Water reducers for the high alumina cement-silica fume system

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ABSTRACT

High early strength mortars or concretes can be produced with high alumina cement. However, at later ages, particularly at temperatures higher than 20°C, there is a strength loss caused by a transformation of hexagonal hydrates into the cubic form.

Silica fume is capable of hindering or blocking this transformation. However, a water reducing admixture is required to counterbalance the higher amount of mixing water caused by the very high specific surface area of silica fume.

Since traditional water reducers (based on sulphonated naphtalene or melamine polymers) are not effective with high alumina cement, two alternative candidates have been tested: sodium tripoliphosphate and carboxylic acrylic ester.

The sodium tripoliphosphate admixture is capable of reducing the mixing water; however, the simultaneous presence of silica fume and sodium tripoliphosphate causes a surprising and not yet fully-explained strength loss (only at 20°C with liquid water), although the transformation of hexagonal hydrates into the cubic form is truly hindered.

In the presence of the carboxylic acrylic ester admixture, the amount of mixing water is reduced without any side effect on the strength loss of the high alumina cement-silica fume system. Therefore, the combination of silica fume with carboxylic acrylic ester appears to be a successful solution to produce mortars or concrete mixes based on high alumina cement content without any strength loss at later ages.

RÉSUMÉ

Des mortiers et des bétons développant des résistances mécaniques élevées à court terme peuvent être produits avec les ciments alumineux. Toutefois, au cours du temps, en particulier pour des températures supérieures à 20 °C, une diminution de la résistance mécanique survient suite à la transformation des hydrates hexagonaux en structure cubique.

La fumée de silice est capable de ralentir ou de bloquer cette transformation. Toutefois, il faut ajouter un réducteur d'eau afin d'équilibrer la plus haute teneur en eau de gâchage requise par la surface spécifique importante de la fumée de silice. Puisque les réducteurs d'eau traditionnels (basés sur le naphtalène sulphonate ou sur la mélamine) n'ont pas d'action sur les ciments alumineux, deux produits alternatifs ont été testés : le tripolyphosphate de sodium et l'ester carboxylique acrylique.

Le tripolyphosphate de sodium est capable de réduire l'eau de gâchage, mais la présence simultanée de fumée de silice et de tripolyphosphate de sodium conduit à une surprenante et non encore expliquée diminution de la résistance (seulement à 20°C avec l'eau liquide), bien que la transformation des hydrates hexagonaux en hydrate cubique soit vraiment limitée.

En présence d'ester carboxylique acrylique, la quantité d'eau de gâchage est réduite sans avoir de diminution de la résistance mécanique du système ciment alumineux-fumée de silice. C'est pourquoi la combinaison fumée de silice-ester carboxylique acrylique semble être une bonne solution pour produire des mortiers ou des bétons ne subissant pas de perte de résistance à long terme.
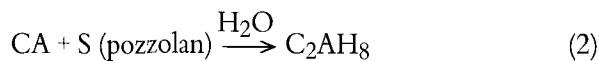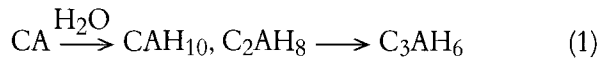
1. INTRODUCTION

High alumina cement, based on calcium aluminate (CA), is used to produce mortar or concrete mixes with high early strength, particularly in cold weather. However, the strength can be significantly reduced at later ages, especially in hot weather (> 20°C) and/or at relatively high water-to-cement ratios (> 0.40). The reduction in strength is associated with the conversion of the hexagonal hydrates (CAH_{10} and C_2AH_8) into the cubic hydrate (C_3AH_6) according to reaction (1). In order to block this conversion and the corresponding

strength loss, mixtures of high alumina cement with pozzolanic materials in the form of ground blast furnace slag, fly ash or silica fume have been used [1-6]. In the presence of reactive silica of the pozzolanic materials, gehlenite hydrate (C_2ASH_8) is formed according to reaction (2), and therefore no strength loss occurs since the transformation of hexagonal aluminate hydrates into the cubic hydrate is hindered:

$$CA \xrightarrow{H_2O} CAH_{10}, C_2AH_8 \longrightarrow C_3AH_6 \qquad (1)$$

$$CA + S \text{ (pozzolan)} \xrightarrow{H_2O} C_2AH_8 \qquad (2)$$

From a practical point of view, fly ash does not appear to be successful in forming C_2ASH_8 even when it replaces a relatively high percentage (20-40%) of high alumina cement.

