Adsorption of Superplasticizers on a Model Powder

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1 Introduction

Dispersion of agglomerated cement particles is known to be the main way by which superplasticizers improve the workability of concrete. Superplasticizers (SP) are anionic polyelectrolyte polymers with generally carboxylate and/or sulfonate groups. 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. The computation of interparticle forces [1,2] allows the prediction and evaluation of rheological properties [3]. A key factor in such theoretical approaches is knowledge of the amount and the conformation of the adsorbed superplasticizers (SP).

In this study we used an MgO powder as a model powder. The advantages of using a model powder for cement in studying the interactions with SPs have already been presented [4-6]. Consequently, we will only discuss this topic briefly. Cement suspensions have an inherent complexity which is an obstacle to understanding cement/SP interactions. 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. Such modifications can be avoided with a model powder like MgO that is chemically similar to CaO, which probably dominates the surface composition of the main cement particles (C_3A, C_3S and C_2S). The MgO isoelectric point is at pH 12.45 [6], close to the one of cement. In aqueous solution, the surface of the MgO reacts with water to form $Mg(OH)_2$. Also, during cement hydration, a part of the SP can be consumed by the formation of organo-mineral phases [7]. This consumed SP will not contribute to the dispersion of cement particles, and can thus give a false indication of the inherent dispersion power of the polymer.

The basic solution in contact with the MgO powder has a very low ionic concentration due to the low solubility of MgO and $Mg(OH)_2$ in highly alkaline medium. This allows us to add specific ions and study their influence on the SP adsorption.

Without SPs the main forces governing the interactions between cement particles are electrostatic forces and the dispersion or van der Waals forces [1,2,4,5]. The van der Waals forces are attractive between isotropic particles constituted of the same matter and cause agglomeration of cement particles. In presence of SPs the steric forces are also expected to play a major role.

2 Interfaces and adsorption

2.1 The solid/liquid Interface

The cement minerals can be considered to be constituted of different oxides (CaO, Al_2O_3, Fe_2O_3, SiO_2). These oxides react with water and their surface charge is determined in part by the pH of the solution in which they are immersed [8]. For such systems, the H^+ and OH^- are potential-determining ions due to the reaction:

$$- M - OH_2^+ \xleftarrow[K_+]{H^+} M - OH \xrightarrow[K_-]{OH^-} M - O^- + H_2O$$

Eq. (1)
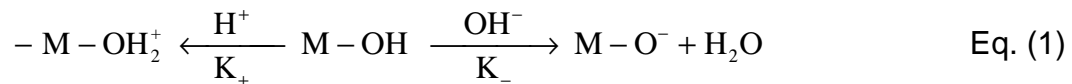
These reactions have corresponding equilibrium constants K_+ and K_-. At the point of zero charge (pzc) there is an equal number of positive and negative charges at the surface.

A charged interface attracts ions and particles of opposite charge and the interfacial zone is generally represented by the double layer model. Close to surface a compact layer, also called the Stern layer, is formed. The ions in this layer have long residence times at the surface and are not affected by the Brownian motion. The region extending from the Stern layer to the bulk solution constitutes a second layer, called the diffuse layer. The ions in this region are influenced by the surface potential and Brownian motion. The potential in the Stern layer is often described as a linearly decreasing function with distance [7]. The electrostatic potential of the diffuse layer is described by the Poisson-Boltzmann equation [8]. The Debye length (κ^{-1}) is defined as follows:

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2e^2 I^2 n_A}}$$

Eq. (2)

Whith ε_0 the permittivity of vacuum, ε the relative dielectric constant of water, k_B the Boltzmann constant, e the elementary charge, $I = 1/2 \sum_i c_i z_i^2$ the ionic strength, c_i the ionic concentration, z_i the number of charge. $1/\kappa$ is a measure of the size of the double layer. The extent of the diffuse layer is of the order of $3/\kappa$ to $4/\kappa$ [7]. As the double layers

interpenetrate they can prevent particles coming into close contact and forming agglomerates.

