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THERMAL ANALYSIS OF HYDRATED FLY ASH–LIME PASTES

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Abstract

Fly ash is the ash precipitated from the exhaust fumes of coal-fired power stations. It consists mainly of active silica and alumina, with large amounts of glass. The aim of this work was to study the pozzolanic activity of fly ash with lime by means of DTA as a function of the lime content and the curing time. The curves revealed that the rate of hydration, as indicated by the residual lime and hydrated compounds, increases with increasing lime content and curing time. It is concluded that fly ash can be used as a blending material in pozzolanic cement.

Keywords: differential thermal analysis, fly ash, lime, pozzolana

Introduction

Fly ash, a pulverized fuel ash, is the ash precipitated electrostatically from the exhaust fumes of coal-fired power stations. It is the most common artificial pozzolana, which is defined as a siliceous or aluminous and siliceous material, which is in itself chemically inert, and possesses little or no cementitious value, but, when in a finely divided form and in the presence of water, reacts with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Fly ash has at least the same fineness as cement, so that the silica is readily available for reaction. The siliceous material used in this study (fly ash) is fully amorphous silica with high hydraulic activity. The active content of fly ash consists of silica (SiO_2) and alumina (Al_2O_3), but the pozzolanic activity can not be judged by chemical composition alone. The major crystalline phases of fly ash are quartz, mullite ($3Al_2O_3$–$2SiO_2$) and comparatively large amounts of glass [1].

The pozzolanic activity of fly ash is defined in terms of the reactions of SiO_2 and Al_2O_3 in fly ash with $Ca(OH)_2$ liberated during the hydration of portland cement to form CSH and calcium aluminate hydrate. In the presence of gypsum, ettringite can be produced. Fly ash is suitable for massive concrete structures because its addition as a partial substitute for cement reduces the heat of hydration, thereby improving the overall durability of the concrete [2, 3].

The pozzolanic activity of fly ash is confirmed by the study of the behaviour of fly ash in saturated lime solution [4]. The determination of free lime in port-

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land cement and in portland cement with fly ash pastes suggests a reaction between $Ca(OH)_2$ and fly ash particles. After one year, a significant amount of $Ca(OH)_2$ is combined with the fly ash to form hydration products such as CSH and calcium aluminate hydrates.

This paper reports the results of an investigation of the fly ash–$Ca(OH)_2$ reaction. Pastes of fly ash with $Ca(OH)_2$ were studied by determining the insoluble residue, free lime and combined water contents and by studying the results of DTA of lime–fly ash pastes hydrated for up to 90 days.

Experimental techniques

Pulverized fly ash and BDH analytical grade $Ca(OH)_2$ were used in this investigation. The chemical analysis of the fly ash gave the following results: SiO_2= 47.40; Al_2O_3=31.26; Fe_2O_3=4.64; CaO=8.57; MgO=0.72; SO_3=1.30; and ignition loss=5.40%. The main constituent of the fly ash is glass in an amorphous state, with small amounts of quartz and mullite. The amorphous materials are SiO_2, Al_2O_3 and Fe_2O_3.

Different mixes were prepared from fly ash and $Ca(OH)_2$ in mass ratios 90:10, 70:30 and 50:50. The dry constituents were mechanically mixed for 1 h in a porcelain ball mill, two balls being used to attain complete homogeneity. The hydration was conducted on a paste. The paste was mixed in a porcelain mortar for 3 min, at a water/solid ratio of 0.40, then left in a desiccator saturated with water vapour (100% relative humidity) and covered with moist cottonwool to minimize carbonation.

After a predetermined curing time, the hydration was stopped, using a technique described elsewhere [5, 6]. The hydration kinetics was studied by the determination of the combined water, free lime and insoluble residue contents of the hydration samples. The free lime content was estimated by the ammonium acetate method [7]. The combined water content was taken as the percentage ignition loss of the dried samples minus the amount of water from free $Ca(OH)_2$ in the samples. Additionally, the insoluble residue was determined by weighing 1 g of dried sample, adding 30 ml cold 1:1 HCl solution and stirring for 15 min [8]. The suspension was filtered on ashless filter paper and washed with hot distilled water till free from chloride. The insoluble residue was determined by igniting the precipitate at 1000°C for 1 h.

The hydration products were identified by a DTA technique (DT-30 Thermal Analyzer Shimadzu Co., Koyoto, Japan). Calcined alumina was used as inert material. A sample of 50 mg (–76 μm) was housed in a small platinum-rhodium crucible and heated at a heating rate of 20°C min^{-1} in atmospheric air.

