



**HAL**  
open science

## Changes in Cement Paste and Mortar Fluidity after mixing induced by PCP: A parametric study

Laure Regnaud, André Nonat, Sylvie Pourchet, Bruno Pellerin, Philippe Maitrassé, Sebastien Georges, Jean-Philippe Perez

► **To cite this version:**

Laure Regnaud, André Nonat, Sylvie Pourchet, Bruno Pellerin, Philippe Maitrassé, et al.. Changes in Cement Paste and Mortar Fluidity after mixing induced by PCP: A parametric study. CANMET/ACI International Conference on Superplasticizers and other chemical admixtures in concrete, Oct 2006, Sorrento, Italy. pp.389-408. hal-00453070

**HAL Id: hal-00453070**

**<https://hal.science/hal-00453070>**

Submitted on 3 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.

# **Changes in Cement Paste and Mortar Fluidity after mixing induced by PCP: A parametric study**

by Laure REGNAUD\*, André NONAT, Sylvie POURCHET, Bruno PELLERIN,  
Philippe MAITRASSE, Jean Philippe PEREZ and Sébastien GEORGES

\* Corresponding author

## **Synopsis :**

The interaction mechanism between polycarboxylate-type superplasticizer (PCP) and cement hydration is not fully understood and incompatibilities between concrete and additive are sometimes observed. In some cases, the fluidity tends to increase (“over-fluidification”) few minutes after mixing. This is a problem because the over-fluidification leads to bleeding of the concrete which could be critical on job site. Our study consisted first in highlighting the phenomenon of “over-fluidification” by slump flow tests on mortar. Next, the time evolution of the rheological behaviour of cement pastes in the presence of PCP was analysed thanks to a rheometry protocol in order to quantify the phenomenon. Later on, a parametric study was undertaken using this methodology. The operating conditions such as temperature and mixing process were studied as well as the effect of PCP structural parameters and the chemical characteristics of cement. In order to understand the origin of the phenomenon, adsorption measurements of PCP on cement particles were performed in the same conditions as those in the rheological measurements. Indeed, the phenomenon of “over-fluidification” could be related to the rate of the initial adsorption and the adsorption kinetics, both of which depend on the parameters of the process, the PCP structure and the cement reactivity.

**Keywords: adsorption; fluidity; “over-fluidification”; PCP; slump flow; sulphate**

**\*Laure REGNAUD** - [laure.regnaud@u-bourgogne.fr](mailto:laure.regnaud@u-bourgogne.fr) : Laure Regnaud works for Chryso during his Ph.D in the University of Bourgogne. His subject deals with interactions between polycarboxylate type superplasticizers (PCP) and the early age of cement hydration in order to understand the changes of fluidity induced by PCP after mixing.

**André NONAT** - [andre.nonat@u-bourgogne.fr](mailto:andre.nonat@u-bourgogne.fr) : André Nonat is a Research Director in CNRS at the University of Bourgogne. His research is based on the reactivity of cement with a special interest in studying the mechanisms of hydration reactions, the thermodynamical and microstructure of hydrates and the mechanism of the setting.

**Sylvie POURCHET** - [Sylvie.pourchet@u-bourgogne.fr](mailto:Sylvie.pourchet@u-bourgogne.fr) : Sylvie Pourchet is an assistant professor at the University of Bourgogne. His research is based on the reactivity of cement with special interest in studying the mechanisms of hydration reactions in presence of organic additives.

LRRS (UMR5613)- Université de Bourgogne DIJON, France

**Bruno PELLERIN** - [Bruno.Pellerin@Chryso-online.com](mailto:Bruno.Pellerin@Chryso-online.com) : Bruno Pellerin is CHRYSO's Research and Development Director. His current research interests are mainly fluidity, strength development and durability for normal concrete and self-leveling concrete.

**Philippe MAITRASSE** - [Philippe.Maitrasse@Chryso-online.com](mailto:Philippe.Maitrasse@Chryso-online.com) : Philippe Maitrasse is a Research Manager of CHRYSO. He's mainly concerned by superplasticizers research, development and relationship with concrete properties.

CHRYSO - Sermaises du Loiret, France

**Sebastien GEORGES** - [sebastien.georges@pole-technologique.lafarge.com](mailto:sebastien.georges@pole-technologique.lafarge.com)

**Jean Philippe PEREZ** - [jean-philippe.perez@pole-technologique.lafarge.com](mailto:jean-philippe.perez@pole-technologique.lafarge.com) : Jean philippe Perez and Sébastien Georges work for Lafarge (LCR) as research engineer on organo-mineral interactions.

LAFARGE-LCR - St-Quentin Fallavier, France

## INTRODUCTION

Polycarboxylate –type superplasticizer has become popular because of its superior water-reducing ability and fluidity retention ability. The interaction mechanism between polycarboxylate polymers (PCP) and cement is not yet fully understood and the dispersibility of PCP on cement particules can be affected by various conditions (1). Indeed, it is assumed that PCP causes dispersion of cement particles by the steric repulsive forces caused by the PCP adsorbed to the surface of solid particles (2).

It has been reported that the cement characters affecting the fluidizing ability of PCP were the amount of alkaline sulphate, the kind and amount of calcium sulphate, and the amount and activity of interstitial phases (3).

Some studies pointed out that the surface area on which PCP was adsorbed and the adsorption amount were the most important factor based on the assumption that PCP works after the adsorption on cement hydrates (4, 5). As for the PCP adsorption, the sulphate ion concentration in solution phase was thought to affect it. The adsorption of PCP decreases in the case of high sulphate ion concentration in aqueous phase because the sulphate ion and PCP are adsorbed on cement particules competitively (6).

In actual placing of concrete, in which PCP was used, it is experienced in some cases that the fluidity of concrete tends to gain few minutes after its mixing. We called

“over-fluidification” this phenomenon. This increase in fluidity makes it difficult to pour the concrete and in the worst case segregation appears. This significant variability in the initial fluidity of the concrete and the stability of this fluidity over time can appear according to the nature of cement, the temperature of the ground or the duration of the mixing.

Our study was thus designed to better understand this phenomenon of “over-fluidification”. Our study first consisted in highlighting the phenomenon and quantifying it on mortar and cement paste thanks to a rheometry tool.

A parametric study of the phenomenon was then undertaken. We studied the parameters related to the manufacturing process, the parameters related to the PCP structure, and the chemical composition of cement.

In order to understand the origin of the phenomenon, the evolution of the rheological properties of cement paste is drawn in parallel with measurements of PCP adsorption on cement particles.

Our study should allow the understanding of the origin of the phenomenon of super-fluidification and the parameters which control the action of the PCP at the beginning of the cement hydration in order to overcome the incompatibility problems.

