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DTA STUDY OF THE INFLUENCE OF LIME CONTENT OF LOW-CALCIUM FLY ASHES ON THE POZZOLANIC REACTION

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ABSTRACT

Three low-calcium fly ashes, similar in fineness, glass content and chemical composition, except for the CaO content which varied from 1.9 to 9.3%, were hydrated at 20, 40 and 55 ° C, with and without added lime, for curing periods ranging from 1 to 70 days, in order to evaluate the influence of CaO incorporated into fly ash on the pozzolanic reaction. It has been found that the fly ash containing the greater CaO content was able to produce, without addition of lime, a calcium silicate hydrate at room temperature. On the contrary, the other fly ashes required higher temperatures and/or addition of lime in order to give the same effect. The contribution made to the pozzolanic reaction by the lime incorporated into low-calcium fly ashes having relatively high CaO contents, is an inherent property of the fly ashes themselves and cannot be related to a greater lime availability for the reaction.

INTRODUCTION

While it is well known that lime plays a substantial role during the hydration of high-calcium fly ashes very little is known about the influence of CaO content of low-calcium fly ashes on the pozzolanic reaction.

This theme of research may be of interest, especially in countries where low-calcium fly ashes, having a great variability in the calcium oxide content, are generated.

In Italy low-calcium fly ashes have a CaO content ranging from 1 to 10%. This depends mainly on the fact that coal is almost entirely imported and comes from a wide range of countries.

A recent investigation [1] on the behaviour of Italian low-calcium fly ashes in Portland cement mortars has shown that fineness, amount of amorphous phase and CaO content are the main fly ash parameters able to influence its technical performance. While the influence of fly ash fineness and glass content on its reactivity is commonly well recognized [2–7], the role played by CaO incorporated into fly ash is not yet well understood.

In this paper the pozzolanic behaviour of some low-calcium fly ashes similar in fineness, glass content and chemical composition, except for the

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CaO content, has been examined. The products of the pozzolanic reaction are ill-crystallized calcium silicate hydrates [8], which easily lose water under moderate heating and can be detected by DTA, an experimental technique widely diffused in the field of cement chemistry.

EXPERIMENTAL

Materials

A large number of samples, containing particles in the range 45–63 μm and obtained by sieve analysis on systematically sampled low-calcium fly ashes generated within all the Italian coal-fired power plants, were examined. Three samples were selected, arising from American, Polish and South African coals, subsequently designated Fly Ashes Nos. 1, 2 and 3, respectively. They had the same glass content (75%) and a similar chemical composition except for the CaO content, which was 1.9, 6.3 and 9.3%, respectively. Their chemical composition, shown in Table 1, was determined through X-ray fluorescence, flame atomic absorption and gravimetric analysis (for sulphates). Loss on ignition was performed by heating to constant weight at 750 ° C.

Glass content was estimated as the ash fraction soluble in a 2 wt.% HF solution, according to Murat's method [9].

For the fly ash–lime mixtures an analytical grade calcium hydroxide, produced by Merck, was used.

TABLE 1

Chemical composition of fly ashes (wt.%)

Compound	Fly Ash no.		
	1	2	3
SiO_2	47.17	46.27	45.74
Al_2O_3	26.83	26.05	25.49
Fe_2O_3	6.42	7.02	5.91
MnO	0.03	0.15	0.03
TiO_2	1.43	1.01	1.47
CaO	1.89	6.34	9.33
MgO	1.95	2.61	2.02
Na_2O	0.53	0.55	0.59
K_2O	2.47	2.23	1.98
SO_3	0.79	0.87	0.75
l.o.i. [a]	7.12	6.57	6.31

[a] Loss on ignition.

Paste hydration

Two series of pastes, A and B, with the same water/solid ratio (0.6), were mist cured at 20, 40 and 55 °C for 1, 2, 3, 5, 7, 10, 14, 21, 28, 35, 42, 56 and 70 days.

