NEW SUPERPLASTICISERS: FROM RESEARCH TO APPLICATIONS

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ABSTRACT. Increasing use of high performance, pumping and self-levelling concrete is driving the leading global producers of chemical admixtures to develop new products. The underlying mechanisms that account for the action of superplasticisers are nowadays not well understood. The increasing variety of superplasticisers currently on the market and the complexity of cementitious systems do not help alleviate incompatibilities and unexpected problems. The above reasons have led us to initiate an European *Eureka* project with the aim to better understand the fundamental aspects of the behaviour of superplasticisers as well as their effect on concrete. The fundamental aspects studied are adsorption, surface charge, and rheology of cement paste. The rheological properties of fresh mortars with the same superplasticisers were also measured. Furthermore, the effect of a grinding aid on properties of cement paste and fresh mortar is shown.

Keywords: Superplasticisers, dispersion mechanisms, adsorption, rheology, grinding aid.

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INTRODUCTION

Even nowadays, the production of quality concrete seems to non-specialists a relatively simple task. The ingredients are well known: Portland cement has been produced for more than one and a half century, sand and gravel are natural products, and water as well. Different admixtures are furthermore at disposal for improving the desired properties: accelerators, retardators, (super)plasticisers, etc. Concrete technologists are only too aware that the situation is not so ideal. Even pure Portland cement can vary in its chemical and mineralogical composition.

Sulphate, C_3A, alkali content influence the properties of fresh and hardened concrete. Blended cement and addition of by-products, which are nowadays commonly used, render the situation still more complex. Aggregates also vary in their chemical and mineralogical composition, shape, particle size distribution and surface properties. Problems of compatibility cement/admixtures are known, and generally avoided by preliminary tests [1]. The precise cause of incompatibility frequently remains unknown. The development of high performance concrete still increases the risk of incompatibility.

Material scientists and chemists involved in the development of chemical admixtures have not only the task to synthesise and formulate new efficient products, indeed they should be able to understand and possibly to foresee the behaviour of the admixtures in complex cementitious systems. Fulfilling these requirements is rendered very challenging because of the complexity of concrete components and the various climatic conditions in which they are used. The influence of a grinding aid, a chemical admixture used for the cement production, will illustrate this point hereafter.

Despite very interesting studies especially carried out since 1970's [2-9], numerous questions remain unsolved. This situation led us to initiate a Eureka project with the aim to study and understand the behaviour of superplasticizers in real cementitious systems. Participants come from university, research and testing laboratory, industry, and practice as well. The scope and the aim of this project are described in more detail in [10].

MECHANISMS OF ACTION OF SUPERPLASTICISERS

Cement particles are always agglomerated in water suspensions. This leads to a viscosity increase by an apparent particle volume increase. A part of the water is entrapped in the porosity of the agglomerates and does not contribute to the flowability. The role of the superplasticizers (polymers) is essentially to break down these agglomerates by modifying the balance of interparticle forces. Four mechanisms might act for the dispersion of cement particles, as well as for other powders. The two most important are linked to polymer adsorption: steric hindrance through the adsorbed layer thickness and electrostatic repulsion through the induced electrical charge. In reality, once the particles are close enough for their adsorbed layers to overlap, both effects come into play. Understanding which mechanism is dominant and what parameters have an effect, is paramount for the design of polymers with improved performances. It should also allow a better use of common polymers. Much has been learned from the field of colloidal science, where surface forces and their role on interparticle interactions has been a subject of ongoing research for many years.
Horn [11] shows how colloidal, surface and interparticle force concepts can be applied to ceramic processing. Russel et al [12] give an extensive treatment of these effects, illustrating how these effects are the regulating factors of the rheology of colloidal dispersions.

Chemical effects are also associated with superplasticizers since they influence the hydration process [2]. For instance, there is a strong indication that sulphonated naphthalene formaldehyde polycondensates (SNFC) molecules can participate in the same type of reaction as the sulphate ions inhibit the early hydration of the aluminate phases. In general, the superplasticizers interfere with the nucleation and growth of aluminate hydrates, ettringite and C-S-H products and affect setting time. The reactivity of the cement with water has a significant influence on the superplasticiser dosage to get a given workability. The lower the reactivity, the lower the superplasticiser demand. A quartz powder requires much less superplasticiser than a C_2S rich cement, which itself requires less superplasticiser than a C_3S or a C_3A rich cement [2].

