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EFFECT OF SILICA FUME ON THE HYDRATION PRODUCTS OF $C_3A-C\bar{S}H_2$ SYSTEM

EFFET DE FUMEE DE SILICE SUR LES PRODUITS D'HYDRATATION DU SYSTEME $C_3A-C\bar{S}H_2$

SUMMARY: The hydration of $C_3A-C\bar{S}H_2$ systems at 20°C has been studied in the presence of quartz (considered to be inert) or silica fume. Moreover, since silica fume is generally used in cement mixes in combination with superplasticizers, the effect of polymer based on naphthalene sulfonated has been also examined.

The hydration products have been identified by thermal analysis (DTG). In some cases XRD analysis has been also carried out.

In the presence of quartz the usual hydration products of the $C_3A-C\bar{S}H_2$ system have been observed: ettringite is initially produced and then it is transformed into monosulfate.

When silica fume replaces quartz the conversion the ettringite into monosulfate is accelerated. Moreover, in the presence of silica fume, beside the monosulfate after some days a new product is formed, with a DTG peak at about 370°C and a group of XRD lines at 5.06, 3.32, 3.11, 2.79, 2.27, 2.02 Å.

On the basis of these data the new product has been identified as a hydrogarnet of chemical composition $C_3AS_xH_{6-2x}$.

With a combined addition of silica fume and naphthalene sulfonated polymer to the $C_3A-C\bar{S}H_2$ system the hydrogarnet production is retarded or completely inhibited (at least up to 28 days) depending on the polymer dosage (0.4 or 2% by weight respectively). Moreover, at the higher dosage of polymer the formation of ettringite and its conversion into monosulfate are both retarded.

Introduction

Since the last few years, it is well known that the need for conserving energy through the lower percentage of clinker in cements has revived the interest in materials having chemical composition and surface properties similar to those of pozzolans.

In recent times research works have been directed towards investigations of silica fume, a by-product resulting from the manufacture of silicon steel. Silica fume appears to possess rather interesting characteristics.

A number of authors (1) have found that, when used as partial substitution of cement, silica fume shows a good pozzolanic activity, because of its high content in amorphous silica and its high fineness (20 m²/g). This extraordinary fineness also results in high demand for mix water to obtain concrete with good workability; yet, the addition of a superplasticizing admixture can conduce to relatively low water/solid ratios again. Moreover, added water being equal, a content of silica fume up to 30% seems to impart improved mechanical properties to concrete.

In the present paper, the influence of silica fume on the C₃A-gypsum system in the presence or absence of superplasticizer is investigated in order to assess the variation both in the kinetics of hydration and in the nature of the hydrated products.

Materials

Four mixes were prepared whose composition is shown in Table 1.

Table 1 Composition of anhydrous mixes (Q=quartz, SF=silica fume, NS=dry polymer of calcium naphthalene sulfonate)

C ₃ A	Q	SF	CSH ₂	NS
50	40	--	10	--
50	--	40	10	--
50	--	40	10	0.4
50	--	40	10	2

Tricalcium aluminate was the same material already used in other works (2,3). Silica fume, with the fineness of 20.70 m²/g was the same which was used in a previous work (4). Finely ground quartz (passing the 37- μ m sieve) was used as an inert material in order to obtain the same amount of C₃A in the mixes without silica fume.

Tricalcium aluminate and silica fume (or quartz) were dry mixed with gypsum and naphthalene sulfonate polymer in powder form, obtained by drying out a proprietary admixture made of a 40% aqueous solution of polymer.

Specimens were hydrated with a given quantity of water in order to obtain a water/solid ratio of 0.5 and then they were maintained at 20°C. At given times, from 6 hours to 28 days, the reaction was blocked by grinding the specimens in methyl alcohol; filtered specimens were tested by thermogravimetric analysis and, in some cases, also by X-ray diffraction.

Results and Discussion

Figure 1 indicates the DTG curves of the C₃A-quartz-gypsum mix. At about 150°C the anhydrous mix shows the peak attributed to bihydrated gypsum. After a 6 hours hydration, one peak at 120°C, due to the thermal decomposition of ettringite, and two peaks (at 200 and 280°C) of monosulfate, are present. At 1 day, the peaks of monosulfate are considerably higher and only traces of ettringite are present. At later ages, monosulfate is the only product of the reaction left, as it had already been found and discussed in a previous work (5).

