



HAL
open science

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

Sylvie Pourchet, Cedric Comparet, A. Nonat, Philippe Maitrasse

► **To cite this version:**

Sylvie Pourchet, Cedric Comparet, A. Nonat, Philippe Maitrasse. Influence of three types of superplasticizers on tricalciumaluminate hydration in presence of gypsum.. 8th CANMET/ACI International Conference on Superplasticizers and other chemical admixtures in concrete., Oct 2006, Sorrento, Italy. pp.151-158. hal-00453194

HAL Id: hal-00453194

<https://hal.science/hal-00453194>

Submitted on 4 Feb 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Sylvie Pourchet*, Cédric Comparet, André Nonat, Philippe Maitrasse

*corresponding author

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: polynaphthalene 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.

Sylvie Pourchet: sylvie.pourchet@u-bourgogne.fr

Université de Bourgogne, LRRS, UMR 5613 bâtiment Mirande, 9 av A. Savary BP 47870, 21078 Dijon Cédex FRANCE

Fax : 33 3 80 39 38 19

Sylvie Pourchet is an assistant professor at the University of Bourgogne (France). Her current research is based on the reactivity of cement with special interest in studying the relation the mechanisms of hydration reactions in presence of organic admixtures.

Cédric Comparet: cedric.comparet@pole-technologique.lafarge.com

Lafarge, L.C.R., 95 Rue du Montmurier BP15, 38291 St Quentin Fallavier FRANCE

Fax: 33 4 74 82 80 11

Cédric Comparet worked for Chryso during his Ph.D on interactions between superplasticizers and hydraulic cement phases. He works for Lafarge (L.C.R.) as research engineer on organo-mineral interactions

Andre Nonat: andre.nonat@u-bourgogne.fr

Université de Bourgogne, LRRS, UMR 5613 bâtiment Mirande, 9 av A. Savary BP 47870, 21078 Dijon Cédex FRANCE

Fax : 33 3 80 39 38 19

André Nonat is a research director in C.N.R.S. at the University of Bourgogne (France). His research is based on the reactivity of cement with special interest in studying the mechanisms of hydration reactions, the thermodynamical and microstructure of hydrates and the mechanism of the setting.

Philippe Maitrasse: philippe.maitrasse@chryso-online.com

Chryso, 7 rue de l'Europe Z.I. 45300 Sermaises du Loiret, FRANCE

33 2 38 39 01 72

Philippe Maitrasse is a research manager of Chryso. He's mainly concerned by superplasticizers research, development and relationship with concrete properties.

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 μm 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.

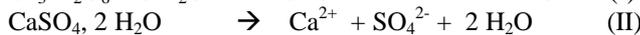
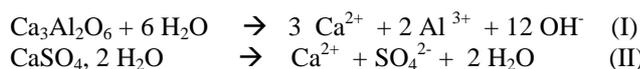
RESULTS AND DISCUSSION

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.

C_3A -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:

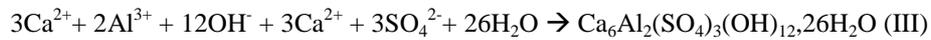


The suspension very quickly becomes supersaturated with respect to ettringite and AFm. Previous studies have clearly shown that although ettringite is the more stable hydrate, AFm phase precipitates at the very beginning of the C_3A hydration and the early AFm precipitation depends on different factors 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 C_3A 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 C_3A 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 C_3A (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 C_3A and gypsum has already been reported [18]. The average rate of ettringite precipitation clearly depends on the C_3A granularity but also on other parameters as sulfate concentration.

Second Part.--This part begins when sulfate concentration becomes equal to zero. C_3A 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 C_3A dissolution which is going on faster and C_4AH_{13} precipitation. Due to C_3A dissolution (I) and C_4AH_{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 C_3A 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 C_3A -gypsum system in a lime saturated solution

The evolution of the electric conductivity during the hydration of a C_3A -gypsum system in a lime saturated solution and in presence of 0.5g of superplasticizer that is to say 5% with respect to the C_3A 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 C₃A-gypsum system hydration in presence of the different superplasticizers.

Diphosphonate.--The C₃A-gypsum mixture was introduced in a lime saturated solution containing 5% of diphosphonate with respect to the C₃A weight. The results are presented in Fig.3. The reference experiment was carried out with the same C₃A sample. As we can see In fig.2 the diphosphonate doesn't modify the duration needed to precipitate ettringite from gypsum and C₃A. 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 C₃A 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 C₃A hydration reactions, small portions of the suspensions were removed, and as usually filtered through 0.3 μm 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 0.1μm filters in order to prevent ettringite from going through. SEM images of the solid collected on the 0.1μm filter one hour after the beginning of the C₃A-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 C₃A 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 C₃A dissolution rate, it mainly acts on ettringite growth giving rise to smaller size of ettringite crystals.