The most commonly used superplasticizers until now are certainly either SNFC (generally the Na salts) or sulphonated melamine formaldehyde polycondensates (SMFC). It is generally believed that the dispersive action of such superplasticiser types is essentially due to the electrical repulsion [5]. They are called of first generation.

Superplasticizers of the new generation are copolymers containing polyethylene glycol as graft chain and carboxylic function in the main chain. These polymers induce less negative zeta potentials (a function of the charge of the particles with adsorbed polymers) than those of the first generation. According to Sakai and Daimon [3], these polymers induce a zeta potential as small as -5 to -10 mV. In this case, the dispersion caused by these superplasticizers is attributed to steric hindrance [6]. Uchikawa et al [7] were led to the same conclusion by measuring surface forces by atomic force microscopy. Nevertheless, the distance at which interaction appears is several times larger than would be expected from the side chain length of the polymers used. Furthermore, they are less incorporated in the hydration products and disperse cement at lower concentration. This leads in general also to a smaller slump loss in time. Further elucidation of the mechanisms and more accurate modelling of the interparticle forces are needed to fully understand and apply these second generation superplasticisers.

EXPERIMENTAL

Materials

The main characteristics of model powders, cements, and silica fume, are give in table 1. Two model powders, MgO and Mg(OH)$_2$, were used for certain measurements in this study. They have similar surfaces properties to calcium oxide, and in particular isoelectric points (zero zeta potential close to the pH=12) as cement suspensions [8]. The main advantage in using such powders is that they are "non-reactive" and the influence of hydration can be avoided.

Two Portland cements obtained from the same clinker were used. The first was ground without any grinding aid.
The second was ground in presence of triethanol amine acetate, a common commercial grinding aid. Grinding times were adjusted so as to obtain two cements with the same specific surfaces.

Table 1 – Cement and silica fume characteristics

Powders used	Specific surface area [m^2/g]

	Blaine	BET (N$_2$)
MgO (Martin Marietta, USA)	-	0.77
Mg(OH)$_2$ (Martin Marietta, USA)	-	11.8
CEM I 42,5 with grinding aid (Olten, CH)	0.349	0.950
CEM I 42,5 without grinding aid (Olten, CH)	0.327	0.963
S.F. Anglefort undensified (Péchiney, F)	-	35.3

Seven structurally different polymers, which are representative of most of the superplasticizers used today, have been selected for this study. They are listed in table 2, along with their average molar mass determined by GPC. Four of these polymers, PCA-1, PCA-2, PCE-3 and SNFC-1 are commercially available. The other three, PCE-1, PCE-2, and PCA-3 are laboratory test products. Apart from the SNFC-1, these polymers are found as concentrated aqueous solutions, with a solid content of about 30-40% by mass.

Table 2 – Chemical nature and molar mass of the polymers

Designation	Chemical Type	Average Molar Mass [g mol^{-1}]
PCA-1	Na-polycarboxylate-polysulphonate	* 16'000 ± 2'000
PCA-2	Na-polycarboxylate-polysulphonate	* 11'500 ± 2'000
PCE-1	Na-polycarboxylate-polysulphonate, containing PEG-ester	* 9'500 ± 1'500
PCE-2	PEG-ester containing polymer, weakly ionic	* 15'000 ± 5'000
PCE-3	Na-polymethacrylic acid, containing PEG-ester, weakly ionic	≠ 10'000 ± 2'000
PCA-3	Na-polyacrylate	≠ 2'500 ± 500
SNFC-1	Sulphonated naphthalene formaldehyde polycondensate, Na-salt	≠ 6'000 ± 1'000

* Number Average Molar Mass   ≠ Mass Average Molar Mass

Zeta potential

The zeta potential was measured at 23-25° C by acoustophoresis. In this method, particles are put into movement by an acoustic wave. The field that their surface charge induces allows calculation of the zeta potential. The suspensions were prepared by dispersing 20 g of powder in 300 ml NaOH 0.01M (pH 12.0 ± 0.1 at 20°C) under vigorous agitation and sonification. The superplasticizers were progressively added as concentrated aqueous solutions with a microdispenser.