Figure 2 shows the DTG curves of the reaction products of the C₃A-silica fume-gypsum mix. The substitution of quartz with silica fume, which is more reactive, determines interesting variations of both the hydration kinetics, and, above all, the type of products obtained. At 6 hours the conversion of ettringite into monosulfate is almost completed. Moreover, the XRD analysis indicates that the percentage of hydrated C₃A appears to be higher in the presence of silica fume than in the presence of quartz. An analogous behaviour has been pointed out in other publications in connection with the hydration of C₃A, pozzolan and gypsum mixes (6,7). The conversion of ettringite into monosulfate is completed after 1 day. At 3 days, a new peak at about 370°C appears, in

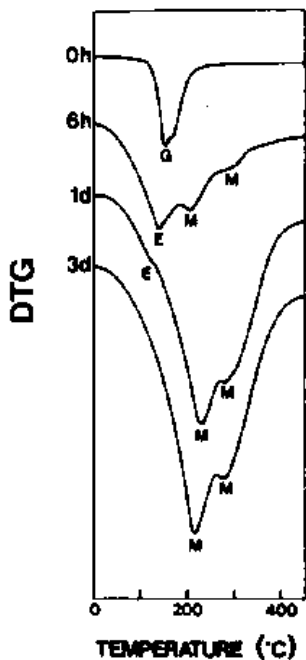


Fig.1 DTG curves of the hydration products of the C₃A-quartz-gypsum mix. G=gypsum; M=monosulfate; E=ettringite.

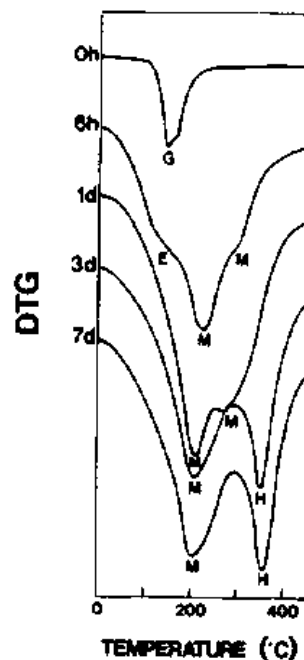


Fig. 2 DTG curves of the hydration products of the C₃A-silica fume-gypsum mix. H=hydrogarnet.

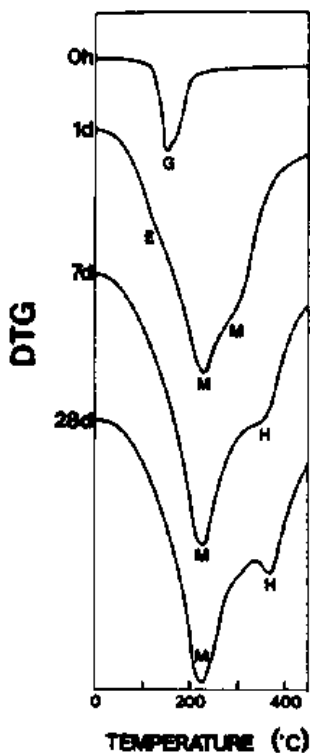


Fig.3 DTG curves of the hydration products of the C₃A-silica fume-gypsum mix in the presence of 0.4% superplasticizer.

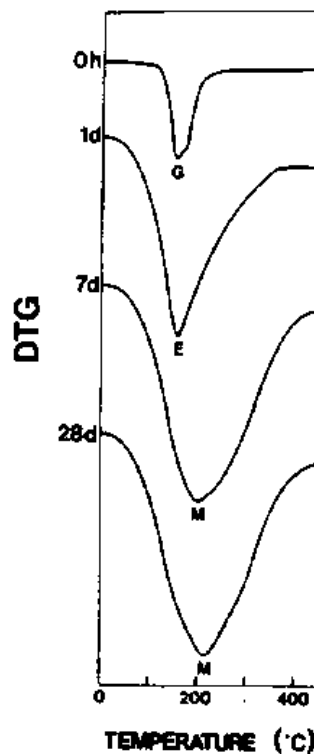


Fig.4 DTG curves of the hydration products of the C₃A-silica fume-gypsum mix in the presence of 2% superplasticizer.