REFERENCES

1. Uchikawa, H. *Hydration of cement and structure formation and properties of cement paste in the presence of organic admixture*. in *Conference in tribute to Micheline Moranville-Regourd. Importance of Recent Microstructural Developments in Cement and Concrete*. 1994. Sherbrooke, Canada, E.C. Canada, Editor. p. 63-117.
2. Uchikawa, H., S. Hanehara, and D. Sawaki, *The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture*. *Cement and Concrete Research*, 1997. **27**(1): p. 37-50.
3. Tagnit-Hamou A., A.P.C., *Cement and superplasticizer compatibility*. *World Cement Research and Development*, 1993. **24**(8): p. 38-42.
4. Hanehara, S. and K. Yamada, *Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology*. *Cement and Concrete Research*, 1999. **29**: p. 1159-1165.
5. Aïtcin, P.-C., C. Jolicoeur, and J.G. MacGregor, *Superplasticizers: how they work and why they occasionally don't*. *Concrete International*. **16**(5): p. 45-52.
6. Yamaguchi, O., H. Nakajima, and M. Takahashi, *The effect of paste and mortar containing various type of water-reducing agents*. *JCA Proceedings of cement and concrete*, 1995. **49**: p. 216-221.
7. Kato, H., K. Yoshioka, and M. Ushiyama, *Influence of sulfate ion on steric hindrance in the performance of superplasticizers*. *JCA Proceedings of cement and concrete*, 1997. **51**(258-263).
8. Jiang, S., B.-G. Kim, and P.-C. Aïtcin, *Importance of adequate soluble alkali content to ensure cement/superplasticizer compatibility*. *Cement and Concrete Research*, 1999. **29**: p. 71-78.
9. Okamura, T., H. Harada, and M. Daimon, *Influence of calcium sulfate in belite-rich cement on the change in fluidity of mortar with time*. *Cement and Concrete Research*, 1998. **28**(9): p. 1297-1308.
10. Nawa, T., H. Ichiboji, and M. Kinoshita. *Influence of temperature on fluidity of cement paste containing superplasticizer with polyethylene oxide graft chains*. in *Superplasticizers and other chemical admixtures in*

- concrete. *Proceedings Sixth International Conference CANMET. SP-195*. 2000. Nice, France: ACI International, V.M. Malhotra, Editor. p. 195-210.
11. Jolicoeur, C. and M.-A. Simard, *Chemical admixture-cement interactions: phenomenology and physico-chemical concepts*. Cement & Concrete Composites, 1998. **20**: p. 87-101.
 12. Bonen, D. and S.-L. Sarkar, *The superplasticizer adsorption capacity of cement pastes, pore solution composition, and parameters affecting flow loss*. Cement and Concrete Research, 1995. **25**(7): p. 1423-1434.
 13. Coppola, L., Troli, R., Zaffaroni, P., Colleparidi, M. *Influence of the sulfate level in the clinker phase on performance of superplasticized concretes*. in *Proceedings of the fourth CANMET/A.C.I. Inter. Symp. on advances in concrete technology SP-179 (Recent Advances in Concrete Technology)*. 1998. Michigan: American Concrete Institute. p. 271-281.
 14. Jolicoeur, C.S., J.; Otis N.; Lebel A.; Simard, M.A.; Page, M. *The influence of temperature on the rheological properties of superplasticized cement pastes*. in *Fifth CANMET/ACI International Conference on Superplasticizers and other Chemical Admixture in Concrete*. 1997, V.M. Malhotra, Editor. p. 379 -405.
 15. Breval, E., *C₃A hydration*. Cement and Concrete Research, 1976, 6: p129-138
 16. Taylor, H.F.W., *Cement chemistry* (second edition) 1997. Thomas Telford edition
 17. Tang, F.J. Gartner, E.M., *Influence of sulphate source on Portland cement hydration*. Advances in Cement Research, 1988. **1** (2) p 67-74
 18. Minard, H., *Etude intégrée des processus d'hydratation, de coagulation, de rigidification et de prise pour un système C₃S-C₃A-sulfates-alcalins*. 2003, Thesis: Dijon France. Université de Bourgogne.
 19. Sakai, E., J.K. Kang, and M. Daimon, *Influence of superplasticizers on the very early hydration of Ca₃Al₂O₆ in the presence of gypsum, CaSO₄ 0.5H₂O and CaO*. Cement Science and Concrete Technology, 2002. **56**: p. 36-41.
 20. Comparet, C., *étude des interactions entre les phases modèles représentatives d'un ciment portland et des superplastifiants du béton*. Thesis Université de Bourgogne Dijon France, 2004.
 21. Simard, M.A. and P.-C. Aïtcin, *Calorimetry, rheology and compressive strength of superplasticized cement pastes*. Cement and Concrete Research, 1993. **23**(4): p. 939-950.
 22. Hekal, E.E. and E.A. Kishar, *Effect of sodium salt of naphthalene-formaldehyde polycondensate on ettringite formation*. Cement and Concrete Research, 1999. **29**: p. 1535-1540.
 23. Afridi, M.U.K., et al., *Effects of polymer modification on the formation of high sulfoaluminate or ettringite-type AFt crystals in polymer-modified mortars*. Cement and Concrete Research, 1994. **24**(8): p. 1492-1494.
 24. Sakai, E., et al., *Influence of sodium aromatic sulphonates in the hydration of tricalcium aluminate with or without gypsum*. Cement and Concrete Research, 1980. **10**(3): p. 311-319.
 25. Slanicka, S. *Influence of water soluble melamine formaldehyde resin in hydration of C₃S, C₃A+CaSO₄.2 H₂O*. in *International Congress on the Cement Chemistry*. 1980. Paris, France: Septima. p. 161-166.

