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Interaction between ettringite and a polynaphthalene sulfonate superplasticizer in a cementitious paste

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Abstract

It has been recognized that the interaction between a superplasticizer and C3A is crucial when controlling the rheology of Portland cement grouts, mortars and concretes. In spite of the fact that a great deal of research has been done to understand the exact nature of this interaction using different experimental techniques, there is not yet a clear understanding of all the basic principles which command that interaction. In an attempt to cast some complementary light in the type of interactions developed between C3A, Portland cement and a polynaphthalene sulfonate superplasticizer in the presence of calcium sulfate, the rheological behavior of a particular cementitious system in which only calcium aluminates or calcium sulfoaluminates hydrated phases could be formed has been studied. This study has shown that superplasticizer molecules are not only adsorbed on unhydrated cement phases but also and perhaps more on some of their hydrates. This adsorption on the hydrates slows down drastically or even stops the growth of ettringite germs. However, when all the initial superplasticizer molecules have been consumed normal growth of ettringite resumes. This interaction between superplasticizer molecules and ettringite can be used to explain the important water consumption in the early stages of mixing as well as the never answered question: where are all the superplasticizer molecules in a hardened concrete. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Ettringite; Hydration products; Retardation

1. Introduction

Superplasticizers represent today an essential family of admixtures when formulating modern durable concretes [1]. As soon as superplasticizers molecules enter in contact with cement particles some of them are adsorbed on cement particles creating negatively charged particles repulsing each other so that cement particles do not flocculate anymore [2–5].

It has been found from experience that superplasticizers must be used at an appropriate dosage if unwanted secondary effects have to be avoided [6]. In some cases, these secondary effects result in a rapid and unrecoverable slump loss, in other cases in a very strong retardation, in other cases in a severe segregation or excessive bleeding. Some researchers have pointed out that the adsorption of superplasticizer molecules on cement particles could not explain the large amount of superplasticizer consumed during the initial phase of cement hydration [3]. Finally, there is always the question that has not received a final answer: where are going all the superplasticizer molecules in the hydrated cement paste [3,6]?

Some recent research tend to show that superplasticizer molecules are not only adsorbed on cement particles but that there are becoming part of the hydrated calcium aluminate phases [7,8]. Recently, Fernon [9] has shown the existence of mixed products formed by the absorption of superplasticizers molecules within structural sheets of hexagonal aluminates. She found that these mixed compounds were:

- well crystallized when a low dosage of superplasticizer was used and when superplasticizer molecules had essentially a linear structure;
- highly disorganized or even amorphous when the superplasticizer dosage was high or when the superplasticizer molecules were showing some branching.

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If the existence of such mixed compounds can be used to explain where the superplasticizers molecules are trapped in the hardened concrete, the existence of these mixed compounds cannot explain the high early consumption of water during the initial phase of cement hydration [3]. In fact, if the right amount of calcium sulfate is added in a Portland cement, hydrated tetracalcium aluminate phases should not be formed during the early stages of cement hydration. Tetracalcium aluminate hydrates usually appear several hours or days after setting when all sulfate ions have been consumed by the formation of calcium sulfoaluminate hydrates and that there is still some unreacted C3A.

Usually, ettringite is first formed during the early stages of cement hydration. Its transformation into calcium monosulfoaluminate occurs several hours after setting when the cement paste is already well hardened. Therefore, it is rather in the interaction between ettringite and the superplasticizer that the important initial water consumption must be looked for. The purpose of the simple following experiments has been to show how the presence of a superplasticizer in a reacting cementitious system can influence its setting time and the cristallinity of the ettringite formed.

2. Methodology

In order to study the action of superplasticizers on portland cement compounds, a direct synthesis technique by mixing appropriate solutions has been already proposed [9,10]. If with this technique it is easy to detect the newly formed phases, the final results that are obtained could not always apply when the reacting medium is composed of solid constituents. In fact, in such a case, the dissolution rate of the solids is an essential factor in the involved chemical processes. For example, when calcium sulfate is added in portland cement, the crystalline form of this calcium sulfate, and particularly its dissolution rate plays an almost as important role as the total amount of calcium sulfate on the rheological properties of the mixture [11].

