

## **Influence of three types of superplasticizers on tricalciumaluminate hydration in presence of gypsum.**

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### **Synopsis**

Different types of superplasticizers have been widely used over the past few decades in order to produce a more fluid or very high strength and durable concrete. These chemical admixtures interfere with the various physico-chemical processes occurring in early cement paste.

In this paper we present results from a study on the influence of superplasticizers on pure tricalciumaluminate hydration in presence of gypsum. The suspensions hydration has been investigated by conductimetry, isothermal calorimetry and total organic carbon analysis of the liquid phase.

The time taken for ettringite formation has been determined without superplasticizer and in presence of three different types of superplasticizers: polynaphtalene sulfonates (PNS), polycarboxylate-polyox (PCP) and diphosphonate terminated polyoxyethylene.

Whereas diphosphonate terminated polyoxyethylene does not seem to modify tricalcium aluminate hydration carried out in presence of gypsum, PCP and even more PNS slow down ettringite formation. This effect seems to be largely due to a decrease of the  $C_3A$  dissolution rate and might be connected to an adsorption of PCP or PNS observed from the early  $C_3A$  hydration. Such an adsorption does not happen with diphosphonate terminated polyoxyethylene superplasticizer. Moreover the presence of PCP superplasticizer causes a decrease in the size of the ettringite crystals formed.

**Keywords: hydration, superplasticizer, tricalcium aluminate.**

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## INTRODUCTION

Superplasticizers are polymers which added to concrete, increase the fluidity at early age without affecting the setting and hardening behaviour of concrete. For that purpose different polymers are used. Whereas polynaphthalene sulfonates (PNS) are often reported to act on cement particles dispersion by electrostatic repulsion, polycarboxylate with polyoxyethylene graft chains (PCP) or diphosphonate terminated monofunctional polyoxyethylene polymer are given to disperse cement particles because of the steric hindrance effect resulting from the extension of their graft chains away from the surface of cement particles [1, 2]

Moreover it is reported that the type of superplasticizer (SP) and the mixing method as preparations conditions or the surrounding environment of concrete could significantly affect the fluidity of the paste [3-14].

The main purpose of our study was to investigate the influence of the chemical structure of various SPs on the interaction with early cement hydration products in order to have a better understanding of the paste fluidity evolution.

Portland cement mainly consists of four mineral phases: the most abundant phases are tricalcium silicate ( $C_3S$ , alite) and bicalcium silicate ( $C_2S$ , belite) and the other phases are tricalcium aluminate,  $Ca_3Al_2O_6$  ( $C_3A$ ) and calcium aluminoferrite  $Ca_4Al_2Fe_2O_{10}$  ( $C_4AF$ , celite). Moreover gypsum  $CaSO_4 \cdot 2H_2O$  is added to clinker to

regulate the reactivity of the aluminate phases. When cement is mixed with water, it undergoes a dissolution reaction generating calcium ions, hydroxyde, silicate, aluminate and sulfate anions in the interstitial solution. Very soon, new hydrates of low solubility precipitate from the initially dissolved phases and these hydrates modify the fluidity of the paste and then, give rise to the hardening of concrete. Because of the very high reactivity of the aluminate phase in presence of water, the fluidity of the paste at the early age will be governed by early hydration reactions of aluminate phase. Consequently, in order to control the fluidity of the cement paste at early age in presence of superplasticizers it is useful to study the hydration reactions of aluminate phase in presence of the different superplasticizers.

Previous studies [15-16] showed  $C_3A$  hydration leads to same hydrates when  $C_3A$  hydrations are carried out in paste or in suspension. Furthermore hydrates formed in a lime saturated solution are mainly the same as those obtained in water. Therefore, due to the experimental methods used,  $C_3A$  hydration was studied in suspension. Because adsorption of polymers largely depends on the chemical composition of the solution,  $C_3A$  hydration was studied in a lime saturated solution in order to mimic the pore solution. Moreover early  $C_3A$  hydration is known to depend on the type of calcium sulphate [17]. In this paper we will focus on  $C_3A$  hydration carried out in presence of gypsum.

## MATERIALS AND EXPERIMENTAL METHODS

### Materials

Three types of superplasticizers were investigated for this study. Their chemical structures and molecular weights are described in Table 1. The pH of these additives was adjusted to 9.60 by adding 1M NaOH in order to neutralise all the acidic functions present in the additive. Since adsorption mechanisms are governed by the concentration of the additive in the solution, the superplasticizer dosages were calculated in order to have the same concentration in solution as in the pore solution of a typical concrete. The three superplasticizers were:

- A polycarboxylate-type superplasticizer with a polyoxyethylene graft chain (PCP) produced by Chryso. The main carboxylic and grafted polyoxyethylene chain lengths are reported in Table 1.
- A polynaphthalenesulfonate polymer (PNS) produced by Handy Chemical (Dysal) was also used.
- A diphosphonate terminated monofunctional polyoxyethylene polymer synthesized by Chryso and with a very well defined chemical structure reported in Table 1.
- $C_3A$  was synthesized by Lafarge by mixing and pulverizing in accordance with stoichiometric equation using calcium carbonate and alumina, and repeating the process to calcine them at 1400°C for 3 hours in an electric furnace twice.  $C_3A$  obtained was analysed by XRD.
- As calcium sulfate, pure gypsum (R.P. Normapur prolabo) was used. The molar ratio gypsum/ $C_3A$  was adjusted to 0.2 by mixing 7.3 mmol of pure gypsum (1.25g) with 37mmol of  $C_3A$  (10 grammes).