## EXPERIMENTAL

In the following sections, the characteristics of the material (polymers and cement) and the details of the method used in the experiments of the present study are described.

### I-Materials:

#### **Polycarboxylate superplasticizers:**

##### Industrial reference:

The industrial HRWRA selected as reference is a standard PCP (called PCP<sub>ref</sub>) used for ready mix applications, characterized by a charge amount (COO<sup>-</sup> concentration/g of polymer) of 0.94 m.eq/g. Some slump increases with time were reported when using this HRWRA.

##### Model PCP:

In order to analyse the influence of the PCP structure, we worked with several PCP model with different charge amount.

The PCP were synthesised by copolymerizing methacrylic acid (CA) and methoxy(polyoxyethylene) methacrylate of Mw = 1100 g/mol (CE) at different molar ratio.

We obtained a range of five PCPs with charge amount between 0.53 m.eq/g and 2.6 m.eq/g. The average molecular weights (Mw) of these polymers were about 45 000 g/mol with a polydispersity index about 2,5. (Table 1)

All the polymers were neutralized with NaOH to a pH value of 7.

#### **Cements and Clinker:**

##### Cement:

Lafarge Portland cement named Cement H was used to study the influence of process parameters and of PCP structure. It is characterized by a low tricalcium aluminate

phase and low alkaline sulphate quantity. (Composition in Table 2, Calcium sulphate : 2/3 gypsum, 1/3 hemi-hydrate)

#### Clinker:

In order to control the type of calcium sulphate added and the proportion of alkaline sulphate, we used an industrial clinker containing low alkaline sulphate, namely the clinker L. (Composition in Table 2)

In order to investigate the influence of the type of calcium sulphate introduced, we added a certain amount of calcium sulphate to the clinker in order to have 3.7% of total  $\text{SO}_3$ . Different kinds of calcium sulphate were used: gypsum only or a mixture of gypsum and hemi-hydrate at different ratios. The calcium sulphate and the clinker were mixed in an asymmetrical mixer during three days.

To investigate the influence of the proportion of alkali sulphate, we introduced  $\text{Na}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$  to the solution before mixing with the clinker powder.

### **II-Mixture proportion :**

Most of the experiments were carried out on cement paste but we also worked with a mortar in order to evaluate the results on the two different systems.

All manipulations were performed with a constant PCP dosage of 0.16% and at a temperature of 20°C except the case of the temperature influence. The water content varied with the nature of the mineral composition and admixture in order to retain the same initial viscosity of about 2 Pa.s at 50 s<sup>-1</sup> for the cement paste and a spread of slump flow of 280 mm for the mortar except in the case of the study of the process parameters where the W/C remains constant. This adjustment guarantees to have the same initial state for all the different conditions thus assuring reliable comparisons.

### **III-Experimental procedures:**

#### **Slump flow of mortar**

The fluidity of mortar was approximately evaluated by flow value. Cement and sand were mixed for 30s in a mortar mixer. We added water mixed with superplasticizer and we mixed everything for 1 min 30s at a constant rotational speed. The fluidity of the paste was evaluated by the spread measured when a truncated cone (Abrams (7) of Ø 100 mm and Ø 50 mm and 150 mm of height) filled with the mortar was pulled away vertically. In order to examine the change in the flow value over time, we measured the flow value every 0, 15, 30, 45, and 60 minutes after initial mixing with a mixing of 30s before each measurement. The slump flow on mortar highlighted the phenomenon of “over-fluidification”.

#### **Rheometry protocol on cement paste**

In order to work with a simple system and to more precisely examine the phenomenon of “over-fluidification”, we developed a rheometry protocol.

This protocol permits to measure the apparent viscosity of the cement paste at 0, 15 and 30 minutes after mixing in the same conditions as the slump flow test.

As a cement paste is close to a Bingham fluid (8), its apparent viscosity  $\eta_{app}$  depends on the shear rate applied  $\dot{\gamma}$  and on the yield stress  $\tau_y$ , considering the law:

$$\eta_{app} = \frac{\tau}{\dot{\gamma}} = \frac{\tau_y}{\dot{\gamma}} + \mu_p$$

with  $\mu_p$  : plastic viscosity  
 $\tau$  : stress

We used an ARES rheometer with a rheo reactor geometry illustrated in Fig. 1. In order to ensure good reproducibility (8), the cement paste was mixed in the rheo reactor. Thanks to a vibrating spatula, the cement was progressively mixed with the solution (water + PCP) previously introduced in the tank. When all the powder is introduced the cement paste was mixed for one minute at a shear rate of  $80 \text{ s}^{-1}$ . After that, the plastic viscosity is measured at a shear rate ranging from 50 to  $0.2 \text{ s}^{-1}$ . To do so, the tank turns at different rotation rates and the sensor measures the torque that the cement paste creates on the agitator. After a rest of 15 minutes, the paste was again mixed for 30 s at a rate of  $50 \text{ s}^{-1}$  and we again measure the viscosity. The same operation was repeated 30 minutes later after initial mixing.

In this way we measured the variation in apparent viscosity versus shear rate at different times after initial mixing.

In order to quantify the phenomenon of “over-fluidification”, we calculated a “% of over-fluidification” which corresponds to the percentage of decrease in viscosity between 0 min and 30 min after initial mixing, for each shear rate.

$$\% \text{ over - fluidification}_i = \left( \frac{\eta_{app_i}(t = 3 \text{ min}) - \eta_{app_i}(t = 30 \text{ min})}{\eta_{app_i}(t = 3 \text{ min})} \right) * 100 \quad [1]$$

The results show that this % of over-fluidification corresponds well to slump flow measurements for rates between  $10 \text{ s}^{-1}$  and  $50 \text{ s}^{-1}$ . Indeed, the scale of shear rates applied on a fluid during gravitating flow is  $1 \text{ s}^{-1}$  to  $10 \text{ s}^{-1}$  (9). During the slump flow on mortar, the cement paste undergoes both the shear of the flow and the shear of the aggregates so the scale of shear rates which correspond with rheometry protocol seems coherent.

Thus in order to make a comparison, we calculated the average of the % of over-fluidification for rate between 10 and  $50 \text{ s}^{-1}$ :

$$\% \text{ over - fluidification}_m = \frac{\sum_i \% \text{ over - fluidification}_i}{j} \quad [2]$$

with j being the number of measurements made with shear rate between 10 and  $50 \text{ s}^{-1}$  and i being the shear rate between 10 and  $50 \text{ s}^{-1}$

For each condition, the experiments were repeated 5 times and we calculated an average of the results.

