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Ettringite formation: A crucial step in cement superplasticizer compatibility

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Abstract

The rheology of cementitious system containing superplasticizer is the consequence of a physical process due to the electrostatic repulsion between particles, but also of a chemical process linked to the nature of the phases that are formed. Ettringite crystallization play as a key role in this matter and the nature of the sulfate phase added to control cement setting is as important as its dosage. Alkali sulfates, which provide only SO_4^{2-} ions, do not promote the formation of ettringite for which the presence of large amounts of Ca^{2+} is necessary. The adsorption of superplasticizer molecules on hydrated cement grains slows down the dissolution rates of the constituents and modifies the nature of the compounds formed. It could result in a modification of the ettringite morphology.

Keywords: Ettringite; Sulfate; Rheology; Superplasticizer

1. Introduction

Cement-superplasticizer compatibility is becoming a source of major concern in the concrete industry due to the increasing use of high performance concretes having low W/C ratios [1]. Experience shows that some cement-superplasticizer combinations can be used to make low W/C concretes that keep a slump of 200 mm during more than 1 h, while drastic slump losses, within 10–15 min, are experienced with other combinations [2,3].

Several studies have shown the crucial role of the calcium sulfate added to control Portland cement setting with water reducers [4–6] and with superplasticizers [7–9] in these compatibility problems. The nature of the calcium sulfate is as important as its dosage, because it controls the dissolution rate, which commands the rheology of the cementitious systems containing water reducers as well as superplasticizers.

The presence of natural anhydrite has always been found in systems presenting compatibility problems [5,7–9]. Natural anhydrite has the lowest dissolution rate of the different forms that calcium sulfate can take (gypsum, hemihydrate, deshydrated hemihydrate, synthetic calcium sulfate, natural anhydrite) even though the final equilibrium that is reached is relatively high.

Ettringite crystals that grow in the presence of a polynaphthalene sulfonate are found to have a morphology quite different from the ones observed in the absence of superplasticizers [10–12]. In the presence of a superplasticizer ettringite crystals grow as small and massive crystals, which shape contrasts with the long needle-like ones usually observed in the absence of superplasticizer. The size of these ettringite crystals seems to decrease when the superplasticizer dosage increases [12].

In order to have a better understanding of the role played by SO_4^{2-} and Ca^{2+} ions and ettringite formation on the rheological behavior of cementing systems containing a certain amount of superplasticizer, a very simple experimental study was undertaken.

2. Methodology

Instead of conducting such a study on different Portland cements with different C_3A contents and different dissolution rates of their calcium sulfates it was rather decided to study a cementitious system where the natural product of

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hydration should essentially be ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$). The rheology and the mechanical properties of such a system in the absence of any chemical admixtures have been studied by one of the authors [13]. This system is composed of calcium hydroxide, sulfates and a source of alumina. A similar approach has already been followed [14,15].

Such a simple system has been selected for three reasons:

- there is no other mineral species that is formed except calcium aluminate hydrates, ettringite and monosulfate aluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}13H_2O$).
- there are no other interferences, which could alter the action of the superplasticizer during their formation, which is most probably the case when using Portland cement.
- in a cementitious system containing Portland cement, C_3A content is generally ranging from 6% to 10%, so that the amount of calcium aluminates formed represents, in the best cases, a small amount of the total system that is under investigation. This is not particularly advantageous if X-ray diffraction and differential thermal analysis are used to make qualitative and quantitative analyses.

3. Materials and experimental techniques

A commercial grade of calcium hydroxide containing 98% of $Ca(OH)_2$ was used; it contributes to calcium ions as well as basicity. The anhydrite used is 98% pure and contributes to sulfates ions. Finally, a silico-aluminous powder containing 20% Al_2O_3 and 15% SiO_2 was used.

These powders were first thoroughly dry mixed before demineralized water was added. When a superplasticizer was used, it was a sodium salt of polynaphthalene sulfonate having a 42% solid content. It has been always dissolved in the mixing water prior its addition in the mixture. The pastes that were obtained were molded in water tight molds and stored at 40 °C until these were tested. Before testing, hydration was stopped using acetone; samples were then dried and ground.

