

## ADSORPTION OF LIGNOSULFONATES AND POLYCARBOXYLATES DEPLETION AND ELECTROACOUSTIC METHODS

F. Perche, Y.F. Houst, P. Bowen, H. Hofmann

Swiss Federal Institute of Technology (EPFL), Powder Technology Laboratory (LTP),  
1015 LAUSANNE, Switzerland

### Synopsis

The adsorption of superplasticizers onto cement particles is a key factor in the rheology of cement and concrete. The adsorbed amount is generally measured as the difference between the amount of polymer present in the aqueous phase before and after contact with cement (depletion method).

Adsorption isotherms of well characterized lignosulfonate and polycarboxylate admixtures have been measured on a model powder (MgO) using the depletion method and on an ultrafine cement by using an electroacoustic method. This method allowed us to follow the variation of zeta potential of the same suspensions as a function of increasing amounts of superplasticizers.

It was found that the influence of the adsorption of superplasticizers on zeta potential measured by electroacoustic technique are significantly lower than those measured earlier with preceding instruments. These differences are due in part to the models used for the zeta potential computation. Apart from improvements in the instrumentation, errors were due to the particle size distribution of cement particles not fully sampled by electroacoustic techniques.

It is shown that the electroacoustic method is also both useful and complementary for studying the adsorption of superplasticizers. It measures zeta potential values necessary for interparticle force calculations. Differences in polymer structures and the effect of different ions on polymer adsorption can be observed.

**Keywords:** Adsorption, Electroacoustic characterization, Lignosulfonates, Model Powder, Polycarboxylates, Superplasticizer.

## INTRODUCTION

This article presents results from the research project *Superplast (5<sup>th</sup> European Framework Programme)*. An overview of the first results is given in (1). The elucidation of superplasticizer structure-function relationships is one of the aims of the project. Contrary to many other research projects, modified lignosulfonates (LS) and tailored polycarboxylate polymers (PCP) have been especially prepared to help elucidate their behavior. They vary in molar mass, number of ionisable groups and for the polycarboxylates, length of the backbone and of the side chains. All polymers have been thoroughly characterized by techniques like gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) of <sup>1</sup>H and <sup>13</sup>C, and chemical analysis.

The adsorption of superplasticizers is a key factor for the production of low water content concrete. The computation of interparticle forces to predict and help the evaluation of rheological properties (2-3) is another aim of the project and the amount and the conformation of the adsorbed superplasticizer a key point. The interaction forces are being measured by atomic force microscopy (AFM) by another participant in the project. We used two different techniques to follow the adsorption: the depletion method and the electroacoustic technique. Both allow us to evaluate the amount of adsorbed superplasticizer. Electroacoustics provide us furthermore with the zeta potential value as a function of the adsorbed amount.

Measurements were made on a model inert powder (MgO) to simplify interpretation and ensure the whole particle size distribution was taken into account during the electroacoustic measurements.

## MODEL SUSPENSIONS

The advantages of using a model powder for cement in studying the interactions with superplasticizers have already been presented several times (3-6). Consequently, we only discuss this topic briefly below.

Cement suspensions have an inherent complexity which is an obstacle to understanding cement/superplasticizer interactions. Indeed, cements are reactive multimineral powders, the surfaces of which evolve in time. Mineralogical and chemical compositions of the different particle size fractions can be different. Certain cements also contain mineral additions, like silica fume, fly ash, slag or filler. Organic grinding aids are generally used in the production route and remain on cement grain surfaces. Cements also have variable C<sub>3</sub>A contents, the reactivity of which can also vary. The importance of the C<sub>3</sub>A reactivity on the rheology of cement slurries is well known (7). 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 (7).

Superplasticizers are anionic polyelectrolyte polymers with generally carboxylate and/or sulfonate groups. The pH of the aqueous phase of cement suspensions being between 12.5 and 13.5, the acidic functions are essentially dissociated. The conformation of these polymers is influenced by the pH and the ionic composition of the pore solution, and this point should be taken into consideration when trying to understand their performance.

Dispersion of agglomerated cement particles is known to be the main way by which superplasticizers improve the workability of concrete. The fluidifying effect of superplasticizers is essentially linked to their adsorption onto cement surfaces. A major factor

is to ensure that the polymer adsorbs onto the particles and has a configuration which maximizes its capacity to disperse agglomerated particles.

During cement hydration, a part of the superplasticizer can be consumed by the formation of organo-mineral phases (8). This part will no longer be able to contribute to the dispersion of cement particles, and can thus give a false indication of the inherent dispersion power of the polymer.

Another characteristic of cement suspensions important for the SP adsorption is that the electrostatic surface potential of the particles is very close to zero at high pH. Getting exact values of surface potentials near the isoelectric point (pH of zero zeta potential) is a difficult task and both slightly positive or negative  $\zeta$  potentials can be found in the literature (9-11). For what we are concerned with, however, it suffices to state that cement suspensions are very close to their isoelectric point and have a very small surface charge even though they are in a highly alkaline suspension.

MgO has an isoelectric point of 12.4 (12). Moreover, it is chemically similar to CaO, which probably dominates the surface composition of the main cement particles ( $C_3A$ ,  $C_3S$  and  $C_2S$ ) leading the positive zeta potential of cement (8,13). MgO fulfils the two main conditions to be representative for cement suspensions: a low surface charge and a relative inertness at high pH. The basic solution in contact with the powder near its isoelectric point has a very low ion content due to the very low solubility of MgO and  $Mg(OH)_2$  in highly alkaline medium. So, it is possible to add specific ions to study their influence on the SP adsorption and the resulting zeta potential.

## EXPERIMENTAL

### Powders

The selected dead burnt MgO was from Martin Marietta Magnesia Specialties Inc. (type MagChem P-98, Baltimore, U.S.A.). Part of this MgO was air classified to obtain a powder with particles finer than 10  $\mu m$ . This fraction called MgO P98-C was necessary for electroacoustic measurements described below.