In order to figure out the influence of the dissolution rate of solid constituents, a particular ternary system has been selected for this study. This system can generate only few well-identified hydrates. It is composed of a calcined kaolin, of lime and anhydrite. It has been extensively investigated by one of the authors [12]. The setting and hardening of such a system normally should occur following the development of reaction (Eq. (1)). In such a reaction calcined kaolin brings active silica and alumina while anhydrite brings sulfate ions.

$$\begin{aligned} &Al_2O_3{\cdot}2SiO_2 + 5Ca(OH)_2 + 3CaSO_4 \\ &\quad + 29H_2O \rightarrow Al_2O_3{\cdot}3CaO{\cdot}3CaSO_4{\cdot}32H_2O \\ &\quad + 2[CaO{\cdot}SiO_2{\cdot}H_2O] \end{aligned} \tag{1}$$

In certain conditions, when some sulfate ions are missing, such a system results in the formation of monosulfoaluminate according to reaction (Eq. (2)), or even in the formation of calcium aluminate hydrates according to reaction (Eq. (3) or (4)) when sulfate ions are totally absent.

$$\begin{aligned} &Al_2O_3{\cdot}2SiO_2 + 5Ca(OH)_2 + CaSO_4 + 9H_2O \\ &\quad \rightarrow Al_2O_3{\cdot}3CaO{\cdot}CaSO_4{\cdot}12H_2O \\ &+2[CaO{\cdot}SiO_2{\cdot}H_2O] \end{aligned} \tag{2}$$

$$\begin{aligned} &Al_2O_32SiO_2 + 5Ca(OH)_2 + 3H_2O \\ &\quad \rightarrow Al_2O_3{\cdot}3CaO{\cdot}6H_2O + 2[CaO{\cdot}SiO_2{\cdot}H_2O] \end{aligned} \tag{3}$$

$$\begin{aligned} &Al_2O_3{\cdot}2SiO_2 + 6Ca(OH)_2 + 9H_2O \\ &\quad \rightarrow Al_2O_3{\cdot}4CaO{\cdot}13H_2O + 2[SiO_2{\cdot}CaO{\cdot}H_2O] \end{aligned} \tag{4}$$

The kaolin used in this study was an industrial kaolin containing 85% of kaolinite and 15% of quartz. The lime used was a high purity laboratory Iime and the anhydrite was an industrial by-product containing 97.5% of anhydrite. The superplasticizer used was a sodium salt of a polynaphthalene sulfonate of high quality.The dry powders were first thoroughly mixed in their dry form before adding water. Paste samples were taken from time to time to be observed under X-ray diffraction and thermal analysis.

3. Experimental results

3.1. Influence of the superplasticizer on the setting time of the cementitious system under study

Two almost identical pastes were prepared with a 0.65 water/cementitious ratio. They contained exactly the same amount of kaolin, lime, anhydrite and demineralized water except that in the second one, 2% (by mass of the cementitious powders) of superplasticizer was diluted in the mixing water. The two pastes were molded and cured in closed vessels. Their setting was followed with a Vicat needle.

It has been found that the two pastes followed a completely different setting pattern.

Mix 1 that was prepared with demineralized water only, had its setting completed within 18 h so that the demolding of the specimens could be done at 24 h. On the contrary, Mix 2 which contained the superplasticizer did not set before 5 days, it was rather looking like a gel that was thickening and hardening very slowly with time. The final setting did not occurred before the seventh day. The presence of the superplasticizer modified drastically the hardening process of the cementitious system. This strong retarding effect can be explained in two ways.

Firstly, it can be assumed that superplasticizer molecules when they are adsorbed on the constituents of the cementitious system modify drastically the dissolution rate of the