This protocol therefore results in a quantification of the phenomenon and in comparison of this phenomenon in different operational conditions.

## **Measurement of adsorption**

The dispersion created by the superplasticizer is caused by the adsorption of PCP on cement particle (10). Therefore, along with the rheology study, we measured the adsorption of the PCP during the 30 minutes after initial mixing. We took three measurements of the adsorption at 0 min, 15 min and 30 min after the initial mixing of 1 min at a constant rate with a mixing of 30s before the measurements at 15 and 30 minutes. We thus retained the same operational conditions of mixing as in the rheology measurement.

For each measurement, we worked with a cement paste at  $W/C = 0.5$  mixed in a small mortar mixer at a temperature of  $20^{\circ}\text{C}$ . After mixing, we took a sample of the paste. For each sample, supernatant liquid was separated centrifugally at 3000 rpm from the paste. Then the total organic carbon content of this liquid was measured using Shimadzu TOC-5000 A, and the concentration of the superplasticizer remaining in the supernatant liquid was obtained from a calibration curve prepared in advance. This yielded the amount of superplasticizer adsorbed on the cement as the difference between the amount of superplasticizer added and that remaining into the liquid.

For each condition, the measurements were repeated 3 times and we calculated an average of the results.

So we obtained the evolution of the PCP adsorption during the thirty minutes after initial mixing of cement paste. In order to interpret results, two parameters are calculated, the % of PCP initial adsorption and the relative increase of the adsorption between  $t = 0$  min and  $t = 30$  min.

## **RESULT AND DISCUSSION**

### **I-The phenomenon of over-fluidification :**

Figure 2 shows the results of the slump flow test with the use of  $\text{PCP}_{\text{ref}}$  which leads to a “over-fluidification”. When  $\text{PCP}_{\text{ref}}$  is used we can observe an increase of the spread of the slump flow during the 30 minutes after initial mixing which is representative of the super-fluidification. With the rheometry protocol on cement paste, we are able to follow this increase of fluidity over the time and quantify it precisely.

Figure 3 shows the measurement of viscosity of cement paste according to shear rates over time using  $\text{PCP}_{\text{ref}}$  when a phenomenon of “over-fluidification” is noted. For each shear rate, we note that viscosity decreases between 0 and 30 min. The % of super-fluidification calculated is therefore positive contrary to cement paste without PCP which gives a constant viscosity over time and therefore no over-fluidification. (Fig. 4)

### **II-Parametric study**

#### **Rheology results:**

##### Process parameters :

The influences of temperature and mixing were studied. We can note in Fig. 5 that the higher the temperature, the lower the % of super-fluidification. This result is in

accordance with the observation that during winter more problems of super-fluidification arise with use of PCP(11).

To measure the influence of mixing, two parameters were studied, the rate of the mixing and the duration of the mixing. We can see in Fig. 6 and 7 that the longer the mixing duration and the stronger the mixing rate, the lower the over-fluidification. Since duration and shear rate of mixing are proportional to the mixing energy, we can say that the higher the mixing energy expended on the cement paste, the lower the over- fluidification.

#### Structural parameters of PCP:

We will now present results concerning the influence of the charge amount of the PCP. Figure 8 documents the influence of the charge amount on the % of over-fluidification. We see that the lower the charge amount up to 1.06 m.eq/g, the more marked the over-fluidification. We can also observe that the lower the charge amount, the higher the E/C, in accordance with the fact that the higher the PCP charge amount, the more it adsorbs it and the more it generates a good dispersion (12). As regards, the charge amount of 0.53 m.eq/g, we can note that with this PCP we do not observe any over-fluidification. Besides, we can observe that with this PCP, the quantity of water needed is very high because this PCP seems to have any dispersion effect.

#### Chemical composition of cement:

In Fig. 9, we can observe the influence of the type of calcium added to the clinker on the % of over-fluidification. First, we remark that in the absence of calcium sulphate, there is no fast setting of the clinker. This result is very surprising and can be explain by the fact that the clinker contains an important amount of sulphate.

Then, we observe that the addition of 100% of gypsum generates a loss of fluidity over time (% over-fluidification <0). Furthermore, we note that super-fluidification is created and accentuated when a certain amount of hemi- hydrate is added. (In this case, more than 40% of the total amount of the calcium sulphate added). This finding indicates that the presence of hemi-hydrate in certain quantities creates the phenomenon of super-fluidification.

In Fig. 10, we can observe that with a constant dosage in PCP, the higher the quantity of  $\text{Na}_2\text{SO}_4$  in solution, the lower the over-fluidification. We can also observe that the water needed to obtain the same initial fluidity increases with the  $\text{Na}_2\text{SO}_4$  concentration. This is in accordance with the fact that there is a competition in adsorption between PCP and sulphates ions (6). We observe the same effect with the addition of  $\text{K}_2\text{SO}_4$ .

#### **Adsorption results:**

##### Process parameters:

Figure 11 shows that the initial adsorption of the PCP varies with the temperature: The higher the temperature, the higher the initial adsorption. We also observe that adsorption increases with time and that this increase depends on temperature.

As regards mixing, the observation is similar (Fig. 12): The longer the mixing duration, the higher the initial adsorption of PCP. We also observe that the evolution of PCP adsorption over time depends on the mixing duration.



#### Structural parameters:

In Fig. 13, we can observe the adsorption results for the PCP model with different charge amount. We observe that the higher the charge amount, the higher the initial adsorption. This finding is in accordance with the fact that the higher the charge amount, the more carboxylic groups contained in the PCP and the higher the adsorption on the cement particles (13). Moreover, for each charge amount, adsorption with time increases and seems dependent on the PCP charge content.

#### Chemical composition of cement:

In Fig. 14, when the clinker contains 50%<sup>m</sup> of hemi hydrate with respect to quantity of gypsum, the initial adsorption of the PCP is low compared to results obtained with the clinker containing gypsum only. We can also observe that the adsorption increase depends on the type of calcium sulphate added. This result can be explain with the fact that the kind of calcium sulphate added affects the initial value of sulphate concentration in interstitial phase. When cement contains hemihydrate mainly, initial sulphate concentration is higher (14) so PCP initial adsorption is lower.

As regards the influence of alkaline sulphate on the PCP adsorption, we observed that increasing amount of alkaline sulphate leads to a strong decrease of the initial PCP adsorption. So, there is no significant adsorption when alkaline sulphate is added during the thirty minutes after mixing.