The particle size distributions were determined by laser diffraction (Malvern Mastersizer, Malvern, G.B.). The BET specific surface areas were determined by adsorption of  $N_2$  (Micromeritics Gemini III 2375; Norcross, U.S.A.). No impurities were detected in the XRD spectrum, MagChem P98 contains only the periclase phase. Its isoelectric point measured by acoustophoresis is 12.45. The powder characteristics are given in Table 1. The particle size distributions of both MgO powders are given in Fig. 1.

The reactivity of this *low reactivity* magnesium oxide was carefully studied by following the formation of hydroxide as a function of contact time in NaOH 0.01M solution by surface area measurements and thermogravimetric analysis (TGA) on filtered and dried powders. The MgO powders were unfortunately not as inert as expected. However, MagChem P98 and its finer fraction MgO P98-C have a specific surface area which can be considered as constant between 30 and 90 minutes contact with a 0.01M NaOH solution, found to be 2.7 and 7.6  $m^2/g$  respectively. More detailed results are given in (6).

### Polymers

Two kinds of very different polymers have been used in this study. They are all laboratory test products. Four Na-polycarboxylate with PEO side chain polymers, called PCP-1, PCP-2, PCP-3 and PCP-4, were produced by Sika A.G. (Zurich, Switzerland). They were provided as

concentrated solutions, with a solid content of about 30-40% by mass. The other polymers are Na-lignosulfonates LS-1, LS-2, LS-4 or Ca-lignosulfonate (LS-3) polymers prepared by Borregaard Lignotech (Sarpsborg, Norway). These polymers are available as solid powders. The main properties of all studied superplasticizers are listed in Tables 2 and 4. More details on these polymers are given in two contributions to this conference (14,15).

### **Depletion method**

Adsorption measurements were performed in suspensions of 10 g of MgO in 18 ml of NaOH 0.011M, previously thermostated in a rotary bath at 200 rpm at 25°C. The suspensions were kept in closed polyethylene flasks to avoid water loss by evaporation. After 30 minutes of mixing, 2 ml of superplasticizer solution is added with a micropipette. The pH of the suspensions is  $12.0 \pm 0.1$  at 25°C. The suspensions are then kept for another 30 minutes in the rotary bath.

At the end of agitation time, the suspensions were centrifuged 5 min at 3'000 rpm, in a thermostatable centrifuge (Jouan, model CR-412; St-Nazaire, France) regulated at the same temperature as the adsorption experiments were carried out. From the supernatant solution, 5 ml, buffered with 30  $\mu$ L of acetic acid (20 mass-%), were filtered through a 0.45  $\mu$ m filter mounted on a dispensable syringe. The first 2 ml were discarded and the rest was analyzed. The calibration standards, apart from containing no powder and not being centrifuged, were treated in the same way.

Lignosulfonate solutions were analyzed by UV spectrometry (Perkin Elmer, mod. Lambda 900; Norwalk, Connecticut, U.S.A.). Polycarboxylate solutions were analyzed by reverse phase chromatography with a high performance liquid chromatograph (Waters, mod. Alliance; Milford, U.S.A.) equipped with a light-scattering detector (Polymer Laboratories, mod. PL-ELS 1000; Amherst, U.S.A.).

### **Electroacoustic Method**

The variation of zeta potential was measured at room temperature (around 25°C) by an apparatus from Colloidal dynamics (model Acoustosizer II; Sydney, Australia). The electroacoustic measurements can be used for determining particle size and zeta potential from the dynamic mobility (16). Electroacoustic measurements allow us to study the adsorption of polymers (17). The characterization of cement suspensions by acoustophoresis has been recently discussed in the literature (18). Only particles below about 10  $\mu$ m give a signal with this instrument. So, the use of MgO P98-C was preferred.

The standard titration method proposed by the manufacturer was used. The suspensions were prepared by dispersing 53 g of powder in 200 ml NaOH 0.01M (pH  $12.0 \pm 0.1$  at 25°C, volume fraction: 6.9 %) under vigorous agitation and ultrasonic treatment for 15 minutes. The suspension is then allowed to cool down to 25°C for another 15 minutes under magnetic agitation. Once the suspension is loaded into the sample reservoir and pumped up through the measurement cell. Polymer solution is then added by increments as aqueous solutions with a microburette. Between two additions, the suspension is allowed to equilibrate for 3 minutes. Zeta potential is calculated using Smoluchowsky's model (19). This model considers that the measured zeta potential is independent of the particle size and shape (all particles are considered as hard spheres).

## RESULTS AND DISCUSSION

### Adsorption onto MgO powders in NaOH (0.01M)

The adsorption isotherms obtained by the depletion method for polycarboxylates and lignosulfonates are given in Figs. 2a) and 2b) respectively. The figures represent the averaged results obtained from two different adsorption measurements for each polymer. Although the Langmuir adsorption model is not applicable for polymer adsorption, all curves are fitted using a Langmuir equation to estimate the adsorption plateau and they present a similar shape: an increase of the polymer adsorbed amount to a plateau value in a very short range of bulk solution concentration.

Electroacoustic measurements were performed on MgO P98-C for all superplasticizers. The influence that polycarboxylates and lignosulfonates have on zeta potential is shown in Figs. 3a) and 3b) respectively.

The adsorption isotherms (Fig. 2a) for the polycarboxylate superplasticizers allowed us to calculate the plateau value given in Table 2. Considering that all acid groups are ionized at pH=12, the quantity of adsorbed dissociated (charged) groups were calculated from the amount of carboxylate groups per molecule, depletion results and the polymer structure.

Except for PCP-3, adsorbed amount increases to a plateau value which varies as a function of studied polymer. For PCP-1, PCP-2 and PCP-4, all isotherms are similar. For PCP-3 at a concentration higher than 4 mg/g, the adsorbed PCP-3 amount seems to increase linearly with the PCP-3 concentration in the supernatant. These results suggest a precipitation of the polymer on the MgO particles or some micellization process which may lead to the removal of the micelles by filtration.