Adsorption

Adsorption measurements were performed in suspensions of 5 g of $Mg(OH)_2$ in 20 ml NaOH 0.01M (pH 12.0 ± 0.1 at 20°C), previously thermostated in a rotary bath (different amounts were taken to achieve similar volume fractions). Superplasticizers were added as concentrated aqueous solutions (10-15% solid content by mass) with a microdispenser.

After 30 min in the rotary bath, the suspensions were centrifuged. From the supernatant, 5 ml, buffered with acetic acid, were filtered and a part was analysed by reverse phase chromatography with a high performance liquid chromatograph (HPLC) [8].

The diode array detector, which only detects molecules that absorb in the UV or visible range, has limited the number of polymers whose adsorption could be studied. Polymers PCE-1 and PCA-2 were selected. They are detectable by UV, have similar molar masses, and HPLC chromatograms suggest that the molar mass distributions are also similar. Finally, they have a similar structure, but differ mainly by the insertion of some PEG-ester units into PCE-1.

Rheology

Samples were inserted into the sample holder of a coaxial cylinder device mounted on a rheometer thermostated at 25°C. The gap between both cylinders is 0.85 mm. Over this gap, the velocity gradient is assumed to be constant. More details are given in [13].

Flow table spread

The tests were performed according to DIN 18555 on mortars made with 1 part of cement and 3 parts of sand $(0 - 4$ mm) by mass.

Heat generation

The temperature variations as a function of time were measured by means of thermocouples placed in the centre of mortars identical to those used for the flow table spread test.

RESULTS AND DISCUSSION

Zeta potential

Electrostatic repulsion, one of the possible mechanisms involved in dispersion and water reduction, is intimately linked to zeta potential. The influence that all superplasticizers used in this study have on the zeta potential of $Mg(OH)_2$ suspensions is shown in figure 1. Potentials are plotted as a function of superplasticiser added, given in mg of their dry mass by m^2 of $Mg(OH)_2$ in suspension. Results show that the polymers PCA-1,-2,-3 and SNFC-1 induce the more negative final potentials (around -23 mV), while the polymers PCE-1,-2,-3 induce potentials ranging from -5 to -18 mV. The main reason for these differences is that the first group of polymers are all strong electrolytes, while the others are weak or very weak electrolytes, due to the insertion of PEG-ester units. This acts as a charge spacer and decreases the charge density of the PCE-type polymers.
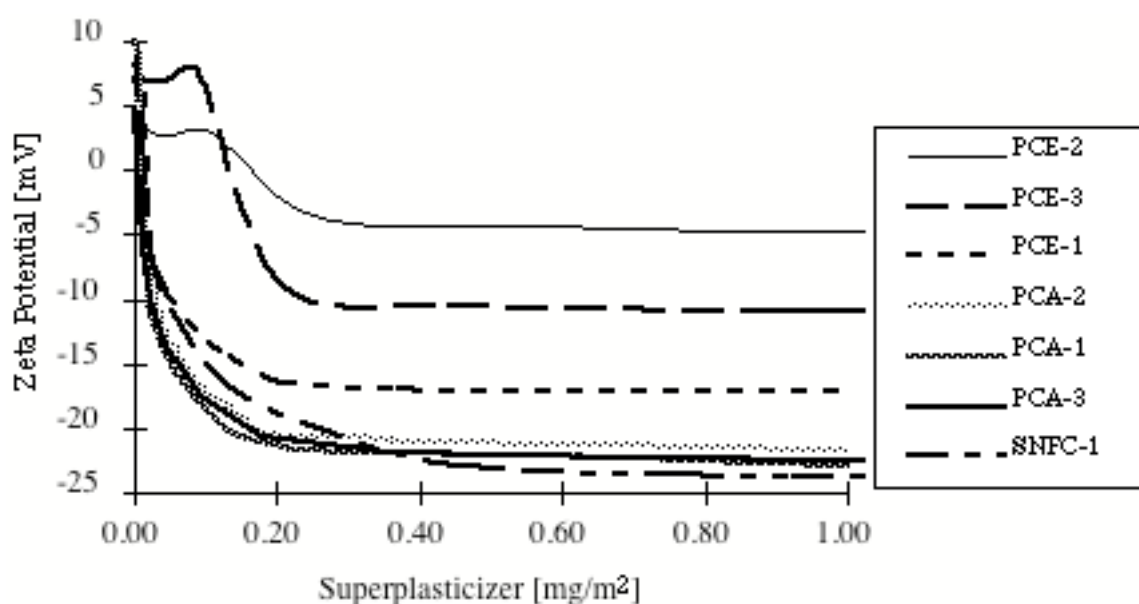

Figure 1. Zeta potential of magnesium hydroxide suspensions as a function of the added mass of superplasticizers [8].

