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**INTERACTION OF SUPERPLASTICIZERS WITH MODEL POWDERS  
IN A HIGHLY ALKALINE MEDIUM.**

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**Synopsis:** It is broadly recognized that the adsorption of superplasticizers on cement particles is a key factor in determining the rheology of concrete. In order to avoid the problems linked to the hydration of cement, the adsorption of superplasticizers is often studied on unreactive model powders. However, in order for the model system to remain as close as possible to cement, the surface should have a similar charge and a similar chemical nature. Furthermore, the pH of the solution should be close to that of the hydrating cement (about 12.5). Under these conditions, cement has been shown to have a positively charged surface. The model powders used in this study were  $Mg(OH)_2$  and dead burnt  $MgO$ , which have nominal isoelectric points of 12.0 and 12.4 respectively, and which are chemically similar to  $Ca(OH)_2$  and  $CaO$ .

The surface charge of such model suspensions was studied as a function of added superplasticizer. These were either commercially available or currently under development, ranging from strongly to very weakly ionic.

Adsorption isotherms for two polymeric superplasticizers, with similar structures but with different ionic group spacing, have been measured for both  $MgO$  and  $Mg(OH)_2$  at pH 12 and 11.3 respectively and between 10 and 40°C. Results showed a strong temperature dependence for the adsorption of the less ionic polymer on  $MgO$ .

**Keywords:** Acoustophoresis, Admixtures, Adsorption, Model Powders, Superplasticizers, Temperature Influence, Zeta Potential.

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## INTRODUCTION

Superplasticizers, also known as High Range Water Reducers (HRWRs), are today of great help in the production of high performance concrete. They are polymeric dispersants, which when added to concrete, allow high water reduction for the same workability. This in turn leads to denser and more durable concrete. The mechanisms through which these polymers act are linked to a change in interparticle forces (1, 2). Defloculation and/or dispersion are terms often used to describe these phenomena. However, a detailed understanding of the underlying mechanisms has not yet been reached. Whether the observed effect is due to electrostatic, steric, entropic or capillary effects or any combination of these, is still a matter of much debate (3-5). A typical illustration of this lack of knowledge is the impossibility to explain rationally the incompatibilities observed between some superplasticizers and some cements (3).

In this study, structurally different water-soluble polymers, which are or could be used as HRWRs, are considered. These polymers were chosen from the three types of anionic polymers (anionic polyelectrolytes) currently used in superplasticizers: Sulfonated Naphthalene-Formaldehyde-Polycondensates (SFNC), Polycarboxylic Acid Polymers (PCA) and Polycarboxylic Ester-polymers (PCE).

The introduction of Polyethyleneglycol-Ester units in the PCE-type polymers allows a larger spacing of ionic groups than in a standard PCA. By using a PCA and a PCE of similar molar mass and containing the same ionic groups, the effect of charge spacing has been investigated. The temperature dependence of the adsorption of two such polymers was studied. The zeta potential that a wide range of these polymers induce on model powders is also presented and the results are

discussed in the light of evaluating the importance of electrostatic effects on cement rheology.

### MODEL SUSPENSIONS

Studying the action of HRWRs in cement suspensions is a tedious task. Cements are reactive multiminerall powders, the surfaces of which evolve in time. Mineralogical and chemical compositions of the different granulometric fractions can be different. Some cements also contain mineral additions, like silica fume, fly ash, slag or filler. Grinding aids are generally used in the production route and remain on cement grains. Cements have variable  $C_3A$  content, the reactivity of which can also vary. The importance of the  $C_3A$  reactivity on the rheology of cement slurries is well known. The dissolution of sulfate ions must be balanced with the reactivity of  $C_3A$  (3). Not only do the surfaces of the hydrating minerals evolve in time, but also the chemical composition of the solution is changing in the period between the mixing and placing of concrete.

Because of this complexity, superplasticizers and other dispersing agents have often been studied using model suspensions of inert powders (5-10). The information that such experiments provide is an indication of the initial interaction of superplasticizers with cement particles.

Nkinamubanzi (6) and Pierre et al (9) found that the adsorption of SNFC on  $TiO_2$  strongly depends on the pH of the suspension. It has a maximum at pH 3 and does not adsorb in the alkaline region. This behavior is rationalized by taking into account the change in surface charge of  $TiO_2$  with pH. Titanium dioxide has an isoelectric point at pH 5.5-6. Below this value, its zeta potential is positive and above it, it is negative. This explains the pH dependent adsorption of the SNFC which is a anionic polymer.

In order to relate adsorption on a model powder in a model suspension to that on Portland cement in a cement suspension, the powder must therefore have a similar zeta potential. Nägele (11) found this potential to be positive by a couple mV. The behavior of a polymer in aqueous solution and its action at the interface of a solid is determined by specific structural characteristics of the solvated macromolecules. These characteristics, apart from depending on the polymer structure (electric charge, number, type, distribution and spacing of the functional side-groups), are strongly influenced by the pH of the solution.

A second condition therefore appears in the choice of model systems. It is that the pH of the suspension should be similar to that of a hydrating cement paste (about 13). Suspensions such as those containing titanium dioxide can not simultaneously fulfill both conditions (high pH and positive zeta potential). Though they can provide some information on adsorption, it would not be wise to use such data to differentiate the effects involved in superplasticizing of concrete. As a matter of fact, very few systems can fulfill simultaneously the above mentioned conditions and conserve the essential inertness required for a model system. To the best of our knowledge, no adsorption experiments have been carried out at pH around 12 with model powders that are positively charged.

The powders used in our study: dead burnt magnesium oxide and magnesium hydroxide, have nominal isoelectric points respectively at pH 12.4 and 12 (12). They were studied in suspensions at pH 12 and 11.3 (pH reached in suspensions prepared with NaOH 0.01M), giving in both cases a zeta potential positive by a couple mV.

Magnesium, which lies above calcium in the periodic table, has a similar outer electronic shell and a smaller radius than calcium. This makes its bonding to oxygen much stronger than that of calcium. This stronger bond makes magnesium oxide almost insoluble. Its solubility can be further decreased by dead burning, producing a very interesting model powder. The main cement phases (calcium silicates and calcium aluminates) contain calcium oxide, which is probably the dominant surface leading to the positive zeta potential of cement (4). It is therefore possible that the initial effects involved in superplasticizing will be closely linked to the adsorption of superplasticizers on calcium oxide-like surfaces. This makes magnesium oxide an even more interesting model powder. As for magnesium hydroxide it offers a surface expected to offer many similarities to that of the hydrated cement phases.

## EXPERIMENTAL

### Powders

MgO dead burnt and Mg(OH)<sub>2</sub> from Martin Marietta Magnesia Specialties Inc. (type: P-98 and MH-10 respectively; Baltimore, USA) were carefully sampled. A representative part of the MgO was then sieved. The fraction below 50 μm was sampled and used in our experiments.