PCP can be classified according to the mean adsorbed polymer amounts at the plateau (except for PCP-3), in decreasing order:

$$\text{PCP-2 (1.51 mg/g)} > \text{PCP-1 (1.26 mg/g)} > \text{PCP-4 (1.16 mg/g)}.$$

PCPs adsorption is assumed to take place through electrostatic interactions between the negative charges of the methacrylate groups of the backbone and the positively charges at the surface of the MgO particles, whereas the non-adsorbing polyethylene oxide grafts dangle in the aqueous environment. Lafuma *et al.* (LPCM, CNRS, Paris, France) have determined that adsorbed PCPs have a brushlike conformation (Fig. 5). The polymethacrylate interfacial conformation is probably somewhat loopy due to screening effects.

To determine which structural parameter influences the polymer adsorption on the model powder, the number of adsorbed molecules necessary to cover all the surface of the MgO particle ( $N_{\max}$ ) has been estimated and compared with the number of adsorbed PCP molecules obtained from depletion measurements ( $N_{\text{exp}}$ ).

At high pH, all carboxylate groups are supposed to be dissociated and repulsion between ionic groups is maximal. So, the polymeric chain expands linearly to minimize the electrostatic repulsion. Moreover, the polymer molecule is assumed to adsorb via the backbone on the MgO particle. The surface occupied by a PCP molecule ( $s$ ) is considered to be a rectangle which dimensions corresponds to the PCP stretched backbone. Assuming that MagChem P98 has a specific surface area of 2.74 m<sup>2</sup>/g after 60 min contact with a 0.01M NaOH solution, the number of adsorbed molecules necessary to cover all the surface of the MgO particle ( $N_{\max}$ ) can be estimated. The fractional coverage of the MgO surface ( $R$ ) can be calculated using Eq. 1:

$$R = \frac{N_{\text{exp}}}{N_{\text{max}}} \quad (1)$$

Results are given in the Table 3.

The number of polymer molecules adsorbed was compared with superplasticizer structures (Table 2 and Fig. 4) to determine which structural parameter influences their adsorption on the model powder:

- PCP-1 and PCP-2 have similar side chain length but different backbone chain lengths. In analyzing depletion results, PCP-2 has a lower adsorbed amount on MagChem P98. The number of PCP molecules adsorbed is function of the backbone length of the polycarboxylate.
- In analyzing PCP-1 results, only 75 % of the particle surface seems to be covered. PCP-1 has side chains of small length (about 1000 g/mol); their steric effect could be considered as weak and should not influence the polymer adsorption in an important way. So, this covering rate could indicate that PCP molecules adsorb in a disordered way, leaving sockets of free surface too small to be occupied by a polymer molecule. This hypothesis seems to be confirmed with PCP-2. PCP-2 has a longer backbone length than PCP-1 and the fractional coverage (R) is smaller than PCP-1.
- PCP-1 and PCP-4 have similar backbone length, but PCP-4 has a longer side chain length (about 5 times longer than PCP-1). From depletion results, only 25 % of particle surface seems to be covered (around 3 times less than PCP-1). The steric effect of the longer PEO chains seems to significantly limit the PCP-4 adsorption. This may be a positive effect whereby increasing polymer side chain length, less adsorbed polymer is necessary to disperse MgO suspensions.

In conclusion, PCP adsorption is influenced by both the side chain and backbone lengths of the polymer and PCP seems to adsorb in a disordered way.

From PCP electroacoustic results (Fig. 3a), polycarboxylate polymers can be classified according to the mean potential value at the plateau, in decreasing order:

$$\text{PCP-1} (-8.2 \text{ mV}) > \text{PCP-2} (-6.7 \text{ mV}) > \text{PCP-3} (-5 \text{ mV}) > \text{PCP-4} (-2.4 \text{ mV})$$

Zeta potential is a function of the surface charge of the particles. At pH=12, MagChem P98 has a positive surface charge and most of PCP's acid groups are ionized. PCP-1 presents the highest zeta potential magnitude at the plateau. Having a similar structure but a longer backbone length, PCP-2 shows slightly a lower zeta potential magnitude. As the polymer backbone length influences the adsorption less PCP-2 molecules are adsorbed (4 times less). Even though the backbone is longer, the number of ionic groups by unit length is slightly lower. This explains the slightly lower magnitude of the zeta potential of PCP-2.

PCP-1 and PCP-3 have similar backbone but the second one has a side chains which are about 2 times longer than PCP-1. By comparing their electroacoustic results, zeta potential magnitude decreases with side chain length. This tendency is confirmed by PCP-4 results. However, zeta potential is calculated using Smoluchowsky's model (19). This model considers particles as hard spheres and ionic mobility does not influence zeta potential. In increasing side chain length, the adsorbed layer increases and adsorbed polymeric molecules may interfere with the flow of fluid across the particle surface and even push the shear plane, where the zeta potential is measured, out from the particle surface (20). So, Smoluchowsky's model might be not well adapted to PCPs having long side chains. So, zeta potential measurements for PCP-3 and PCP-4 may not be directly comparable.

Electroacoustic measurements are influenced by the side chain length and by the backbone length, but they neither give information about the adsorbed amount or about parameters which could influence the adsorption of the polymer, e.g. molar mass.

The adsorption isotherms (Fig. 2b) for the lignosulfonate superplasticizers allowed us to calculate the plateau value given in Table 4.

From depletion results, LS superplasticizers can be classified according to the mean adsorbed polymer amounts at the plateau, in decreasing order:

$$\text{LS-3 (3.31 mg/g)} > \text{LS-2 (2.79 mg/g)} > \text{LS-4 (2.57 mg/g)} > \text{LS-1 (1.15 mg/g)}$$

LS superplasticizers are all found as random coils in alkaline solutions and their chemical characteristics are listed in Table 4.

- LS-2 and LS-3 have molar mass in the same range (respectively 12'000 and 18'000 g/mol) and have a number of LS molecules adsorbed in the same range within experimental errors.
- LS-1 has a molar mass of about 157'000 g/mol, which means that it is about ten times longer than LS-2 and LS-3. But it has an adsorbed amount on MagChem P98 of 1.15 mg/g (which is approximately 2-3 times lower than LS-2 and LS-3). The polymers already adsorbed on the MgO particles might produce a steric barrier, which limits the adsorption of new polymeric molecules, especially polymers with long chains (high molar mass).