Blast furnace slag is able to form C_2ASH_8 and therefore to block the strength loss at later ages. However, the percentage of alumina cement which must be replaced by slag is so high (25-50%) that the typical high strength of pure alumina cement does not occur at early and later ages [6].

Only silica fume is able to form C_2ASH_8 and thus to block the strength loss at later ages by replacing relatively small percentages (10-20%) of high alumina cement [5]. On the other hand, because of the very high specific surface area of silica fume, the amount of mixing water needed to produce the mix at a plastic consistency is too high, and a water reducing chemical admixture is required.

Unfortunately, the traditional plasticizing or superplasticizing admixtures (sulphonated naphtalene or melamine polymers) generally used for Portland cement concrete mixes [7] are either not effective for high alumina cement or retard the hydration process. The purpose of the present work is to investigate whether or not a more effective water reducer can be found for the high alumina cement-silica fume system.

2. MATERIALS AND METHODS

Two candidates have been taken into account as a water reducer for the high alumina cement-silica fume system: sodium tripoliphosphate which has already been proposed by Marcdargent *et al.* [8] for this system and carboxylic acrylic ester (CAE) which has already been used as a superplasticizer for Portland cement mixes [9-12] but has never been tested as a water reducer for high alumina cement.

Sodium tripoliphosphate (TPP) has been proposed by Marcdargent *et al.* [8] as a deflocculating agent at a concentration of 0.5% by weight of alumina cement and silica fume. In the present work, a concentration of 0.3, 0.6 and 1.2% TPP, or of 0.9% CAE, has been used for a cement paste based on 80% high alumina cement and 20% silica fume. Due to the presence of TPP or CAE, the same water-to-solid ratio (w/s) of 0.30 has been adopted as that of the alumina cement in the absence of silica fume. On the other hand, for the high alumina cement-silica fume system in the absence of TPP or CAE, the w/s ratio was 0.45 in order to attain a plastic

consistency. Table 1 summarizes the composition of all the mixes. The chemical compositions of the silica fume and high alumina cement have been shown in a previous paper [5], whereas the CAE composition has been presented in reference [9].

After mixing all the ingredients, the workability of the cement paste has been determined through a modified Marsh cone test by measuring the flow time required for 600 cm^3 of cement paste to leave the cone which has been placed on a vibrating table. The lower the flow time, the more workable is the cement paste. A flow time of 4 sec to 30 sec is considered to be adequate for placing the cement mix at a plastic consistency.

The cement paste specimens have been cured into the forms (40 mm-cube) at 5°C, 20°C and 50°C. At 6 hr, the specimens were demoulded and kept at the same original temperature either under water or in the air at a R.H. of 95%. For the 50°C specimens, after 7 days the temperature was reduced from 50°C to 20°C in order to simulate the practical thermal change in a massive concrete structure cured at room temperature.

Compressive strength measurements and X-ray diffraction (XRD) analysis were carried out from 6 hr to 180 days.

3. RESULTS AND DISCUSSION

Fig. 1 shows the flow time of cement pastes (measured by the modified Marsh cone test) as a function of the time after mixing. The high alumina cement-silica fume mix without admixture (HAC-SF curve in Fig. 1) appears less workable than the high alumina cement alone (HAC curve in Fig. 1) although the w/s ratio was much higher (0.45 versus 0.30). In general, the addition of TPP improves the workability of the high alumina-silica fume system (TPP 0.3, TPP 0.6, TPP 1.2 curves in Fig. 1). However, at TPP concentrations lower or higher than 0.6%, there is a significant workability loss at 15 min after mixing. In particular, for the 0.3% TPP, there is a surprising workability increase (between 5 and 15 min) and then a rapid workability loss. Therefore, only the most reliable HAC-SF system with 0.6% TPP will be compared later (for compressive strength and XRD analysis) with HAC-SF and HAC, both in the absence of TPP.