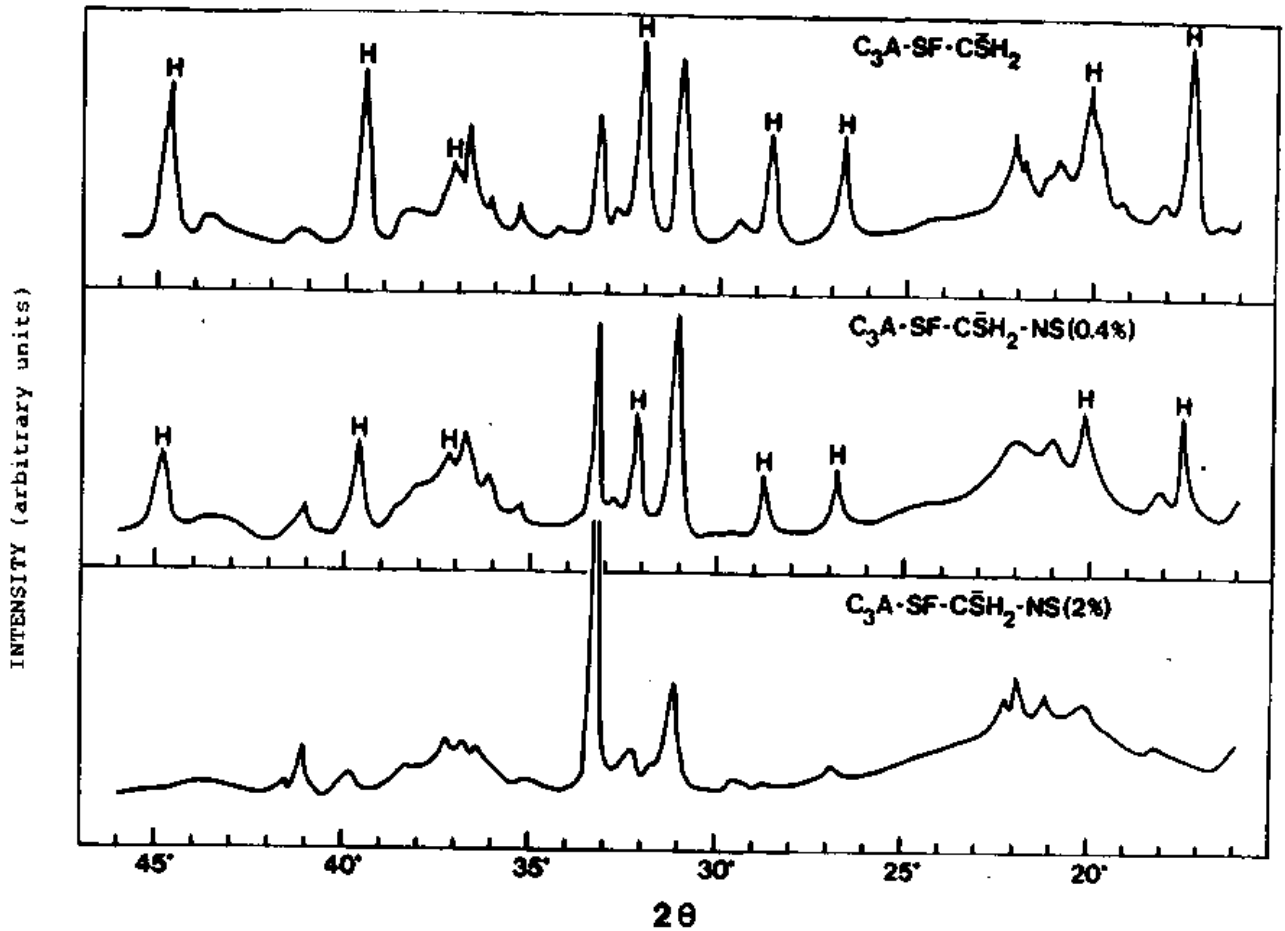


Fig. 5 XRD patterns of the hydration products of the C_3A -silica fume-gypsum mix. H = hydrogarnet

addition to the peak already mentioned. Comparing the XRD patterns obtained with the existing data in the literature (8) allowed to identify this new peak as hydrogarnet ($C_3AS_2H_6 \cdot 2x$).

