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THE INFLUENCE OF POZZOLANIC MATERIALS ON THE MECHANICAL STABILITY OF ALUMINOUS CEMENT

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ABSTRACT

High alumina cement paste, in the presence of silica fume, shows an increasing strength trend even at 20°C and 40°C, since this pozzolan causes the formation of gehlenite hydrate (C_2ASH_8) and therefore strongly reduces the transformation of hexagonal aluminate hydrates (CAH_{10}, C_2AH_8) into the cubic hydrate (C_3AH_6) which is responsible for the strength loss of high-alumina cement mixes at higher temperatures (>20°C).

On the contrary, fly ash is not suitable for reducing the transformation of hexagonal hydrates into the cubic phase. Consequently, the strength at 20°C and 40°C of the fly ash-high alumina cement mixes decrease as well as the high alumina cement pastes in the absence of pozzolan.

Introduction

High alumina cement is particularly suitable for manufacturing sulphate resistant concretes and in particular cement mixes which are able resist the sea water aggression. Moreover, due to early high its strength, this cement, has been widely used in structural engineering in the sixties. However, in the following decade, the first drawbacks were reported which have been connected with a strength reduction in time.

Considerable efforts have been devoted to this cement and to investigate the main causes of reduction in strength. It has been established that high water\cement ratios as well as high curing temperatures cause a progressive strength decrease associated with the conversion of hexagonal calcium aluminate hydrates (CAH_{10} and C_2AH_8) into the cubic hydrate (C_3AH_6) with a lower specific weight. Substantially, this conversion causes the remarkable increase in porosity which is responsible for the strength decrease, because of the transformation of the voluminous hexagonal hydrates into the more dense cubic phase. Due to this reason, the French standard specifications allow the use of high alumina cement for concrete devoted to structural applications provided that the water\cement ratio is not higher than 0.40, so that the strength decay is negligible or even zero.

Many attempts have been made to avoid this strength loss by using products which could stabilize the hexagonal hydrates. In particular it has been found [1,2] that the addition of calcium carbonate has a beneficial effect, but the problem has yet not been completely resolved. More recently, some researchers have suggested the use of mixtures of high alumina cement and ground blast furnace slag [3-6] or high alumina cement and pozzolan [6,7] as a solution for this problem. In fact, the use of these mixtures seems to inhibit or strongly hinder the strength decrease. The results obtained in these researches have also been patented [8,9]

The aim of the present work is to check the validity of these proposals with particular reference to the mixture of high alumina cement and pozzolans in the form of silica fume or fly ash.

Materials and methods

Three groups of cement paste specimens (40 X 40 X 160 mm) have been prepared. In the first group only high alumina cement (Ciment Fondu, Lafarge) has been used as binder.

In the second group, part of the cement has been replaced by silica fume (15% and 30% by weight) and in the third group the high alumina cement has been partially replaced by fly ash (20% and 40% by weight). The chemical analysis of the high alumina cement, silica fume and fly ash used are reported in Table 1.

TABLE 1

Chemical composition of the aluminous cement

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
4.00	38.70	16.50	39.20	0.52	0.02	0.11	0.15

Chemical composition of the fly ash

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
46	30	4.2	4.8	1.1	1.1	0.3	5.5

Chemical composition of the silica fume

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
98	0.1	0.1	0.1	0.2	0.1	0.1	1

The three binding systems have been hydrated by using a water\solid ratio of 0.4. Obviously, in the specimens containing silica fume or fly ash as partial substitutes for high alumina cement, the use of the same water\solid ratio (0.4) involves a water\cement ratio which increases by increasing the amount of pozzolanic material to replace the high alumina cement. In the specimens containing silica fume a naphtalene-based superplasticizer has been used to produce an adequate workability for the placement of the cement mixes. The specimens were demoulded after one day of curing at room temperature (20°C) and each group was further divided into three parts. Each part was then immediately placed in its own curing environment consisting of water at 5°C, 20°C and 40°C.

Periodically, between 1 and 12 months, compressive strength tests and X-ray diffraction analyses were carried out on all the specimens, in order to detect the relationship existing between strength and kinetics of formation and\or conversion of hydrated calcium aluminates.

Results and discussion

Figure 1 shows the strength behaviour of specimens produced by high alumina cement alone as a function of time, at different curing temperatures.