From electroacoustic results (Fig. 3b), the LS-3 zeta potential does not reach a plateau value. It cannot be compared with the other polymers for this analysis. The other lignosulfonates can be classified according to the mean potential value at the plateau, in decreasing order:

$$\text{LS-1 (-18.4 mV)} > \text{LS-2 (-17.7 mV)} > \text{LS-4 (-13.4 mV)}$$

- Zeta potential is a function of surface charge of the particles. From depletion results, LS-1 and LS-2 have a similar adsorbed charge amount. From electroacoustic results, they have similar zeta potential values at the plateau within experimental errors (around  $-18 \pm 0.5$  mV).
- LS-4 has a PEG chain grafted on the backbone chain. This induces a more extended steric barrier and could influence the LS-4 adsorption. The LS-4 molar mass is not available and its effect could not be estimated.

### **Ionic influence**

The influence of ions, present in cement suspension because of hydration, on polymer adsorption was simulated and studied with the MgO suspensions by addition of various ions. Suspensions were prepared by mixing MgO P98-C with solutions of different compositions: (a) NaOH 0.01M; (b) KCl 0.01M; (c) NaOH 0.1M; (d) NaOH 0.1M + Na<sub>2</sub>SO<sub>4</sub> 0.1M, (e) final mixture: a veritable "soup" of ions which should simulate very closely a typical pore solution (Ca<sup>2+</sup> 0.012 M + Na<sup>+</sup> 0.276 M + SO<sub>4</sub><sup>2-</sup> 0.1M + OH<sup>-</sup> 0.1 M).

Possible adsorption of the sulfate ions was studied using the depletion method. Standards were prepared by mixing 75 ml of NaOH (0.01M) with various amounts of Na<sub>2</sub>SO<sub>4</sub>. All samples were prepared by dispersing 6.77 g of MgO P98-C in 75 ml of NaOH (0.01M) and sulfate added as similar to the standard solutions. To study the competition between polymer and sulfate, various amounts of ultrafiltrated PCP-1 were added in some standards (from E8 to E11) and in some samples (from A8 to A12). All supernatant solutions were analyzed by ionic chromatography at Sika Technology AG (Switzerland). Fig. 6 presents the expected and the measured sulfate concentrations (in mass-%) in the standards (Fig. 6a) and in the samples (Fig. 6b).

In Fig. 6a), the measured sulfate concentrations present lower values than the expected ones. The difference between concentration values seems to be constant (around 15-20 %). In Fig. 6b), the measured sulfate concentrations present lower values than the introduced ones in the samples which contain powder. From these results, it appears that no adsorption takes place under these experimental conditions.

Depletion measurements were performed in NaOH (0.01M) and in the “soup” for LS-3 polymer onto MagChem P98 and MgO P98-C. The adsorption isotherms are given in Figs. 7a) and 7b) respectively. The figures represent the averaged results obtained from two different adsorption measurements. All the curves are fitted using a Langmuir equation.

For the LS-3 adsorption onto MagChem P98, the adsorbed amount increases to a plateau value. The polymer concentration needed to reach the plateau and the plateau value is similar for both ionic solutions studied. Only the slope at the beginning of the isotherms presents a slight difference.

For the LS-3 adsorption onto MgO P98-C, the adsorbed amount does not reach a plateau. This is simply explained by the SSA of the powders. MgO P98-C has a higher SSA ( $7.55 \text{ m}^2/\text{g}$  after a contact time of one hour in NaOH 0.01M) than MagChem P98 ( $2.74 \text{ m}^2/\text{g}$ ). A plateau should be reached for a LS-3 dosage contained between 15 and 20 mg polymer / g powder.

Calcium and sulfate ions do not seem to influence the final amount of LS-3 which adsorbs on the powder, but they might influence the kinetics of the adsorption.

Electroacoustic measurements were performed on MgO P98-C in all ionic solutions for PCP-1 and LS-3 polymers and the results are reported in Figs. 8a) and 8b).

For both polymers, zeta potential decreases to a plateau, the value of which varies with ionic solutions. With NaOH (0.01M), the lowest plateau value is obtained (-19 mV). With the ionic “soup” and  $\text{Na}_2\text{SO}_4$  (0.1M) / NaOH (0.1M) solutions, similar plateau values were obtained within experimental errors (-14 mV).

Initial and plateau zeta potential values for MgO P98-C were plotted as a function of the added ionic concentration for two superplasticizer contents: one without superplasticizer (corresponding to 0 %) and the other containing 20 mg polymer/g powder (corresponding to 2 %). These zeta potential values are also plotted versus the ionic strength  $I$  of various solutions. The ionic strength  $I$  of the solution containing ions is calculated by Eq. (2).

$$I = \frac{1}{2} \sum (C_i \times z_i^2) \quad (2)$$

The results are given in Figs. 9a) and 9b). The error bar represents the experimental error of the Colloidal Dynamics Acoustosizer II measurement.

For samples containing 20 mg/g of superplasticizer, the magnitude of the zeta potential decreases as the solution ionic strength increases towards a plateau. Similar curves were observed with the solvent ionic strength. So, zeta potential is predominantly influenced by the ionic concentration of the suspension solution phase. Sulfate and calcium ions seem not to influence the zeta potential of these samples, do not show specific adsorption and are not potential determining ions.

For samples without polymer, zeta potential decreases as a function of ionic concentration.

Yamaha had studied PCP adsorption onto normal portland cement (21). He has noticed that the PCP adsorption is significantly affected by sulfate ions. Contrary to his results, sulphate ions do not seem to influence superplasticizer adsorption in this study.



## CONCLUSION

The LS and PCP adsorptions onto MgO and cement were studied using two different techniques: depletion and electroacoustic methods. Zeta potential shows the variation of electrostatic effects due to polymer adsorption but contrary to depletion measurements it does not indicate directly the adsorbed amount. Both techniques are complementary. Both analyses have shown that polymer adsorption is influenced by the side chain length, the length of the backbone and the ionic charge of the polymer. Increasing the backbone length as well as increasing the side chain length decreases the adsorbed amount.

The influence of main ions, present in cement suspension because of hydration, on polymer adsorption was studied. Neither sulfate or calcium ions seem to specifically adsorb onto MgO surface and thus do not affect directly the surface potential nor compete with the polymer adsorption. Only an ionic strength effect has been observed on the zeta potential measurements.