In the presence of carboxylic acrylic ester (CAE 0.9 curve in Fig. 1), the rheological behaviour of the HAC-SF system is as good as that in the presence of 0.6% TPP; there is a workability loss only at 45 min after mixing.

Figs. 2 and 3 show the compressive strength development of the HAC system under two different curing conditions: in air at 95% R.H. and under water, respectively. The latter appears more effective at later ages in the absence of the conversion from the hexagonal hydrates into the cubic form at 5 °C; the compressive strength at 180 days is 140 MPa when the system is cured under water (Fig. 3), whereas it attains about 90 MPa in air at 95% R.H. (Fig. 2). On the other hand, the presence of liquid water seems to favour the above conversion and the corresponding strength loss at 20°C or 50/20°C.
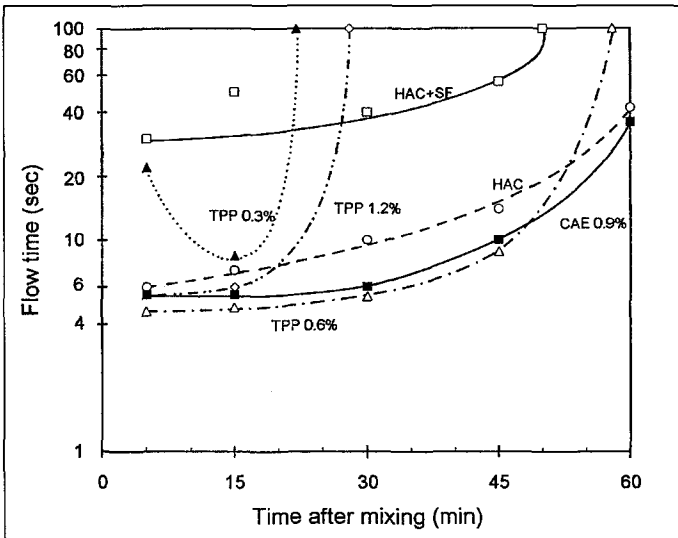
Fig.1 – Workability determined by flow time as a function of the time after mixing.

Fig.2 – Compressive strength as a function of curing time (95% R.H.) for HAC alone.