The rheological study was done using the minislump test [16]. Phase characterization was done on X-ray diffractometer using a copper anticathod (40 kV, 30 mA) and a thermogravimetric balance operating in a nitrogen atmosphere.

4. Influence of SO_4^{2-} ions on paste rheology

In order to pinpoint the role of SO_4^{2-} ions provided by calcium sulfate on the rheology of the cementitious system under study, two types of mixtures were prepared with demineralized water; their W/C ratio was 0.35 due to the use of a limestone filler. The superplasticizer was used at a 2% dosage (solids).

The first mix (mix 1) contained 22% of silico-aluminous powder, 22% of calcium hydroxide, 5% of anhydrite and 51% of limestone filler. After mixing, a quite fluid mixture was obtained. Its rheology expressed as the spread of the minicone as a function of time is represented in Fig. 1. This curve shows that the paste experiences first a slight slump loss that is recovered progressively later on due to the dispersing action of superplasticizer molecules.

The second mix (mix 2) contained exactly the same proportions of the different constituents except that anhydrite ($CaSO_4$) was replaced by a ground siliceous sand having almost the same grain size distribution as the previous anhydrite. The rheology of this mix is presented also in Fig. 1. The initial spread of the minicone is almost the same, but this time the spread drops drastically and definitively quite rapidly.

As anhydrite is the only difference between the two mixes and as the ground siliceous sand used is nonreactive, it appears then that, like in Portland cement pastes, the addition of some calcium sulfate neutralize the flash set probably due to the formation of ettringite.

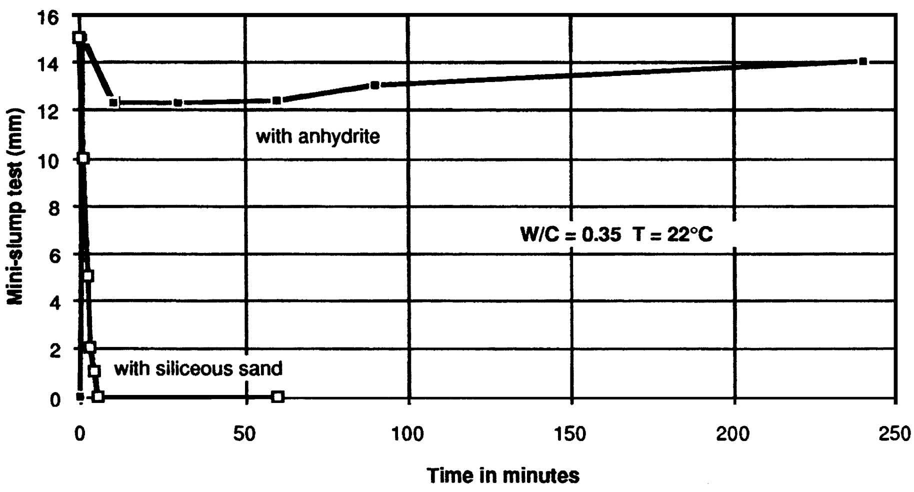

Fig. 1. Rheology of the mixes containing $CaSO_4$ and siliceous sand.

5. Influence of ettringite on the rheology of cementitious pastes

The rheology of cementitious system containing superplasticizer is the consequence of a physical process due to the electrostatic repulsion between particles, but also of a chemical process linked to the nature of the phases that are formed. Ettringite crystallization play as a key role in this matter as already pointed out by some other researchers [10,14].

In order to show that it is not sufficient to have SO_4^{2-} ions in the system to control its rheology but rather have conditions favoring the growth of ettringite, a third mixture (mix 3) was prepared. In this mixture, anhydrite was replaced by sodium sulfate as a source of SO_4^{2-} ions.

When mixed at the same W/C ratio this new paste was not plastic at all, and it was impossible to cast a minicone. Even for a 0.80 W/C ratio, the paste was still too sticky. This drastic difference in the rheological behavior of mixes 1 and 3 is due to the nature of reaction products. Indeed, from mix 1 containing anhydrite ($CaSO_4$), the main product that crystallized is ettringite as shown in Fig. 2. On the contrary, from mix 3 that contains sodium sulfate (Na_2SO_4), ettringite is not present at all (Fig. 3). It is probably the crystallization of gypsum or some calcium aluminates that explain the rapid set of this mix 3 but the peaks of these products are not clearly recognizable in Fig. 3 due to the presence of large amount of limestone filler.