Table 1--Chemical structures of te different Superplasticizers

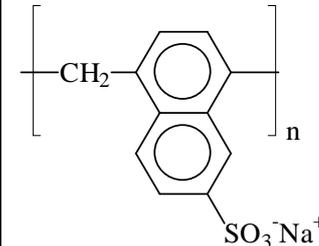
SP name	Chemical formula
Diphosphonate	$\text{CH}_3\text{-}[\text{O-CH}_2\text{-CH}_2]_n\text{-N}^+\text{-H}$ $\begin{array}{l} \diagup \text{CH}_2\text{-PO}_3^{2-}, 2\text{Na}^+ \\ \diagdown \text{CH}_2\text{-PO}_3^{2-}, 2\text{Na}^+ \end{array}$
PCP	$\left[\left(\text{CH}_2\text{-}\overset{\text{CH}_3}{\underset{\text{COO}^-\text{Na}^+}{\text{C}}}\text{-} \right)_n \left(\text{CH}_2\text{-}\overset{\text{CH}_3}{\underset{\text{C=O}}{\text{C}}}\text{-}\text{O-}\left(\text{CH}_2\text{CH}_2\text{O}\right)_m \right)_p \right]_q$ <p style="text-align: center;">n ~ 0.4 p ~ 0.6 m ~ 15</p>
PNS	 <p style="text-align: center;">SO_3^-Na^+</p>

Table 2--Specific area of different hydrates formed during C₃A-Gypsum hydration

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

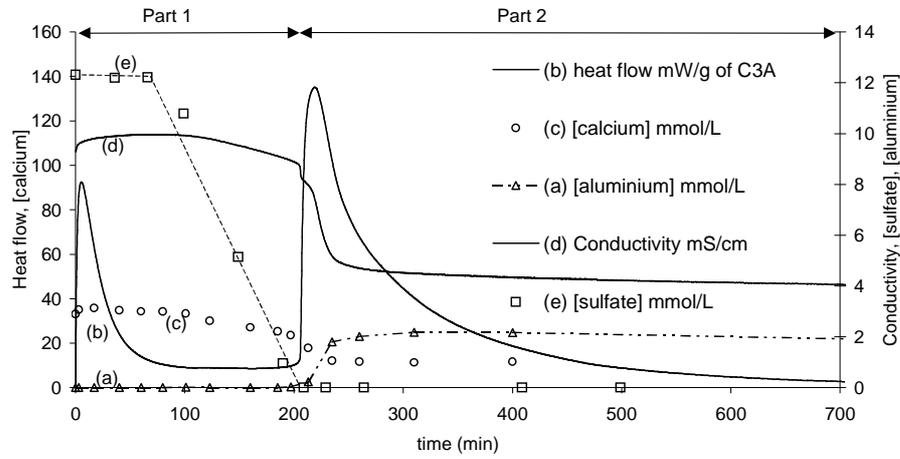


Fig.1--Evolution of heat flow, electric conductivity and ions concentration during C₃A hydration (10g) in saturated lime solution in presence of 1.25g of gypsum. The liquid to solid ratio was adjusted to 25