The potential at the plane of shear is known as the zeta potential (ζ). A considerable body of evidence has accumulated suggesting that ζ is equal to, or very close to, the potential characterizing the onset of the diffuse part of the double layer [7]. The surface potential Ψ_s, at the particle surface can be approximated using Eq. 3 [8]:

$$\Psi_s = \zeta \exp(\kappa d) \qquad\qquad\qquad \text{Eq. (3)}$$

With d the thickness of the compact or Stern layer, that is of the order of 0.5 nm, the size of a hydrated ion [7].

We have seen that the origin of the surface charge is due to the dissociation of amphoteric groups as described by Eq. (1). A large part of the oxide surface charge is balanced by the adsorption of counterions into the compact layer. The adsorption of monovalent ions onto charged surface sites reduces the magnitude of $|\zeta|$ but do not, normally, change its sign. In contrast, divalent ions like SO_4^{2-} and Ca^{2+} may change the sign of the ζ potential [8]. This point is particularly relevant for cement as such divalent ions are common in cement pore solutions.

Another characteristic of cement suspensions important for SP adsorption is that the electrostatic surface potential of the particles is very close to zero at high pH. Getting exact values of potentials near the isoelectric point (iep, pH of zero zeta potential) is a difficult task and both slightly positive or negative ζ potentials can be found in the literature [10-12]. Variations of ζ potentials can also be due to variations in composition of cements and time of hydration. For what we are concerned with, however, it suffices to state that cement suspensions are very close to their iep and have a very small net surface charge even though they are in a highly alkaline suspension.

2.2 The solid/liquid Interface with polymers

The pH of the aqueous phase of cement suspensions being between 12.5 and 13.5, the acidic functions are fully dissociated. The conformation of certain polycarboxylates polymers in solution has been established [13] according to the mean-field model developed for non-ionic comb-like polymers. They were all found to be in the flexible backbone wormlike regime (FBW). A 2D schematic representation of two polycarboxylate polymers is given in Fig. 1.
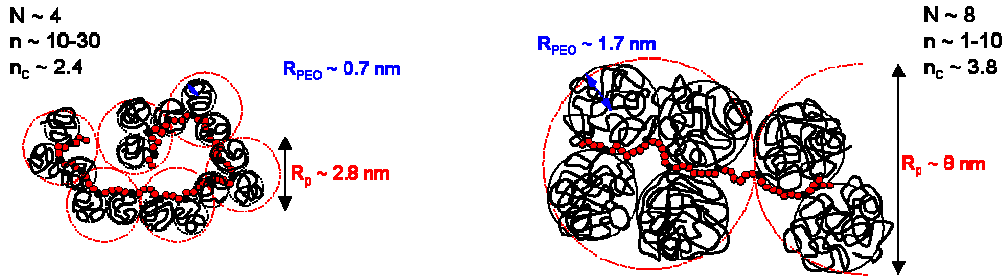
Figure 1 - Conformation of polycarboxylates PCP-1 (left) and PCP-4 (right) in solution [13].