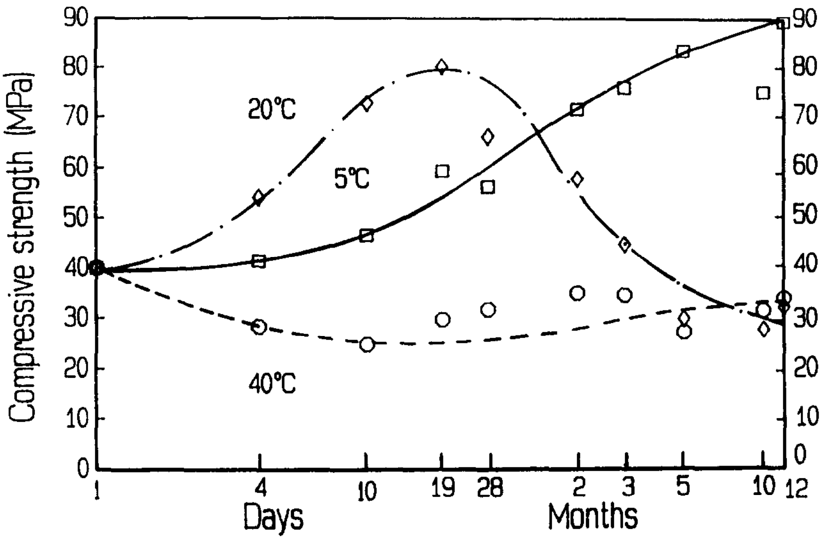

FIG. 1
Compressive strength of specimens with only high alumina cement.

In particular, for the samples kept at 5°C, the compressive strength increases and at the end it achieves a maximum of 90 MPa. For the specimens kept at 20°C, the maximum strength value (80 MPa) has been recorded after only 19 days. Afterwards, the strength value rapidly decreases up to 30 MPa at 1 year's curing time. At 40°C, a moderate decrease in strength during the first 10 days can already be noticed. Then there is a slight increase up to 30 MPa.

The X-ray diffraction patterns of Fig.2 show the remarkable influence of the temperature on the conversion of hexagonal hydrates (CAH_{10}, C_2AH_8) into the cubic hydrate (C_3AH_6) which is responsible for mechanical decay. At 40°C the transformation from the hexagonal hydrates into the cubic phase is completed in the first 28 days. At 5°C the XRD peaks of the cubic hydrate are small even after 300 days.

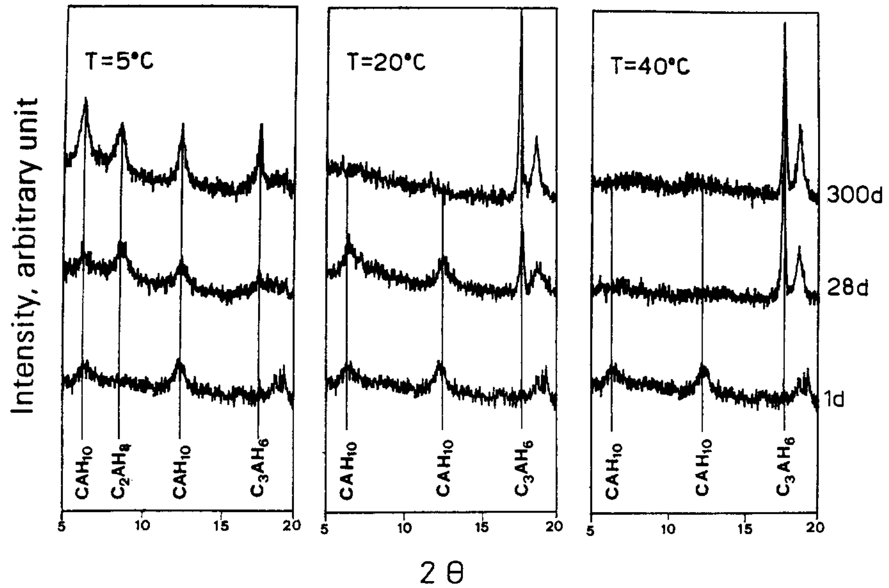

FIG. 2
X-Ray patterns of mortar samples with only high alumina cement.

The fact that the transformation may or may not occur, reflects the strength behaviour at the three different curing temperatures.