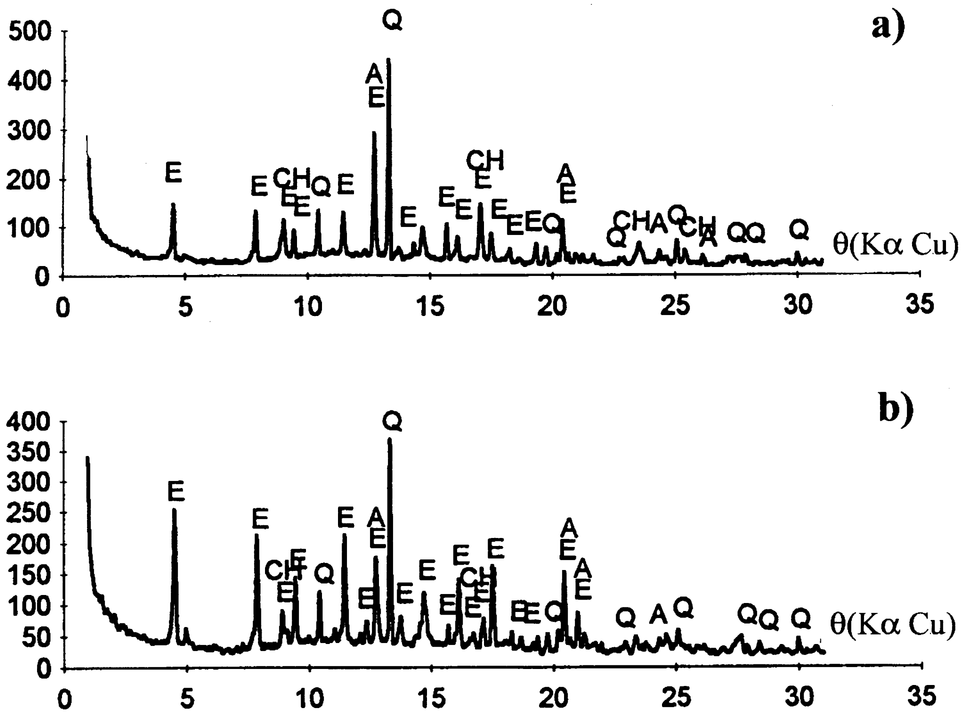

Fig. 1. X-ray diffractograms obtained from Mix 1 (no superplasticizer): (a) 2 h after mixing; (b) 24 h after mixing. E = Ettringite; Q = Quartz; CH = Lime; A = Anhydrite.

constituents reducing the crystallization rate of ettringite which is in any case responsible for the setting of the paste. If such a hypothesis is to be true, set retardation should be essentially of kinetic origin, ettringite, being formed very slowly during all the setting and its amount increasing with time.

Secondly, it can be supposed that superplasticizer molecules are adsorbed not only on the unreacted constituents but also on ettringite germs just after their formation. In such a case, compounds that do not have the binding properties of usual ettringite should be formed. If such a hypothesis is found to be true it can be concluded that the superplasticizer has modified the crystallization and growth of ettringite.

These two hypotheses do not exclude each other and it could be possible that at the same time a slow down in the dissolution rate of the constituents of the cementitious system and an inhibition of ettringite crystallisation can happen simultaneously. In order to better understand what is actually happening in the system under study, the evolution of the hydrated phases has been followed par X-ray diffraction and thermal analysis.

3.2. Influence of the superplasticizer on the products of reaction

Fig. 1 represent the X-ray diffractograms obtained on samples of the two pastes, 2 and 24 h after their mixing.

For Mix 1 prepared with demineralized water, Fig. 1a shows that ettringite, characteristical peaks are easily observed after two hours and that their intensity increases until 24 h (Fig. 1b). Thermal analysis curves (Fig. 2) confirm this analysis. It is easily seen that the 105 °C peak