The particle size was determined by laser diffraction (Malvern Mastersizer; Malvern, GB). The BET specific surface area was determined by adsorption of N<sub>2</sub> (Micromeritics Gemini III 2375; Norcross, USA). No impurities were detected in the XRD data collected on the MgO. The Mg(OH)<sub>2</sub> contained a small amount of MgO, possibly formed at the surface by excess drying during the production. The powder characteristics are given in Table 1.

Fig. 1, 2 show SEM pictures of these powders. MgO has a morphology relatively close to cement. Mg(OH)<sub>2</sub> is a solid aggregate of small crystallites. It might include a non negligible porosity.

### Polymers

Seven structurally different polymers which are representative for most of the superplasticizers used today have been used in this study. They are listed in Table 2, along with their average molar mass determined by GPC with a UV or light scattering detector.

Three of these polymers - PCE-3, PCA-3 and SNFC-1 - are commercially available. The other four - PCA-1, PCA-2, PCE-1 and PCE-2 - 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.

### Zeta potential

Zeta potential was measured at 23-25° C by acoustophoresis (Penkem, system 7000; Bedford Hills, USA). 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. There is debate in the literature as to the exact way by which this potential must be calculated (13). However, not being aware of a definitive study on the question, the standard method proposed by the manufacturer and outlined by Marlow et al (14) was used. A slight vacuum was maintained in the measuring cell to avoid bubble formation which attenuates the

signal. The suspensions were prepared by dispersing 20 g of powder in 300 ml NaOH 0.01M (pH  $12.0 \pm 0.1$  at  $20^\circ\text{C}$ ) under vigorous agitation and sonification for 15 min (150 W, 20 kHz). Prior to measuring, they were degassed for 5 min ( $\approx 20$  torr). The superplasticizers were progressively added as concentrated aqueous solutions with a microdispenser.

### **Adsorption**

It was found by high performance liquid chromatography (HPLC) that excessive residence of the superplasticizers in a solution at pH around 12 can lead to a partial hydrolysis of the polymer. The adsorption experiments were designed to minimize the necessary residence time of the polymer in suspension, while achieving complete adsorption.

Adsorption measurements were performed in suspensions of 10 g of MgO or 5 g of  $\text{Mg}(\text{OH})_2$  in 20 ml NaOH 0.01M (pH  $12.0 \pm 0.1$  at  $20^\circ\text{C}$ ), previously thermostated in a rotary bath at 200 rpm (different masses were taken to achieve similar volume fractions). The suspensions were kept in closed polyethylene flasks to avoid change in concentration by evaporation. Superplasticizers were added as concentrated aqueous solutions (10-15% solids content by mass) with a microdispenser. This concentration range allows a viscosity small enough to obtain a precise dosage with microdispensers, while keeping added volumes sufficiently small not to change the systems behavior due to dilution. Nevertheless, the dilution was taken into consideration when calculating the adsorption mass balance.

After 30 min in the rotary bath, the suspensions were centrifuged 5 min at 3'000 rpm, in a thermostatable table centrifuge from Jouan (mod. CR-412; St-Nazaire, France) regulated at the same temperature as the adsorption experiments were carried out. From the supernatant, 5 ml, buffered with 25  $\mu\text{l}$  of  $\text{CH}_3\text{COOH}$  (30% V/V), were filtered through a 0.45  $\mu\text{m}$  filter mounted on a dispensable syringe. The first 2 ml were discarded and the rest was analyzed by reverse phase chromatography with a high performance liquid chromatograph from Waters (mod. Alliance; Milford, U.S.A.) equipped with a diode array detector. The calibration standards, which, apart from containing no powder and not being centrifuged, were treated in the same way. Each sample was analyzed at least twice.

The diode array detector, which only allows one to study products which absorb in the UV or visible range, has limited the number of polymers whose adsorption could be studied. Other detectors are currently being considered to extend this method to all types of superplasticizers.

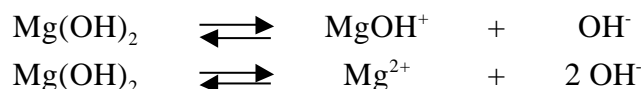
Polymers PCE-1 and PCA-2 were selected for adsorption measurement. They are detectable by UV, have similar molar masses and HPLC chromatograms suggest molar mass distributions are also similar (Fig. 3). Finally, they have a similar structure, but differ by the insertion of some PEG-ester units into PCE-1.

## **RESULTS AND DISCUSSION**

### **Stability of suspensions**

The pH of the  $\text{Mg}(\text{OH})_2$  suspensions dropped to 11.3, while it remained at  $12.0 \pm 0.1$  with MgO. The pH change of the  $\text{Mg}(\text{OH})_2$  suspensions is believed

to result from the precipitation of hydroxides by dissolved impurities. A further pH decrease is limited by the following equilibria:



### **Zeta potential**

Electrostatic repulsion (ER), one of the possible mechanisms involved in dispersion and water reduction, is intimately linked to zeta potential. In Fig. 4, the influence that superplasticizers have on this potential is shown for  $\text{Mg(OH)}_2$  suspensions. Potentials are plotted as a function of superplasticizer added, given in mg of their dry mass by  $\text{m}^2$  of  $\text{Mg(OH)}_2$  in suspension. Results show that the polymers PCA-1, 2, 3 and SNFC-1 induce the largest final potentials (around -23 mV), while the polymers PCE-1, 2, 3 induce lower 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.

From these results, it is concluded that dispersion by electrostatic repulsion (ER) may be less likely for the PCEs than for the PCAs or the SNFC. However, they can all be successfully used as water reducers. Dispersion by PCE-type polymers should therefore involve at least one mechanism other than ER. It may be steric, entropic or capillary and may also be involved in the dispersion with PCA and SNFC.

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.

Fig. 5 a, b show the change in zeta potential that both polymers PCA-2 and PCE-1 induce respectively on MgO and  $\text{Mg(OH)}_2$ . Here, the superplasticizer added is given in molar units instead of mass of solids content. Both figures show similar differences between the potentials induced by the PCA-2 and the PCE-1, though the potentials of the saturated powders are smaller (in absolute value) on MgO than on  $\text{Mg(OH)}_2$ .

Fig. 5 indicates that the adsorption continues after the surface has acquired a negative charge. This might be because zeta potential is the potential measured at the shear plane and not the surface, or because of a non-electrostatic interaction involved in the adsorption process. However, the most probable explanation is a surface charge inhomogeneity on the particles. Hoogeveen et al (15) in their study of the adsorption of cationic polyelectrolytes on oxides ( $\text{TiO}_2$  and  $\text{SiO}_2$ ) found this the most likely explanation.

### **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, which corresponds to surface saturation of the solid phase. It is not the point of this paper to discuss the many existing adsorption models. However, it may be noted that a step function generally indicates an irreversible

process, while a less steep function can indicate a less favorable process (chemical equilibrium for the substance at surface and in the liquid, or kinetic limitation such as pore accessibility).