From these results, it is concluded that dispersion by electrostatic repulsion (ER) may be much smaller for the PCEs than for the PCAs or the SNFC. However, they can all be successfully used as water reducers and superplasticizers. Dispersion by PCE-type polymers should therefore involve at least one mechanism other than ER.

Since the surface charge induced by the PCA and SNFC strong electrolytes were all found to be very similar, it is expected that dispersion due to electrostatic repulsion will be similar. Any major differences in the dispersion efficiencies would therefore be a consequence of non-electrostatic effects.

Adsorption

For a substance in suspension at a fixed temperature, an adsorption isotherm gives the concentration of this substance at the surface of the solid phase versus its concentration in the bulk of the liquid phase. Usually, these isotherms have a horizontal asymptote (a plateau concentration), which corresponds to surface saturation of the solid phase.

Plateau concentration of adsorption isotherms of PCA-2 and PCE-1 as a function of the temperature are given in figure 2. It appears that the adsorption of PCE-1 on MgO increases with temperature, while the one of PCA-2 do not show significant temperature dependence. Adsorption of polymers onto surfaces is mainly linked to either polymer-surface, solvent-surface, polymer-polymer or polymer-solvent interactions. One of these factors, or a combination of them, should explain why the plateau concentration of PCE-1 adsorbed on MgO increases with temperature.
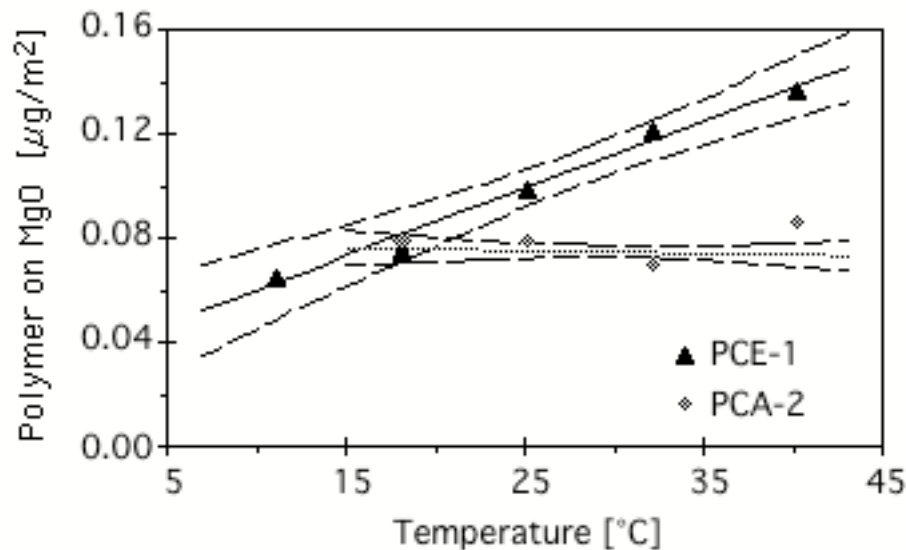

Figure 2 – Temperature effect on the adsorption of PCA-2 and PCE-1 on MgO. The full straight lines are obtained by a linear regression and the dotted lines show the 95% confidence interval.

The PCE-1 polymer is similar to the PCA-2, but its anionic groups are further apart, due to the insertion of PEG-ester groups. Consequently, its electrostatic attraction towards the positively charged surfaces must be smaller than it is for PCA-2. Mechanisms are discussed in more details in [8].

Such different behaviours of almost similar superplasticizers can have important practical implications. For instance, it could be assumed that the workability with PCE-1 is very much influenced by the temperature.