### **III- Parallel between adsorption and the phenomenon of over-fluidification :**

In order to draw a parallel, we reported the % of initial adsorption and the % of the relative increase in adsorption during the 30 minutes after the initial mixing as a function of the % of over-fluidification obtained with the rheology study for each parameter which influence super-fluidification. Results are reported in Fig. 15 for the temperature, Fig. 16 for the duration of mixing, and Fig. 17 for the charge amount of PCP and 18 for the kind of calcium sulphate added.

First, we observe a link between the initial adsorption, the % of the relative increase in adsorption and the % of over-fluidification. Indeed, for each parameter, if the % of over-fluidification increases, the % of initial adsorption decreases and the % of relative increase in adsorption increases. There is a single exception at a point which corresponds to the PCP which has a charge amount of 2.6 m.eq/g (Fig. 17). With this PCP, the phenomenon of over-fluidification is very slight, its initial adsorption is high, but its increase in adsorption is also high. We think that the evolution of adsorption for this PCP has no effect on the fluidity of the paste because its initial adsorption is sufficient to assure the maximal dispersion.

We can therefore conclude that there is a link between the phenomenon of over-fluidification, and the evolution of adsorption of the PCP. The lower the initial adsorption and the higher its relative increase with time, the more marked the phenomenon of over-fluidification.

If we compare the ratio  $A = \frac{\Delta\% \text{ of over - fluidification}}{\Delta\% \text{ of initial adsorption}}$  and

the ratio  $B = \frac{\Delta\% \text{ of over - fluidification}}{\Delta\% \text{ of relative increase of adsorption}}$ , we observe that  $A >$

$B$  for each parameter. Then, the initial adsorption seems to be the parameter the most critical for the phenomenon of over-fluidification.

With regards to the alkaline sulphate, we have observed that the decrease in the phenomenon of over-fluidification related to the alkaline sulphate concentration is linked to a strong decrease in the initial adsorption of the PCP. This is caused by the competition of adsorption between sulphate and PCP (5). So, assuming a constant dosage of PCP, the increase in the amount of alkaline sulphate creates a major decrease in the adsorption of PCP. In these conditions, the PCP becomes inoperative and loses all dispersion effect. Consequently, the phenomenon of over-fluidification disappears because this phenomenon seems to be the consequence of the PCP adsorption.

## CONCLUSION

This study first highlights the phenomenon of over-fluidification by slump flow tests on mortar. The rheometry protocol used here precisely quantifies this phenomenon on cement paste. This protocol provides information in agreement with slump flow tests on mortar.

Thanks to this rheometry protocol, we conducted a parametric study of the phenomenon of over-fluidification. We have observed that the temperature, the mixing, the charge amount of the PCP and the kind of calcium sulphate added have a significant effects on the phenomenon of over-fluidification. A study of PCP adsorption in the same conditions showed that when the phenomenon takes place, the adsorption of the PCP increases with time. We observed a link between the phenomenon of over-fluidification, the initial adsorption and the evolution of the PCP adsorption over time: the lower the initial adsorption of the PCP and the higher the relative increase of this adsorption over time, the more marked the phenomenon of over-fluidification.

We now need to study the causes of this low initial adsorption and this evolution of adsorption over time. As regards the nature of the parameters which have an effect on the phenomenon, we think that the PCP adsorption is related to the sulphate concentration of interstitial phase and the reactivity of cement in the first instants of hydration.

## REFERENCES

1. 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.
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. Matsuhisa, M., et al., *Effects of cement character on the fluidity of cement paste added with beta-naphthalene sulfonate type or polycarboxylate type superplasticizers*. Proceedings of the Japan Concrete Institute, 1998. **20**(2): p. 67-72.
4. Negishi K., N.H., Sugaya H., Goto T., *Fluidity of paste added with polycarboxylate-type superplasticizers*. Cement science and Concrete Technology, 1998. **52**: p. 138-139.

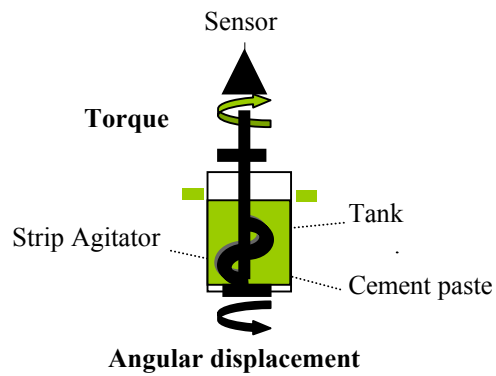
5. Yamada K, H.S., Honma K. *The effects of naphthalene sulfonate type and polycarboxylate type superplasticizer on the fluidity of belite-rich cement concrete.* in *Proceeding of Int. Workshop on Self-Compacting Concrete.* 1999.
6. Yamada, K., s. Ogawa, and S. Hanehara, *Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate concentration in aqueous phase.* Cement and Concrete Research, 2001. **31**: p. 375-383.
7. Saak, A.W., H.M. Jennings, and S.P. Shah, *A generalized approach for the determination of yield stress by slump and slump flow.* Cement and Concrete Research, 2004. **34**(3): p. 363-371.
8. William D.A., S.A.W., Jennings H.M., *The influence of mixing on the rheology of fresh cement paste.* Cement and Concrete Research, 1999. **29**: p. 1491-1496.
9. Barnes H.A., H.J.F., and All, *An introduction to Rheology.* 1989, Elsevier: Amsterdam. p. 13.
10. Uchikawa H, H.S., Sawaki D, *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**: p. 37-50.
11. Yamada K, Y.T., Hanehara S. *Influence of temperature on the dispersibility of polycarboxylate type superplasticizer for highly fluid concrete.* in *Proceedings of Int. Conf. of Self-compacting concrete.* 1999. Stockholm: RILEM.
12. Comparet, C., *Etude des interactions entre les phases modèles représentatives d'un Ciment Portland et des superplastifiants du béton.* 2004, université de Bourgogne.
13. Yamada, K., et al., *Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer.* Cement and Concrete Research, 2000. **30**: p. 197-207.
14. Nakajima Y., Y.K., *The effect of the kind of calcium sulphate in cements on the dispersing ability of poly-naphthalene sulphonate condensate superplasticizer.* Cement and Concrete Research, 2004. **34**: p. 839-844.

