pozzolanic properties (poor and active pozzolan mixed together) is frequently used in so-called 'high performance' concrete technology [1, 2].

The admixtures taken into account in this study have their counterparts in the components of some waste materials. As it has been mentioned earlier, silica fume is produced in some metallurgical processes. In turn, $CaSO_4$ or $CaCl_2$ occur in desulphurisation wastes or as by-products in some chemical technologies. These materials can be used to produce the mixtures for different purposes, e.g. soil stabilisation, underground works, concrete and many others. Thus it may be possible to improve the hydraulic properties of waste product from power industry – fly ash – by use of other wastes (by-products). This is significant from the natural environment point of view. However, application of $CaCl_2$ containing materials must be limited, because of the corrosion hazard.

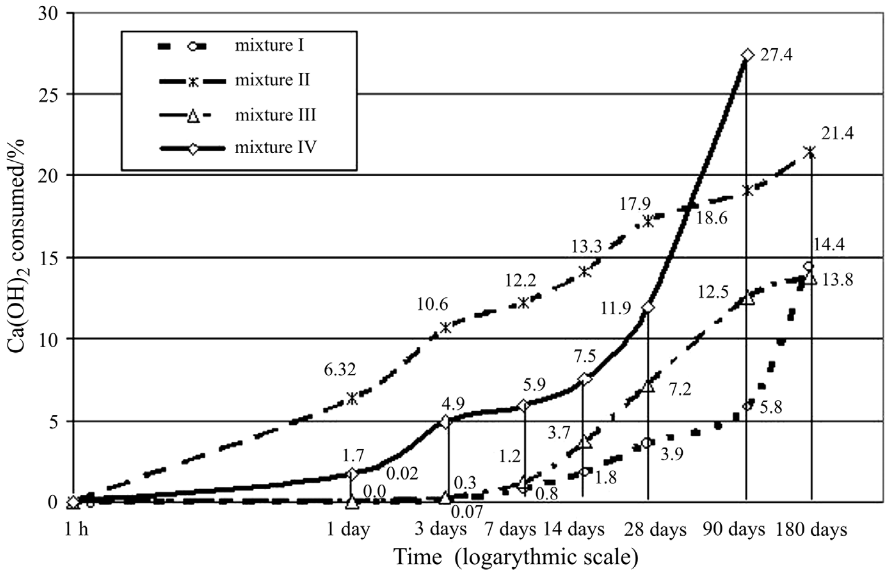

Fig. 6 $Ca(OH)_2$ consumed in pozzolanic reaction by reactive components of mixtures I– IV *vs*. time of hydration

Conclusions

- The reaction between $Ca(OH)_2$ and fly ash, which is relatively slow and thus limiting the fly ash implementation as a component of cementitious mixtures, can be successfully monitored using the DTA-TG method.
- The pozzolanic reaction in the system $Ca(OH)_2$–fly ash can be significantly accelerated by use of additives, such as silica fume, anhydrite $CaSO_4$, $CaCl_2$. The kinetics of $Ca(OH)_2$ consumption can be evaluated by TG; DTA is helpful in the determination of the mechanism of fly ash–$Ca(OH)_2$–additive interaction.

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