### General trends

With  $\text{Mg}(\text{OH})_2$  as the solid phase, all isotherms are similar. They have two distinct steps: an initial vertical rise (probably an irreversible process), followed by a gradual rise to saturation. An illustration of this is given in Fig. 6.

When  $\text{MgO}$  is the solid phase, isotherms of PCE-1 and PCA-2 are quite different. With PCA-2, isotherms show step functions, as in Fig. 7(a). With PCE-1 a larger dispersion of results is encountered and more data had to be collected. In this case, the isotherms can be described by a Langmuir functionality as shown in Fig. 7(b).

From fitted isotherms, it appears that the adsorption of PCE-1 on  $\text{MgO}$  increases with temperature, while all other adsorption isotherms do not show any significant temperature dependence (Fig. 8). This confirms results of a preliminary study (16). These temperature effects are discussed in more detail in the following section. The temperature dependent adsorption of the  $\text{MgO}$  is not believed to be linked to a modification of the polymer due to temperature because standards and calibration curves are not effected by temperature, no effect is seen with  $\text{Mg}(\text{OH})_2$  and the HPLC chromatograms of the filtered suspensions do not indicate a modification of the polymer.

### Temperature effect

Surface concentrations at saturation (plateau values) of all the isotherms have been calculated by averaging all experimental data considered as representative of the saturated powders. A linear regression was then performed, allowing the calculation, among other parameters, of the p-value of the temperature effect on surface concentrations at saturation (Annex 1). A p-value is a measure of the error made if the assertion that a given parameter (temperature) does not have an influence on a measurement (surface concentration of the polymer at saturation). The p-values considered as small enough to validate a hypothesis vary depending on the field of application. However, the most widely used is of 5%. With this criteria, values in Table 3 indicate that a temperature effect can only be accepted when PCE-1 is in an  $\text{MgO}$  suspension. This effect is found to be  $2.6\% \text{ } ^\circ\text{C}^{-1} \pm 0.5\% \text{ } ^\circ\text{C}^{-1}$  at  $25^\circ\text{C}$ . Fig. 8b shows this temperature dependence with the corresponding fitted isotherms. For the three other cases, values of the temperature effect at  $25^\circ\text{C}$  are also given. These however are only indicative of possible trends since this effect is rejected based on their high p-values (more precisely, the assertion that temperature does not effect adsorption can not be rejected). All errors given in Table 3 were calculated for 95% confidence intervals (Annex 1).

Fig. 9 and 10 show adsorption behavior (plateau concentrations) of polymers PCE-1 and PCA-2 as a function of temperature on  $\text{MgO}$  and  $\text{Mg}(\text{OH})_2$  respectively. Full lines give the predicted trends and dotted lines the 95% confidence intervals. Errors are larger with the hydroxide, mainly because less points could be used to calculate plateau value of the isotherms. More data was not acquired, because the effect of temperature did not appear to be significant.

### Temperature dependent adsorption

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.

Polymer PCE-1, similar to PCA-2, has less anionic groups due to insertion of PEG-ester fragments. If as in (15) adsorption is mainly influenced by electrostatic attraction, adsorption enthalpy ( $\Delta H_{\text{ads}}$ ) of PCE-1 should be smaller and than that of PCA-2. Because adsorption entropy ( $\Delta S_{\text{ads}}$ ) should be negative and both  $\Delta H_{\text{ads}}$  and  $\Delta S_{\text{ads}}$  should vary little with temperature, adsorption free energy ( $\Delta G_{\text{ads}}$ ) of PCE-1 may be more easily influenced by temperature ( $\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}$ ). This might lead to a conformation change of PCE-1 (less anchor points per polymer molecule), resulting in an increase of plateau concentrations.

The smaller  $\Delta H_{\text{ads}}$  of PCE-1 might also allow competitive adsorption of hydroxyl ions, making its adsorption dependent on solvent-surface interactions. In this case, a temperature rise would desorb hydroxyl ions, allowing a higher surface coverage by the PCE-1 molecules. Such a competition may not exist in  $\text{Mg}(\text{OH})_2$  suspensions, because pH (11.3 instead of 12), which corresponds to a concentration of hydroxyl ions lower by a factor of five.

Polymer-solvent interactions can also influence adsorption. For instance, water is known to desorb from hydroxypropylmethyl cellulose polymers (HPMC) (17). This should lead to adsorbed polymer molecules occupying smaller areas and in turn allowing higher plateau concentrations as temperature rises.

Water desorption from polymers due to temperature increase is believed (18) to explain why attraction between polyethylene oxide polymers (PEO) coated surfaces, increases with temperature over similar ranges (19). Claesson et al (19) observed that the surface occupied per polymer molecule decreased when temperature increased. At the same time they observed an increase in the thickness of the film. Since PEO polymers are similar to PCE-1, this observation would be compatible with the PCE-1 remaining on the surface but being linked by less anchor points. If the as with PEO, attraction between PCE-1 polymers increases with temperature, this might also lead to multiple layer adsorption.

The reason why adsorption plateau concentrations do not increase on  $\text{Mg}(\text{OH})_2$ , due to the above mentioned solvent-polymer and polymer-polymer interactions, might be due to the pH or different polymer-surface interactions. Porosity on the  $\text{Mg}(\text{OH})_2$  powder might also sterically prevent multiple layer adsorption

Finally, it should be noted that at higher temperatures, desorption would be expected. These experiments were not carried out because the polymers are not expected to be very stable at temperature greater than 50°C.

### **Links with zeta potential**

Zeta potential changes induced by adding polymers can be compared with the adsorption of these polymers by plotting both measurements as a function of the total amount of polymer added. However, because the liquid to solid ratios used in both measurements are not equal, data cannot be correlated directly unless as for PCA-2 on MgO, polymers added adsorb until saturation is reached. This corresponds to a vertical rise in the adsorption isotherms. With  $\text{Mg}(\text{OH})_2$ , this behavior is observed at first. The isotherms then become incurved, as for PCE-1 on MgO. In these situations, an equilibrium between the adsorbed polymers and polymers in solution may be expected and the ratio between their concentrations should not be greatly influenced by changing the solid to liquid ratio. If the suspension is less concentrated as for zeta potential measurements, more polymer has to be added to achieve the same amount of adsorbed polymer.



Fig. 11 shows zeta potential and adsorption in MgO suspensions for PCA-2 and PCE-1. A similar comparison for Mg(OH)<sub>2</sub> suspensions is given in Fig. 12. For MgO, it is assumed that all the polymer is adsorbed until the plateau value is reached. Vertical dotted lines show the point where adsorption reaches 95% of the plateau. A fairly good correlation is seen between the adsorption and zeta potential plateaux. For Mg(OH)<sub>2</sub>, the initial part of the plot is similar to those obtained with MgO corresponding to the vertical segment on the original isotherms. It is followed by a more gradual rise. A first vertical line shows the end of the first segment, while the second corresponds to 95% of plateau value. Between both amounts of added polymer, the zeta potential varies very little. This could indicate that after this step, the additional polymers are adsorbed in difficultly accessible pores, which would not effect zeta potential (20). Preliminary measurements indicate a non negligible amount of pores smaller than 10 nm in diameter.