Thermal analysis curves were recorded from the pastes obtained 10 min after the mixing. The DTA curve of mix 1 containing calcium sulfate (Fig. 4a) shows clearly a peak at 87 °C corresponding to the decomposition of ettringite and a small one at 165 °C, which may be attributed to monosulfate aluminate. These peaks are not on the curve of mix 3, which contains Na_2SO_4 (Fig. 4b). However, both diagrams contain a peak of about 430–460 °C, which is due to the dehydration of calcium hydroxide, and another one around 800 °C corresponding to the decarbonation of the limestone filler calcite.

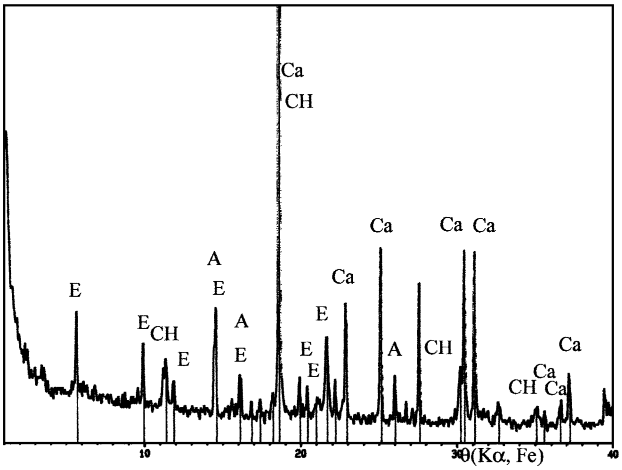

Fig. 2. XRD of the mix 1 containing anhydrite ($CaSO_4$). A = Anhydrite, CH = calcium hydroxide, Ca = calcite, E = ettringite.

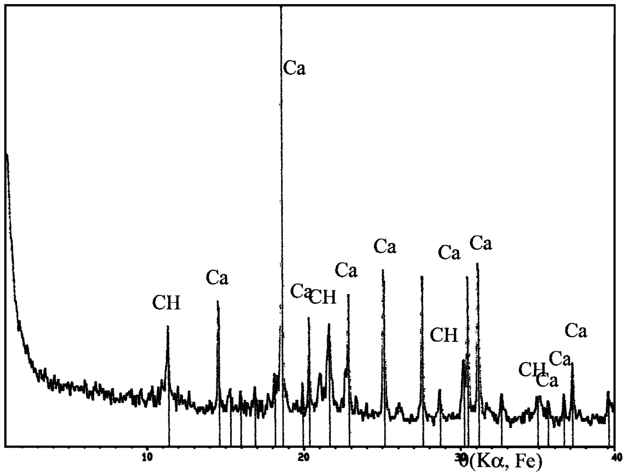

Fig. 3. XRD of the mix 2 containing Na_2SO_4. CH = Calcium hydroxide, Ca = calcite.

Finally, it appears that ettringite does not crystallize easily in the presence of the large amount of alkali-sulfate and despite the presence of some gypsum. The explanation