Rheology

It is shown in [13] that a simple model such as the two parameters Bingham model is insufficient to account for the complete shear rate-shear stress curves. Above a certain superplasticiser dosage, all curves indicate very similar flow behaviours. Increasing the shear stress allows us to identifying the yield stress. Up to a certain value of shear stress, the shear rate is equal to zero. Then, there is a sudden increase in shear rate. This limiting stress value is the yield stress.

The flow curves with the cement with and without grinding aid, with PCA-1 and PCA-2, have been measured. It has been found that optimum dispersion was obtained just before the saturation level observed in adsorption isotherms with PCA-2. This is in agreement with similar studies with model powders [9]. With PCA-1, the optimum dispersion was obtained with an amount exceeding the saturation level observed in adsorption isotherm. This can be attributed essentially to a difference in adsorption kinetics. PCA-1, however, allows us to obtain suspensions with a lower yield stress. These properties can be related to the chemical structure and molar mass distribution of the two superplasticizers, the latter being significantly different.

The presence of a grinding aid influences the rheological properties of cement suspensions. The minimum yield stresses of the cement without grinding aid are slightly higher than those with grinding aid, but the amount of polymer required is smaller, with respect to adsorbable amounts [13], i.e. more polymer is needed when using a grinding aid, but the overall result is better.

Flow table spread

Numerous measurements were carried out on different mortars made with different cements, different superplasticizers and dosages, and different w/c. As examples, results obtained with the superplasticizers SNFC-1 and PCE-2 and the cement with and without grinding aid are given in figures 3 and 4 respectively.