Within Series A the solids to be hydrated were formed by the three fly ashes alone. Within Series B the solids were three fly ash–lime mixtures with a 15 : 1 fly ash/lime weight ratio.

DTA tests

At the fixed aging times, the hydration was stopped by grinding under acetone, followed by washing with ether. The hydrated samples were then stored in a desiccator in the presence of P_2O_5. The then dried pastes were submitted to DTA.

The equipment used was a Dupont 900 apparatus; the operating conditions were, heating rate $10\,°C\ min^{-1}$ and DTA sensitivity $80\ mV\ in^{-1}$.

The weight of all the specimens submitted to DTA was 50 mg. For the Series A pastes only containing Fly Ashes Nos. 2 and 3, specimens of 12.5 and 10 mg in weight, respectively, were also tested.

RESULTS AND DISCUSSION

Series A at 20 °C

Up to the longest aging time (70 days) Fly Ashes Nos. 1 and 2 do not react at all with water. On the contrary, Fly Ash No. 3 gives a calcium silicate hydrate, whose presence after 28 days is revealed by the endothermal peak at about 90 °C (Fig. 1). This result proves that some low-calcium fly ashes are self-hydraulic like high-calcium fly ashes, although the hydration rate of the latter is considerably higher.

Series A at 40 and 55 °C

Owing to the well-known favourable effect of curing temperature on the pozzolanic reaction, the fly ash behaviour at room temperature after very long curing periods may be foreseen by means of hydration tests performed at higher temperatures for shorter aging times.

However an increase to 40 °C of curing temperature has no effect, within the aging times examined, on the hydration of both Fly Ashes Nos. 1 and 2. At 55 °C, on the contrary, these fly ashes behave differently. While Fly Ash No. 1 still does not react with water, for Fly Ash No. 2 the signal of calcium silicate hydrate is clearly distinguishable after 42 days (Fig. 2).

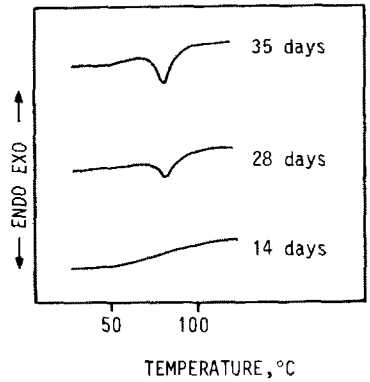

Fig. 1. Thermograms of Fly Ash No. 3, Series A at 20 °C.

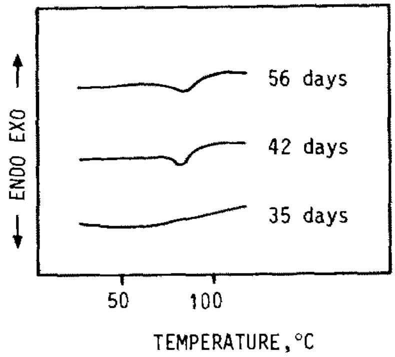

Fig. 2. Thermograms of Fly Ash No. 2, Series A at 55 °C.

As far as Fly Ash No. 3 is concerned, the aging times at which the first appearance of the reaction product was observed were 14 and 10 days, at 40 and 55 °C respectively (Fig. 3).

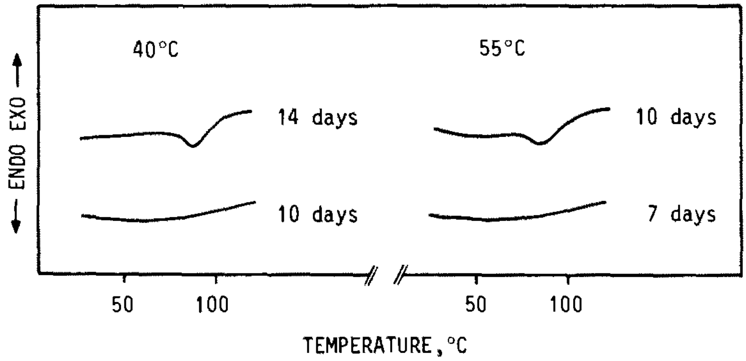

Fig. 3. Thermograms of Fly Ash No. 3, Series A at 40 and 55 °C.