### Experimental methods

The  $C_3A$ -gypsum mixture was hydrated at 25°C in dilute lime saturated suspensions with a liquid/solid ratio equal to 25 under inert atmosphere in order to avoid

carbonation. The suspension was continuously subjected to mechanical stirring. The chemical evolution was followed by isothermal calorimetry (Tian-Calvet Setaram) and by electric conductivity measured with an XE 150 electrode (Tacussel).

To determine concentrations of species in solution ( $[Ca^{2+}]$ ,  $[Al^{3+}]$ ,  $[SO_4^{2-}]$ ) or the polymer adsorption during the  $C_3A$  hydration reactions, small portions of the suspensions were removed, filtered through 0.3  $\mu m$  millipore filters and acidified to avoid carbonation. A carbon analyser, model TOC 5050 (Shimadzu) was used to determine the evolution of the adsorption of the polymer during the  $C_3A$  hydration. Atomic Absorption Spectrometry (Perkin Elmer) was used for the calcium and aluminium concentrations and ionic chromatography (Dionex) equipped with a conductivity cell was used to determine sulfate concentration.

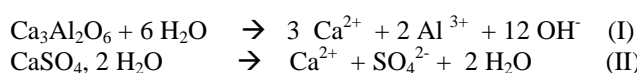
## RESULTS AND DISCUSSION

In order to analyse the effect of the different superplasticizers on the  $C_3A$  hydration in presence of gypsum, the hydration of  $C_3A$ -gypsum mixture was first carried out without superplasticizer in a lime saturated solution.

### C3A-gypsum hydration without superplasticizer

The reference experiment was carried out by adding 37mmol of  $C_3A$  and 7.25mmol of gypsum to 250mL of lime saturated solution. The evolution of the sulfate, calcium and aluminium ions concentrations and the heat flow deduced from the isothermal calorimetry are reported in Fig. 1. The Fig. 1 shows two parts. During the first part, sulfate ions are still present in the solution and they are consumed to precipitate a hydrate. That is the situation during the workability period. The second part begins when the sulfate concentration becomes equal to zero.

First part -- When  $C_3A$ -gypsum mixture is introduced in a lime saturated solution without additive, it undergoes dissolution reactions generating calcium ions, hydroxyde, aluminate and sulfate anions in the interstitial solution according to the dissolution reactions:

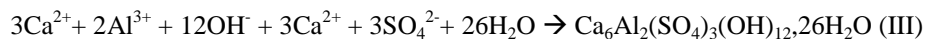


The suspension very quickly becomes supersaturated with respect to ettringite and AFm. Previous studies have clearly shown that although ettringite is the more stable hydrate, AFm phase precipitates at the very beginning of the  $C_3A$  hydration and the early AFm precipitation depends on different factors as for example the sulfate type used,  $C_3A$  granularity or superplasticizer presence [18, 19]. Consequently the exothermic peak obtained at the beginning of the first part expressed the very high reactivity of the system and this peak results from the exothermic  $C_3A$  dissolution and AFm and/or ettringite precipitation.

This peak is followed by a period of a low thermic activity. Under the experimental conditions, there is still solid gypsum at the beginning of the  $C_3A$  hydration giving rise to the sulfate concentration plateau, because of the limited solubility of gypsum in lime saturated solution which is equal to 12.5mmol/L.

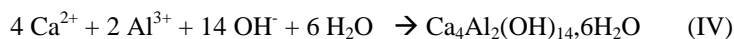
Since aluminium concentration remains constant and very low so that it is not detectable, we can deduce all the aluminium ions liberated by the dissolution are

consumed by ettringite precipitation. Namely, under these conditions, the supersaturation level is the highest for ettringite which is then the more stable phase. Ettringite precipitates according to the reaction :



Ettringite precipitation consumes calcium, aluminium and sulfate ions which causes further  $\text{C}_3\text{A}$  and gypsum dissolution. A stationary state is then established resulting from dissolution reactions and from ettringite precipitation reaction. When gypsum is totally dissolved, ettringite precipitation rate can be deduced from the decrease of sulfate ions concentration. As usually reported and observed in these systems, the average rate of ettringite precipitation from  $\text{C}_3\text{A}$  and gypsum, is decreasing according to time. For instance Fig.1 shows that 70 minutes (duration of the “sulfate plateau”) are needed to precipitate 1.4 mmol of ettringite from 4.2 mmol of gypsum and 1.4 mmol of  $\text{C}_3\text{A}$  (according to reactions I, II and III), while 140 minutes are needed to “convert” the last 3 mmol of sulfate into 1 mmol of ettringite. Moreover, because sulfate concentration decrease is linear, we assume ettringite precipitation is quite constant during this period. Such an evolution on the rate of ettringite precipitation from  $\text{C}_3\text{A}$  and gypsum has already been reported [18]. The average rate of ettringite precipitation clearly depends on the  $\text{C}_3\text{A}$  granularity but also on other parameters as sulfate concentration.

Second Part.--This part begins when sulfate concentration becomes equal to zero.  $\text{C}_3\text{A}$  hydration without sulfate leads to a metastable calcium hydroaluminate precipitation according to the reaction:



The exothermic peak appearing at the beginning of this period is attributed to  $\text{C}_3\text{A}$  dissolution which is going on faster and  $\text{C}_4\text{AH}_{13}$  precipitation. Due to  $\text{C}_3\text{A}$  dissolution (I) and  $\text{C}_4\text{AH}_{13}$  precipitation (IV), calcium ions concentration decreases and consequently conductivity too, whereas aluminium ions concentration increases. In the same time monosulfoaluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4, 12\text{H}_2\text{O}$ ) becomes more stable than ettringite and consequently precipitates by using sulfate ions liberated by ettringite dissolution. This last reaction is very slow and ettringite is still present two days later.