At the interface, the polymers compete with simple ions which may modify their conformation. At high pH, their negatively charged carboxylate groups are expected to interact with $-M-OH_2^+$ sites of the surface. As the polymer has many points of contact with the surface it forms trains and loops [14]. In the case of polycarboxylates, another fixation mechanism is likely to be the complexation of carboxylate groups by cations such as Ca^{2+} (or Mg^{2+} with our model powder). It has been demonstrated that sodium polyacrylate forms bidentate complexes with Ca^{2+} that precipitate due to their loss of solubility on the surface of calcite [15]. The surface complexation of calcite by carboxylates in water was also shown. In this case, the adsorption site is a $-Ca^+$ site that is complexed by to carboxylates, similarly to the complexation of Ca^{2+} in solution.
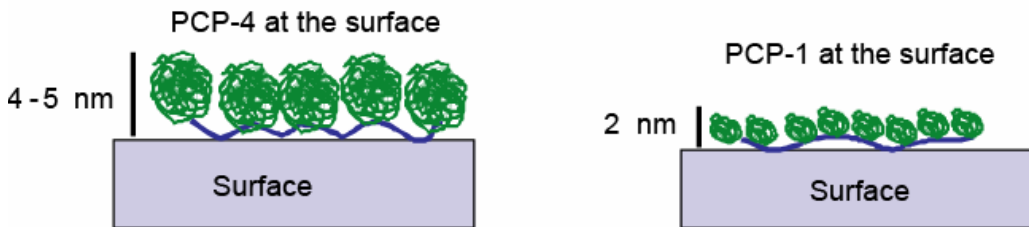

Figure 2 - Conformation of 2 polycarboxylates estimated form AFM measurements [16].

A more detailed description of the behavior and properties of polymers at interfaces are out of the scope of this paper. Interested readers may consult the specific literature, for instance [14].

3 Experimental

3.1 Materials

The model MgO used was a dead burnt MgO (called P98). A part was classified (P98-C) to give particle sizes below 10 μm for electroacoustic

measurements. Both powders can be regarded as non-reactive for a period between 30 minutes and 2 hours after first water contact. During this period all surfaces of the MgO grains are expected to have a thin layer of $Mg(OH)_2$ [6].

Six different polycarboxylate polymers (PCPs) containing grafted PEO moieties (Fig. 3) were supplied by SIKA. The amount of grafting (τ) varies between 12 and 30 %. Their main characteristics are given in Tables 1 and 2. The polymers were purified by ultrafiltration to eliminate low molar mass compounds.
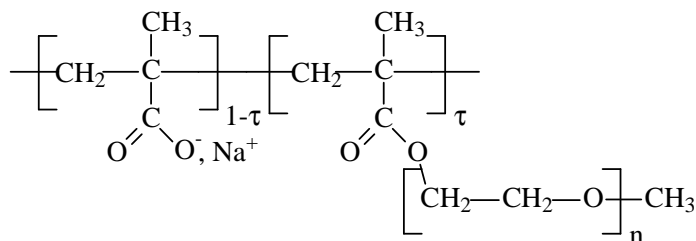

Figure 3 – Molecular structure of the polycarboxylate polymers.

Table 1: Characteristics of the polycarboxylates

Polymer		PCP-1	PCP-2	PCP-3	PCP-4	PCP-5	PCP-6
Molar mass (g/mol)	M_w	23'000	112'000	25'000	61'000	48'000	32'500
	M_n	13'000	45'000	18'000	28'000	30'000	16'600
	M_w/M_n	1.8	2.5	1.5	2.2	1.6	2.0
Side chain length		average	average	long	very long	short/ long	average

More details on the materials can be found in [18].

3.2 Adsorption and ζ potential measurements

The amount of the adsorbed polymer was measured by the depletion method. A solution of polymer is brought into contact with the powder (solution/powder = 1.8 g/g) for 30 min. The solid and liquid phases were separated and the amount of polymer in the solution was measured. The difference in the concentration before and after contact with the powder is assumed to be the adsorbed polymer amount. The majority of measurements were carried out in a solution of NaOH 0.01M (pH 12) and the influence of different ions was studied by adding salts to the solution. The temperature was kept constant at 25 ± 0.5 °C.

Electroacoustic measurements were carried out to determine zeta potential from the dynamic mobility [19]. They also allowed us to study the adsorption of the polymers. An aqueous polymer solution was added to the suspension by increments with a micro-burette and the zeta potential was calculated for each increment using Smoluchowsky's model [20].