Table 1 – Composition of the mixes

Mix	Ciment fondu (%)	Silica fume (%)	Sodium tripoli-phosphate (%)	Carboxylic acrylic ester (%)	W/C
HAC	100	0	0	0	0.30
HAC + SF	80	20	0	0	0.45
HAC + SF + TPP	80	20	0.3	0	0.30
	80	20	0.6	0	0.30
	80	20	1.2	0	0.30
HAC + SF + CAE	80	20	0	0.9	0.30
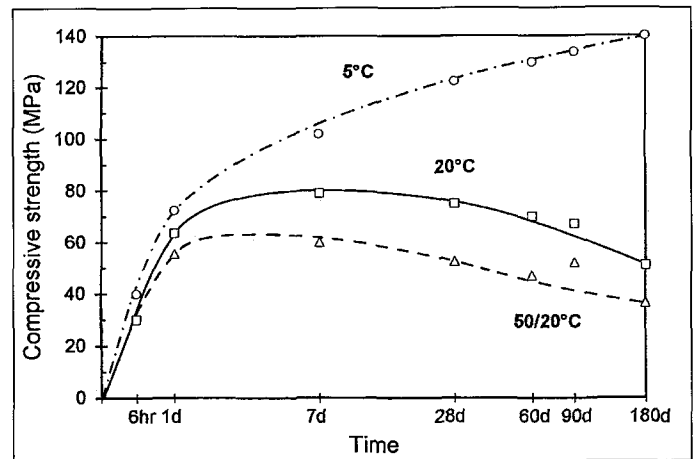
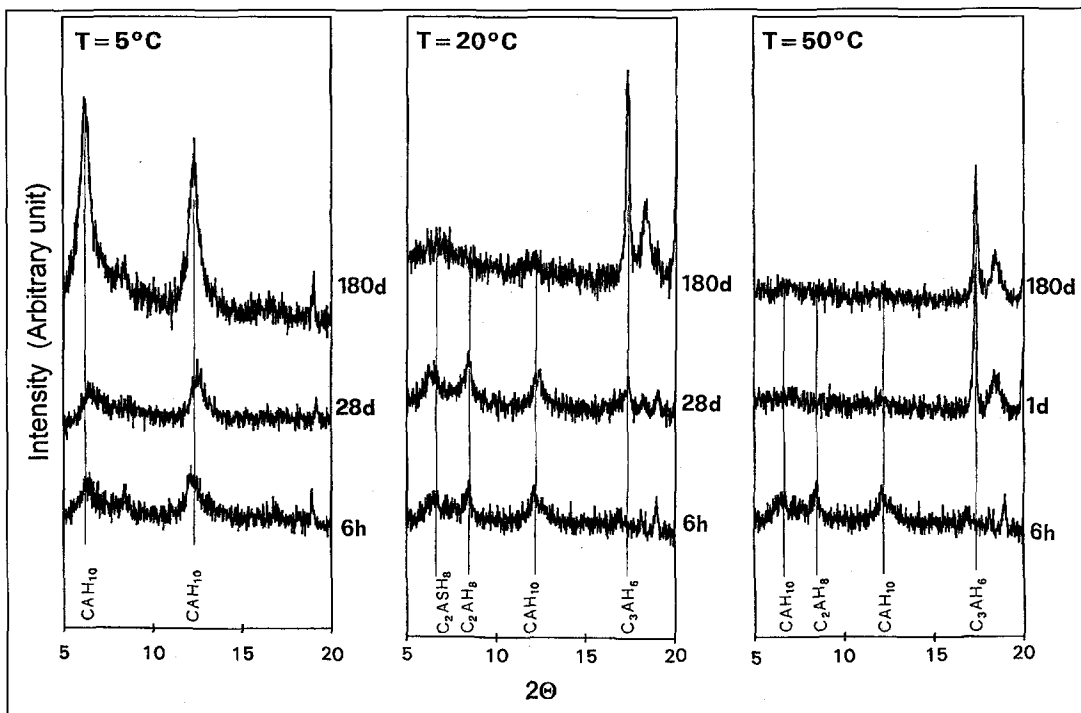Fig.3 – Compressive strength as a function of curing time (under water) for HAC alone.