Finally, all these reactions give rise to a stationary state.

Consequently, the conductivity curve allows us to determine the duration of the first step which corresponds to the precipitation of 2.4 mmol of ettringite under our conditions from  $\text{C}_3\text{A}$  and gypsum. Moreover, the evolution of sulfate ions concentration allows us to determine the time needed to precipitate total ettringite and also the first 1.4 mmol.

### **Effect of the superplasticizers on the reactivity of the $\text{C}_3\text{A}$ -gypsum system in a lime saturated solution**

The evolution of the electric conductivity during the hydration of a  $\text{C}_3\text{A}$ -gypsum system in a lime saturated solution and in presence of 0.5g of superplasticizer that is to say 5% with respect to the  $\text{C}_3\text{A}$  weight is represented in

Fig.2. From these curves it appears that the diphosphonate doesn't modify the duration of ettringite precipitation whereas both PNS and PCP decrease the rate of ettringite formation. Next Figures (Fig.3,4,6) represent the evolution of the ionic concentrations during the  $C_3A$ -gypsum system hydration in presence of the different superplasticizers.

Diphosphonate.--The  $C_3A$ -gypsum mixture was introduced in a lime saturated solution containing 5% of diphosphonate with respect to the  $C_3A$  weight. The results are presented in Fig.3. The reference experiment was carried out with the same  $C_3A$  sample. As we can see In fig.2 the diphosphonate doesn't modify the duration needed to precipitate ettringite from gypsum and  $C_3A$ . The same experiment was also carried out with higher levels of gypsum (2 and 2.5g of gypsum) and again, the time needed to precipitate the ettringite is the same with or without the diphosphonate, as reported in Fig.3. The only noticeable difference is relative to the initial conductivity. The slight increase observed in presence of the diphosphonate can be attributed to the ability of the diphosphonate to form a complex with calcium ions and consequently increases the solubility of lime. [20]

PNS.--The average rate of ettringite precipitation is drastically decreased in the presence of PNS; the time needed is approximately multiplied by four in the experimental conditions (Fig.2). The decrease of the rate depends on the PNS dosage as shown in the Fig.4. Moreover Fig.4 shows the decrease of the precipitation rate when the sulfate concentration is at the plateau level and also when it decreases. Figure 5 suggests that the time needed to precipitate ettringite in the presence of PNS could be correlated with the initial adsorption level of PNS. The slowing down of the ettringite precipitation is maybe linked to a decrease of  $C_3A$  dissolution rate.

PCP.--Figure 2 shows a slowing down of ettringite precipitation as a result of the PCP presence. Under the experiment conditions the time needed to precipitate the ettringite is multiplied by 1.5 in presence of 5% of PCP. Moreover an increase of the PCP amount (5 to 6 % ) leads to higher duration (Fig.7). As the slope of the sulfate concentration decrease is linked to the rate of ettringite precipitation we conclude that PCP slows down the rate of ettringite precipitation.

Nevertheless it appears that the rate of ettringite precipitation is not affected when the sulfate concentration is high enough and at the "plateau" value (Fig.7). In the same time, the size of ettringite crystals precipitated in the presence of PCP during this period, is smaller than usually. Indeed in order to determine concentrations of species in solution during the  $C_3A$  hydration reactions, small portions of the suspensions were removed, and as usually filtered through 0.3  $\mu\text{m}$  millipore filters. However in the presence of PCP, aluminium, calcium and sulfate concentrations proved that ettringite crystals were present in the filtered solution (Fig.8). In this case a new filtration was done using 0.1 $\mu\text{m}$  filters in order to prevent ettringite from going through. SEM images of the solid collected on the 0.1 $\mu\text{m}$  filter one hour after the beginning of the  $C_3A$ -gypsum hydration in saturated lime solution in the presence of PCP are presented in Fig.9. PCP clearly decreases the size of the ettringite crystals formed.

Consequently, the presence of PCP induced a slowing down of the rate of ettringite precipitation and a decrease of the size of ettringite crystals. The PCP may act on ettringite precipitation by decreasing its growth rate. Previous studies already showed such a decrease of the growth rate or a modification of the ettringite morphology as a

result of a polymer adsorption [21-25]. However the average rate of ettringite precipitation is not affected when the sulfate concentration is high enough and at the “plateau” level. Namely when the sulfate concentration is high enough and at the plateau level, ettringite nucleation might take place and by this way the rate of ettringite precipitation would not be decreased during this period.

#### **Study of the adsorption:**

Preliminary adsorption isotherms were established on pure ettringite, monosulfoaluminate and  $C_3AH_6$  for each superplasticizer in saturated lime solution and with a liquid to solid ratio adjusted to 25. They are reported in Fig.10.

The specific surface area determined by B.E.T. using nitrogen are reported in Table 2. As expected, the adsorption level mainly depends on the specific area of the hydrate and consequently the adsorption level on monosulfoaluminate and ettringite is similar and larger than that on  $C_3AH_6$  phase. Therefore the adsorption should be larger again on platey hexagonal  $C_4AH_{13}$  crystals. Moreover PNS and PCP show larger ability to adsorb than the diphosphonate. By using these informations we are able to approximately determine the amount of each superplasticizer likely to be adsorbed on 2.4 mmol of ettringite that is to say on ettringite which will precipitate during  $C_3A$  hydration under our conditions. By this way about 9mg of diphosphonate and 30 mg of PNS or PCP should adsorb on ettringite as represented in the Fig.12.

The evolution of the superplasticizer adsorption during the  $C_3A$ -gypsum hydration is reported in Fig.11. An initial adsorption is only observed for both PCP and PNS. In the case of the PNS, a large part of the superplasticizer, about 150mg ( 30%), is adsorbed during the first minutes. The initial adsorption could happen on the anhydrous phases but also on the AFm formed at the very beginning of the  $C_3A$  hydration, because of its important specific surface area.