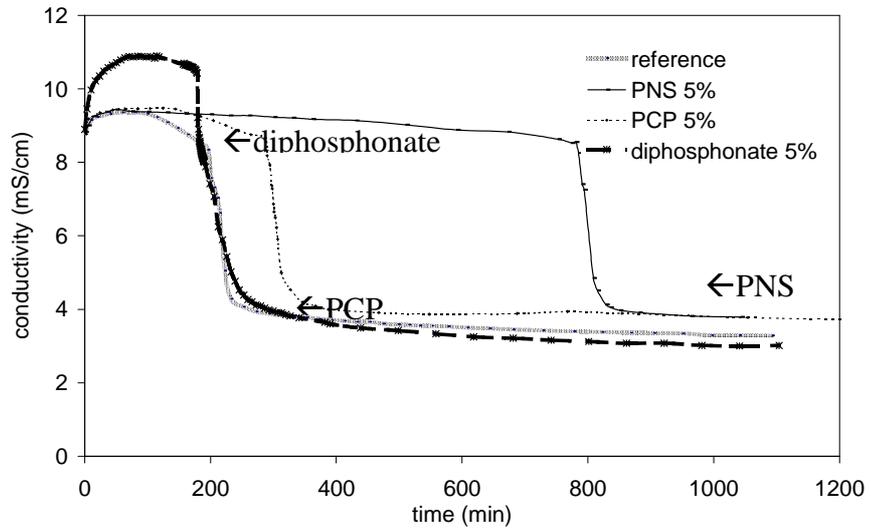


Fig 2--Evolution of the electric conductivity during C₃A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and in presence of 0.5g of superplasticizer. The liquid to solid ratio was adjusted to 25.

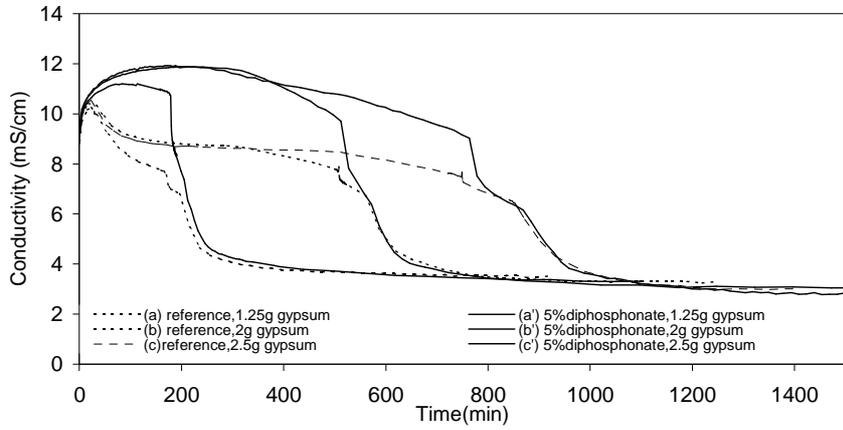
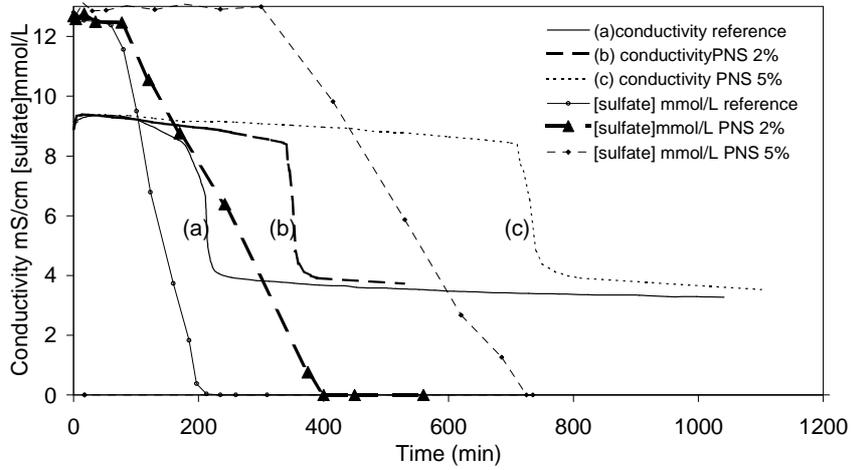


Figure 3

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.