### **Surface coverage**

In Table 3, adsorption concentration is used to calculate the surface area occupied by a molecule. The radius of spheres from a compact monolayer is also given. Because, as discussed above, the extent of adsorption on Mg(OH)<sub>2</sub> might be influenced by porosity, it is wiser only to consider values obtained with MgO. The radius of the PCA-2 is about 2.5 nm and PCE-1 2.2 nm. The thickness of the adsorbed layer can therefore be estimated to be between 4 and 6 nm. This result is interesting to estimate steric interactions. When calculating the errors on these radii, errors of molecular mass and surface area were considered. They were not considered previously because this would have led to an incorrect interpretation of the effect of temperature on adsorption.

## **CONCLUSION**

Electrostatic Repulsion (ER), one of the mechanisms commonly put forward when discussing the superplasticizing effect, is linked to zeta potential. In model suspensions dispersed with highly ionic polymers such as Sulfonated Naphthalene-Formaldehyde-Polycondensates (SFNC) and Polycarboxylic Acid Polymers (PCA), zeta potential was found to be independent of the polymer type. Lower zeta potentials were observed with Polycarboxylic Ester-polymers (PCE), which contain Poly Ethylene Glycol-ester (PEG-ester) fragments as a charge spacer. The amounts of PCE-1 adsorbed were larger than those of PCA-2, but this difference is not sufficient to induce a larger zeta potential (in absolute value). Zeta potential remains mainly influenced by the concentration of ionic groups in the polymer. Therefore the contribution of ER to the superplasticizing effect is expected to be similar for all the highly ionic polymers since they all induce a similar zeta potential. In the dispersion of suspensions containing PCE-type superplasticizers the relative importance of other effects (steric, entropic or capillary) is expected to be greater.

The effect of temperature on the adsorption of two anionic superplasticizers, PCA-2 and PCE-1, was studied. These two polymers have similar structures, but the PCE-1 contains PEG-ester groups which act as charge spacers.

It was observed that on MgO, at pH was 12, PCE-1 adsorption plateau concentrations increase significantly with temperature. With PCA-2 and MgO, no effect was seen. With Mg(OH)<sub>2</sub>, where pH was 11.3, no effect was seen with either polymer. The reasons for these behaviors are believed to be linked to polymer-surface, solvent-polymer, polymer-polymer or polymer-solvent

interactions. In particular, it appears that electrostatic interaction between these polymers and MgO might be an important factor in determining their adsorption properties. When studying adsorption on model powders this aspect must not be overlooked, particularly at elevated pH values as those found in cement suspensions. The model powders studied therefore offer promising perspectives for studying mechanisms of superplasticization in highly alkaline suspensions.

The mechanism by which adsorption changes with temperature and how this may affect dispersion has not yet been established. However, this could have some major practical implications for the use of such superplasticizers.

This study has provided fundamental information concerning behavior of highly alkaline model suspensions. It will help to orient and interpret data from the rheological studies, which are planned in the near future, to understand which mechanisms are involved in the dispersion of cement: which are the most effective ones, why, and which factors might influence them. Calorimetric measurements might also provide valuable information concerning the heat of adsorption of these polymers onto the model surfaces chosen. Such knowledge will be as important in understanding cement and superplasticizer incompatibilities as well as in the design and production of new and even more efficient superplasticizers.

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**Annexe 1: Statistical treatment of data**

The effect of temperature T on the amount of adsorbed polymer y, was evaluated for each combination of polymer and powder using a linear regression. At each temperature T, n<sub>T</sub> measurements of were performed, giving an average y<sub>T</sub> and an uncertainty σ(y<sub>T</sub>), the standard deviation of y at temperature i. All values of T are known exactly. The slope b and its variance var(b), the ordinate a and its variance var(a), as well as the covariance of slope and the ordinate cov(a,b) can be calculated by well established methods (20).

The standard deviation σ(μ<sub>T</sub>) for the prediction μ<sub>T</sub>, of the expectation y<sub>T</sub>, is given by:

$$\sigma(\mu_T) = \sqrt{\text{var}(\mu_T)} = \sqrt{\text{var}(b T + a)} = \sqrt{\text{var}(a) + T^2 \text{var}(b) + T \text{cov}(a, b)}$$

Because at each temperature a finite number of measurements are used to calculate σ<sub>T</sub>, these values are approximations. This is taken into account by correcting when calculating the confidence intervals Δy<sub>T</sub> on a prediction μ<sub>T</sub>. Bilateral Student factors are used instead of a the normal law. The number of degree of freedom is the total number of measurements minus two (number of parameters estimated in the regression) minus the number of temperatures studied (number of σ(μ<sub>T</sub>) estimated). Confidence intervals of 95% were systematically used. The p-value of the temperature effect is obtained with a unilateral Student law, the ratio σ(b)/b and the same number of degree of freedom given above.

The relative importance of temperature was reported as ratio of the slope obtained by the linear regression to the predicted amount of adsorbed polymer for a temperature of 25°C. When calculating the error associated with this ratio, we must take into account the fact that these parameters are not independent of each other. The error for such a ratio is given by (22):

$$\sigma\left(\frac{b}{\mu_{25^\circ C}}\right) = \sqrt{\text{var}\left(\frac{b}{\mu_{25^\circ C}}\right)} = \frac{b}{\mu_{25^\circ C}} \sqrt{\frac{\text{var}(b)}{b^2} + \frac{\text{var}(\mu_{25^\circ C})}{\mu_{25^\circ C}^2} - \frac{2 \text{cov}(b, \mu_{25^\circ C})}{b \mu_{25^\circ C}}}$$

Where:

$$\text{cov}(b, \mu_T) = \text{cov}(b, a + b T) = \text{cov}(a, b) + T \text{cov}(b, b) = \text{cov}(a, b) + T \text{var}(b)$$

Table 1 - Powder characteristics.

	Mg(OH) <sub>2</sub>	MgO
Specific Surface Area	11.8 ± 0.5 m <sup>2</sup> g <sup>-1</sup>	0.77 ± 0.03 m <sup>2</sup> g <sup>-1</sup>
Median Volume Diameter	10.5 ± 0.5 μm	15.0 ± 0.5 μm

Table 2 - Characteristics of the polymers used.

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

<sup>≠</sup> Mass Average Molar Mass

\* Number Average Molar Mass

Table 3 - Effect of temperature on adsorption.