Although MgO powders are unfortunately not as inert as expected, electroacoustic measurements on cement and model powders give similar results. From results on rheological studies on the MgO and cements (22), the MgO seem to reproduce the general trends seen for cements. The use of MgO therefore allows us to study the effect of modifications of the polymers and the effect of the pore solution composition without the complication of the cement hydration.

These findings used in conjunction with observed layer thickness measurements from AFM and rheological properties of cement and model powder suspensions to elucidate how these new superplasticizers function as water reducing agents.

## ACKNOWLEDGMENTS

This work was carried out within the 5<sup>th</sup> European Framework Programme (Contract G5RD-CT-2001-00435) and received a financial support from the Swiss Federal Office for Education and Science (contract No 00.0273-1).

## REFERENCES

1. Kauppi A., Banfill P.F.G., Bowen P., Houst Y.F., Lafuma F., Mäder U., Perche F., Petersen B.G., Reknæs K., Schober I., Siebold A., Swift D., "Improved Superplasticizers for High Performance", Proceedings of the 11<sup>th</sup> International Congress on the Chemistry of Cement, Durban, 2003.
2. Flatt R.J., Houst Y.F., Bowen P., Hofmann H., "Electrosteric Repulsion Induced by Superplasticizers Between Cement Particles: an Overlooked Mechanism?", in 6<sup>th</sup> CANMET/ACI International Conference on Superplasticizers and other Chemical Admixtures in Concrete, (Malhotra V.M. Ed.), SP 195, American Concrete Institute, Farmington Hills, Mi, USA, 2000, pp. 29-42.
3. Flatt R.J., "Polymeric Dispersants in Concrete", Polymers in Particulate Systems. Properties and Applications (Hackley V.A., Somasundaran P, Lewis J.A., Eds), Marcel Dekker, Inc., New York, 2002, pp. 247-294.
4. Flatt R.J., Houst Y.F., Bowen P., Hofmann H., Widmer J., Sulser U., Maeder U. and Bürge T.A., "Interaction of superplasticizers with model powders in a highly alkaline medium", Proceedings of the 5<sup>th</sup> Canmet/ACI International Conference on

Superplasticizers and Other Chemical Admixtures in Concrete (editor: Malhotra V.M.), American Concrete Institute, Farmington Hills, Mi, USA. SP-173, 1997, pp. 743-762.

5. Flatt R.J., Houst Y.F., Bowen P., Hofmann H., Widmer J., Sulser U., Mäder U., Bürge T.A., "Effect of Superplasticizers in Highly Alkaline Model Suspensions Containing Silica Fume", 6<sup>th</sup> CANMET/ACI International Conference on Fly-Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Bangkok, Tailand, 1998. (Malhotra V.M. Ed.), SP 178, American Concrete Institute, Farmington Hills, Mi, USA, 1998, Vol. 2, pp. 911-930.
6. Flatt R.J., Houst Y.F., Siebold A., Bowen P., "Cement model powder for superplasticizer properties studies", Proceedings of the 11<sup>th</sup> ICCI, Durban, 2003, accepted.
7. Hewlett, P.C., "Lea's Chemistry of Cement and concrete", Fourth edition, Arnold, , London, 1998
8. Flatt R.J., Houst Y.F., "A simplified view on chemical effects perturbing the action of superplasticizers", Cement and Concrete Research, Vol. 31, 2001, pp.1169-1176.
9. Nägele, E., "The Zeta-Potential of Cement", Cement and Concrete Research, Vol. 15, 1985, pp. 453-462.
10. Nägele, E., "The transient zeta potential of hydrating cement", Chemical Engineering Science, Vol. 44, No. 8, 1989, pp.1637-1645.
11. Lewis J.A., Matsuyama H., Kirby G., Morissette S., Young J.F., "Polyelectrolyte Effects on the Rheological Properties of Concentrated Cement Suspensions", Journal of the American Ceramic Society, Vol. 83, No 8, 2000, pp. 1905-13.
12. Parks, G.A. "The Isoelectric Points of Solid Oxides", Solid Hydroxides and Aqueous Hydroxo Complex Systems, Chemical Reviews, Vol. 65, 1965, pp. 177-198.
13. Sakai E., Daimon M., "Mechanisms of Superplastification", Materials Science of Concrete IV, The American Ceramic Society, Westerville, OH, 1995, pp. 91-111
14. Reknes K., Gundersen S.A., Myrvold B.O., Petersen B.G., "Novel lignosulfonate with superplasticizer performance", Contribution to this conference.
15. Schober I., Mäder U., "Compatibility of Polycarboxylate Superplasticizers with Cements and Cementitious Blends", Contribution to this Conference.
16. O'Brien R.W., "Electroacoustic effects in a dilute suspension of spherical particles"; Journal of Fluid Mechanics, Vol. 190, pp. 71-86, 1988.
17. O'Brien R.W., Cannon, D.W., Rowlands, W.N., "Electroacoustic Determination of Particle Size and Zeta Potential", Journal of Colloid and Interface Science, Vol. 173, 1995, pp. 406-418.
18. Flatt R.J., Ferraris C.F., "Acoustophoretic Characterization of Cement Suspensions", Materials and Structures, Vol. 35, No 253, pp. 541-549, 2002.
19. Hunter, R.J., "Measuring Zeta Potential in Concentrated Industrial Slurries", Colloids and Surfaces, Vol. 195, 2001, pp. 205-214.
20. Hunter, R.J., "Recent Developments in the Electroacoustic Characterisation of Colloidal suspensions and Emulsions", Colloids and Surfaces, Vol. 141, section A, 1998, pp. 37-65.

21. Yamada, K., Ogawa, S., Hanahara, S., “Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizers by sulfate ion concentration in aqueous phase”, Cement and Concrete Research, Vol. 31, 2001, pp. 375-383.
22. Swift, D.S., Banfill, P.F.G., “Effects of superplasticizers, powder fineness and solution electrolyte content on the rheology of model paste systems”, Contribution to this Conference.