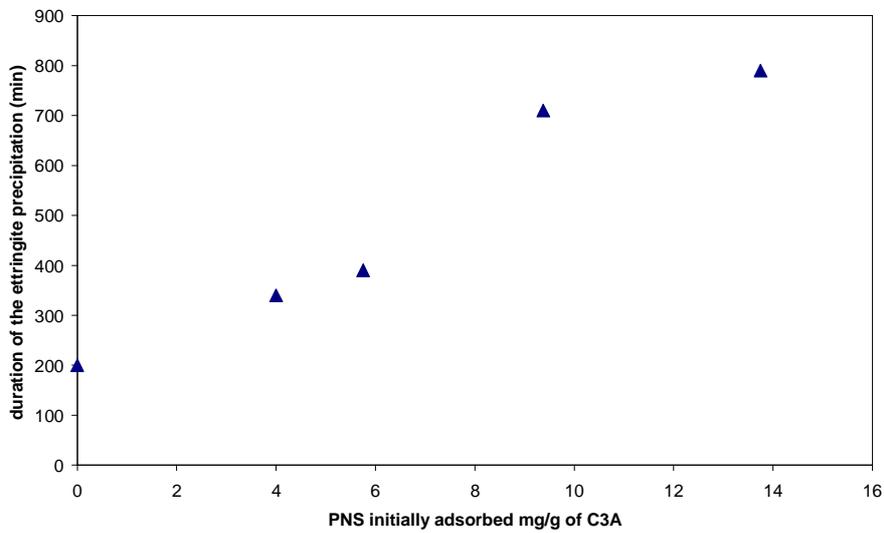


figure 5

Evolution of the duration of the ettringite precipitation versus the initial adsorption level of the PNS. 10g of C_3A were hydrated in 250ml of a lime saturated solution and in presence of 1.25g of gypsum.

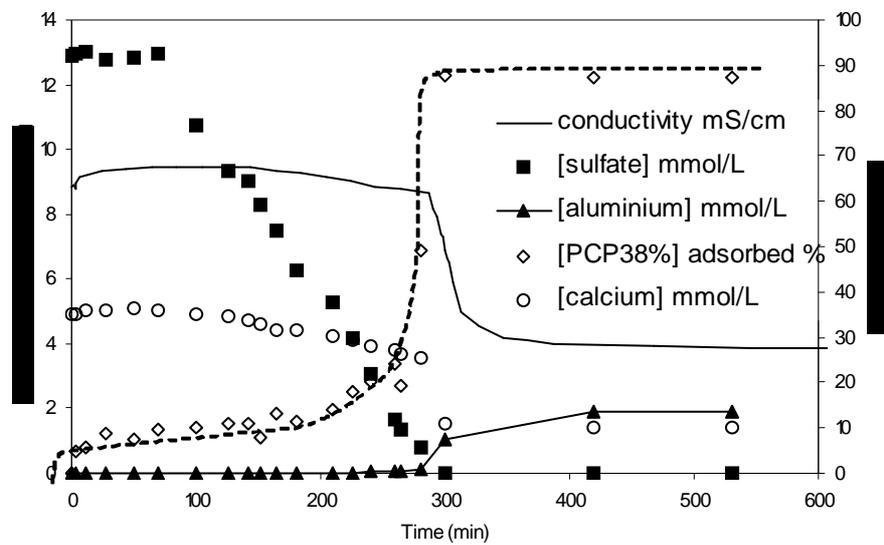


Figure 6

Evolution of the electric conductivity and ions concentration during C_3A 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