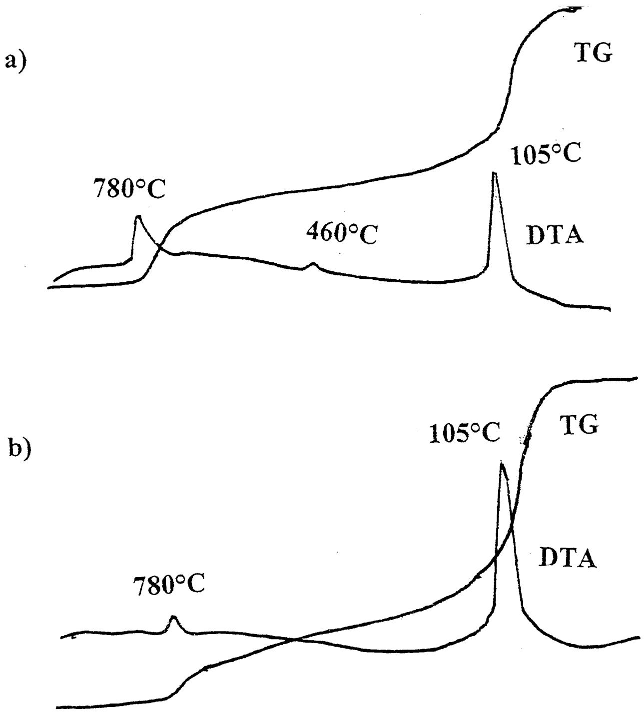

Fig. 2. Thermal analysis curves of the reaction products obtained from Mix 1 (a) 2 h after the mixing; (b) 24 h after the mixing.

corresponding to ettringite dissociation grows in size between 2 and 24 h.

For Mix 2, containing the superplasticizer, ettringite peaks are clearly seen in the sample observed at 2 h (Fig. 3a) but they have almost completely disappeared at 24 h (Fig. 3b). Between 24 h and the fifth day there are almost absent in the X-ray diffractograms while the paste remains essentially viscous but is thickening very slowly. After the fifth day, ettringite peaks reappear and their intensity increases until the seventh day (Fig. 3c). The crystallization observed in this case corresponds exactly to the end of setting. It seems that a strong interaction occurs between the initial ettringite and superplasticizer molecules. This interaction being translated by an amorphisation of the firstly formed crystals and an inhibition of their crystalline growth.

These observations lead to the following partial conclusions.

(1) Firstly, in the presence of a superplasticizer, the dissolution rate of the constituents is not nihil since some ettringite is formed and easily seen during the first hours following the mixing. This ettringite will be later on called primary ettringite.

(2) Secondly, it should be pointed out that if the lengthening of setting period was only due to a slow down of the dissolution rate of the different ionic species, there should be no reasons to see any retrogression of ettringite crystallization and stopping of its formation. On the contrary, the amount of ettringite formed should have increased slowly with time. All occurs as if the paste is progressively transformed into a gel, which do not give the usual ettringite peaks when submitted to X-rays. It is probable that during this phase the crystallites that are formed include superplasticizer molecules so that the natural periodicity of ettringite crystal structure is broken.

(3) Thirdly, if ettringite starts again to crystallize between the fifth and seventh day it is because the conditions that inhibited its growth or totally desorganized it are no more prevailing. There is probably no more superplasticizer molecules available to block the natural growth of ettringite crystals.