The mortars prepared with the cement without grinding aid have always a higher spread than those prepared with the cement containing a grinding aid. The spread loss in time is not influenced by the grinding aid. With SNFC-1, the spread loss is high already after 30 min. The mortars with PCE-2 and the highest superplasticiser dosage (0.6%) exhibit very few spread loss. This is certainly due to a dosage higher than the saturation in adsorption isotherm. This compensates the fraction of superplasticiser incorporated in hydration products.
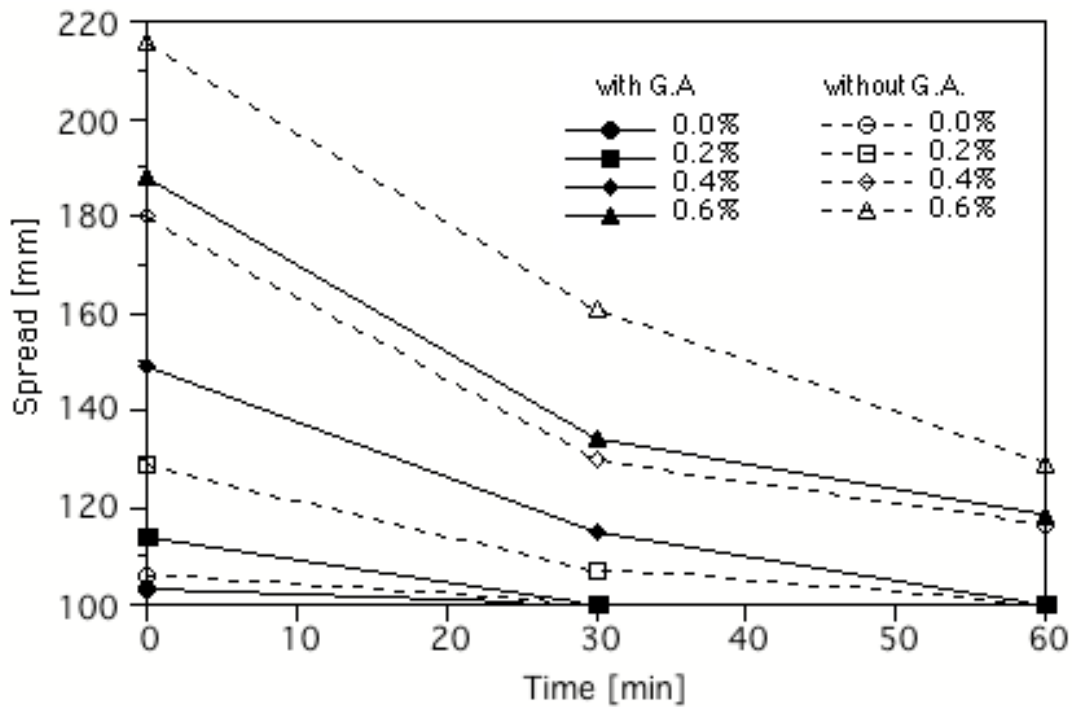
Figure 3 – Flow table spread of mortars prepared with various dosage of superplasticiser SNFC-1 on a CEM I with and without grinding aid (w/c=0.36).
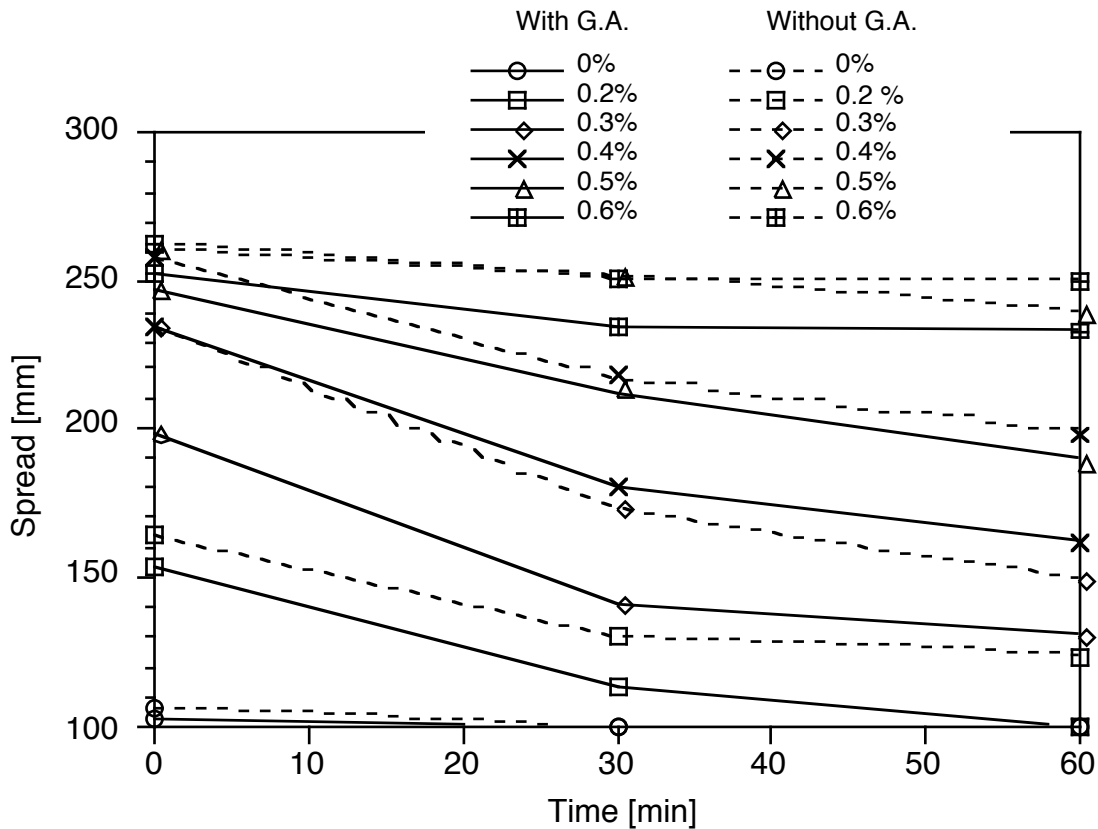

Figure 4 – Flow table spread of mortars prepared with various dosage of superplasticiser PCE-2 on a CEM I with grinding aid and without grinding aid (w/c=0.36).

Heat generation

The maximum of the heat generation is usually attributed to the crystallisation of $Ca(OH)_2$ and to the dissolution of C_3S and the formation of C-S-H. The maximum temperatures measured on mortars are reported in figure 5. The grinding aid has no influence on the reference mortars without any superplasticiser. On the other hand, all superplasticizers delay the maximum temperature, this trend being amplified by increasing superplasticiser dosage. A noticeable difference can be observed between superplasticizers PCA-1 and PCA-2 or PCE-1. The grinding aid has no effect with PCA-1, but it does have an effect with PCA-2 and PCE-1. Their effects are opposed: grinding aid increases the effect of PCA-2 and decreases the one of PCE-1.