TABLE 1 – POWDER CHARACTERISTICS

Powders	MagChem P98	MgO P98-C
Specific Surface Area (m <sup>2</sup> /g)	0.87 ± 0.01	2.51 ± 0.01
Median Volume Diameter (µm)	18.30 ± 0.5	2.90 ± 0.5

TABLE 2 – CHARACTERISTICS AND MAIN DEPLETION RESULTS OF POLYCARBOXYLATES USED

Polymer	PCP-1	PCP-2	PCP-3	PCP-4
Molar mass (M <sub>w</sub> )* (g/mol)	23'000	110'000	25'000	60'000
Relative side chain length**	1	1	2	5
Number backbone units per molecule	41	139	52	38
Calculated polymer plateau (mg/g)	1.26	1.51	No plateau	1.16
Number of polymer molecules (adsorbed) (nmol/g)	53.8	13.4	No plateau	19.1
Total dissociated ionic group (adsorbed) (µmol/g)	1.67	1.43	No plateau	0.63
Total dissociated ionic group (adsorbed) (µmol/g)	1.67	1.43	No plateau	0.63

\* M<sub>w</sub>: mass-average molecular mass

\*\*side chain length relative to PCP-1

TABLE 3 – ESTIMATION OF NUMBER OF PCP MOLECULES ADSORBED

Polymer	s (nm <sup>2</sup> )	N <sub>max</sub>	N <sub>exp</sub>	R
PCP-1	6.2	4.4 × 10 <sup>16</sup>	3.2 × 10 <sup>16</sup>	0.73
PCP-2	21	1.3 × 10 <sup>16</sup>	0.8 × 10 <sup>16</sup>	0.61
PCP-3	7.8	3.5 × 10 <sup>16</sup>	No plateau	-
PCP-4	5.7	4.8 × 10 <sup>16</sup>	1.2 × 10 <sup>16</sup>	0.24

TABLE 4 – CHARACTERISTICS AND MAIN DEPLETION RESULTS OF LIGNOSULFONATES USED

Polymer	LS-1	LS-2	LS-3	LS-4
Molar Mass Distribution M <sub>w</sub> (g/mol)	157'000	12'000	18'000	Not available
Organic sulphur (Mass - %)	5.8	5.5	4.2	4.3
Weak Acid Groups (COOH) (Mass - %)	3.5	2.3	9.4	5.4
Calculated polymer plateau (mg/g)	1.15	2.79	3.31	2.57
Number of polymer molecules (adsorbed) (nmol/g)	7.3	239	184	-
Total dissociated ionic group (adsorbed) (µmol/g)	1.55	2.98	8.29	-