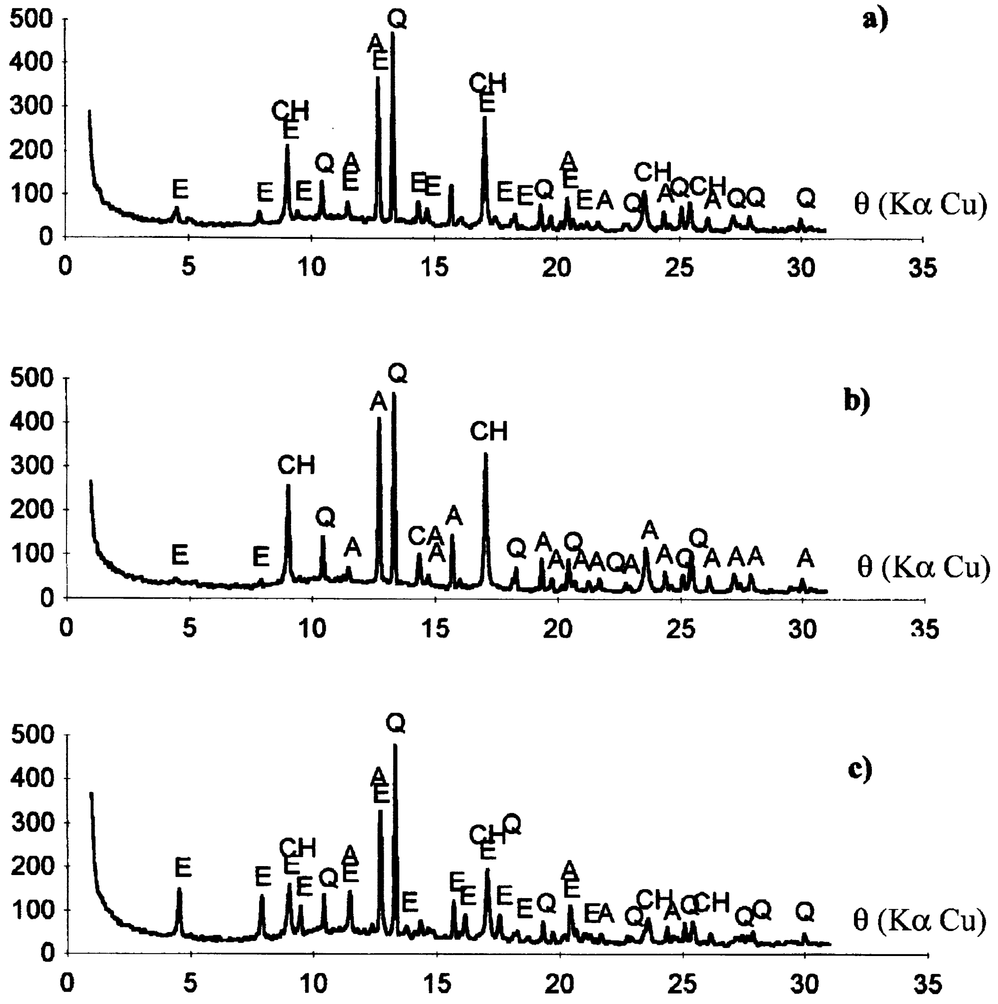

Fig. 3. X-ray dffractograms obtained from Mix 2 (containing superplasticizer): (a) 2 h after mixing; (b) 24 h after mixing; (c) 7 days after mixing. E = Ettringite; Q = Quartz; CH = Lime; A = Anhydrite.

In short, from the sequence of reactions observed in the particular cementitious system understudy, it comes out that there is a very strong interaction between superplasticizer molecules and ettringite germs. Ettringite germs are probably maintained in a short-range organization looking like an amorphous material. Superplasticizer molecules are progressively consumed within this amorphous looking like paste. The usual ettringite crystals start to grow again when all superplasticizer molecules have been consumed. In order to confirm this hypothesis the morphology of hardened pastes containing or not superplasticizer molecules has been observed under a scanning electron microscope

3.3. *Influence of the superplasticizer on the morphology of the hardened paste*

The samples have been taken 7 days after the mixing and have been observed under a scanning electron microscope, with two different magnitudes.

Fig. 4 corresponds to the mixture in which no superplasticizer was added. The paste contains very thin needles, which connect the initial granular particles. Ca, Al and S are clearly identified on EDAX diagram.

Fig. 5, which corresponds to the paste incorporating the superplasticizer, is quite different. On a looking like amorphous background, there are some small and massive clusters of crystallites. On the EDAX diagrams of the background and of the crystallites, the same peaks Ca, Al, S, Na are detected showing that both of them are composed with the same basic ions, Na ions coming from the superplasticizer. The presence of the superplasticizer has resulted in a definite modification of ettringite morphology as it was shown by other authors.