PCP	Charge amount (m.eq/g)	Mw (g/mol)	Ip
1	2.6	/	/
2	1.43	45 777	2.59
3	1.23	47 462	2.6
4	1.06	51 471	2.65
5	0.53	/	/

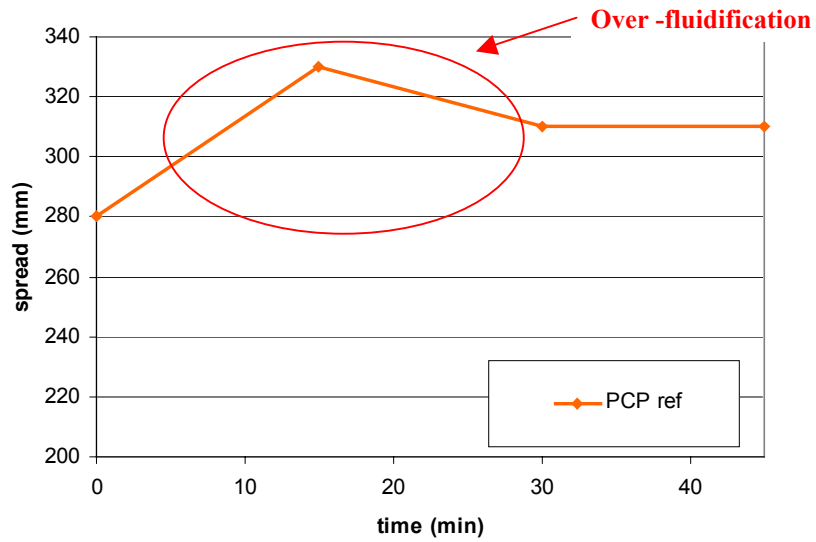
*Table 1: Structural parameters of PCP models*

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>
Cement H	20.47	4.77	1.75	65.78	1.04	0.144	0.263	3.7
Clinker L	20.72	5.29	1.75	68.01	1.15	0.2	0.07	1.55

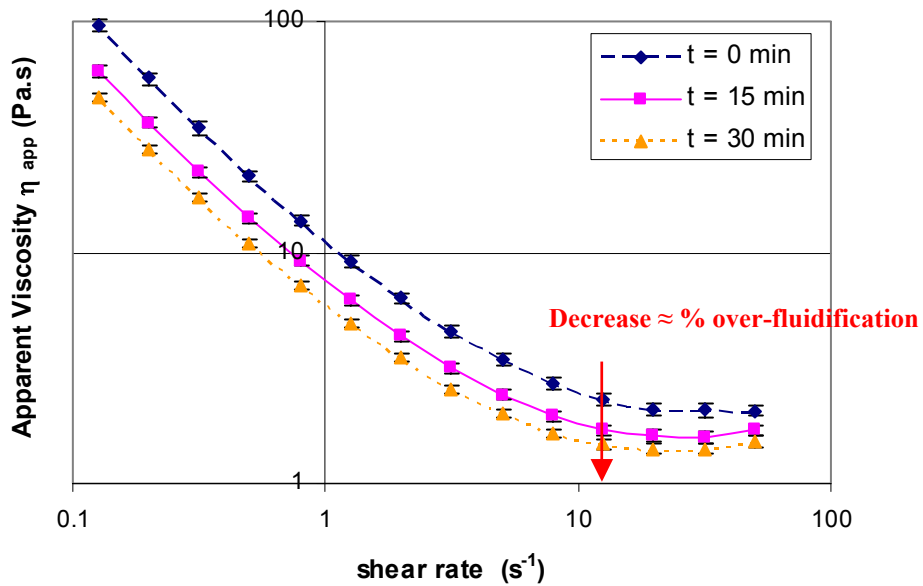
*Table 2: Composition of Cement H and Clinker L (mass %)*



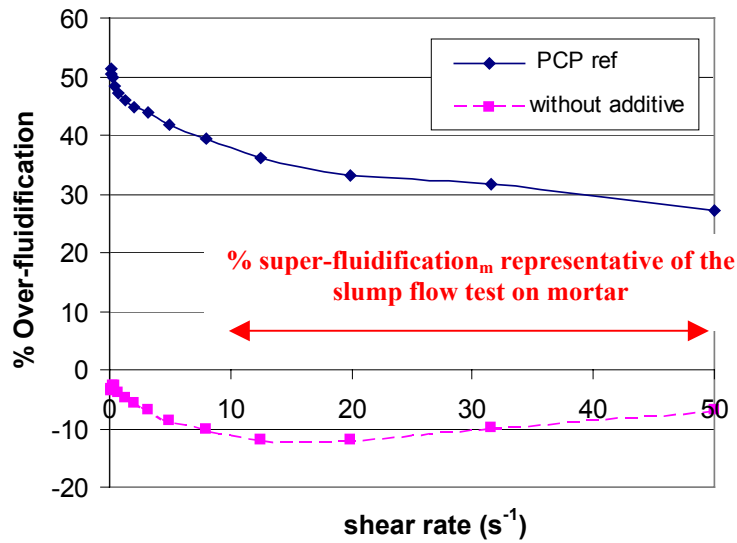
*Fig. 1: Geometry rheo-reactor used*



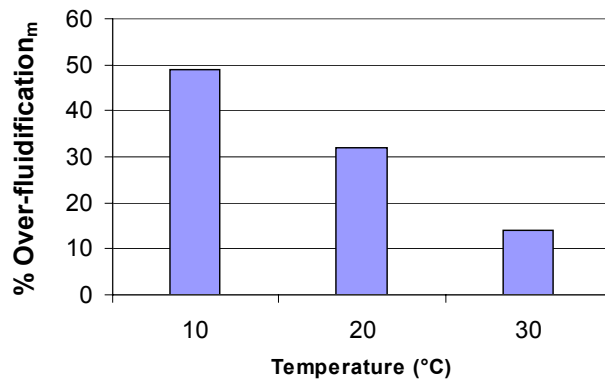
**Fig. 2: Evolution of the spread of Mortar over time (slump flow tests), PCP ref = 0.16%, W/C = 0.4, Cement H**



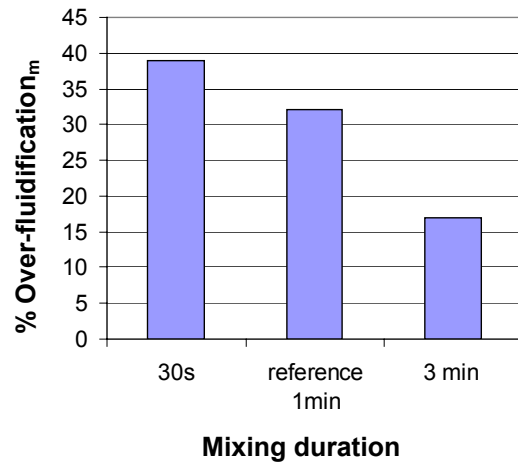
**Fig. 3: Evolution of Apparent Viscosity versus Shear rates over time after initial mixing for a Cement paste with PCPref = 0.16%, W/C = 0.32, Cement H: A decrease of viscosity is observed with time after mixing**