Powder Polymer	MgO		Mg(OH) <sub>2</sub>	
	PCE-1	PCA-2	PCE-1	PCA-2
Temperatures [°C]	11, 18, 25, 32, 40	18, 25, 32, 40	25, 32, 40	25, 32, 40
Quantile of temperature effect [%]	100	69	93	89
Slope [nmol/m <sup>2</sup> /°C]	2.6 ± 1.1	-0.1 ± 0.4	0.4 ± 0.9	0.5 ± 1.2
Adsorption at 25°C [nmol/m <sup>2</sup> ]	99 ± 7	75 ± 3	75 ± 1	51 ± 6
Surface per polymer molecule [nm <sup>2</sup> ]	17 ± 5	22 ± 6	22 ± 5	33 ± 1
Polymer radius on powder surface [nm]	2.2 ± 0.3	2.5 ± 0.3	2.5 ± 0.3	3.1 ± 0.5
<b>Temperature Effect [%]</b>	<b>2.6 ± 0.5</b>	<b>-0.1 ± 0.4</b>	<b>0.4 ± 0.2</b>	<b>0.9 ± 0.6</b>

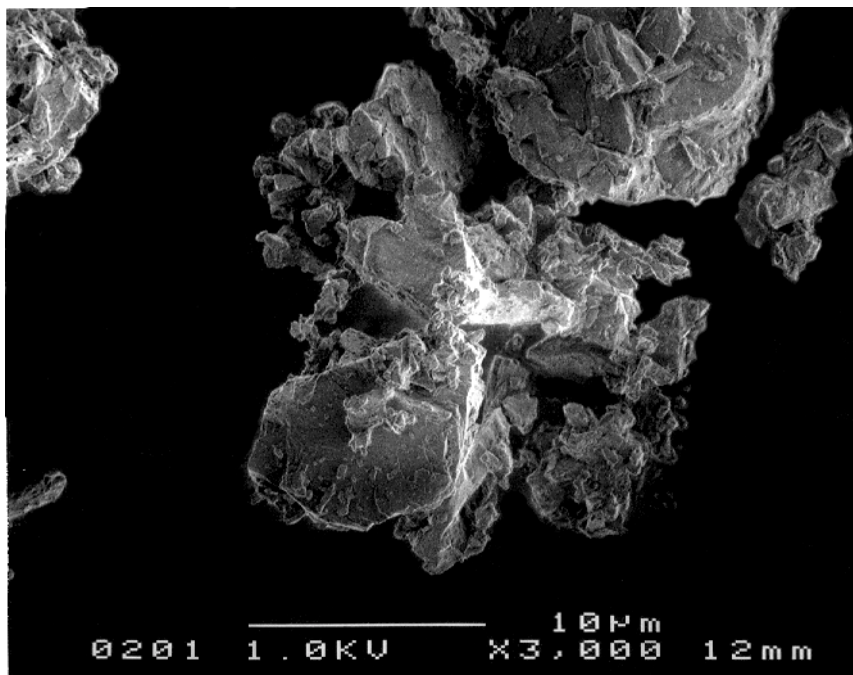


Fig. 1 - SEM picture of MgO.

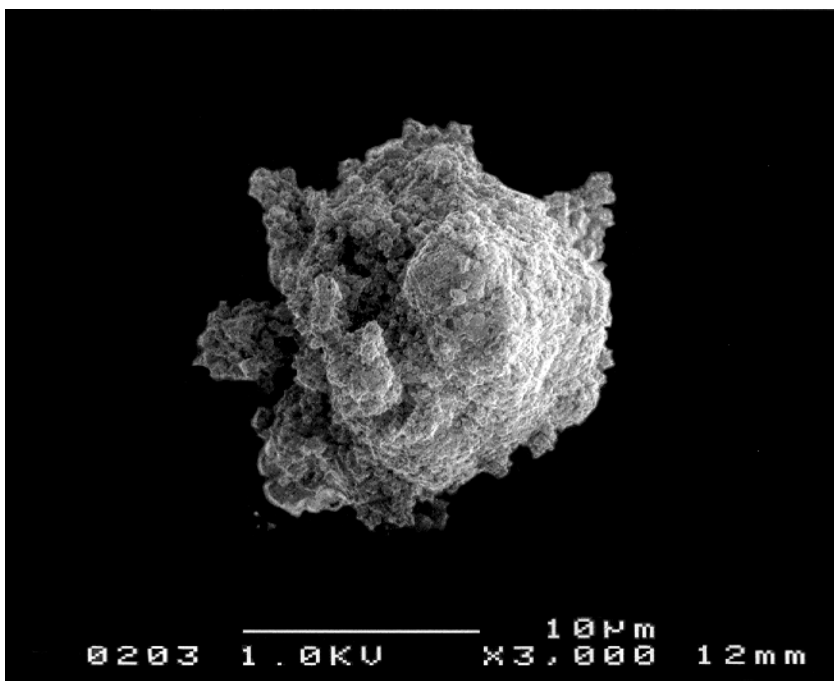


Fig. 2 - SEM picture of Mg(OH)<sub>2</sub>.

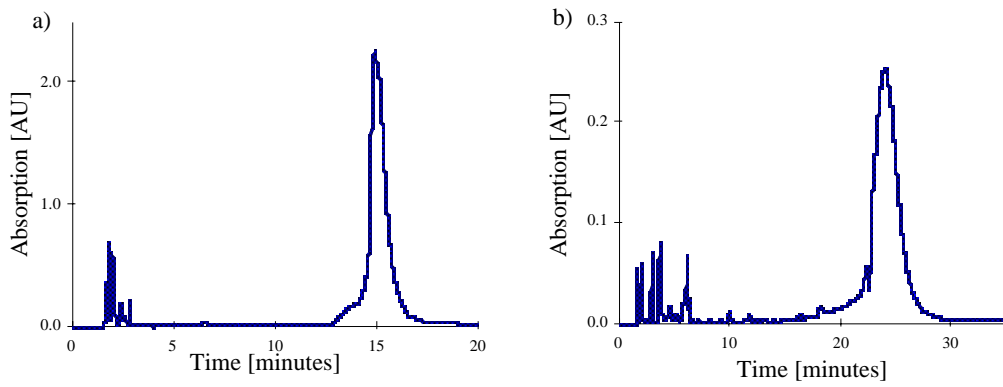


Fig. 3 - Example of an HPLC chromatograms. a) PCA-2. b) PCE-1.