4 Results and discussion

Adsorption isotherms were carried out at pH≈12 (NaOH 0.01M). All adsorption curves have the same trend, a linear portion followed by a non-linear section ending in a plateau (Fig. 4) with the exception of PCP-3. The linear section indicates that the adsorbed quantity is proportional to the amount of superplasticizer added. The experimental points of this part were fitted by Eq. (4).

$$y = ax \hspace{6cm} \text{Eq. (4)}$$

The calculated slopes (a) are given in Table 2. The steeper the slope, the higher the affinity of the superplasticizers for the surface of the powders. Unfortunately, the limited number of polymers studied does not show clear trends. The second part of the curve is non-linear and the adsorbed polymer amount increases up to a plateau value. The experimental points of this part of the adsorption curves were fitted by Eq. (5).

$$y = \frac{bcx}{1+cx} \hspace{5cm} \text{Eq. (5)}$$

b and c are constants. b is the plateau value ($x \rightarrow \infty$) and is reported in Table 2. Such an equation is identical to the Langmuir adsorption equation. The plateau values, where we expect to have a fully covered surface with a constant adsorbed layer thickness, allowed us to estimate the amount of polymer needed for AFM and rheological property measurements. Also electroacoustic measurements were made to follow the change in zeta potential as a function of adsorbed polymer.

Except for PCP-3, adsorbed amount increases to a plateau value which varies as a function of studied polymer. For PCP-1, PCP-2, PCP-4, PCP-5 and PCP-6, 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.

Table 2 . Radii of gyration (R_g), hydrodynamic radii (R_h), adsorbed layer thickness (L_{AFM}) (8 < pH < 12.8 and 0.03 < I < 0.4 M), affinity (a) and adsorption plateau values (b) for the PCPs.

	PCP-1	PCP-2	PCP-3	PCP-4	PCP-5	PCP-6
$\overline{R_g}$ (nm)	5.0±0.7	9.1±0.5	5.2±0.8	7.9±0.4	6.7±0.3	6.2±0.3
$\overline{R_h}$ (nm)	4.9±0.3	10.1±1.0	4.4±0.1	9.3±0.1	5.9±0.3	4.7±0.3
L_{AFM}	1.5±0.5	4.0±1.0	3.5±0.5	4.5±0.5	3.0±1.0	1.5±1.0
Affinity a [-]	0.37	0.48	0.74	0.40	0.46	0.58
b (mg/g)	1.14	1.28	No plat.	1.01	1.45	1.99

It has been shown for a neutral polymer that the amount of adsorbed polymer increases with its molar mass [14]. The studied polymers contain 70 to 88 % of PEO (neutral polymer) and they have essentially a neural character. However, no simple relationship between adsorbed amount and molar mass can be observed. This is probably due to the significant variations in structure of the polycarboxylates.
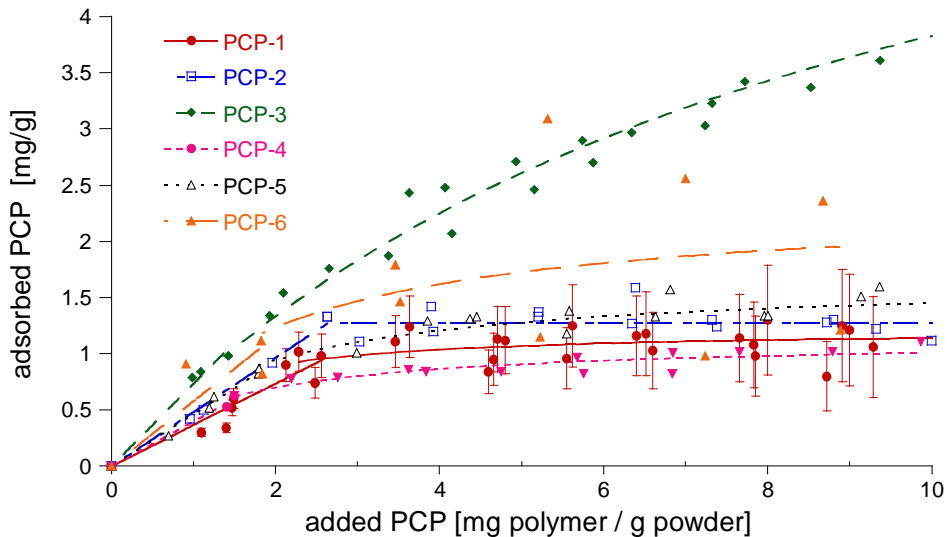

Figure 4 - Adsorption curves of PCPs onto MgO P98 in NaOH 0.01M.