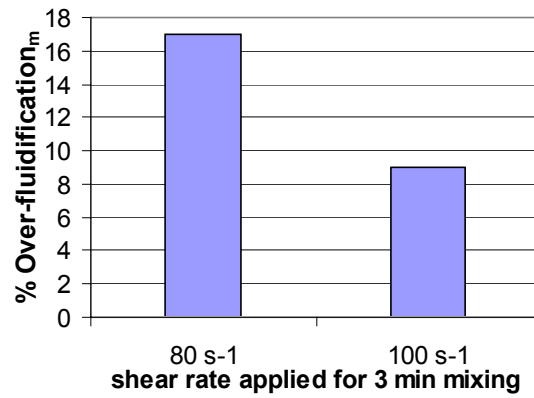
**Fig. 4: Comparison of the % of super-fluidification (see equation 1) obtained for a cement paste with PCP ref and a cement paste without additive: Shear rates between 10 and 50 s<sup>-1</sup> are representative of the result obtain with slump flow test**



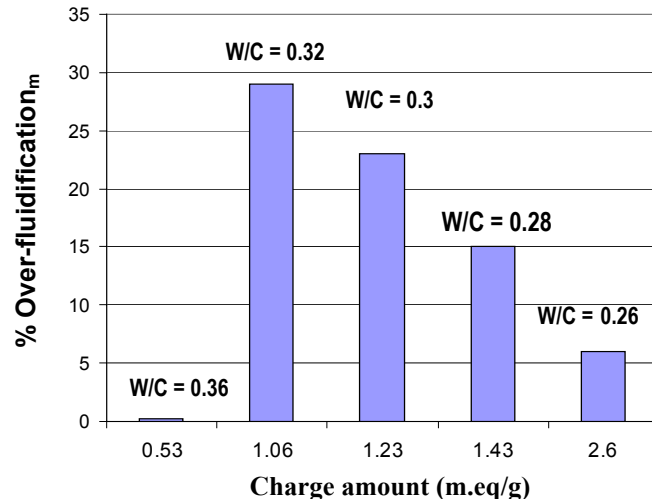
**Fig. 5: Influence of the temperature on the % of over-fluidification<sub>m</sub> (see equation 2) Cement H paste with PCP ref = 0.16%, W/C = 0.32, initial mixing: 1 min, 80 s<sup>-1</sup>**



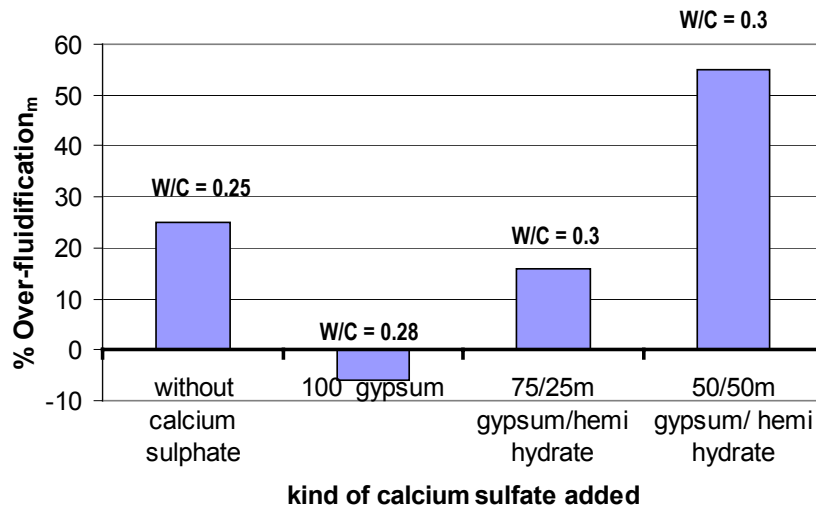
**Fig. 6: Influence of mixing duration on the % of over-fluidification<sub>m</sub>**  
 (see equation 2): Cement H paste with PCP ref = 0.16%, W/C = 0.3,  
 shear rate of mixing =  $80s^{-1}$ ,  $T = 20^{\circ}C$



**Fig. 7: Influence of the shear rate of mixing on the % of over-fluidification<sub>m</sub>**  
 (see equation 2): Cement H paste with PCP ref = 0.16%, W/C = 0.3,  
 Mixing duration = 1 min,  $T = 20^{\circ}C$

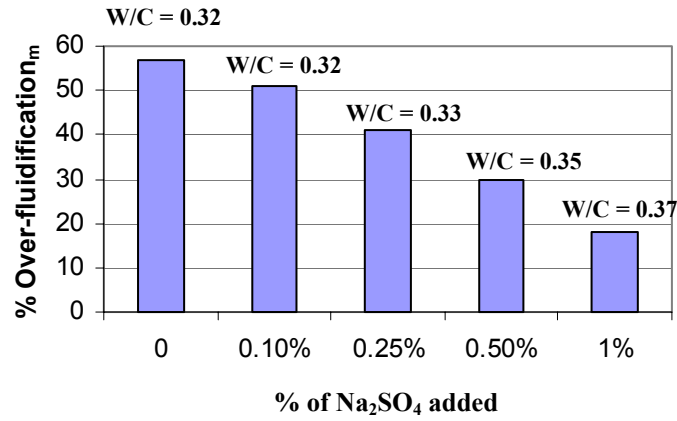


**Fig. 8:** Influence of the PCP charge amount on the % of over-fluidification<sub>m</sub> (see equation 2) : Cement H paste with additive = 0.16%, W/C adjusted to get the same initial viscosity, T= 20°C, initial mixing : 1 min, 80 s<sup>-1</sup>

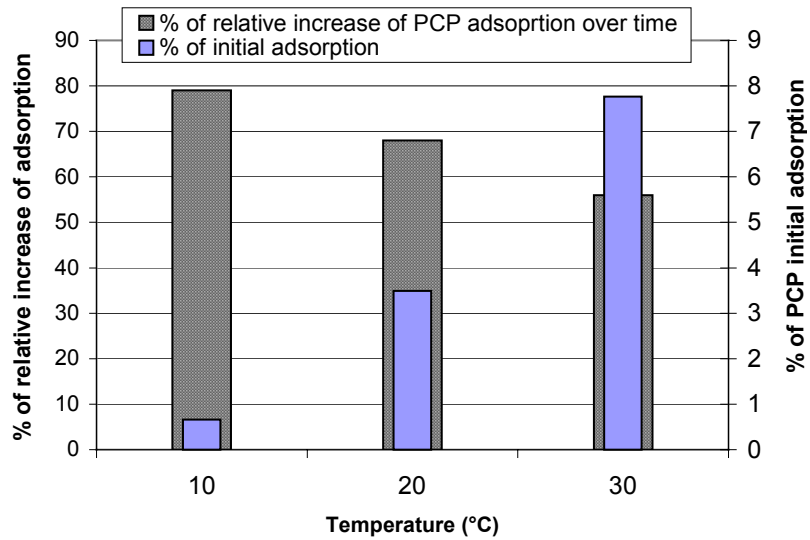


**Fig. 9:** Influence of the kind of calcium sulphate added to Clinker L on the % of over-fluidification<sub>m</sub> (see equation 2) : Cement paste with PCP ref = 0.16%, W/C adjusted to get the same initial viscosity, initial mixing: 1 min, 80 s<sup>-1</sup>, T= 20°C