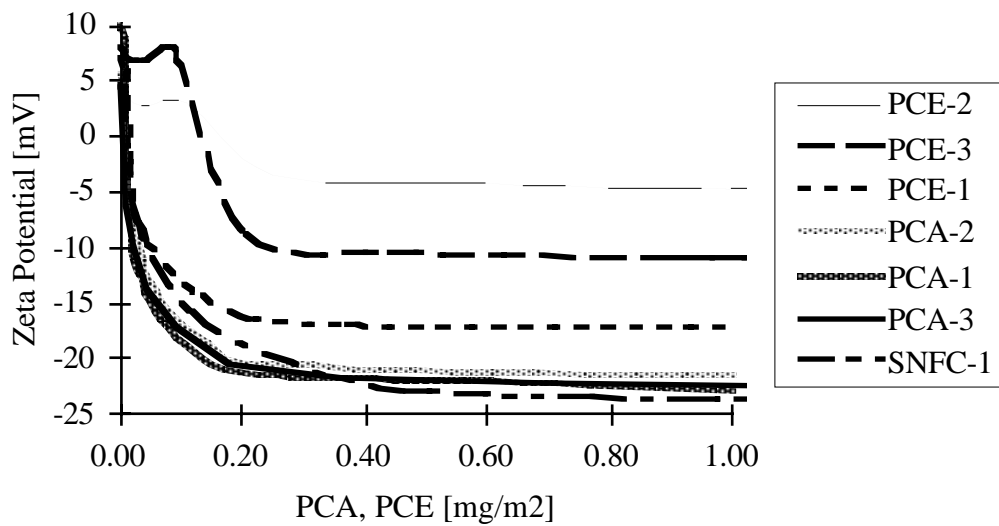


Fig. 4 - Zeta potential of magnesium hydroxide suspensions plotted as a function of the added mass of superplasticizers.

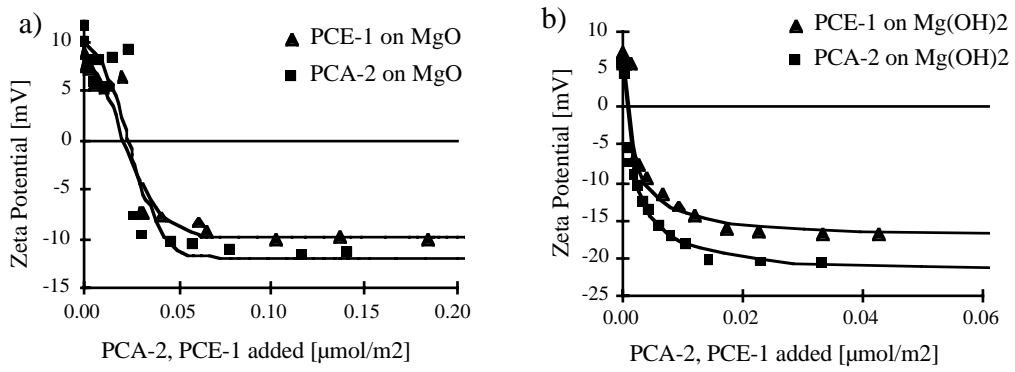


Fig. 5 - Zeta potential measured of PCE-1 and PCA-2. a) with MgO. b) with  $\text{Mg}(\text{OH})_2$ . Fitted curves are S-functions for MgO and hyperbolas for  $\text{Mg}(\text{OH})_2$ .

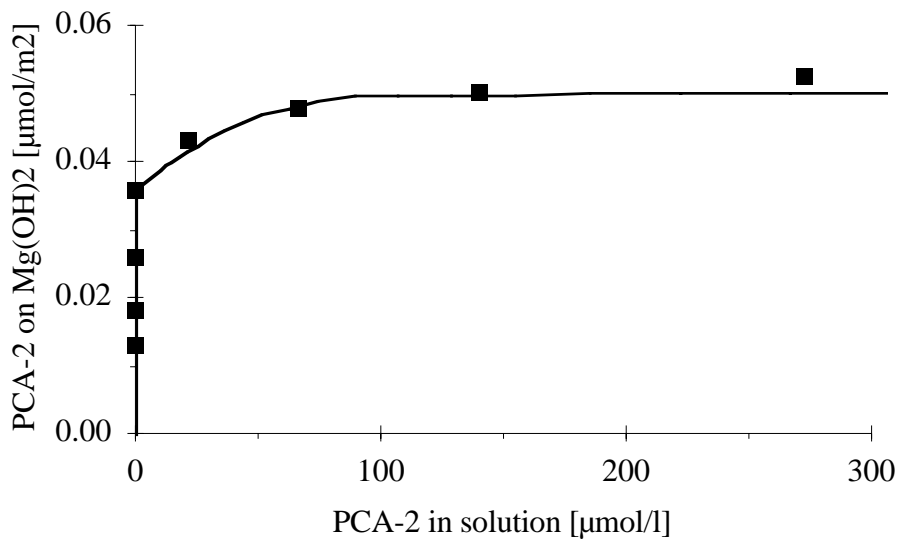


Fig. 6 - Adsorption isotherms of PCA-2 on  $\text{Mg}(\text{OH})_2$  at 25°C. The fitted curve has no particular functionality.



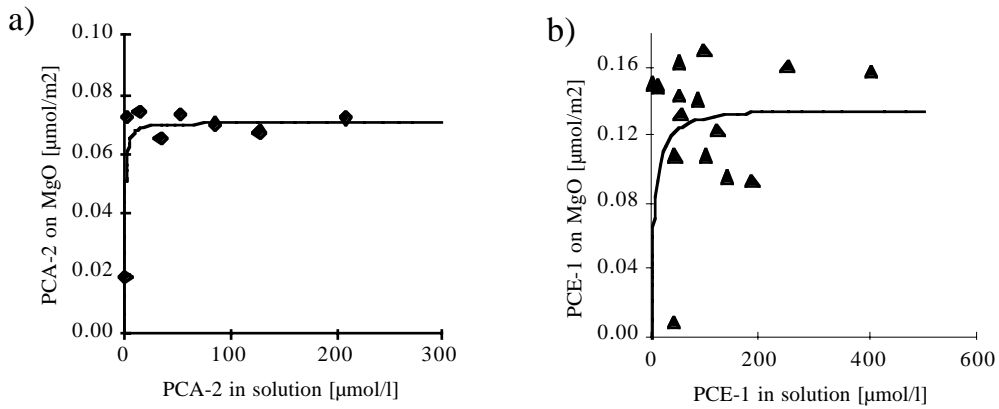


Fig. 7 Adsorption Isotherm on MgO. a) PCA-2 at 32°C. b) PCE-1 at 40°C.