The electrical charge of MgO should decrease as the adsorbed amount of SP increases and also reach a plateau. This effect was observed by recording the variation of ζ potential (Fig. 5). In this experiment, a polymethacrylate (PMMA), a polymer without grafted PEO, was also added. This polymer has more carboxylate groups and should lead to a more negative ζ potential, as was observed (Fig. 5).
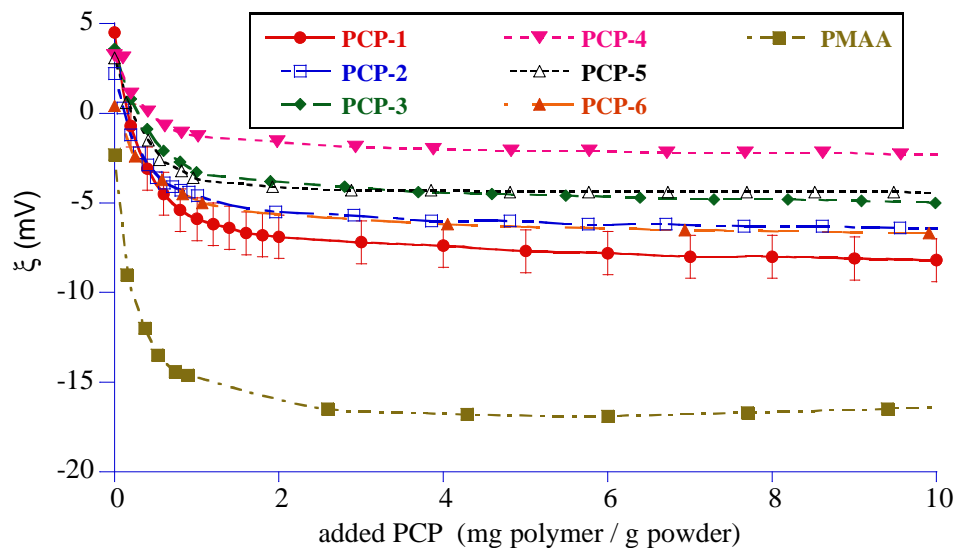
Figure 5 – Zeta potential of MgO P98-C (at pH=12) as a function of added PCP and a poly(methacrylic) polymer (PMMA).

The electroacoustic and adsorption curves of PCP-5 on MgO P98-C are shown in Fig. 6. ζ potential (and consequently the surface charge) of MgO varies with the amount of adsorbed SP. The two curves reach a plateau for an equivalent amount of added SP. This indicates that ζ potential is linked to the adsorption of the polymer. The influence of the amount of adsorbed carboxylate groups is shown in Fig. 7, where the $|\zeta|$ is seen to be proportional to the number of adsorbed charges.
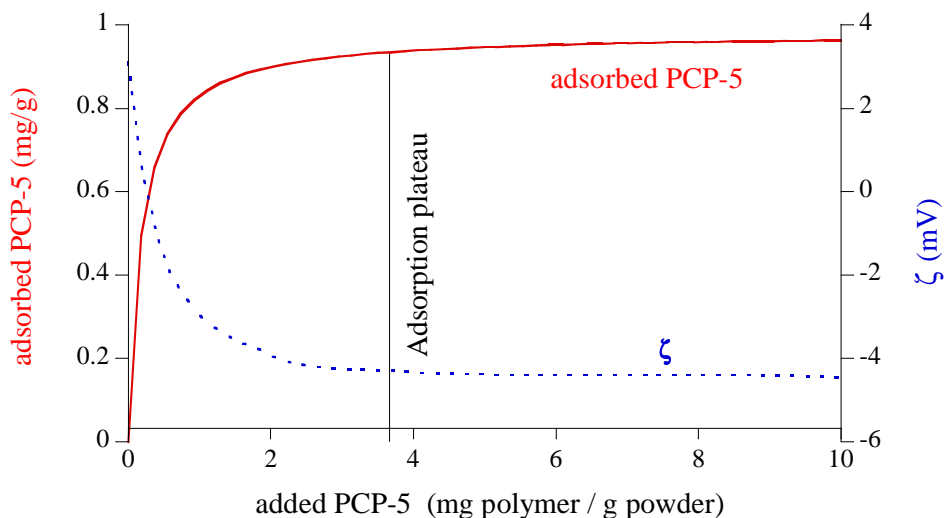