In a second time, a quite linear increase of adsorption is observed during the ettringite precipitation with all superplasticizers. Nevertheless, whereas about 100mg of PCP or PNS are adsorbed on ettringite, only 10mg of diphosphonate seems to be adsorbed on ettringite. These amounts are larger than the values previously calculated for the PCP and PNS (~30mg for PNS and PCP). These values are reported in Fig.12. These differences can result from the adsorption of other phases which could also be formed (AFm for example). Furthermore, we also can suspect a modification of ettringite morphology due to the adsorption of superplasticizer on ettringite giving rise to an increase of ettringite specific surface area. Namely, the previous observations made on the effect of PCP on the size of ettringite crystals lead us to conclude that the superplasticizer adsorption should be higher because of the increase of the specific area of the ettringite formed in this case.

At least, when there is no more sulfate ions in solution, hydroaluminate begins to precipitate, giving rise to a large adsorption of the superplasticizers. The adsorption level gets fastly maximum, all the superplasticizer able to be adsorbed are adsorbed.

### **CONCLUSIONS**

The interaction of superplasticizers with  $C_3A$  when hydration occurs in presence of gypsum was studied with three types of superplasticizers.

Diphosphonate does not modify the average rate of ettringite precipitation. No adsorption happens during the first minutes and the adsorption level of the polymer on ettringite is low.

The PNS slows down the ettringite precipitation. The decrease of the average rate of ettringite precipitation is higher with higher PNS dosages. Moreover, the time needed to precipitate ettringite varies as a function of the initial PNS adsorption level. PNS may act on C<sub>3</sub>A hydration by decreasing its dissolution rate, in consequence of its strong initial adsorption. By using PNS delayed addition, the strong initial adsorption on the aluminate phases can be avoided and consequently more PNS can act efficiently on silicate phases in slowing down its hydration and delaying setting.

PCP also slows down ettringite precipitation, but the decrease of ettringite precipitation is less strong than with PNS. Whereas PCP may decrease the C<sub>3</sub>A dissolution rate, it mainly acts on ettringite growth giving rise to smaller size of ettringite crystals.

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Table 1--Chemical structures of te different Superplasticizers

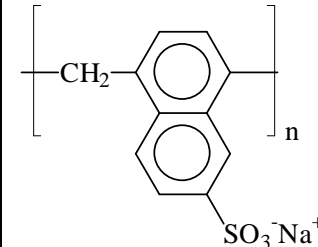
SP name	Chemical formula
Diphosphonate	$\text{CH}_3\text{-}[\text{O-CH}_2\text{-CH}_2]_n\text{-N}^+\text{-H}$ $\begin{array}{l} \diagup \text{CH}_2\text{-PO}_3^{2-}, 2\text{Na}^+ \\ \diagdown \text{CH}_2\text{-PO}_3^{2-}, 2\text{Na}^+ \end{array}$
PCP	$\left[ \left( \text{CH}_2\text{-}\overset{\text{CH}_3}{\underset{\text{COO}^-\text{Na}^+}{\text{C}}}\text{-} \right)_n \left( \text{CH}_2\text{-}\overset{\text{CH}_3}{\underset{\text{C=O}}{\text{C}}}\text{-}\text{O}\text{-}\left(\text{CH}_2\text{CH}_2\text{O}\right)_m \right)_p \right]_q$ <p style="text-align: center;">n ~ 0.4 p ~ 0.6 m ~ 15</p>
PNS	

Table 2--Specific area of different hydrates formed during C<sub>3</sub>A-Gypsum hydration

Compound	Hydrogarnet C <sub>3</sub> AH <sub>6</sub>	ettringite	Monosulfo aluminate
BET Specific surface area (m <sup>2</sup> /g)	3.5	1.1	1.2

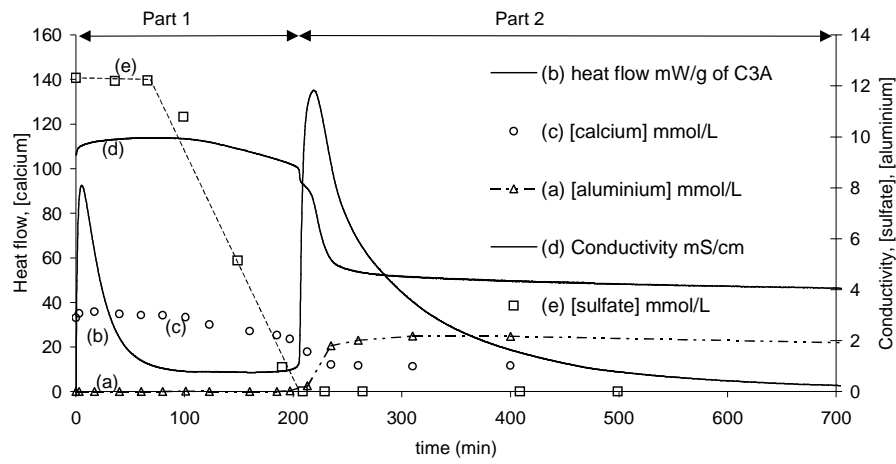


Fig.1--Evolution of heat flow, electric conductivity and ions concentration during C<sub>3</sub>A hydration (10g) in saturated lime solution in presence of 1.25g of gypsum. The liquid to solid ratio was adjusted to 25