Results and discussion

Figure 1 shows DTA curves of a hydrated 90:10 fly ash–lime mixture as a function of curing time. The results indicate four endothermic peaks, at

100–200, 480, 575 and 770°C. The small endothermic effects below 200°C may be due to the dehydration of an interlayer of CSH and of calcium aluminate and sulphoaluminate hydrates. The second endotherm is attributed to the decomposition of $Ca(OH)_2$, while the endotherm at 575°C is from the α, β-quartz conversion [1]. The fourth endothermic peak, at 770°C, is characteristic of the decomposition of $CaCO_3$. The sample hydrated for 3 days exhibits a very small broad peak of calcium silicate and calcium aluminate or sulphoaluminate hydrates, and also marked peaks $Ca(OH)_2$, the α, β-quartz conversion and $CaCO_3$. As the hydration proceeds, the intensity of the $Ca(OH)_2$ peak decreases up to 28 days, and the peak has disappeared by 90 days, with simultaneous increases in the hydrated calcium silicate, aluminate and sulphoaluminate. $CaCO_3$ is still present in all samples, due to the carbonation of $Ca(OH)_2$; as the hydration products have a highly amorphous character, they are readily attacked by atmospheric CO_2. This attack occurred even when the hydrated samples were kept in a desiccator containing soda lime and calcium chloride as desiccants. Meanwhile, the quartz (amorphous silica) was completely consumed by 90 days, due to the reaction with $Ca(OH)_2$ forming hydrated products, as can be seen from the endothermic peak at 575°C.

In fly ash–lime pastes, ettringite is already present after 5 h, and persists up to 28 days without any transformation into monosulphate [9]. The conversion of ettringite occurs in fly ashes with a low SO_3 content [10]. The fly ash–lime pastes applied in this study therefore contain ettringite and/or monosulphate hydrate due to the presence of ~1.30% SO_3.

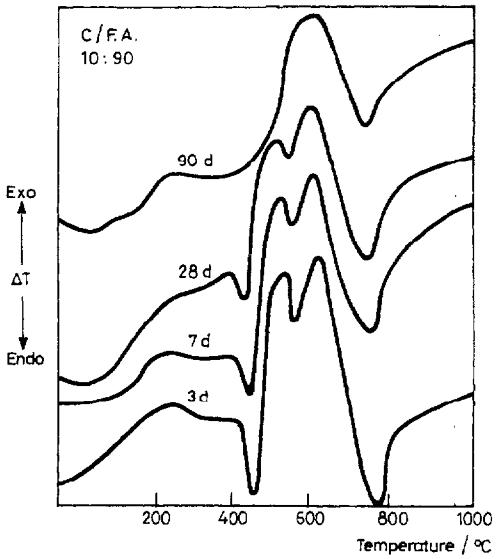

Fig. 1 DTA curves of 10:90 lime–fly ash specimens as a function of curing time

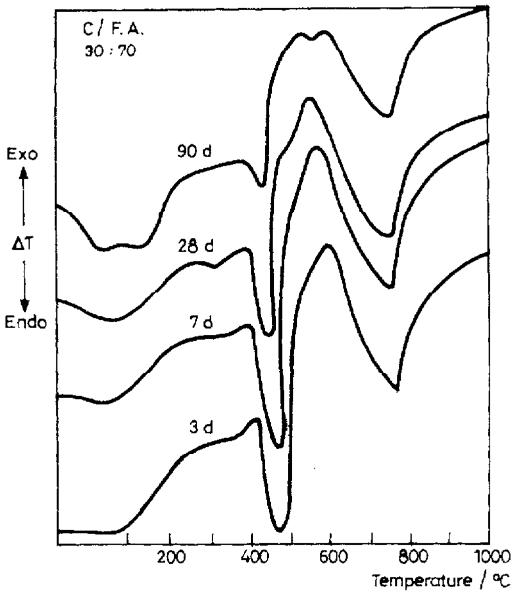

Fig. 2 DTA curves of 30:70 lime–fly ash specimens as a function of curing time

Figure 2 illustrates DTA curves of a hydrated 70:30 fly ash–lime as a function of curing time. At 9 days, a small peak of calcium silicate, sulphoaluminate or aluminate hydrates is distinguished; the peaks characteristic of $Ca(OH)_2$ and $CaCO_3$ appear. As the curing time is increased, the amount of $Ca(OH)_2$ decreases up to 90 days, when it is present in traces. Simultaneously, the amounts of calcium silicate and aluminate hydrates increase with curing time. At 90 days, different hydrates with various compositions and crystalline states are present [11]. A $CaCO_3$ phase is also detected at all stages of hydration. Quartz is not the DTA curve; this may be due to the higher content of $Ca(OH)_2$, which reacts with quartz (amorphous silica) to furnish hydrated CSH products.

The first step in the silica–alumina–lime hydration reaction is the dissolution of these compounds. The dissolved materials react together to give CSH and also calcium aluminate and sulphoaluminate hydrates. As the amount of lime is increased, the residual silica disappears due to the chemical reaction of lime with the silica and alumina constituents of fly ash, leading to the formation of hydrated calcium silicate and aluminate or sulphoaluminate.