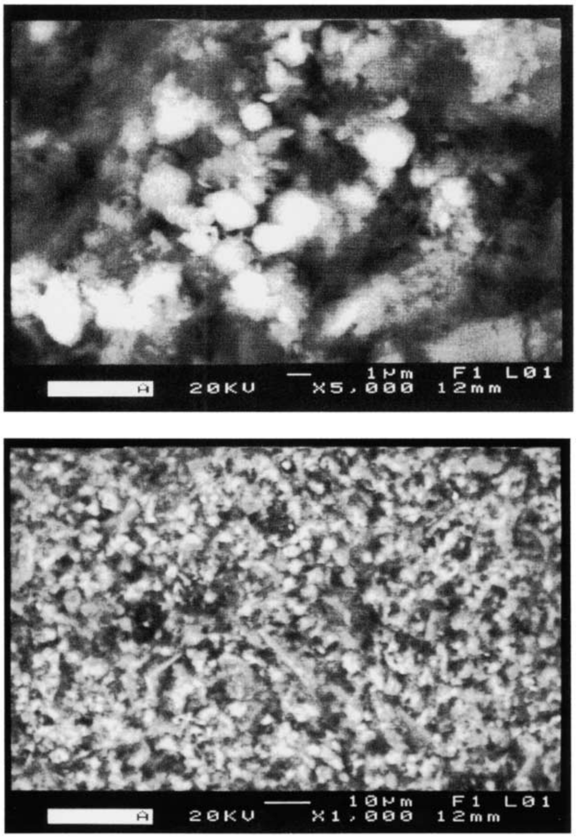

Fig. 4. SEM at two different magnitudes of the paste without superplasticizer.

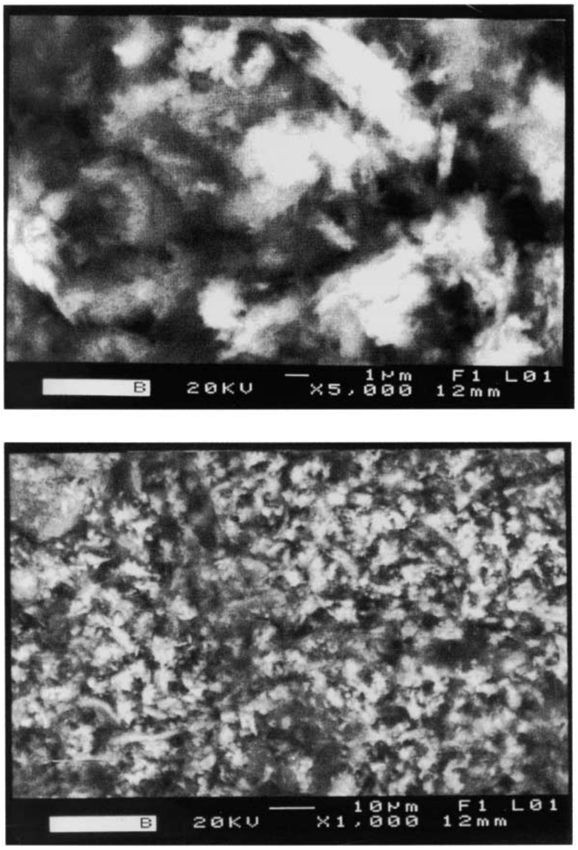

Fig. 5. SEM at two different magnitudes of the paste containing superplasticizer.

In conclusion, the great retardation found in the setting of the cementitious system under study can be explained by a drastic modification of the kinetic of the reactions and of the microstructure of the products of the reaction. If such a long retarding effect is not usually found in Portland cement pastes mortars or concrete it can be due to the greater reactivity of the C3A and the limited amount of C3A and superplasticizer present. During the early stage of hydration C3A liberates significant amounts of $Al(OH)_4^-$ that can generate ettringite crystals. As these ettringite germs consume some superplasticizer molecules, when there are no more superplasticizer molecules available usual ettringite crystals start again to build-up in the system However, when concrete is overdosed in superplasticizer, a strong retardation is observed in the concrete because it takes longer to consume all these superplasticizer molecules. In order to confirm this mechanism another simple experiment was undertaken.

3.4. Influence of the reactivity of the constituents

In order to verify the influence of the reactivity of the constituents, the initial mixture was slightly modified. Instead of using the activated kaolin as a source of alumina, a bauxitic residue rich in active alumina was used. Two mixes were prepared. Mix 3 was mixed using demineralized water while Mix 4 contained 2% superplasticizer diluted in the same amount of demineralized water. In both cases setting was completed within 24 h. In both cases, ettringite crystals have been clearly identified in X-ray diffractograms.

When the ettringite peaks found on Mixes 3 and 4 samples, examined 2 h after mixing, are compared, it is seen that in Mix 4 that contained the superplasticizer (Fig. 6a) ettringite peaks are slightly smaller than those appearing in Mix 3 diffractogram (Fig. 6b). In parallel, lime and anhydrite peaks are of course smaller in the diffractogram of Mix 3 sample. Although ettringite formation was not totally blocked, the introduction of the superplasticizer in the mix resulted in a slow down of the dissolution rate of the initial phases of the mix. Being absord on the constituents of the mix a diffusional barrier was created reducing interfacial exchanges.