Figure 3 shows the DTG peaks of the C_3A -silica fume-gypsum mix, hydrated at 0, 1, 7, 28 days in the presence of 0.4% of superplasticizer by weight of cement. At 1 day, the peaks of monosulfate and a shoulder attributed to residual ettringite are observed. Comparing these results with the one obtained at 1 day without admixture (Fig. 2), it can be concluded that the superplasticizer slightly retards the conversion of ettringite into monosulfate. Only at 7 days, the peak attributed to the hydrogarnet appears at about $370^\circ C$; the presence of the admixture retards its appearance and strongly retards its rising. It does not reach the amount it had in the

mix without admixture at 3 days, not even at 28 days.

The increase in the dosage of superplasticizing admixture (2%) retards the conversion of ettringite into monosulfate strongly (Fig. 4). For example, at 1 day the DTG peak of ettringite at $120^\circ C$ is predominant.

Figure 5 indicates the X-ray diffraction patterns of the C_3A -silica fume- C_5H_2 system hydrated at 7 days with and without superplasticizing admixture. The XRD analysis confirms the presence of hydrogarnet in the sample without superplasticizer and in the sample with a lower dosage (0.4%) of admixture. In the last case, the intensity of XRD peaks is weaker. Even the XRD analysis does not indicate the presence of hydrogarnet in the specimen with a higher dosage of superplasticizer (2%).

Conclusion

The addition of silica fume to the $C_3A-C\bar{S}H_2$ system accelerates the production of ettringite and its conversion into monosulfate. Moreover, it causes the formation of hydrogarnet ($C_3AS_2H_6-2x$) which is strongly evident after $x \times 3^{6-2x}$ days of hydration.

Naphthalene sulfonate based superplasticizer, added at the dosage rate of 0.4% to the C_3A -silica fume- $C\bar{S}H_2$ system, slows down both the conversion of ettringite into monosulfate and the formation of hydrogarnet. The strong effect obtained with the dosage of 2% hinders the production of hydrogarnet at least up to 28 days.

References

- (1) G.G. Carette and V. M. Malhotra, "Silica Fume in Concrete - Preliminary Investigation", CANMET Report 82-1E, Canada, February 1982.
- (2) S. Monosi, G. Moriconi, M. Pauri, M. Collepardi, "Influence of Gluconate, Lignosulfonate or Glucose on the C_3A Hydration", Cem. Concr. Res., 13, 568-574, 1983.
- (3) M. Collepardi, S. Monosi, G. Moriconi and M. Pauri, "Influence of Gluconate, Lignosulfonate or Glucose on the C_3A Hydration in the Presence of Gypsum With or Without Lime", Cem. Concr. Res., 14, 105-112, 1984.
- (4) S. Chatterji, M. Collepardi and G. Moriconi, "Pozzolanic Property of Material and Synthetic Pozzolans: a Comparative Study", First International Conference on the Use of Fly Ash, Silica Fume, Slag and other Mineral By-products in Concrete, Montebello, Canada, July 31-August 5, 1983, Vol. 1, pp 221-233.
- (5) M. Collepardi, G. Baldini and M. Pauri, "Tricalcium Aluminate Hydration in the Presence of Lime, Gypsum or Sodium Sulfate", Cem. Concr. Res., 8: 571-580, 1978.
- (6) M. Collepardi, G. Baldini and M. Pauri, "The Effect of Pozzolans on the Tricalcium Aluminate Hydration", Cem. Concr. Res., 8, 741-752, 1978.
- (7) H. Uchikawa and S. Uchida, "Influence of Pozzolana on the Hydration of C_3A ", 7th International Congress on the Chemistry of Cement, Paris 1980, Vol. III, Theme IV 24-29.
- (8) H.F.W. Taylor, "The Chemistry of Cements", Vol. I, pg 344, Academic press, London, (1964).