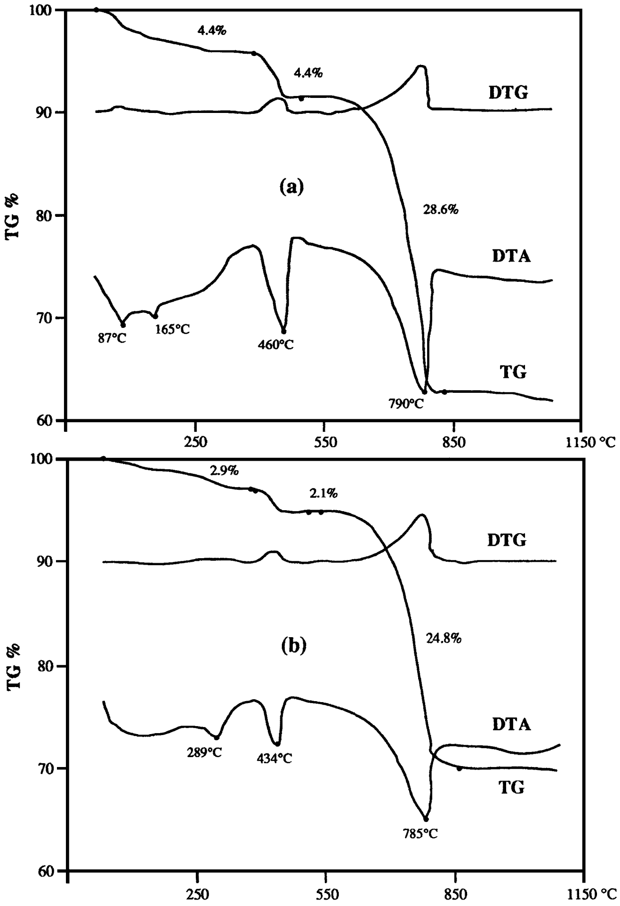

Fig. 4. Influence of the nature of the sulfate. (a) Thermogram of the mix containing anhydrite, (b) thermogram of the mix containing sodium sulfate.

is the following: from the mixes on study, $Ca(OH)_2$ and Na_2SO_4 dissolve according to Eqs. (1) and (2), respectively. Calcium ions react with SO_4^{2-} ions giving gypsum according to Eq. (3).

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \qquad Ks = [Ca^{2+}]*[OH^-]^2 \tag{1}$$

$$Na_2SO_4 \leftrightarrow 2Na^+ + SO_4^{2-} \qquad Ks = [Na^+]^2*[SO_4^{2-}] \tag{2}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O$$

$$Ks = [Ca^{2+}] * [SO_4^{2-}] \tag{3}$$

As Na_2SO_4 is highly soluble, the $SO_4{}^{2-}$ ion concentration in the internal solution is very high and gypsum precipitate according to Eq. (3). Two consequences result from this:

- Firstly, the calcium ion concentration drops drastically in order to maintain the solubility product constant given in Eq. (3).
- Secondly, the decrease of the calcium ion concentration entails the increase of the OH^- ion concentration so as to maintain the constancy of the product of solubility given in Eq. (1).

In this condition, ettringite does not crystallize easily due to the lack of calcium ions in the internal solution and despite the presence of lime in a solid state. This result shows well that the new products crystallize from the solution according to the equilibrium laws of reactions. The composition of the internal solution is the main factor that determines the nature of the reaction products.

Finally, the nature of the sulfate used in the cementitious systems plays an important role in their rheological behaviour.

6. Influence of superplasticizers on cementitious pastes rheology

Some works done on cementitious paste rheology resulted in slightly diverging interpretations on the consequence of the interaction between superplasticizers and some calcium sulfates, particularly anhydrite. Dodson and Hayden [5] have shown that the solubility rate of anhydrite decreases noticeably in the presence of a lignosulfonate. On the contrary, in their comprehensive study on the interaction between a polynaphthalene sulfonate and different forms of calcium sulfate, Aïtcin et al. [3] have shown that, in all cases, the addition of a superplasticizer resulted in an increase of the solubility of the sulfate, without noticeably affecting the dissolution rate of the different forms of calcium sulfate used.

Those results are contradictory only in appearance when the particular experimental conditions are closely examined. In Jolicoeur et al.'s study, the measurements were done by conductimetry in an agitated solution. In such conditions, the dissolution rate is principally controlled by the mineral species (anhydrite, gypsum or hemihydrate) and their specific surface area. On the contrary, Dodson and Hayden [2] made their study on cement pastes. In such a case, the dissolution rate is not only controlled by the nature and the specific surface area of the minerals but also by the diffusion rate of the ions at the solid–liquid interface. This last parameter can become a limiting factor if a diffusional barrier is created at the interface of the reacting powders.

The following experiments have been done to see if a superplasticizer could not create such a barrier that could slow down the dissolution rate of the different constituents of the system.