Figure 3 shows the strength behaviour of specimens prepared with 15% silica fume and 85% high alumina cement. For the specimens kept at 5°C the strength-time curve is similar to that of the alumina cement alone even though the strength values are systematically lower. For the specimens kept at higher temperatures (20°C, 40°C) the strength results are significantly different. In particular, at 20°C, the strength shows a progressive increase during the first two months of curing followed by a slight decrease and stabilization. This trend is very different to that recorded with high alumina cement alone showing in a sharp decrease in strength (Fig.1). At 40°C, no strength decrease can be observed. There is a progressive strength increase up to 40 MPa during the first two months of curing. Then no significant strength change has been found.

These substantially positive results, are probably due to the effect of amorphous silica in silica fume on the kinetics of transformation of hexagonal hydrates favouring the formation of gehlenite hydrate (C_2ASH_8) at the expenses of the cubic phase (C_3AH_6). This hypothesis is confirmed by the results obtained from the X-ray diffraction analyses shown in Fig.4 up to 300 days of curing. It can be observed, that at 20°C the gehlenite hydrate is present instead of C_3AH_6. This can explain the significant strength increase. At 40°C, although silica fume is present, appreciable amounts of C_3AH_6 are formed and consequently the strength is lower than at higher temperatures.

In Fig.5 the strength curves of specimens prepared with 30% of silica fume and 70% of high alumina cement are shown. The addition of high amounts of silica fume at the same water\solid ratio and then at a higher water\cement ratio, negatively affects the development of strength which progressively increases in time, but never reaches values which could be of practical interest.

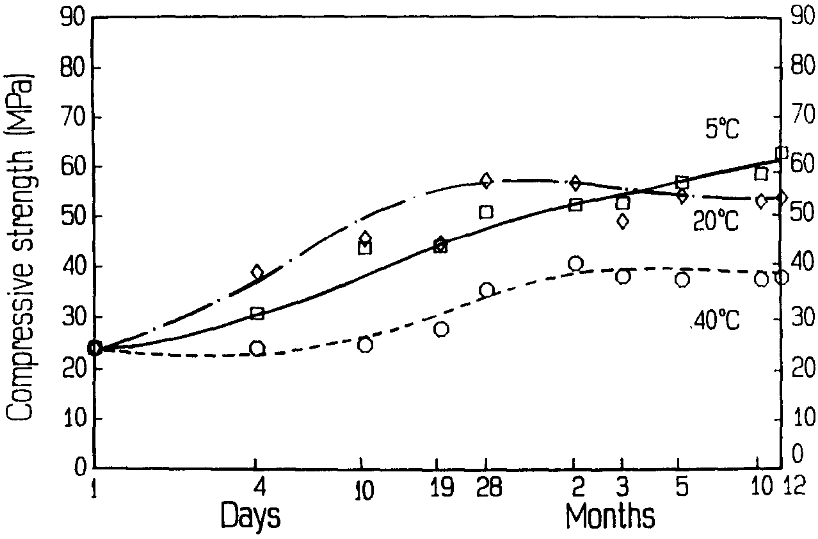

FIG. 3
Compressive strength of specimens with 15% silica fume at 300 days of curing.

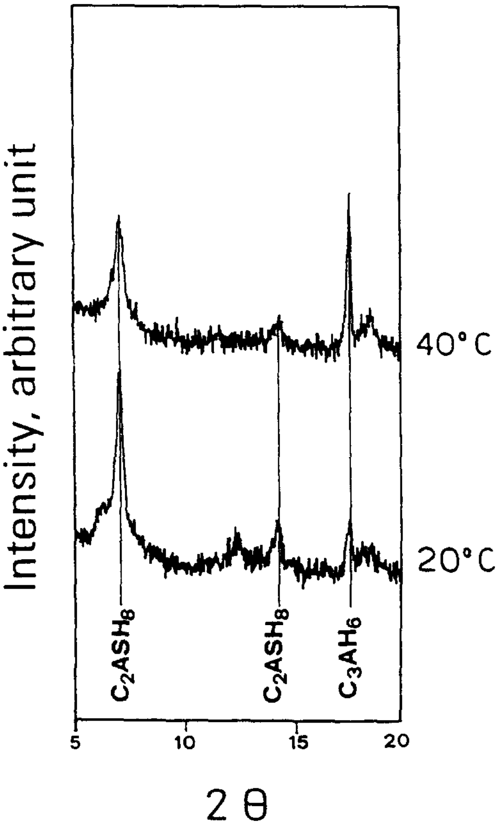

FIG. 4
X-Ray patterns of mortar samples with 15% silica fume at 300 days of curing.