All these effects are linked with the cement hydration and have been extensively studied with SNFC and SMFC superplasticizers. The state of the art has been recently presented [2, chap. 5]. It can be noticed that numerous examples are cited, but almost always without explanation of the fundamental reasons, which cause such behaviours. This shows avenues for new research.
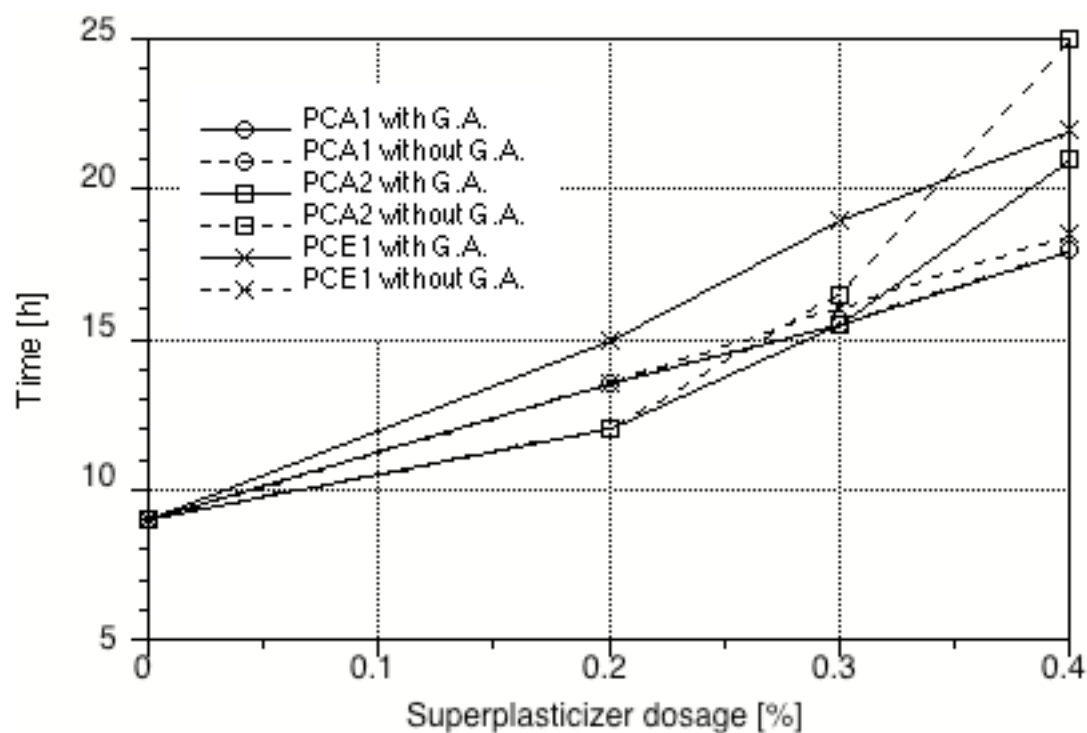

Figure 5 – Influence of superplasticiser dosages on the displacement in time of the maximum of heat generation of mortars made with CEM I with and without grinding aid (w/c=0.36).

CONCLUSIONS

The seven superplasticizers studied belong either to the group of strong electrolytes or to the group of weak or very weak electrolytes. It has been shown that the polymers of the second group, which act essentially by steric repulsion, can be used with success as superplasticizers.

Adsorption isotherms characterise the interaction of superplasticizers-cement surfaces. It was found from rheological measurements that the adsorption plateaux (surface saturation) correspond roughly to the amount of superplasticiser allowing the optimum dispersion.

It has been confirmed that a superplasticiser without sulphonated functions has less spread loss than a SNFC superplasticiser belonging to the first generation of superplasticizers.

The retarding effect of superplasticizers has been confirmed. However, significant differences can be observed, depending on the couple cement/superplasticiser.

A grinding aid, commonly used nowadays in the cement production, interferes with superplasticizers and influences most of the measured properties. This effect is sometimes positive, sometimes negative. The mechanisms behind these effects remain to be elucidated.

The examples given above in this paper show why it is necessary to better understand the mechanisms through which superplasticisers act. The development, the selection and the correct use of these admixtures strongly depend on it.

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