6.1. Effects of the superplasticizer on the kinetics of the reactions

In order to reach a better understanding of the role of the superplasticizer on the reacted products, two new mixes were prepared (mixes 4 and 5); they have the same solid components as mix 1. Mix 4 was made using 2% of superplasticizer, while in the second one (mix 5), no superplasticizer was used. The determination of the phases developed during hydration was made using thermal analysis (TG, DTA and DTG) and X-ray diffraction. The thermal analysis diagrams were recorded directly on samples obtained after hydration of the mixes. On the other hand, X-ray diagrams were recorded on special pastes having the same solid components except that the limestone filler was avoided allowing an easy determination of the newly formed products.

If the X-ray diagrams recorded after 24 h of hydration are considered, it appears that ettringite is the only well-crystallized phase that is formed in both series of mixes. Fig. 5 is an example of diagram obtained from the sample without superplasticizer.

However, if the thermal analysis curves are considered (Fig. 6), some differences are noticed between diagrams obtained from the mixes containing the superplasticizer and those obtained from the mixes that do not contain any superplasticizer.

On the DTA curve of the sample containing the superplasticizer (Fig. 6a), the following peaks are present.

- a small peak at 92 °C corresponding to the decomposition of ettringite,
- a second one at 157 °C that could be attributed to the decomposition of the monosulfate aluminate,
- a third one at 433 °C, which is due to the dehydration of calcium hydroxide,
- a last one around 800 °C corresponding to the decarbonation of the limestone filler calcite.

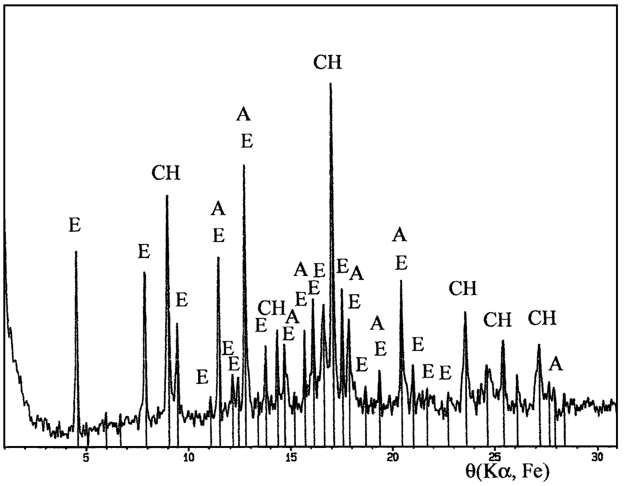

Fig. 5. XRD of the mix 4 recorded after 24 h of hydration. A = Anhydrite, CH = calcium hydroxide, E = ettringite.

On the curve (Fig. 6b), which corresponds to the sample that does not contain any superplasticizer, the same peaks are observed except that there is not a small peak corresponding to the decomposition of the monosulfate aluminate.