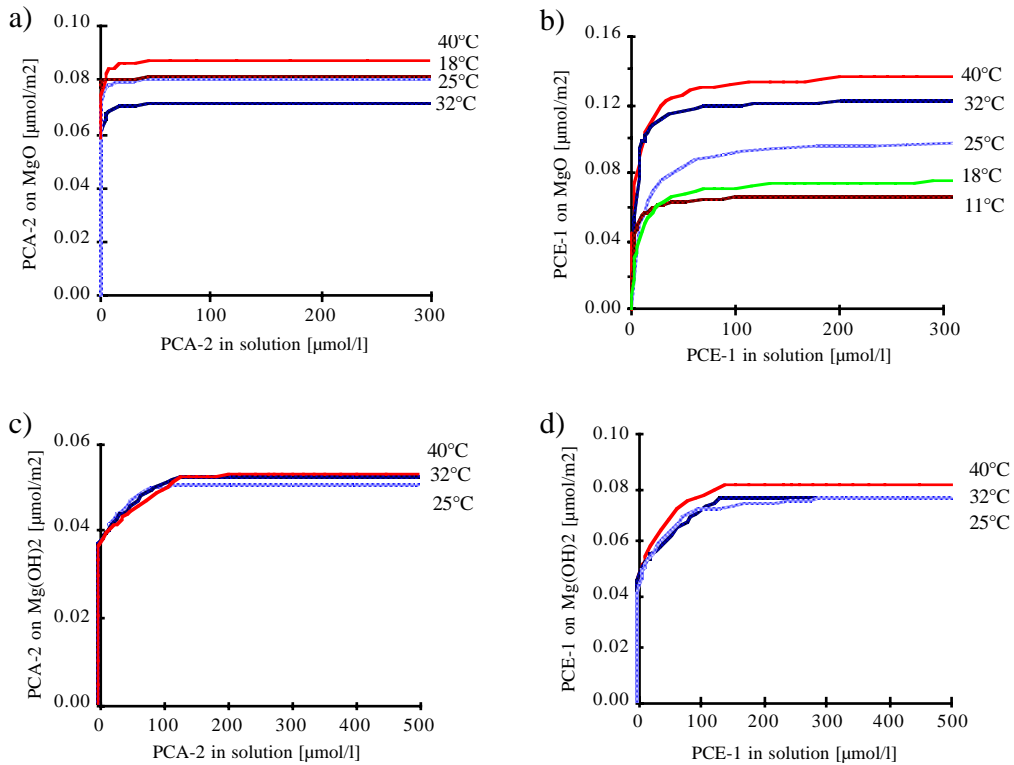


Fig. 8 - Fitted adsorption isotherm curves. a) PCA-2 with MgO. b) PCE-1 with MgO. c) PCA-2 with  $\text{Mg}(\text{OH})_2$ . d) PCE-1 with  $\text{Mg}(\text{OH})_2$ . Only PCE-1 with MgO shows a temperature dependence.

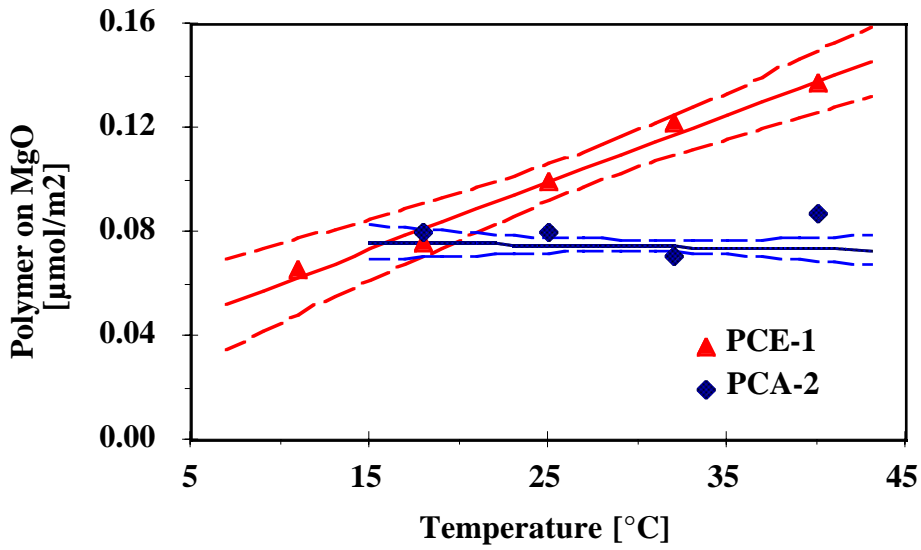


Fig. 9 Temperature effect on the adsorption of PCA-2 and PCE-1 on MgO. The full straight lines are obtained by a linear regression and the dotted lines show the 95% confidence interval.

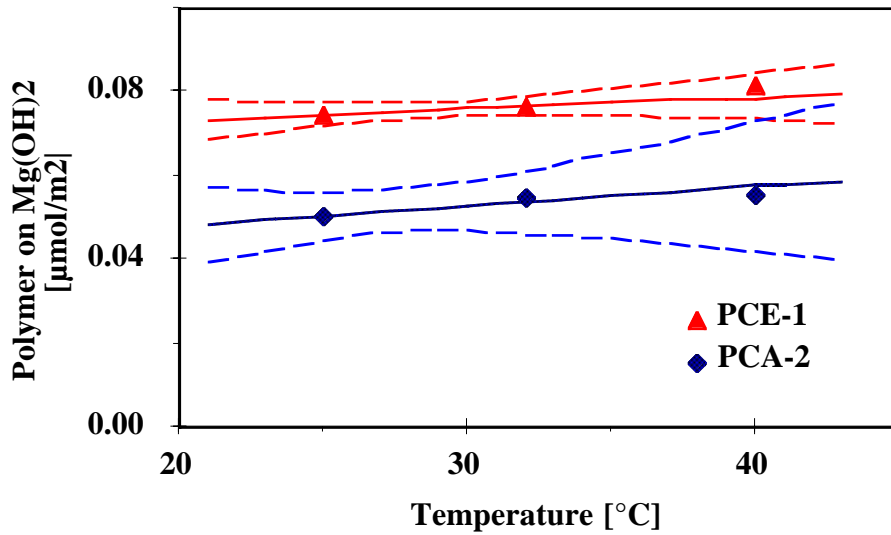


Fig. 10 - Temperature effect on the adsorption of PCA-2 and PCE-1 on Mg(OH)<sub>2</sub>. The full straight lines are obtained by a linear regression and the dotted lines show the 95% confidence interval.