Fig.4 – XRD patterns at 5°C, 20°C and 50/20°C for the HAC paste cured at 95% R.H.
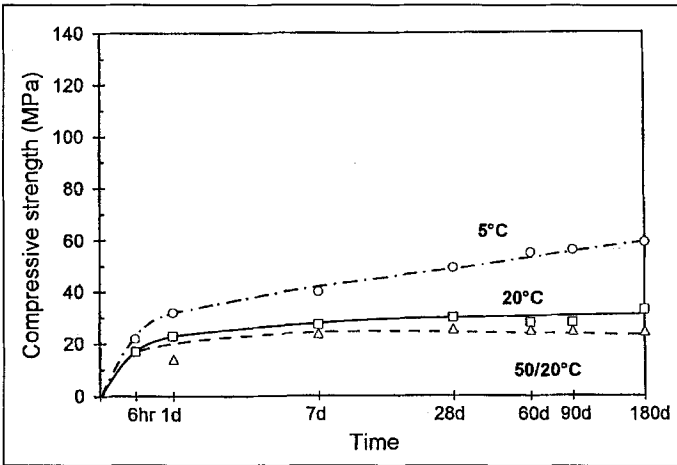
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Fig.5 – Compressive strength as a function of curing time (95% R.H.) for HAC-SF system.
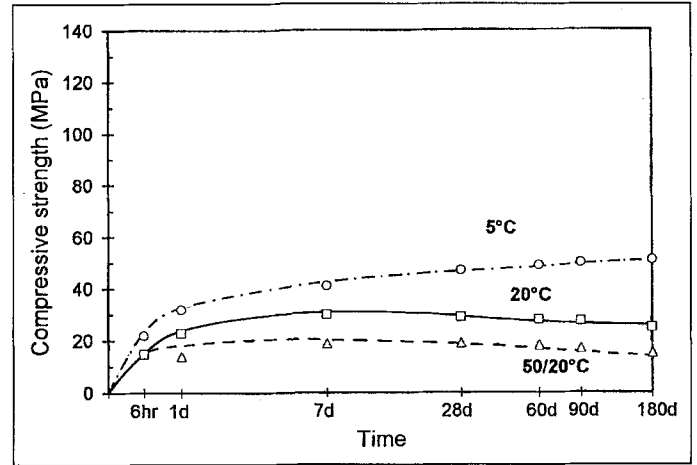

Fig.6 – Compressive strength as a function of curing time (under water) for HAC-SF system.
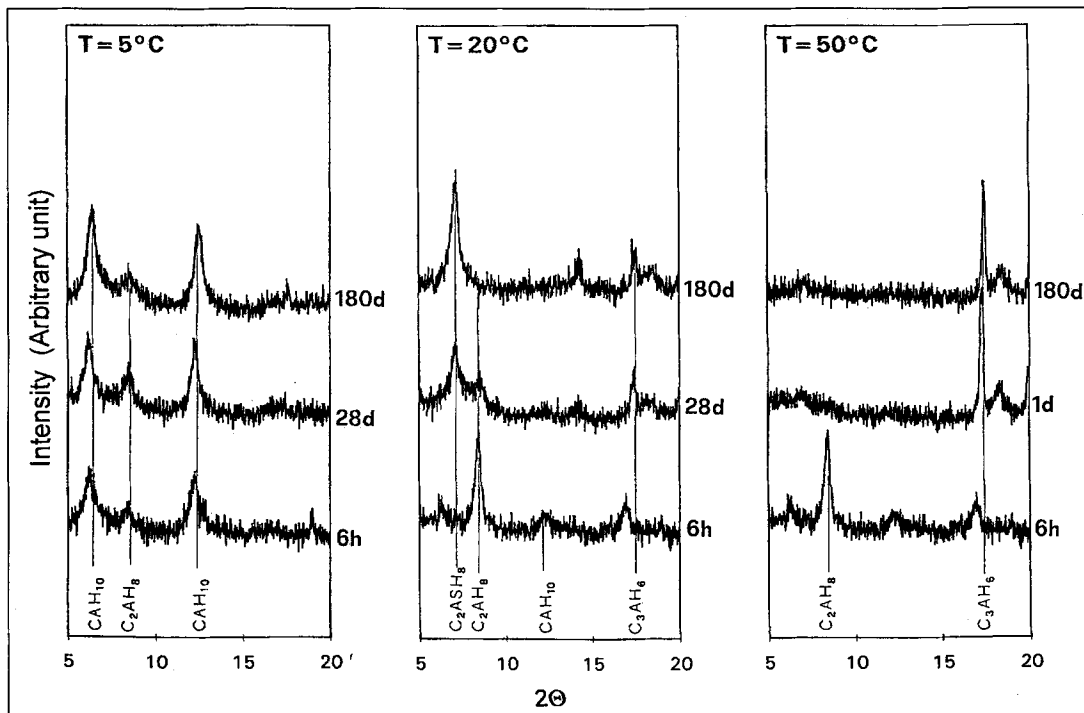