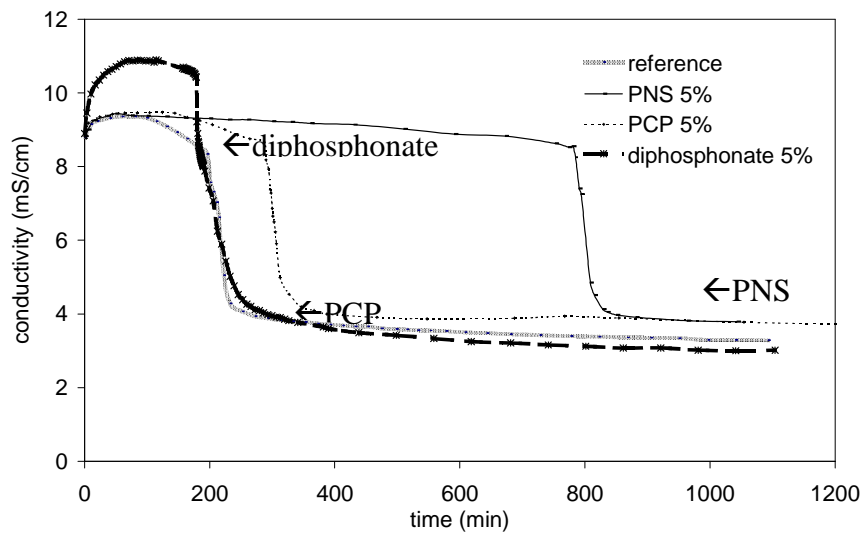


Fig 2--Evolution of the electric conductivity during C<sub>3</sub>A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and in presence of 0.5g of superplasticizer. The liquid to solid ratio was adjusted to 25.

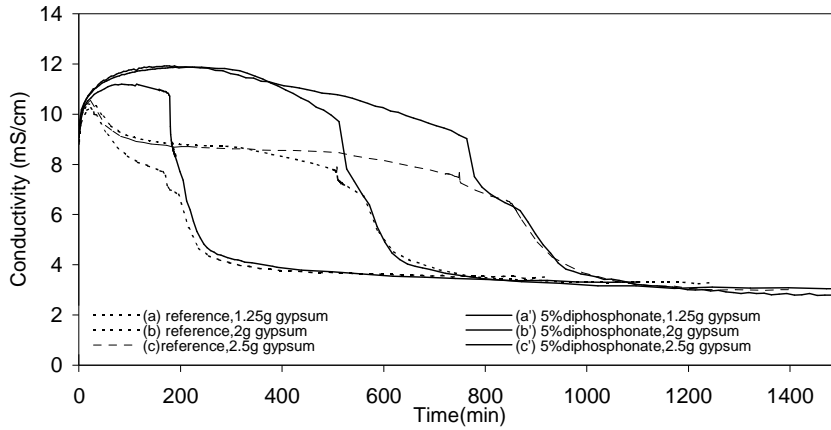
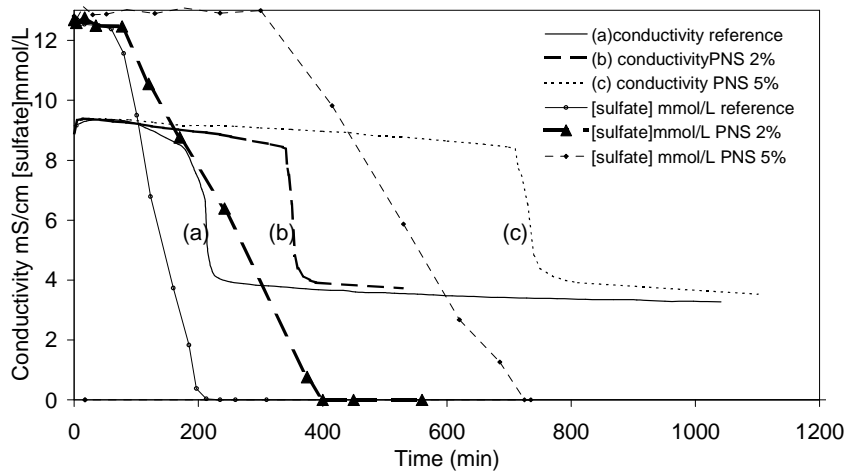


Figure 3

Evolution of the electric conductivity during C3A hydration (10g) in a lime saturated solution with or without 0.5g of diphosphonate and in presence of different quantities of gypsum. liquid/solid =



25.

figure 4

Evolution of the electric conductivity during C3A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and in presence of different amounts of PNS. The liquid to solid ratio was adjusted to 25.

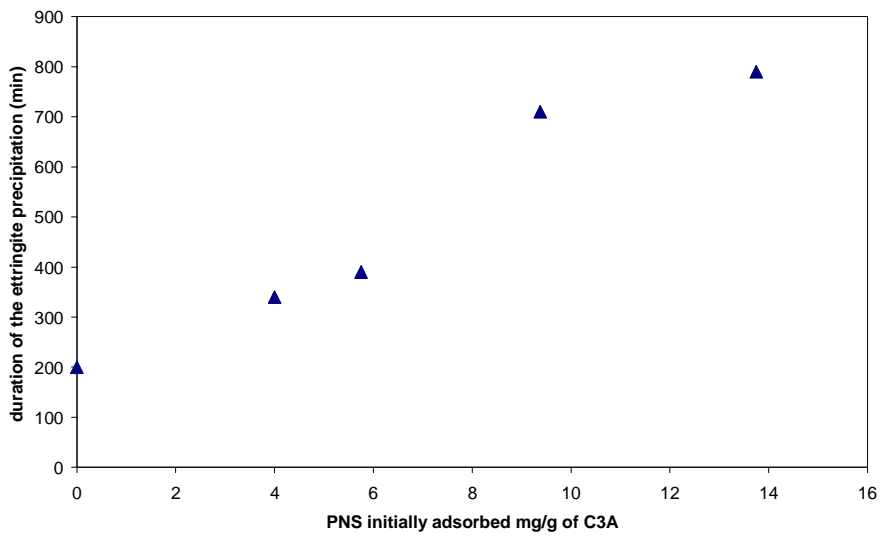


figure 5

Evolution of the duration of the ettringite precipitation versus the initial adsorption level of the PNS. 10g of C<sub>3</sub>A were hydrated in 250ml of a lime saturated solution and in presence of 1.25g of gypsum.