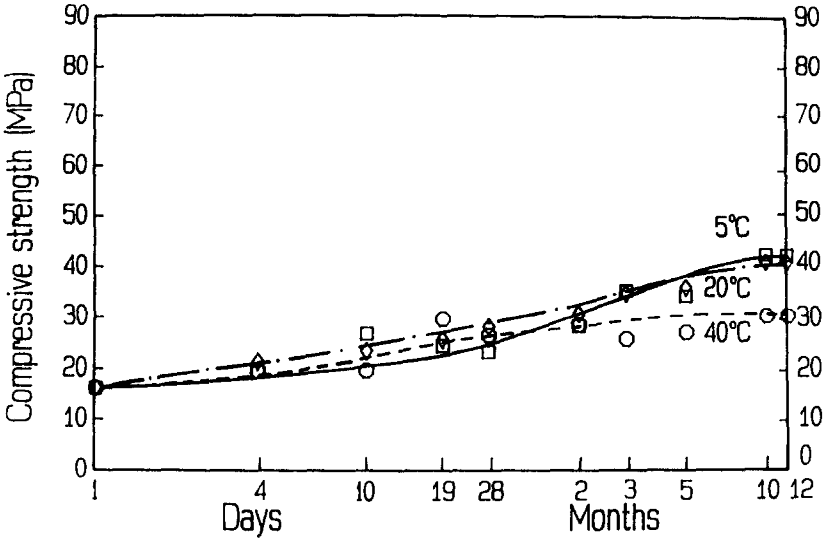

FIG. 5
Compressive strength of specimens with 30% silica fume.

It can also be observed that the specimens prepared with silica fume and high alumina cement show a very low strength level at early curing times (slightly more than 15 MPa at one day). This can be ascribed to both the high water/cement ratio (since pozzolan at early time does not act) and to the retarding effect caused by the naphtalene-based superplasticizer.

Figure 6 shows the compressive strength of specimens prepared with 20% fly ash. The strength-time curves at different temperatures are similar to those recorded for the

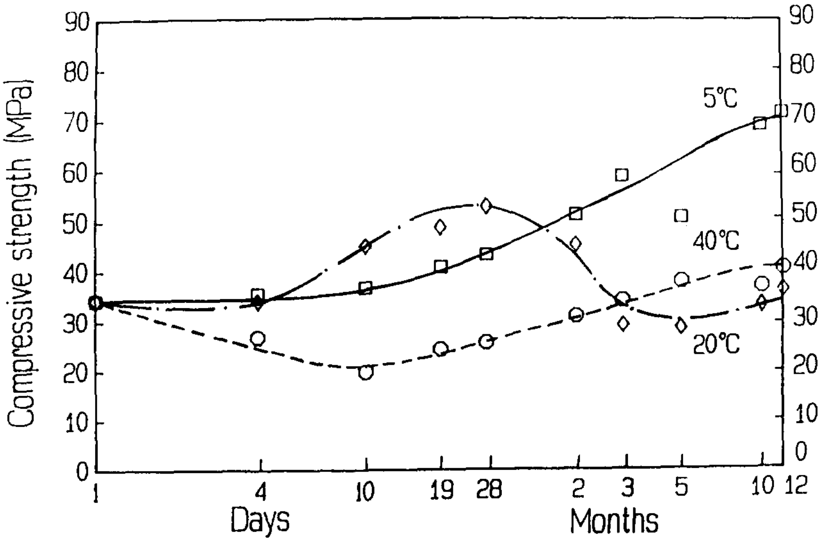

FIG. 6
Compressive strength of specimens with 20% fly ash.

specimens containing high alumina cement alone, but the maximum strength levels are slightly lower. The specimens at 20°C show the characteristic strength decrease after the first 28 days of curing, while at 40°C this decrease occurs in the first 10 days.

Figure 7 shows the X-ray diffraction patterns of the specimens cured for 300 days at 20°C and 40°C. It can be observed that the amount of gehlenite hydrate is quite small, while the peaks belonging to the cubic aluminate hydrate are more enhanced. It seems that the silica of the fly ash is not adequately reactive to form gehlenite hydrate and therefore the conversion of hexagonal aluminate hydrates into the cubic one is avoided or at least negligible.