Fig.7 – XRD patterns at 5°C, 20°C, 50/20°C for the HAC-SF system cured at 95% R.H.
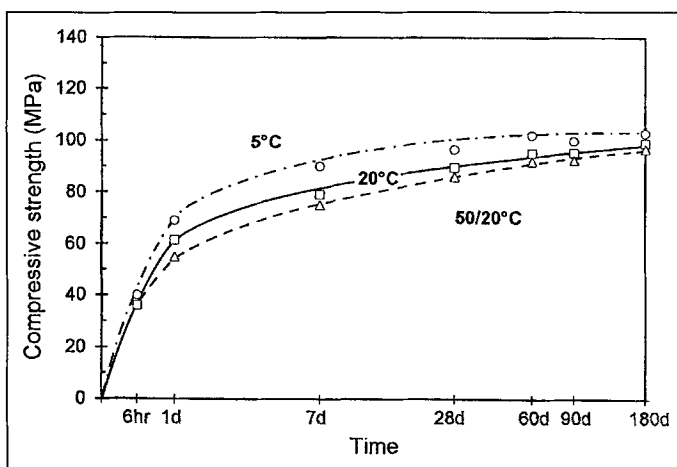

Fig.8 – Compressive strength as a function of curing time (95% R.H.) for HAC-SF system with 0.6% TPP.
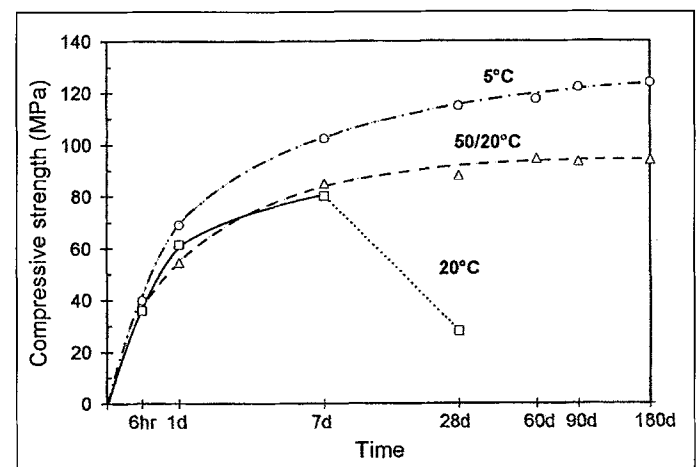

Fig.9 – Compressive strength as a function of curing time (under water) for HAC-SF system with 0.6% TPP.
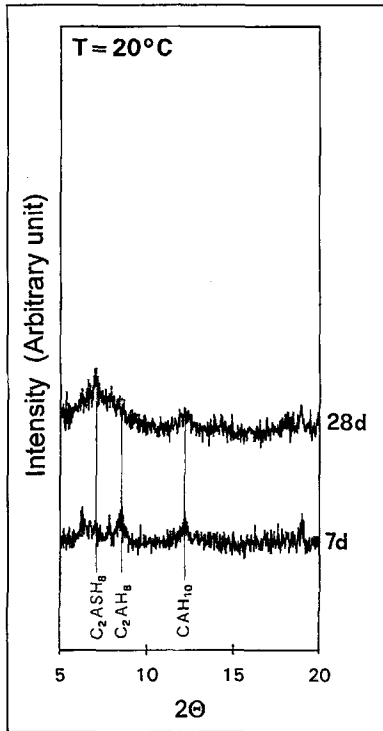
Fig.10 – XRD patterns at 20°C for the HAC-SF system with 0.6% cured under water.
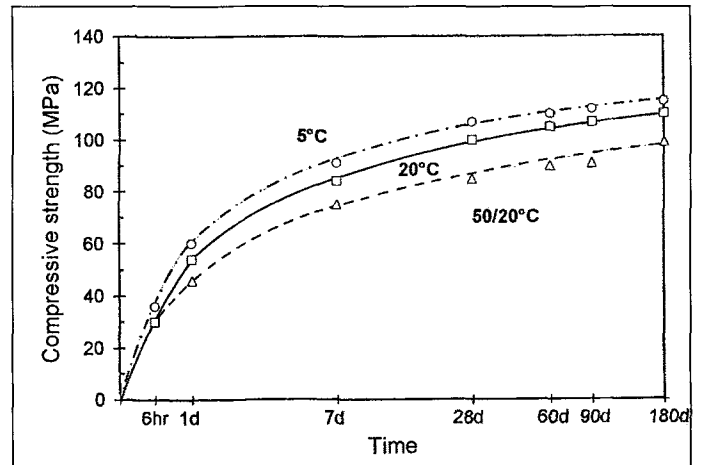