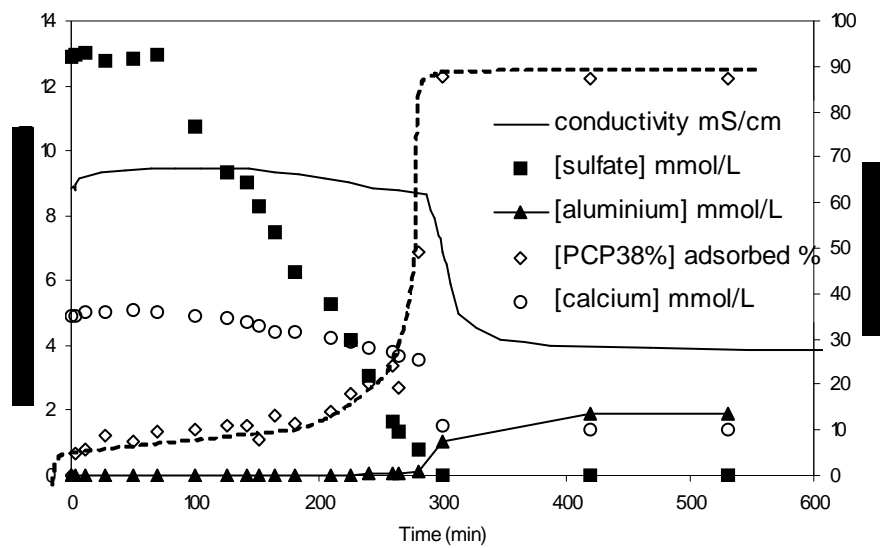


Figure 6

Evolution of the electric conductivity and ions concentration during C3A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and 0.5g of PCP. The liquid to solid ratio was adjusted to

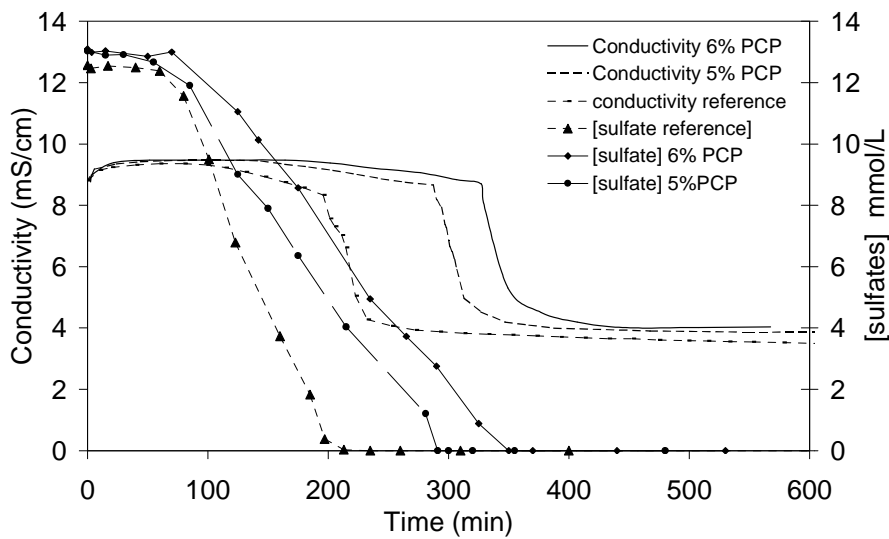


Figure 7 :

Evolution of the electric conductivity and the sulphate concentration during C3A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and in presence of different amounts of PCP

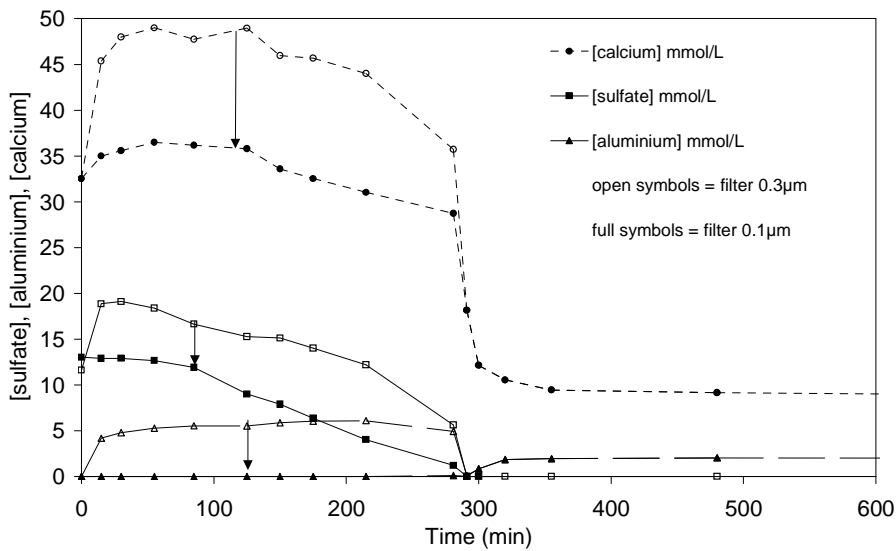
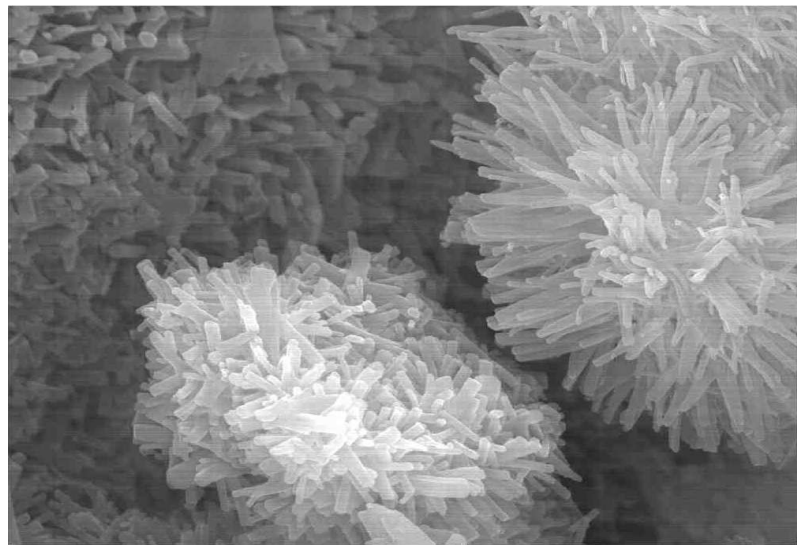