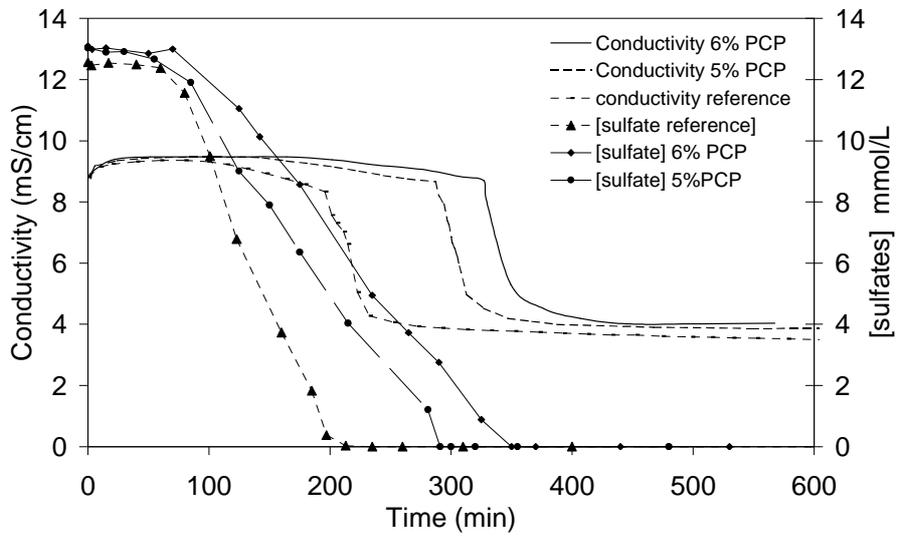


Figure 7 :

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

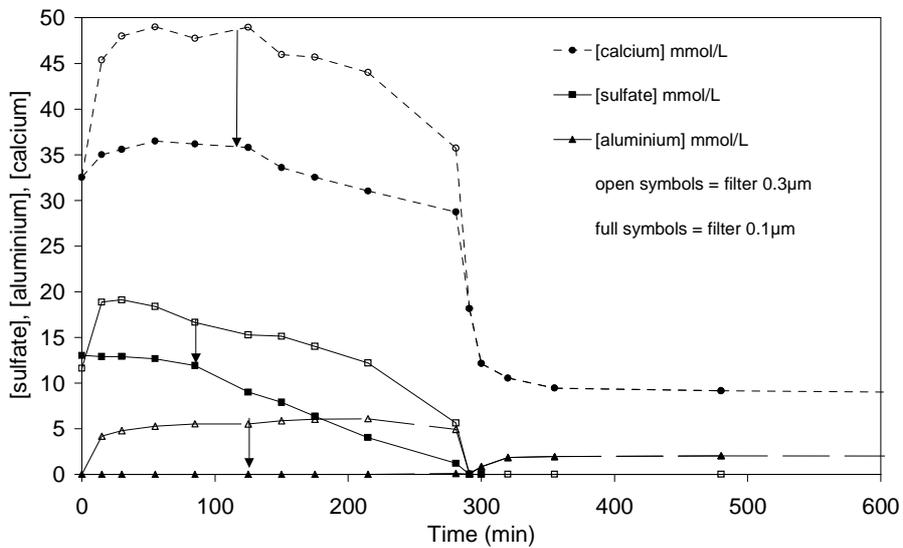
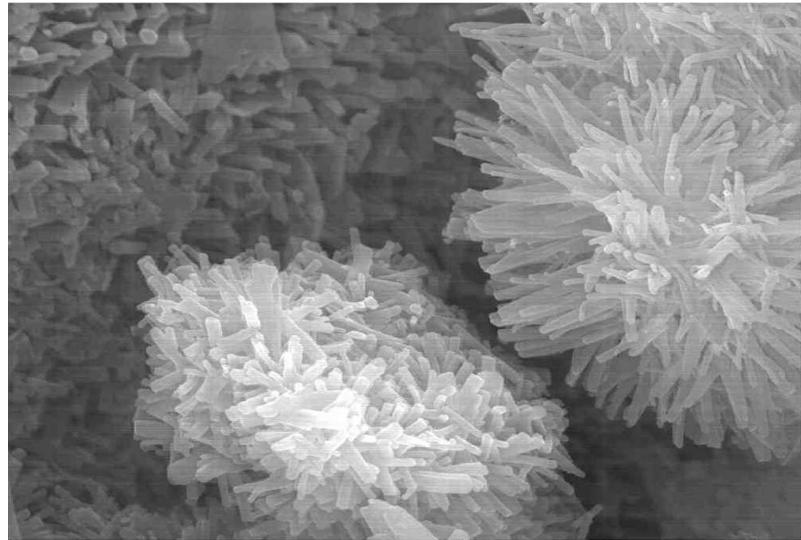


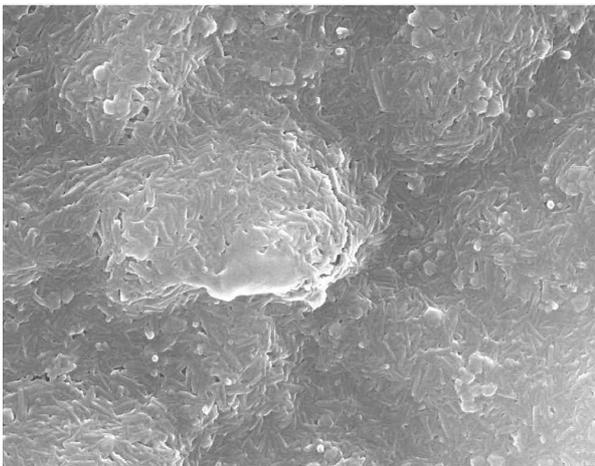
Figure 8

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.