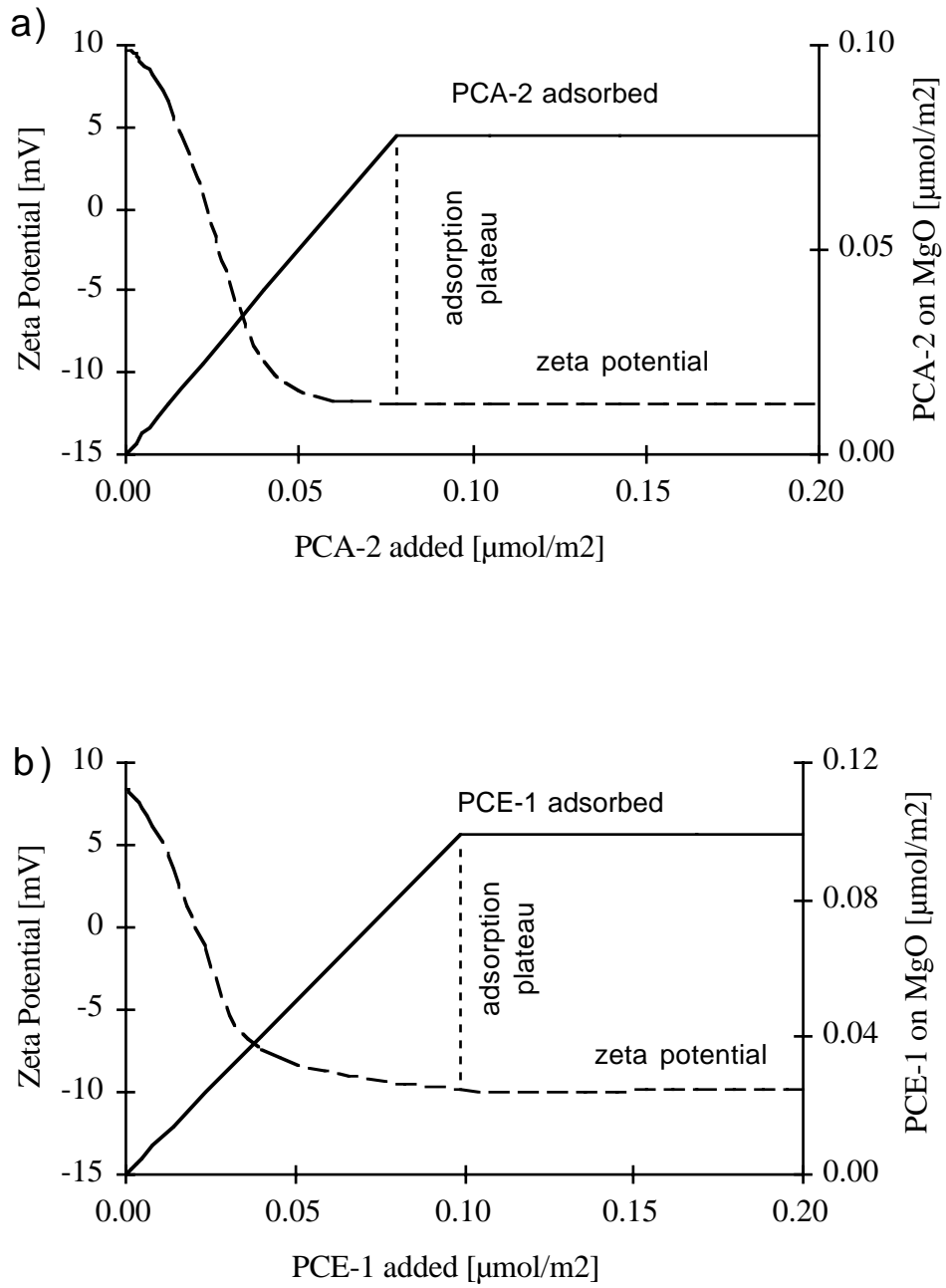


Fig. 11 - Adsorption and zeta potential curves. a) PCA-2 with MgO. b) PCE-1 with MgO.

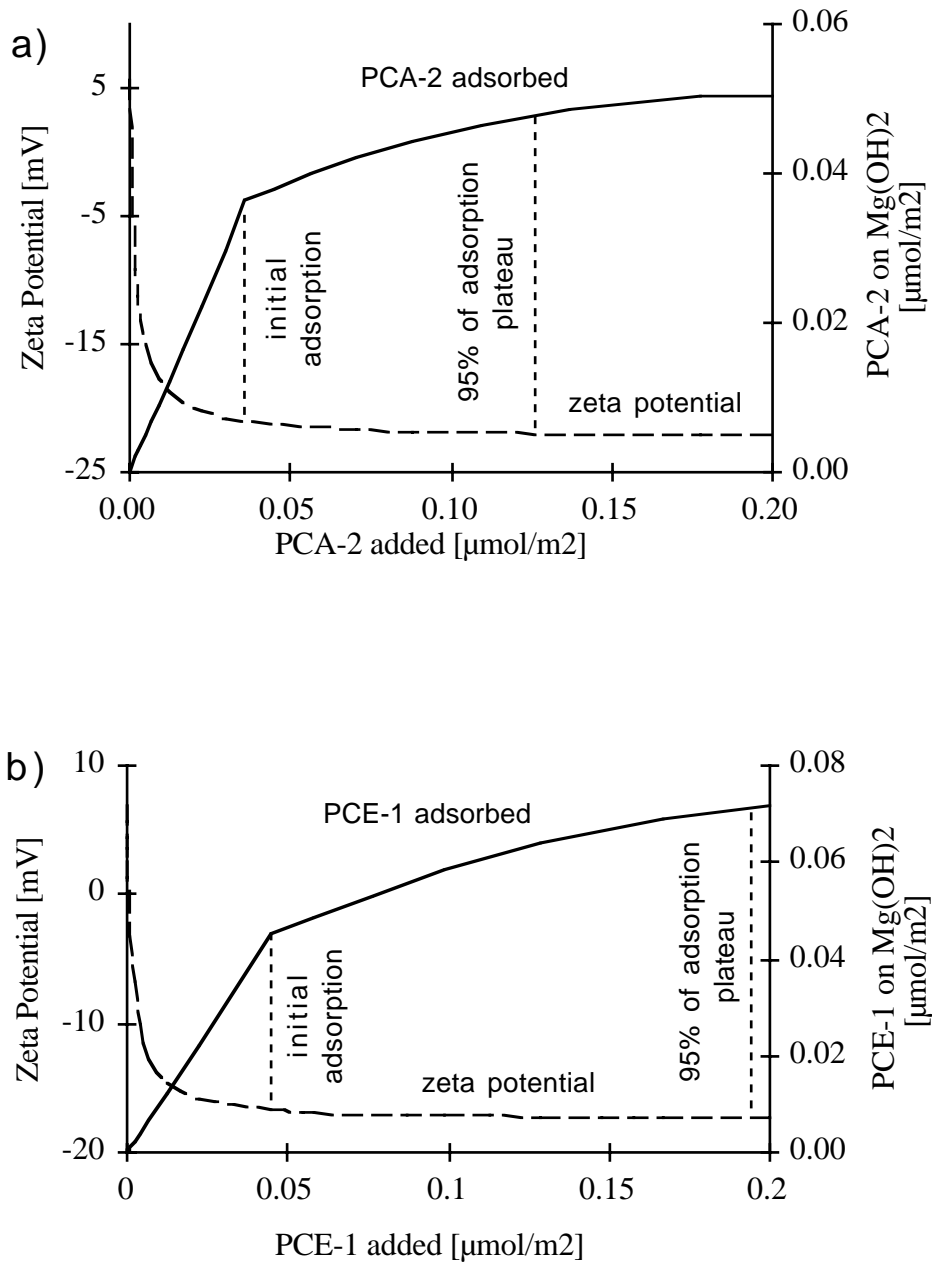


Fig. 12 - Adsorption and zeta potential curves. a) PCA-2 with Mg(OH)<sub>2</sub>. b) PCE-1 with Mg(OH)<sub>2</sub>.