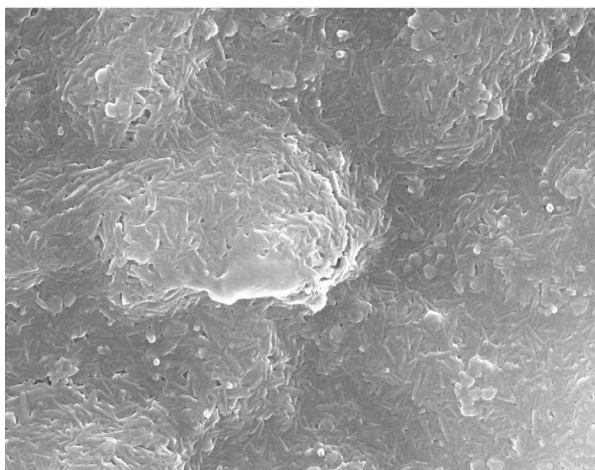
Figure 8

Evolution of the aluminium, calcium and sulfate concentrations of the solution filtered through 0.3 µm or 0.1 µm millipore filters during the C3A-Gypsum hydration in presence of 5%PCP.



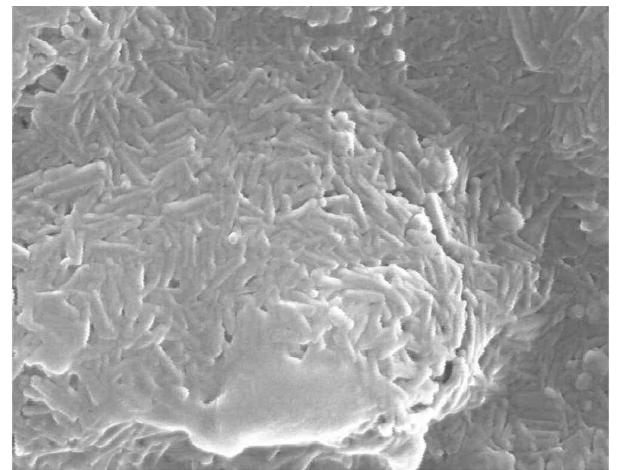
3  $\mu\text{m}$

x 20 000



3  $\mu\text{m}$

x 20 000



1  $\mu\text{m}$

x 40 000

Figure 9: Typical SEM images of ettringite obtained 1 hour after the beginning of the C3A-gypsum mixture hydration without superplasticizer (a) or in presence of 5% of PCP.