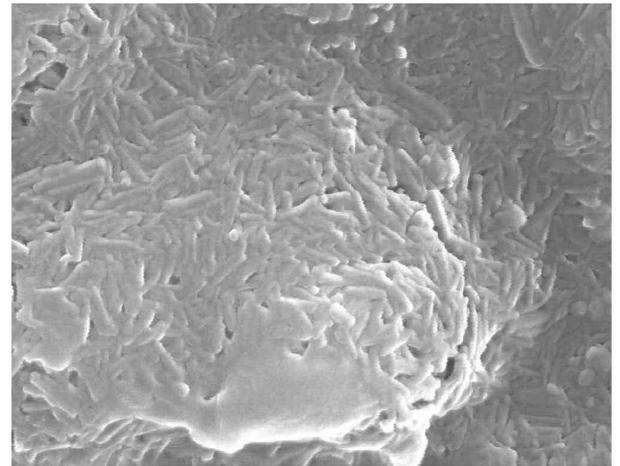
3 μm

x 20 000



3 μm

x 20 000



1 μm

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.

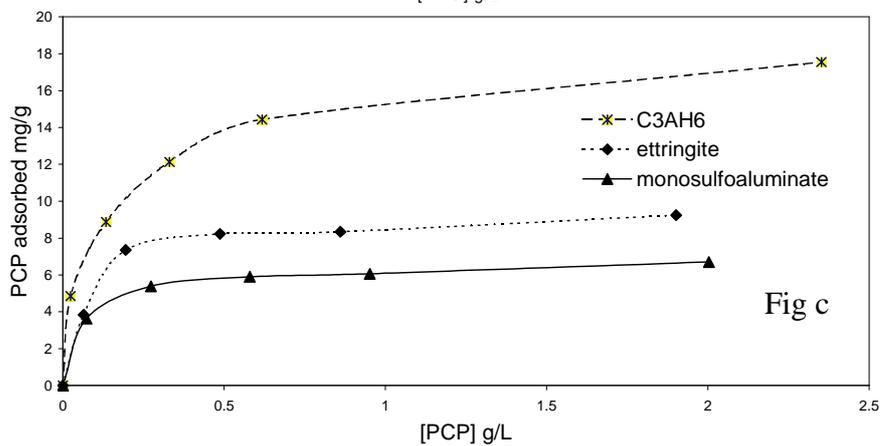
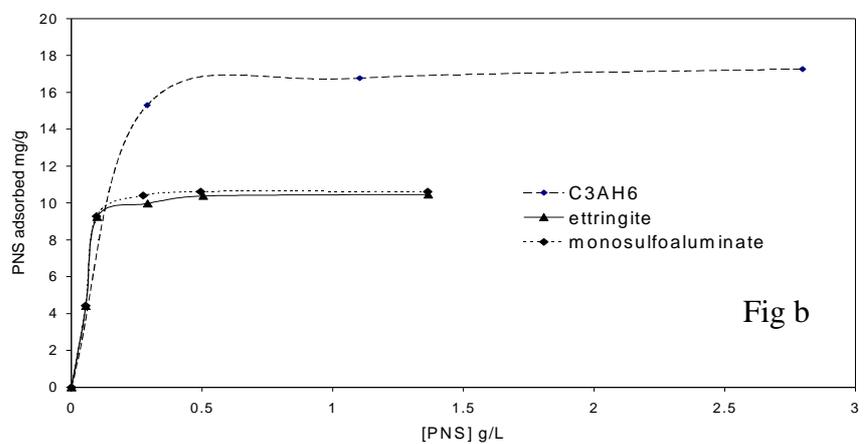
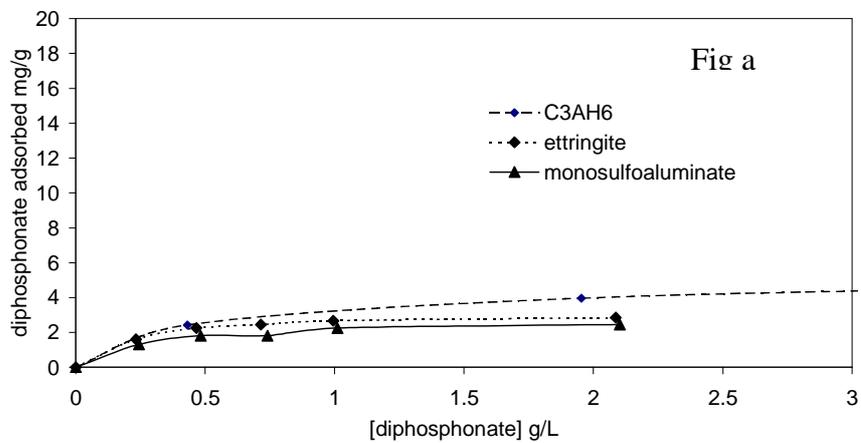