Figure 3 depicts DTA curves of a hydrated 50:50 fly ash–lime as a function of curing time. It is clear that, as the lime content is increased, the residual $Ca(OH)_2$ increases, as do the hydrated compounds such as calcium silicate, aluminate or sulphoaluminate, as indicated by their endothermic peaks. Figure 3 shows the appearance of free $Ca(OH)_2$ at all stages of hydration. The endotherm at 575°C is not seen in the samples at any stage of hydration. This may be due to the complete consumption of quartz (amorphous silica) by the free $Ca(OH)_2$ in the hydrated samples at all stages of hydration.

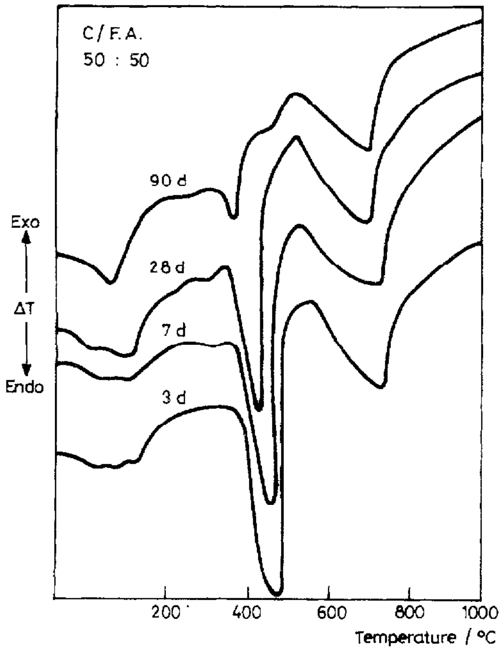

Fig. 3 DTA curves of 50:50 lime–fly ash specimens as a function of curing time

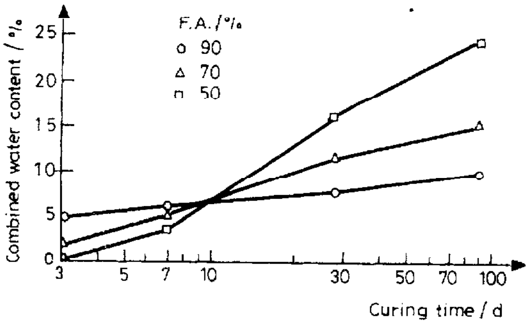

Fig. 4 Combined water contents of hydrated lime–fly ash specimens as a function of curing time

The kinetics of hydration can be studied from the combined water contents of the different hydrated samples as a function of the mix composition and the curing time up to 90 days. These results could be corrected for the hydration products themselves, provided that each mole of free CaO is accompanied by one mole of non-evaporable water. The results obtained are presented graphically in Fig. 4, where the combined water denotes the water of hydration products of fly ash. It is clear that the combined water content increases with time for all hydrated samples, due to the continuous hydration of the lime with fly ash. Increase of the lime content may inhibit the rate of hydration of fly ash during the early stages of hydration. As the amount of lime is increased, the corresponding amount of combined water is enhanced. This indicates that fly ash has pozzolanic activity.

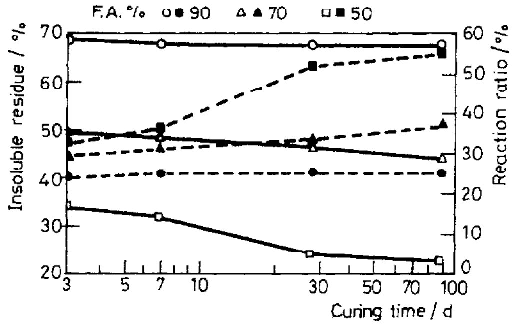

Fig. 5 Insoluble residue and reaction ratio of hydrated lime–fly ash specimens as a function of curing time

Figure 5 shows the relationships between insoluble residue content, reaction ratio and curing time for all mixes up to 90 days. The insoluble residue decreases continuously with curing time. The 10/90 lime–fly ash mix exhibits a very small decrease from 3 up to 90 days. This is largely due to the decrease of the lime content. The DTA curves reveal that free lime is found up to 28 days. This is mainly chemisorbed on the hydrated products. As the lime content is increased the insoluble residue decreases with curing time for the mixes containing 30 and 50% lime. This indicates that there is enough lime to react with the fly ash forming hydrates. The residue also decreases with increase of the lime content. The decrease in the insoluble residue for all mixes from 3 up to 90 days is 0.95, 5.17 and 10.72% for the samples containing 10, 30 and 50% lime, respectively. Further, it is clear that the hydraulic reactivity of the fly ash increases with increase of the lime content. The results relating to the insoluble residue are in good agreement with the combined water findings and those of DTA. It may be concluded that fly ash can be used as a blending material for the preparation of pozzolanic cement.

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