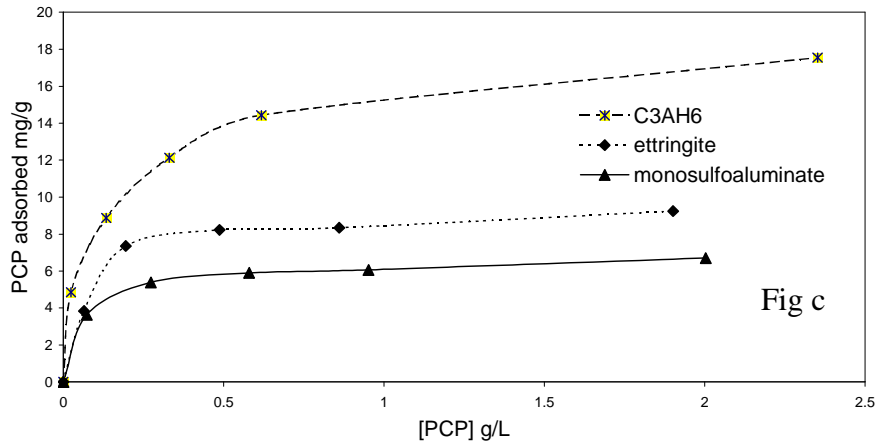
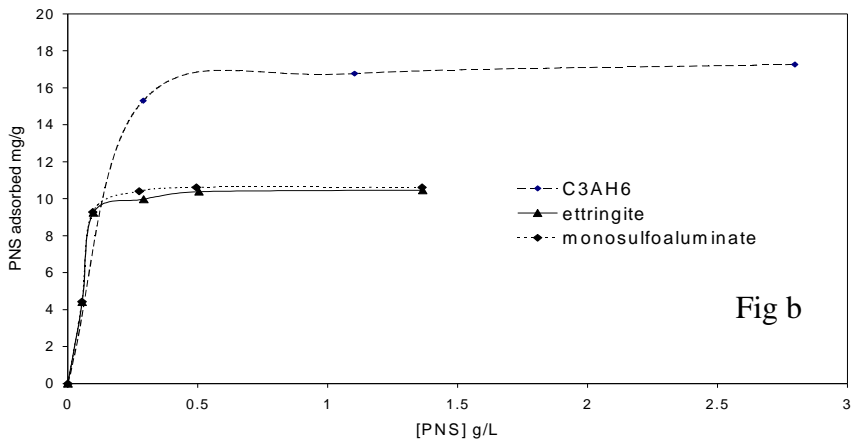
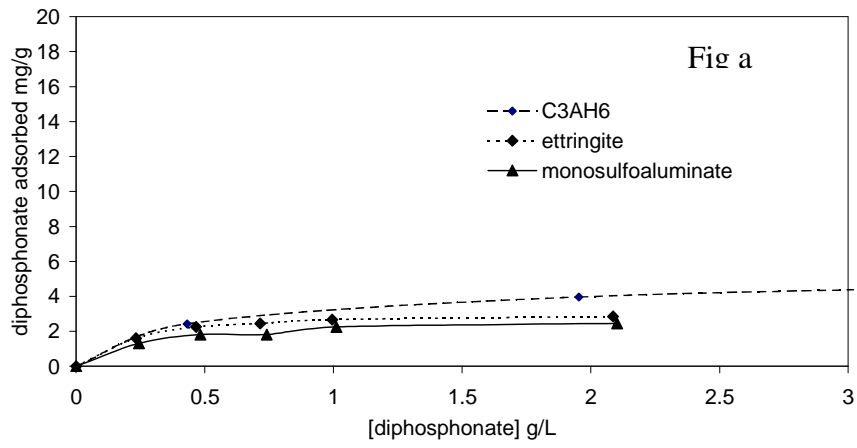


Fig.10 a, b,c.-- Adsorption of the diphosphonate (a), PNS (b) and PCP (c) on aluminate phases:  $C_3AH_6$ , ettringite and monosulfoaluminate in a lime saturated solution and with a liquid to solid ratio adjusted to 25.

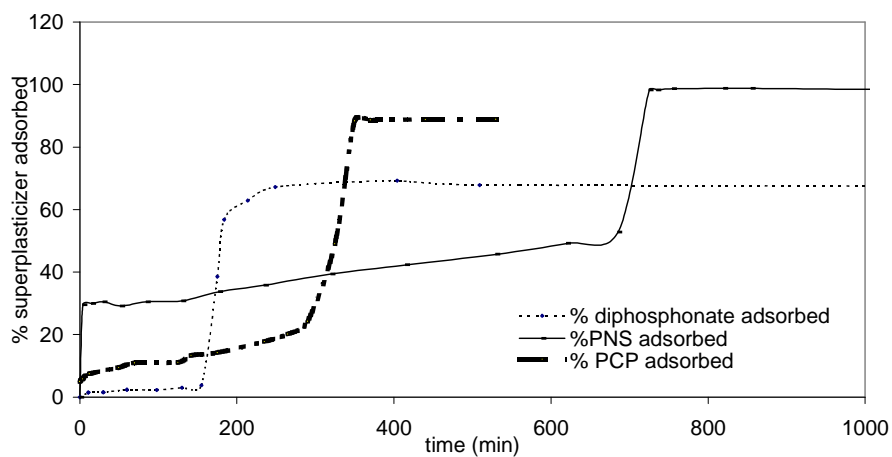


Fig.11--Evolution of the fraction of superplasticizer adsorbed during C<sub>3</sub>A-gypsum hydration in a lime saturated solution. 0.5g of superplasticizer was added to 10g of C<sub>3</sub>A and 1.25g of gypsum. The liquid to solid ratio was adjusted to 25.

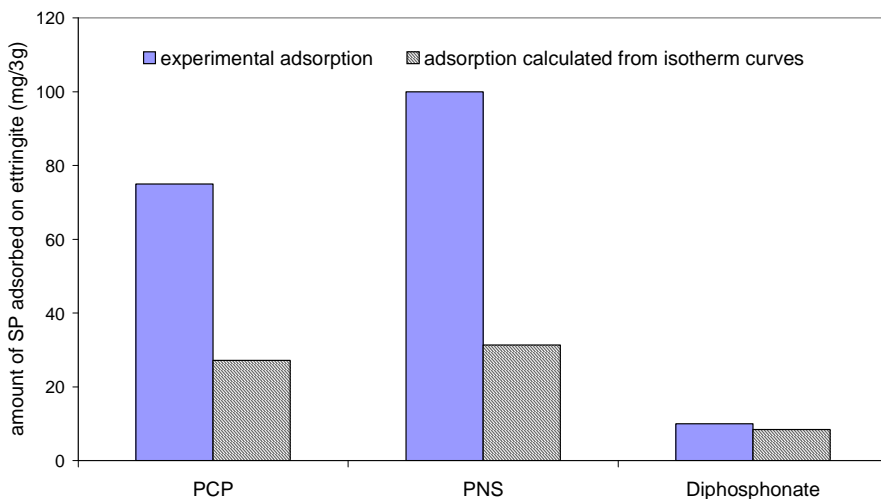


Fig.12--Comparison between the amount of superplasticizer adsorbed during the ettringite precipitation deduced from the adsorption measurements (figure 11) and the amount of superplasticizer adsorbed on ettringite calculated from isotherm adsorption curves represented on the Fig.10