Fig.10 a, b,c.-- Adsorption of the diphosphonate (a), PNS (b) and PCP (c) on aluminate phases: C_3AH_6 , ettringite and monosulfoaluminate in a lime saturated solution and with a liquid to solid ratio adjusted to 25.

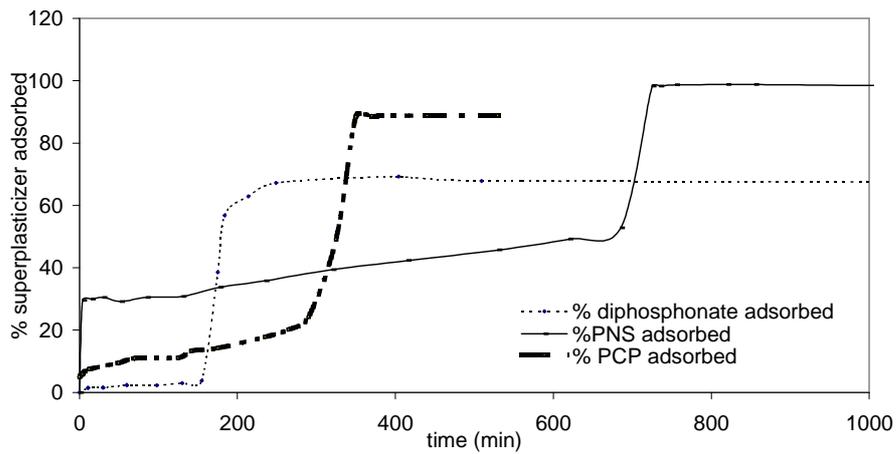


Fig.11--Evolution of the fraction of superplasticizer adsorbed during C_3A -gypsum hydration in a lime saturated solution. 0.5g of superplasticizer was added to 10g of C_3A and 1.25g of gypsum. The liquid to solid ratio was adjusted to 25.

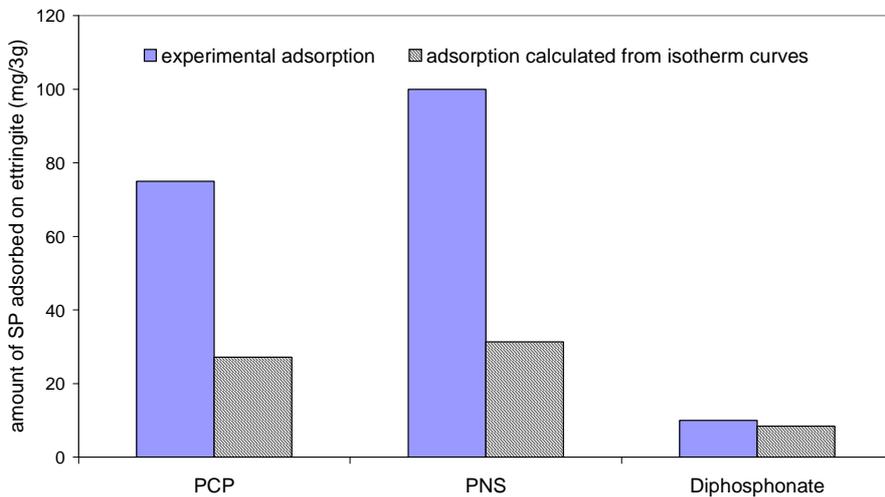


Fig.12--Comparison between the amount of superplasticizer adsorbed during the ettringite precipitation deduced from the adsorption measurements (figure 11) and the amount of superplasticizer adsorbed on ettringite calculated from isotherm adsorption curves represented on the Fig.10