4. Conclusions

The results presented here tend to suggest that superplasticizer molecules were not only adsorbed on the

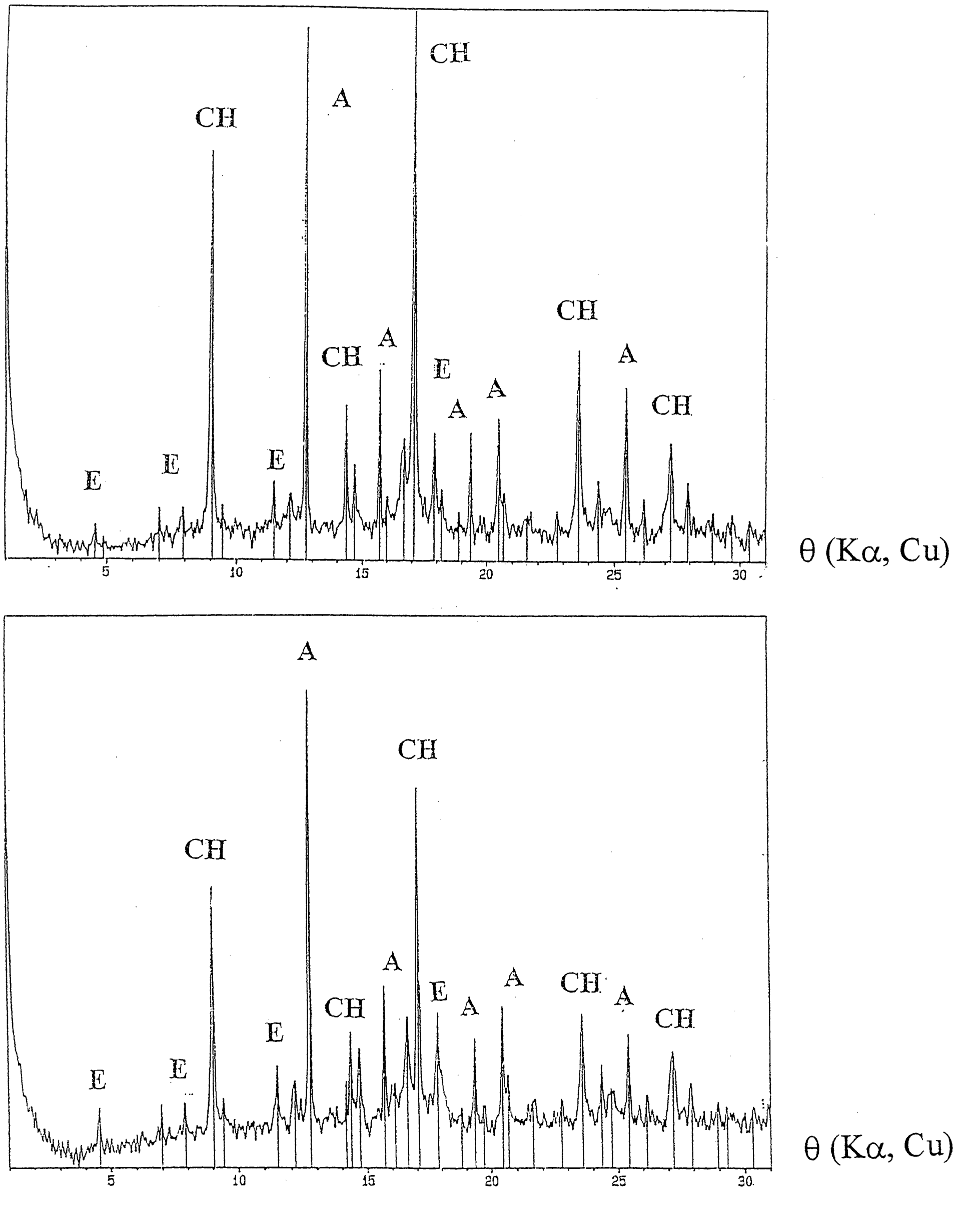

Fig. 6. X-ray diffractograms obtained with the bauxitic residue: (a) from Mix 3 containing the superplasticizer; (b) from Mix 4 prepared without superplasticizer.

anhydrous constituents of the cementitious paste under study but also on the crystalline germs of the first hydrates. Ettringite growth is stopped as soon as these germs are formed so that the usual needle like ettringite crystals cannot developed, rather small massive ettringite clusters appear on an amorphous looking paste. However, when there is no more superplasticizer molecules to block the development of ettringite crystals, they start growing again in their usual shape.