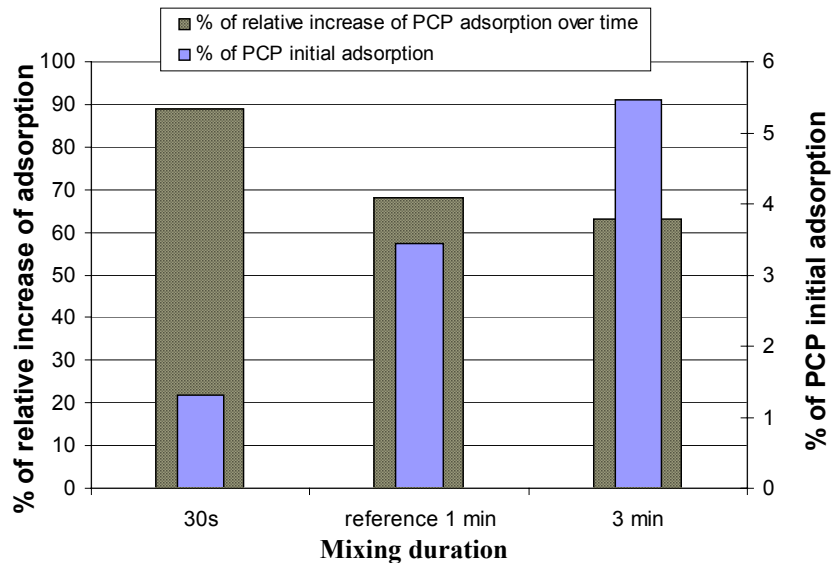




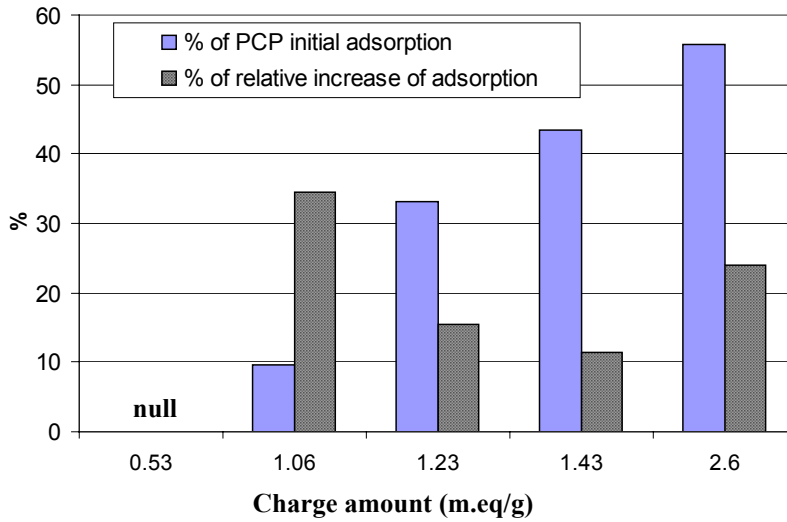
**Fig. 10:** Influence of the quantity of Na<sub>2</sub>SO<sub>4</sub> added on the % of over-fluidification<sub>m</sub> (see equation 2): Cement paste with Clinker L 50/50m gypsum/hemi- hydrate, PCP ref = 0.16%, W/C adjusted to get the same initial viscosity, Initial mixing: 1 min, 80 s<sup>-1</sup>, T = 20°C



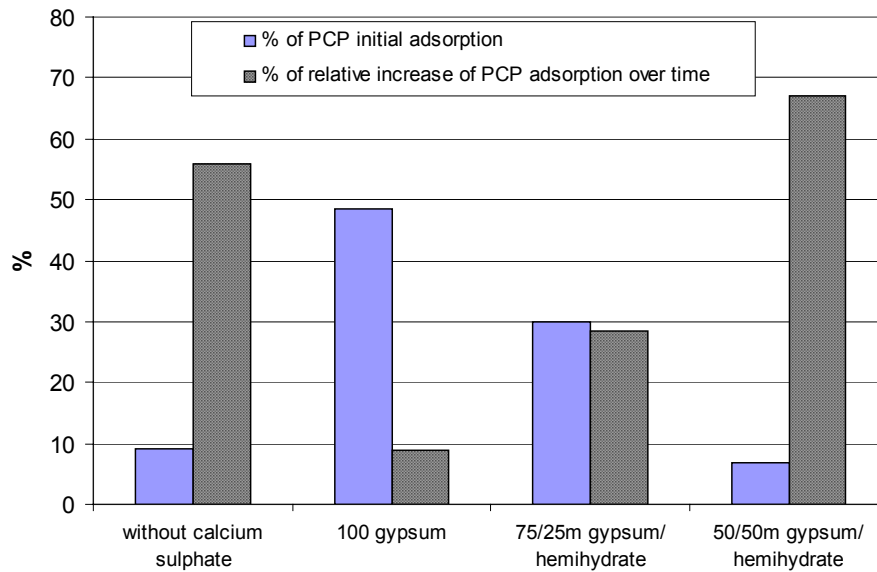
**Fig. 11:** Parameters representative of PCP adsorption evolution over time according to temperature: Cement H paste, PCP ref = 0.16%, W/C = 0.5, T = 20°C, initial mixing: 1 min