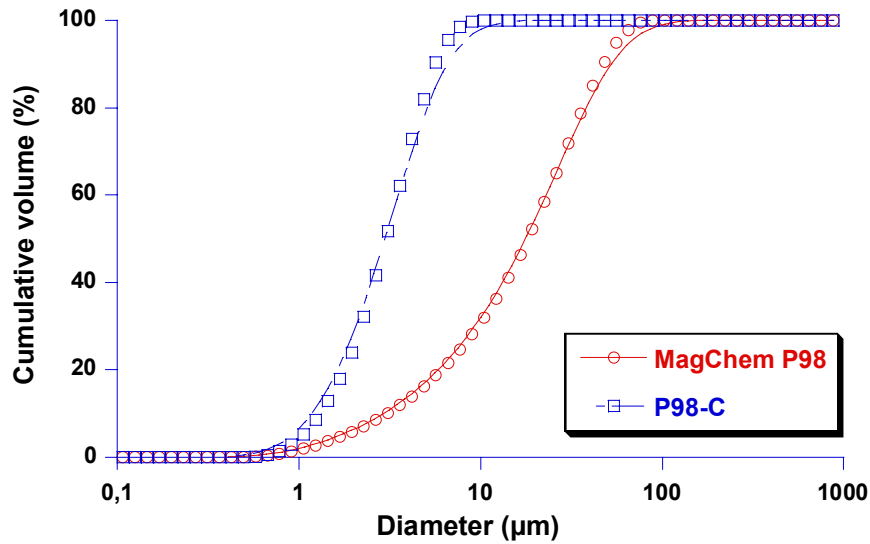


Fig. 1: Particle size distribution of MgO powders measured by laser diffraction

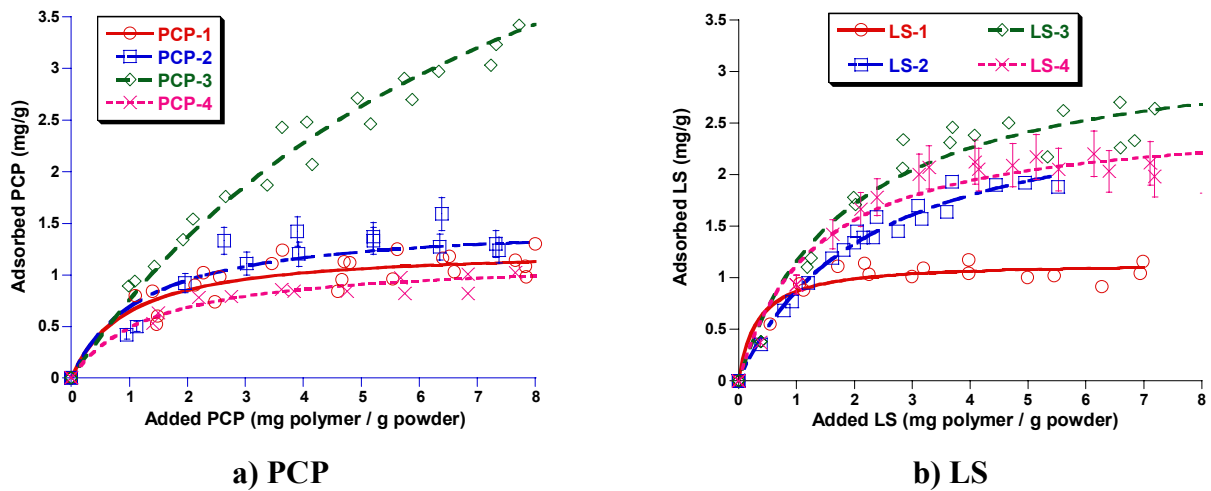


Fig. 2: Adsorption isotherms of superplasticizers on MagChem P98

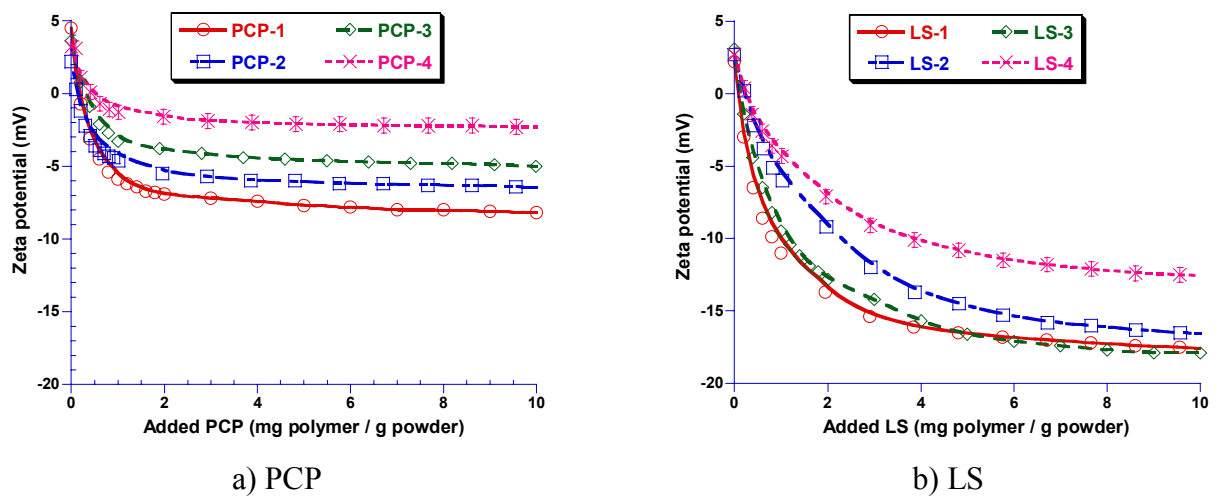


Fig. 3: Zeta potential vs. added Superplasticizer for to MgO P98-C

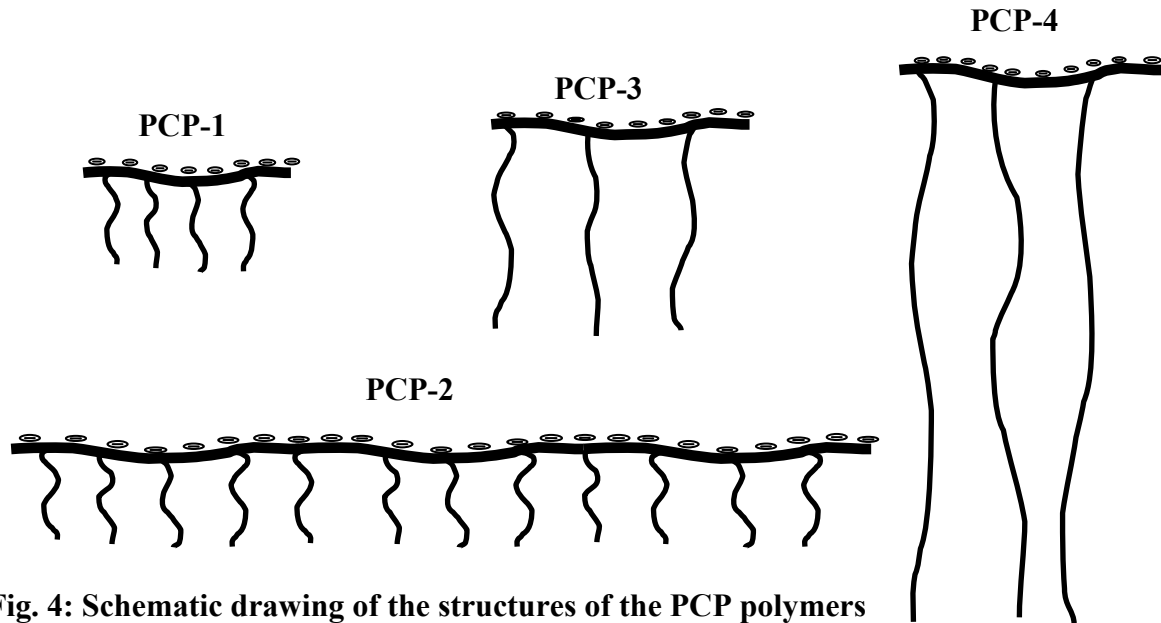


Fig. 4: Schematic drawing of the structures of the PCP polymers

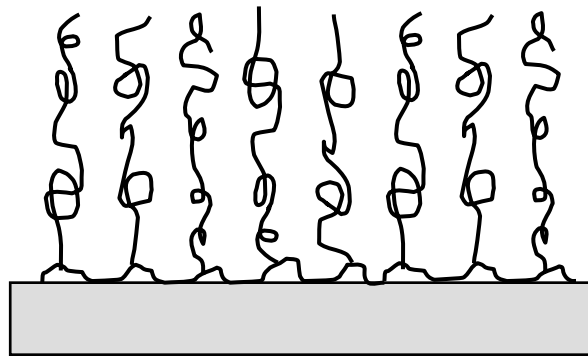


Fig. 5: Expected brushlike conformation of adsorbed PCP polymers

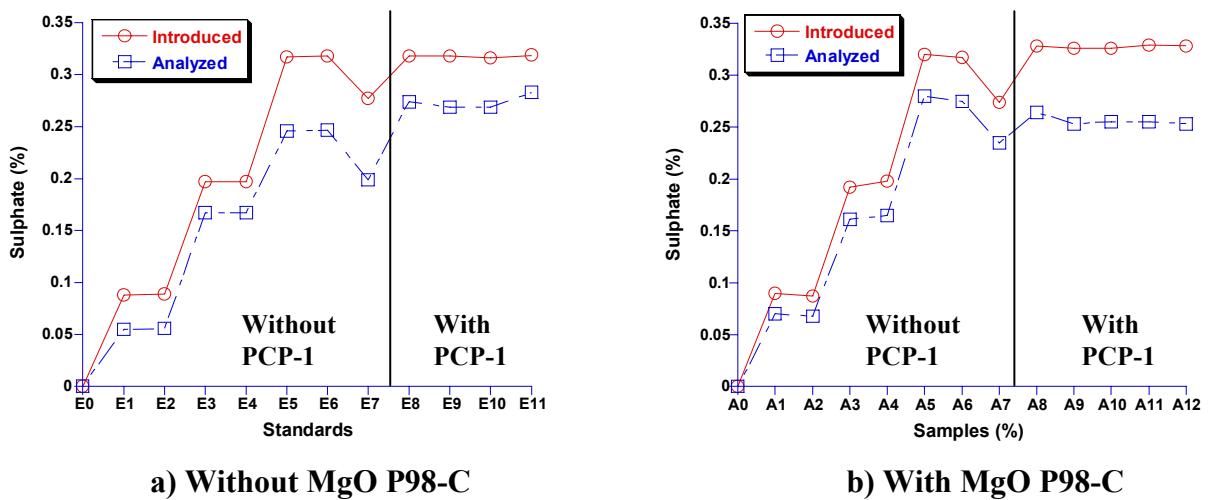
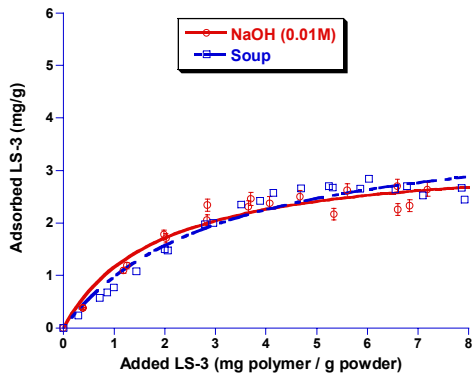