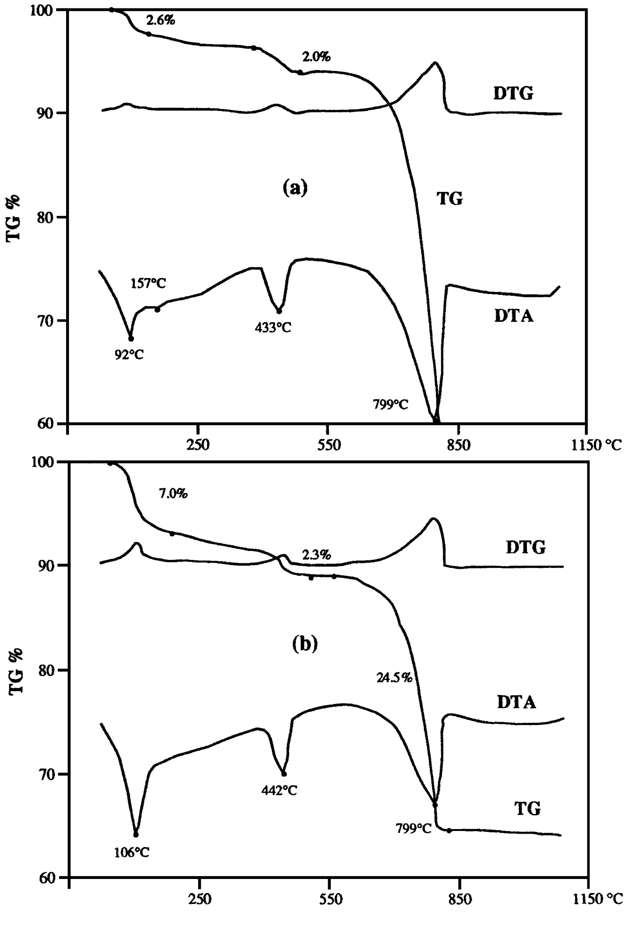

Fig. 6. Effect of the superplasticizer on the phases present 24 h after mixing. (a) Thermogram of the mix containing the superplasticizer, (b) thermogram of the mix without superplasticizer.

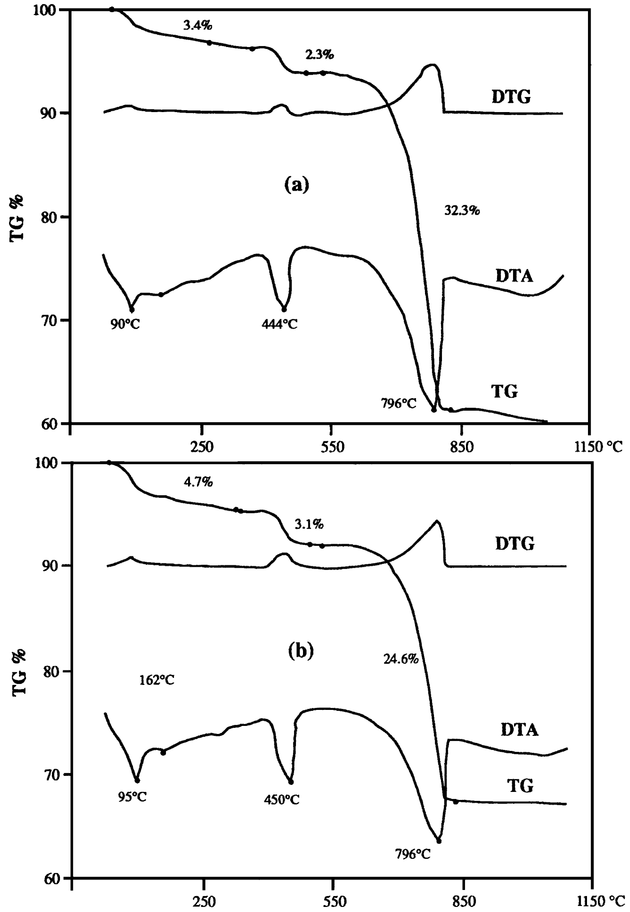

Fig. 7. Effect of the superplasticizer on the phases develops during the first hour after mixing. (a) Thermogram of the mix containing the superplasticizer, (b) thermogram of the mix without superplasticizer.

Instead, a neat peak is observed in all the mixes that were prepared ($0.50 < W/C < 0.80$) and observed between 2 and 24 h. It seems then that the presence of the superplasticizer induced the formation of some monosulfate beside ettringite

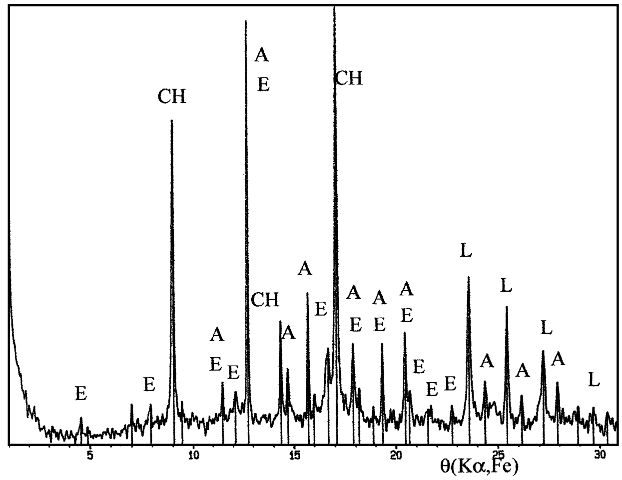

Fig. 8. XRD of the mix 4 containing the superplasticizer (after 1 h of hydration). A = Anhydrite, CH = calcium hydroxide, E = ettringite.