Fig.12 – Compressive strength as a function of curing time (95% R.H.) for HAC-SF system with 0.9% CAE.
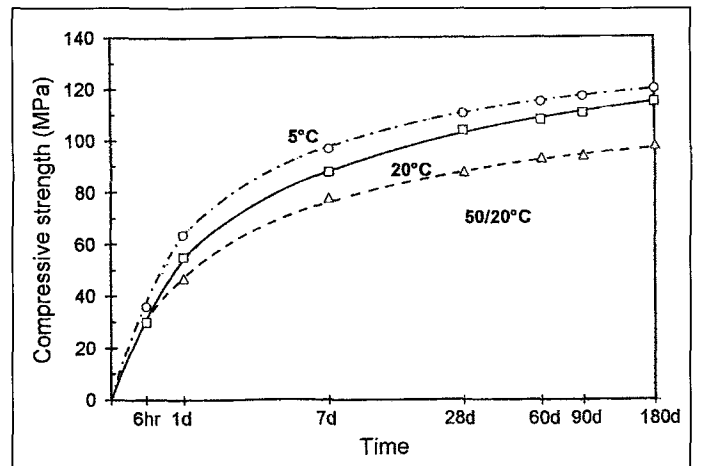

Fig.13 – Compressive strength as a function of curing time (under water) for HAC-SF system with 0.9% CAE.
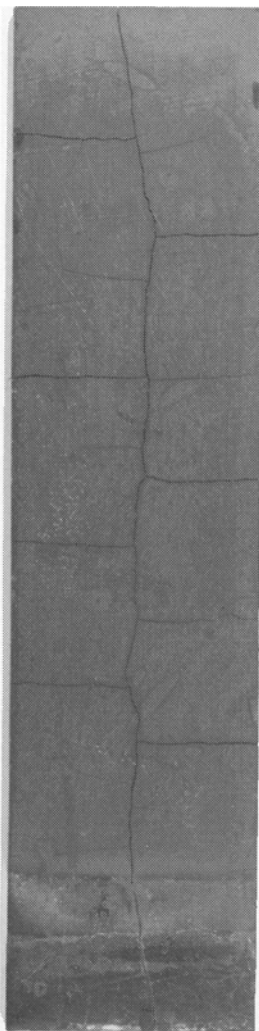

Fig.11 – Picture of cracked specimen produced with HAC-SF-TPP (0.6%).

Some XRD patterns between 6 hr and 180 days are shown in Fig. 4 for the HAC paste cured in air at 95% R.H., which confirms that the strength loss at later ages is related to the reduction of hexagonal hydrates and the formation of the cubic hydrate; the C_3AH_6 peak is increased between 7 and 180 days at 20°C, just when there is a strength decrease from 75 to 55 MPa (Fig. 2). No significant strength loss occurs between 7 and 180 days at 50/20°C (Fig. 2) because the C_3AH_6 has already been formed at 1 day, and no further conversion from hexagonal hydrates into cubic hydrates occurs after 1 day (Fig. 4).