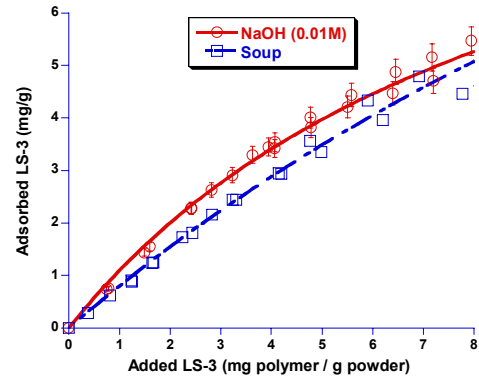


Fig. 6: Interactions of sulfate ions with MgO P98-C powder

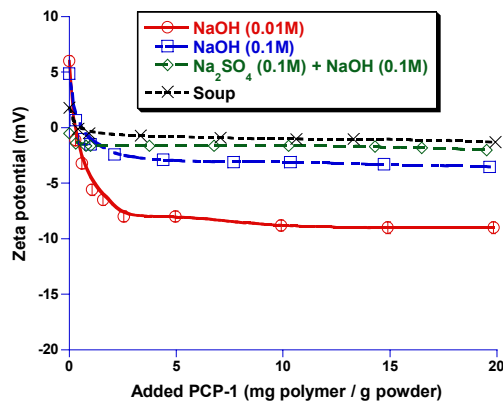


a) MagChem P98

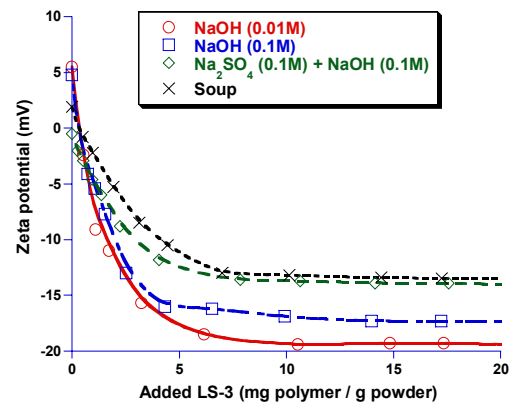


b) MgO P98-C

Fig. 7: LS-3 adsorption isotherms onto MgO powders in various ionic solutions

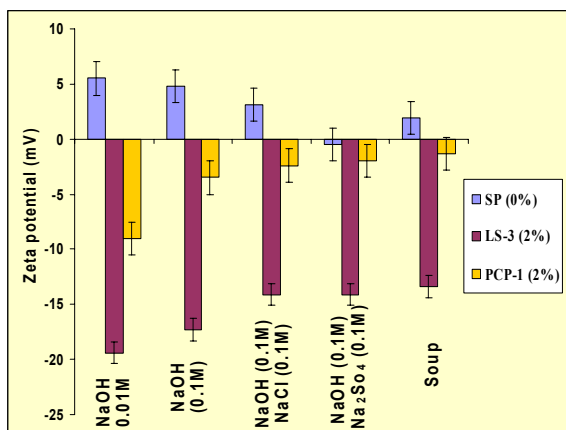


a) PCP-1

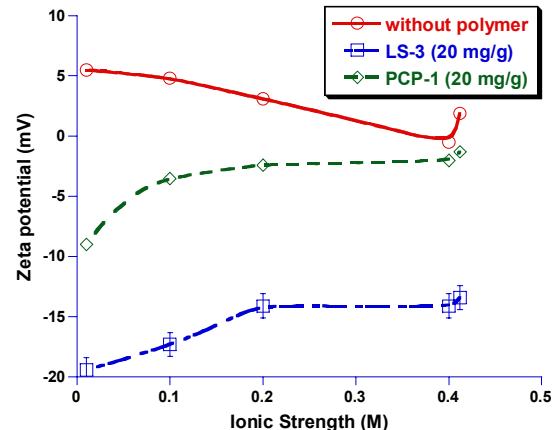


b) LS-3

Fig. 8: Zeta potential of MgO P98-C suspensions vs. added superplasticizers for different ionic solutions



a)



b)

Fig. 9: Zeta potential from electroacoustic measurements on MgO P98-C for a) different ionic solutions b) as a function of ionic strength