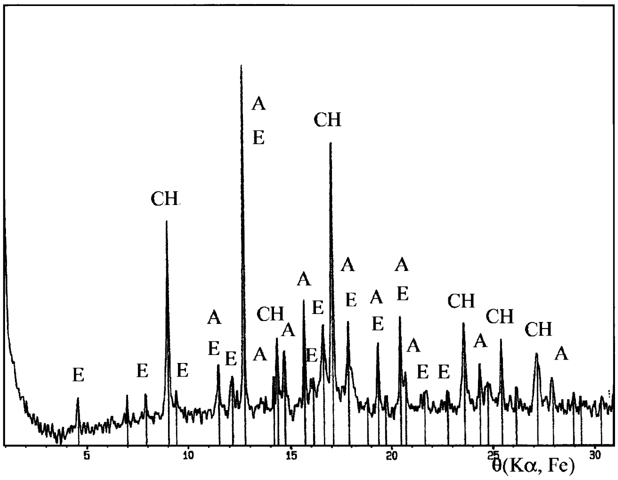

Fig. 9. XRD of the mix 4 without the superplasticizer (after 1 h of hydration). A = Anhydrite, CH = calcium hydroxide, E = ettringite.

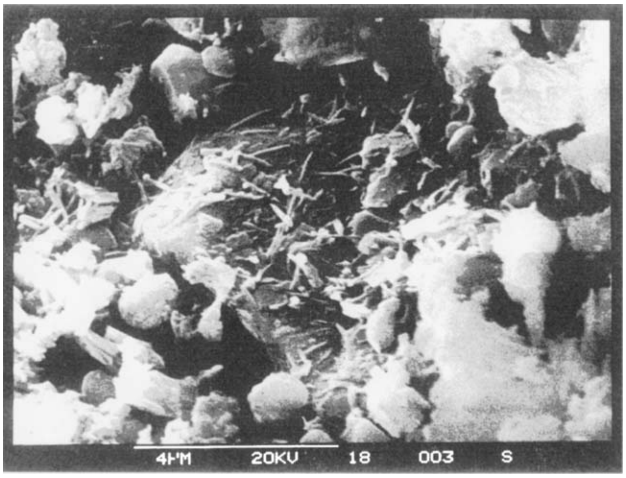

Fig. 10. SEM of the mixture without superplasticizer.

at the early beginning of hydration. Usually, monosulfate aluminate is formed when there is a deficiency in SO_4^{2-} with respect to $Al(OH)_4^-$. It is then possible that the superplasticizer reduces the dissolution rate of the anhydrite.

In order to show that this deficiency in SO_4^{2-} ions can explain the formation of the monosulfate aluminate, the products of hydration developed during the first hour in the presence or absence of the superplasticizer were compared. For such short reaction time when using anhydrite with a low dissolution rate as a source of sulfate, a deficiency in SO_4^{2-} ions should be observed in both cases, which should result in the formation of monosulfate aluminate.

The two thermograms obtained in such conditions are reproduced in Fig. 7. In the presence of the superplasticizer (Fig. 7a), the monosulfate aluminate is formed in an amount almost equal to that of ettringite. In the absence of the superplasticizer (Fig. 7b), ettringite is predominant even if some small amount of monosulfate aluminate is found.

If the X-ray diagrams are considered, the sample containing the superplasticizer shows (Fig. 8) some weak peaks of the ettringite while the calcium hydroxide and anhydrite peaks are still very strong. Conversely, on the diagram of the sample that does not contain superplasticizer (Fig. 9), the ettringite peaks (E) are stronger, while the calcium hydroxide (CH) and anhydrite (A) peaks decrease.