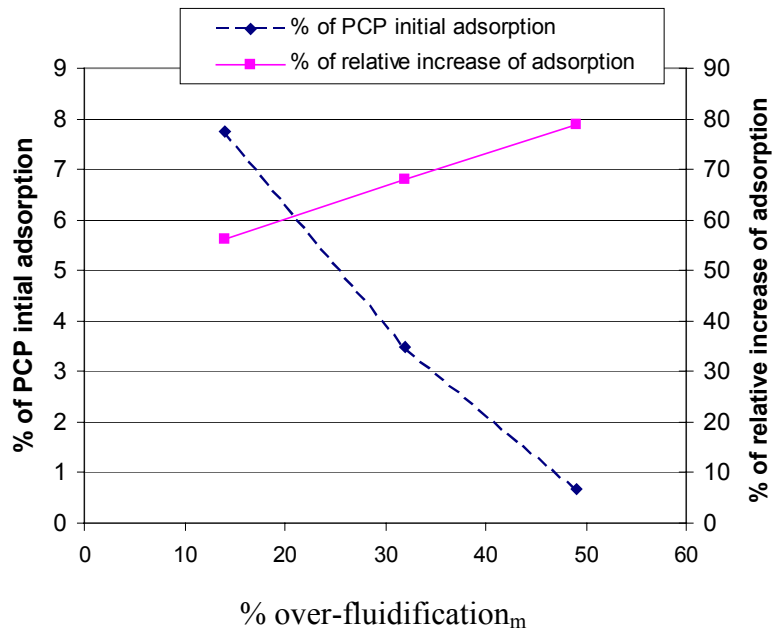
**Fig. 12: Parameters relative to PCP adsorption evolution over time according to duration of mixing: Cement paste, PCP ref = 0.16%, W/C = 0.5, T = 20°C, Initial mixing: 1 min**



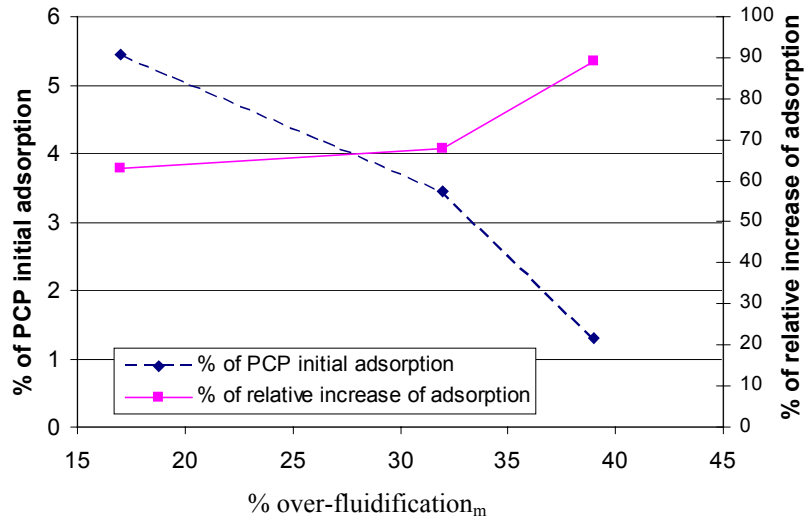
**Fig. 13: Parameters representative of PCP adsorption evolution over time according to the PCP charge amount : Cement paste, Additive = 0.16%, W/C = 0.5, Initial mixing: 1 min, T = 20°C**



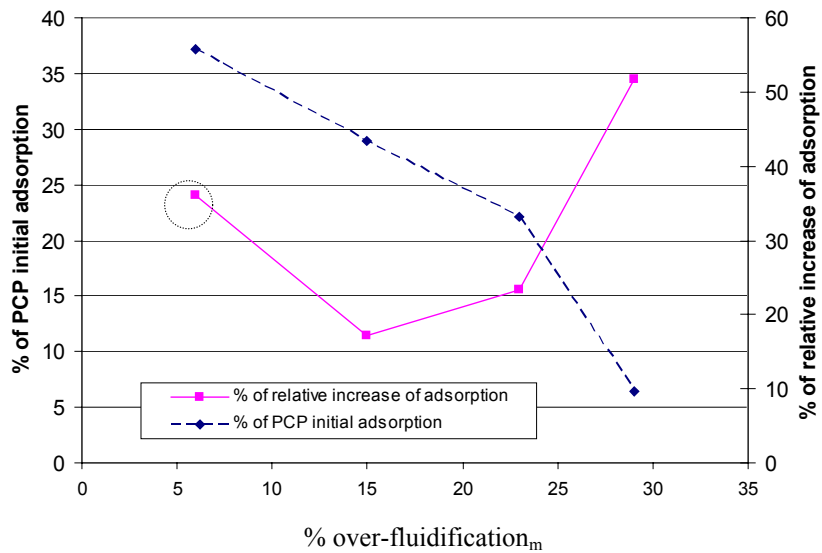
**Fig. 14: Parameters representative of PCP adsorption evolution over time according to the kind of the calcium sulphate added to Clinker L, Cement paste, PCP ref = 0.16%, W/C = 0.5, T = 20°C, Initial mixing : 1 min, 80 s<sup>-1</sup>**



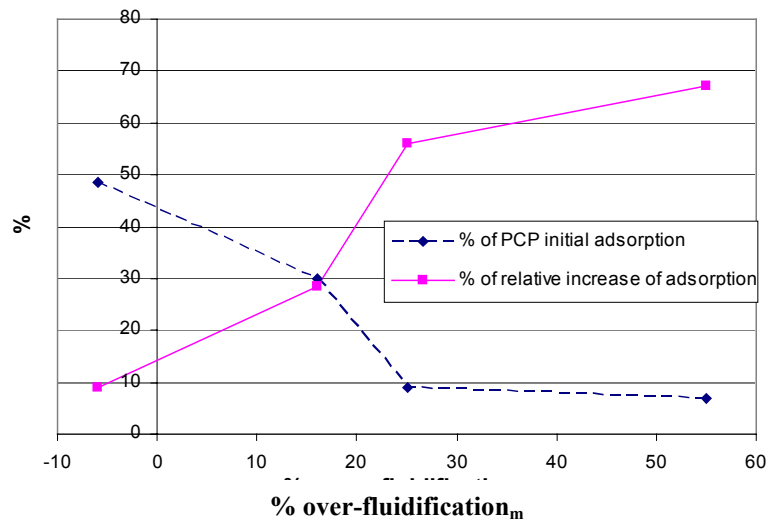
**Fig. 15: Parallel between % of over-fluidification<sub>m</sub>, the % of PCP initial adsorption and the relative increase in this adsorption over time with the results concerning the effect of temperature**



**Fig.16: Parallel between % of over-fluidification<sub>m</sub>, the % of PCP initial adsorption and the relative increase in this adsorption over time with the results concerning the effect of time of mixing**



**Fig. 17: Parallel between % of over-fluidification<sub>m</sub>, the % of PCP initial adsorption and the relative increase in this adsorption over time with the results concerning the effect of PCP charge amount**



**Fig. 18:** Parallel between % of over-fluidification<sub>m</sub>, the % of PCP initial adsorption and the relative increase in this adsorption over time with the results concerning the effect of the kind of the calcium sulphate added to clinker L