The adsorption of superplasticizer molecules on hydrated phases has two beneficial consequences:

- the electrostatically charged germs participate to the electrostatic repulstion so that flocculation is avoided;
- the growth of long needles of ettringite that usually decreases paste flowability and workability is delayed.

In Portland cement concretes, the presence of calcium sulfate prevents flash set because the brutal formation of hexagonal aluminate is replaced by the more progressive formation of ettringite. But ettringite formation consumes many water molecules so that the paste workability decreases due to this consumption of water and the growth of acicular ettringite crystals. When the superplasticizer is adsorbed on ettringite germs it delays the formation of ettringite needles, the paste remains workable for a longer period of time, but if the superplasticizer is overdosed a very strong retardation of setting can be observed.

This interaction between superplasticizer molecules and ettringite germs could explain not only the high consumption of superplasticizer molecules observed in the early stage of hydration but also the place where these molecules can be found in the hardened cement paste.

Acknowledgments

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References

[1] P.-C. Aïtcin, M. Baalbaki, Concrete admixtures: key components of hardened concretes, International RILEM Workshop on Concrete Technology — New Trends, Industrial Application, E & FN SPON, London, UK, 1994, pp. 33–47.

[2] F. Massazza, U. Costa, Effect of superplasticizer on the C_3A hydration, International Conference on the Chemistry of Cement, Pads, (1995) 529–534.

[3] M. Regourd, A Review of the use of proton magnetic resonance to study superplasticizers, Mater. Res. Soc. Proc. 85 (1987) 245–254.

[4] C. Jolicoeur, P.-C. Nkinarnubanzi, M.-A. Simard, M. Piotte, Progress in understanding the functional properties of superplasticizers in fresh concrete, ACI SP-148 (1994) 63–88 (Detroit).

[5] H. Uchikawa, Hydration of cement and structure formation and properties of cement paste in the presence of organic admixture, Proceedings of the Tribute de Micheline Moranville-Regourd available through the Network of Centres of Excellence on High Performance Concrete at Sherbrooke, P.Q., Canada, 1994, 55 pp.

[6] P.-C. Aitcin, C. Jolicoeur, J. MacGregor, Superplasticizers: how they work and why they occasionally don't, Concr. Int. 16 (5) (1994) 45–52.

[7] M.N. Onofrei, M.N. Gray, Adsorption studies of 35S-labelled superplasticizer in cement based Grout, in: Y.M. Malhotra (Ed.), Proceedings of the Third International Conference on Superplasticizers and other Chemical Admixtures in Concrete, ACl SP-119, 1989, pp. 545–660.

[8] H. Poellmann, Carboxylic acid anions: the reaction mechanisms and products with the aluminate phase of cement, Int. Symp. Chem. Cem., New Delhi, 1992, pp. 198–204.

[9] V. Fernon, Caractérisation de produits d'interaction adjuvants/hydrates du ciment, 3e journée techniques adjuvants, les Technodes, Guerville, France, 1994, 140 pp.

[10] K. Luke, P.-C. Aïtcin, Effect of superplasticizer on ettringite formation, in: S. Mindess (Ed.), Advances in Cementitious Materials, Ceramic Transaction, vol. 16, 1991, pp. 103–166.

[11] R. Ranc, Interactions entre les réducteurs d'eau plastiflants et les ciments, Ciments, Bétons, Plâtres, Chaux, No 782-1190 (1990) 19–21.

[12] W. Prince, Etude de la réactivité de matériaux naturels activés par voie therrnique ou mécanique en vue de leur utilisation comme liant, Ph. Thesis, Université de Toulouse, France, Juin 1987, 226 pp.