In Fig.8 the strength behaviour of the samples prepared with 40% of fly ash is shown. The high water\cement ratio, due to the considerable amount of pozzolan replacing the cement, decreases the strength and makes almost negligible the differences among the values obtained at the three curing temperatures.

Conclusions

The use of silica fume to replace 15% of high alumina cement almost completely reduces the strength decrease at 20°C and 40°C, since the presence of this high-silica pozzolan favours the formation of gehlenite hydrate (C_2ASH_8) and therefore the transformation of hexagonal aluminate hydrates (CAH_{10}, C_2AH_8) into the cubic

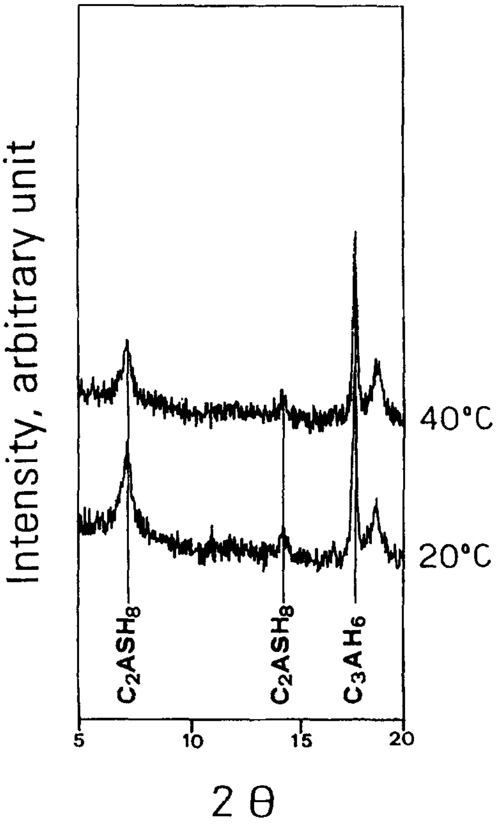

FIG. 7
X-Ray patterns of mortar samples with 20% fly ash at 300 days of curing.

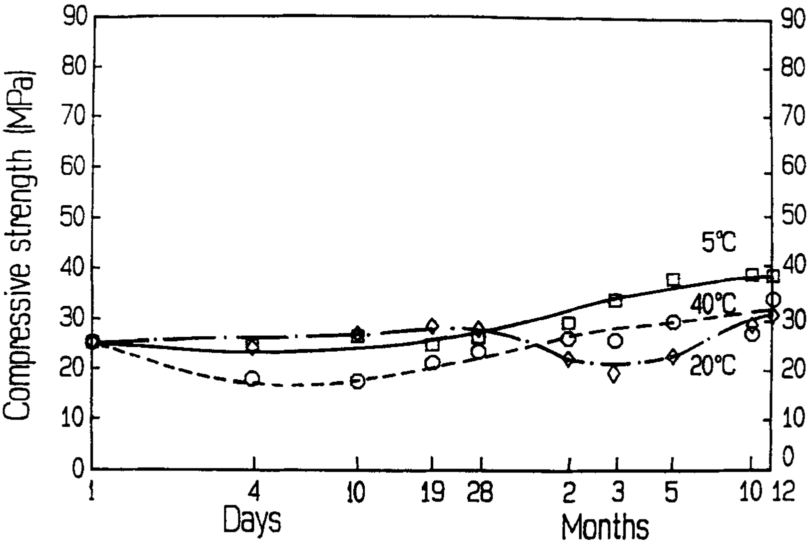

FIG. 8
Compressive strength of specimens with 40% fly ash.

hydrate (C_3AH_6) is hindered. At 5°C the conversion of hexagonal hydrates into cubic hydrates does not occur independently of the presence of silica fume. Therefore strength is reduced at 5°C in the presence of silica fume at all the curing times due to the higher water\cement ratio.

On the other hand the use of fly ash is not particularly advantageous in reducing the transformation of hexagonal hydrates into the cubic phase. In order to detect any effect of fly ash on this transformation, a high amount of pozzolan must be used (40%) and this reduces all the strength levels because of the increase in the water\cement ratio.

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