Therefore, in the cementitious system understudy, the superplasticizer seems to decrease the dissolution rate of anhydrite and acts as it was creating a diffusional barrier at the surface of the reacting powders as shown by Uchikawa et al. [17] and Uchikawa [18]. This effect results in a modification of the sequence in which the different hydrated phases are appearing, for example, some monosulfoaluminate can be initially formed and then be transformed into ettringite, if later on the amount of sulfate ions reaches a sufficient level. The second consequence could be a modification of the morphology of the newly formed phases.

Table 1
Temperature of decomposition of ettringite

Ettringite decomposition temperature (°C)	E/C = 0.50			E/C = 0.80
	10 min	2 h	24 h	24 h
With superplasticizer	90	84	87	92
Without superplasticizer	95	100	95	105

6.2. Hypothesis of modification of the newly formed phase morphology

In a reacting media, it is possible that the size of the crystals formed can vary according to the level of saturation of the different ionic species that are in solution: it is possible to obtain a great number of small crystals or rather a limited number of big crystals.

As previously mentioned, some authors [10–12,15] have found that ettringite that crystallizes in the presence of a superplasticizer loses its needle-like shape to form rather small massive crystals without the definite characteristical

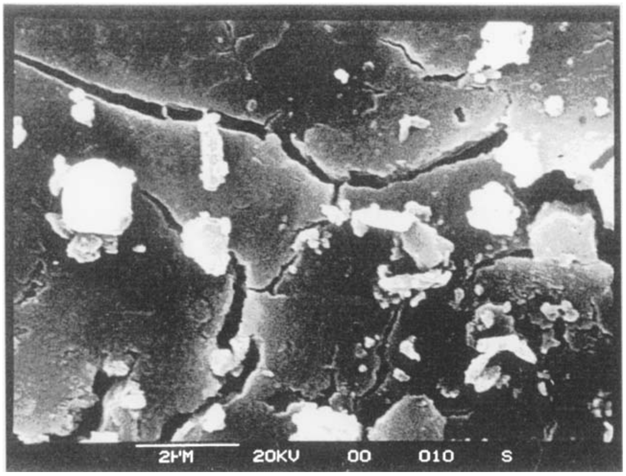

Fig. 11. SEM of the mixture containing superplasticizer.

shape of ettringite. In order to see if such a change in the morphology of the hydration product was occurring in the studied cementitious system, the temperature at which ettringite decomposes has been noted and reported in Table 1 for two mixes: one which contains a superplasticizer and the other one that does not.

Although it is difficult to give an absolute value to this temperature of decomposition, the trend is systematic; decomposition temperature is always lower when the mix contains a superplasticizer because either the superplasticizer acts like a fluxing agent or/and changes ettringite morphology.

Clearly, samples observed under scanning electron microscope show two different aspects. The mixture in which no superplasticizer was added (Fig. 10) contains very thin needles of ettringite, which connect the initial granular particles. The paste incorporating the superplasticizer (Fig. 11) shows an amorphous background with some massive clusters of crystallite. On the EDAX diagrams of the background and of the crystallites, the same peaks, Ca, Al, S and Na, are detected showing that both of them are composed of the same basic ions Na coming from the superplasticizer.

7. Conclusion

The simple experiments presented here confirm that the addition of calcium and sulfate ions in the particular cementitious system under study helped in controlling the rheology of the system. It has been also shown that, in the presence of a high amount of alkalis when using an alkali sulfate rather than calcium sulfate, it is difficult for ettringite to crystallize so that a rapid stiffening of the system is experienced. On the contrary, when calcium sulfate is used, there is no more any flash set and the superplasticizer can fluidize the paste.

Therefore, in order to favor a good rheology within a cementitious paste, it is imperative to favor ettringite crystallization in proportions compatible with the level of fluidity that is looked for.

It has also been found that the adsorption of superplasticizer molecules at the surface of the particles of the cementitious system seems to decrease the dissolution rate of the constituents and modify the nature of the different hydrated compounds. It has also been noted that the adsorption of the superplasticizer results in a decrease of the temperature of decomposition of ettringite. This phenomenon could be linked to the change in ettringite morphology already observed by some authors.

Although this study was done in a particular cementitious system different from Portland cement, it is reasonable to think that the trends that have been observed could be extended to Portland cement.

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