In the presence of silica fume, the compressive strength does not show any significant strength loss either at 95% R.H. (Fig. 5) or under water (Fig. 6) at 5°C and 20°C. A lower strength is obtained when the cementitious system is kept at 50/20°C. The XRD patterns (Fig. 7) show that in the presence of silica fume, some C_3AH_6 is formed at higher temperatures (50/20°C), whereas it is blocked at 5°C and strongly hindered at 20°C. In the absence of water-reducing admixtures, the compressive strength of the high alumina cement-silica fume system is much lower than the pure alumina cement at early and later ages because of the higher amount of

mixing water (Table 1). This drawback substantially off-sets the advantage of reducing the strength loss related to the formation of C_3AH_6. For instance, the early compressive strength at 5°C at 6 hr is reduced from 40 MPa (Fig. 2) to 25 MPa (Fig. 5) by the higher w/s ratio caused by the presence of silica fume. Even at 180 days, the compressive strength at 5°C is reduced from 90 to 60 MPa because of the increase in the w/s ratio caused by silica fume.

The w/s ratio of the alumina cement-silica fume system is reduced by 0.45 to 0.30 by the presence of 0.6% TPP (Table 1). Therefore, at an R.H. of 95%, this system's compressive strength at 5°C (Fig. 8) is similar to that of pure alumina cement (Fig. 2) at early as well as later ages. On the other hand, because of the simultaneous presence of silica fume (20%) and TPP (0.6%), there is no strength loss at 20°C or 50/20°C, and the compressive strength at later ages is distinctly independent of the temperature (Fig. 8). However, this very interesting result is not confirmed when the cementitious system is cured under water (Fig. 9). In such a case, it has been found that a surprising and dramatic strength loss only occurs at a temperature of 20°C, although no conversion from hexagonal hydrates into C_3AH_6 has been recorded at 20°C under water (Fig. 10). The strength loss in the presence of silica fume and TPP is accompanied by severe cracking (Fig. 11). However, the cracking cannot be associated with drying shrinkage because it occurs only under water.

In the presence of the acrylic admixture, there is no strength loss for the HAC-SF system cured at an R.H. of 95% (Fig. 12) or under water (Fig. 13) independently of the temperature. Therefore, the combination of silica fume (20%) with CAE (0.9%) appears to be successful in blocking the typical strength loss for high alumina cement at higher temperatures (>20°C).

4. CONCLUSIONS

Silica fume is capable of retarding or blocking the conversion from hexagonal hydrates into C_3AH_6 by favouring the formation of C_2ASH_8. However, due to the high specific surface area of the silica fume, a higher amount of mixing water is required, and this effect reduces the strength at early and later ages.

Sodium tripoliphosphate is a good water-reducing admixture for the high alumina cement-silica fume system. Therefore, in the presence of TPP, the high alumina cement-silica fume system should be *potentially* capable of quickly attaining a high strength level without any subsequent strength loss caused by the conversion of hexagonal hydrates into C_3AH_6.

The simultaneous presence of silica fume and TPP does actually produce a dramatic failure of the high alumina cement-based system when kept at 20°C under water. There are some surprising events associated with this failure which cannot yet be explained:
- the strength loss is accompanied by cracking;
- the cracking is not associated with drying shrinkage because it occurs *only* under water;

- cracking and strength loss occur *only* at 20°C and not at 5°C or at 50°C;
- cracking and strength loss are not associated with any chemical product detectable by XRD.

In other words, for the high alumina cement-silica fume-TPP system, there is a dramatic strength loss at 20°C in the presence of liquid water, even though the conversion from the hexagonal hydrates into C_3AH_6 is strongly hindered.

In view of the above limits and events, the combined system based on high alumina cement-silica fume-TPP cannot be used *in practice* unless the materials are cured in air in the absence of liquid water.

On the contrary, the combination of silica fume with a carboxylic acrylic ester admixture appears to be successful in blocking both the conversion from hexagonal hydrates into C_3AH_6 and the strength loss independently of the temperature and of the presence of liquid water. Therefore, the addition of silica fume (20%) and CAE (0.9%) appears to be a practical solution for the use of high alumina cement without any strength loss at later ages.

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