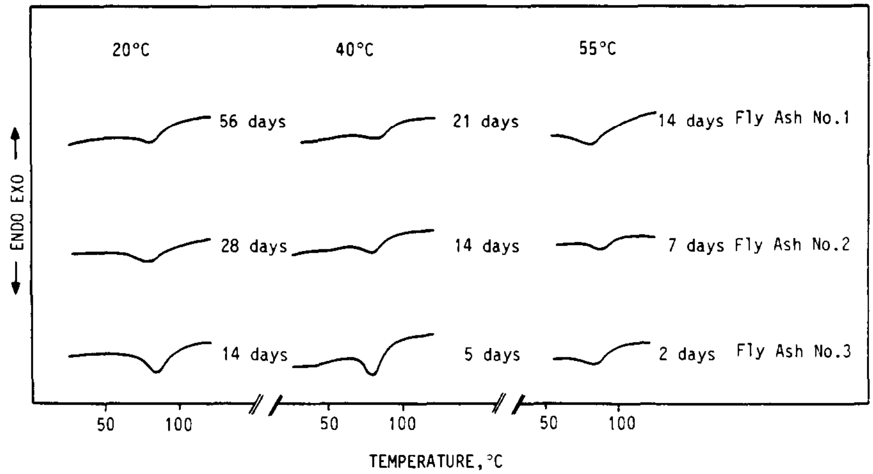

Fig. 4. Thermograms of Fly Ashes Nos. 1, 2 and 3, Series B at 20, 40 and 55 °C.

On the whole the Series A data suggest a reactivity scale regulated by the lime content of fly ash (Fly Ash No. 3 > Fly Ash No. 2 > Fly Ash No. 1). The higher hydration rate of Fly Ash No. 3 does not depend on the fact that a larger amount of lime is available for the reaction, but is an intrinsic property of the fly ash itself; these same results were obtained after reducing, respectively, to 1/5 and 1/4 the weight of Fly Ash No. 3 and No. 2 paste specimens for DTA, in order to have for both these fly ashes about the same absolute amount of lime available for the reaction as that of Fly Ash No. 1.

Series B at 20, 40 and 55 °C

Figure 4 shows the thermograms of the Series B pastes at the aging times for which the first appearance of the reaction product was observed. These times and the corresponding ones for the Series A pastes are collected in Table 2.

TABLE 2

Aging times (days) at which the reaction product was first observed

	20 °C		40 °C		55 °C	
	A	B	A	B	A	B
Fly Ash No. 1	[a]	56	[a]	21	[a]	14
Fly Ash No. 2	[a]	28	[a]	14	42	7
Fly Ash No. 3	28	14	14	5	10	2

[a] Not observed.

It can be noted that the lime addition causes earlier formation of the calcium silicate hydrate generated by the three ashes. The enhancement of the reaction rate of Fly Ashes Nos. 1 and 2 is evidently attributable to the peculiar effectiveness of the contribution of the added lime. As far as Fly Ash No. 3 is concerned, this enhancement has to be mainly related to the increased lime availability. As a matter of fact, the effect of the lime incorporated into Fly Ash No. 3 on the pozzolanic reaction is stronger than that of the lime added. This observation is based on the comparison between two systems containing about the same amount of available lime: Fly Ash No. 3—Series A and Fly Ash No. 1—Series B. Table 2 shows that, at all the examined temperatures, the formation of the reaction product in the former system is earlier.

CONCLUSIONS

The lime content of low-calcium fly ashes can contribute to the formation of calcium silicate hydrates generated in the pozzolanic reaction. This contribution depends on the amount of lime contained in the fly ash: while it is negligible when this amount is low, it can be important and more significant than that of added lime, when the content of incorporated lime is relatively high.

This phenomenon is not related to a greater lime availability within the reaction system, but is an intrinsic characteristic of the fly ash itself.

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