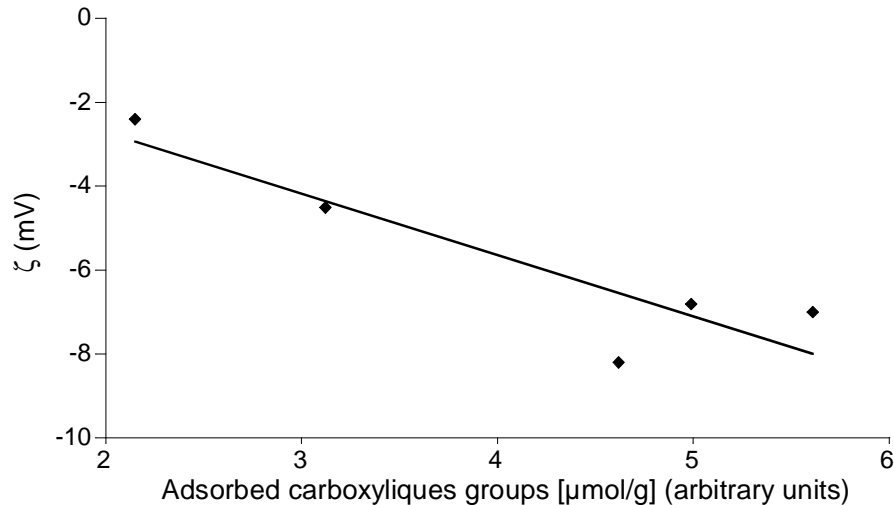Figure 6 – Adsorption and electro-acoustic curves of PCP-5 (at pH=12).

Figure. 7 – ζ potential as a function of adsorbed carboxylate groups.

The zeta potentials of MgO suspensions in presence of different ions are presented in Table 3. We get a positively charged surface at pH 11 and a negative surface at pH 13, as expected from the isoelectric point. However, when Ca^{2+} ions are added they interact with the MgO powder and the zeta potential increases to more positive values with the zeta potential remaining positive at pH 13. Table 3 shows that SO_4^{2-} ions also affect the zeta potential but in this case towards a less positive or a more negative value. This shows that both Ca^{2+} and SO_4^{2-} ions interact with the MgO surfaces. However, other experiments have shown that there is no chemisorption of SO_4^{2-} onto the MgO surface [18]. Apparently the interaction between the MgO surface and the SO_4^{2-} ion is not strong enough to chemisorb but is strong enough to affect the zeta potential which in turn would be expected to affect adsorption as seen in recent work on polycarboxylate-type superplasticizers [21]. The inverse of the Debye length (see Eq. 2) has been calculated and is reported in Table 3. These values give an approximation of the position where ζ potential were determined. It can also be seen that the double layers are considerably reduced at high ionic strength.

The variations of zeta potentials of MgO in presence of one superplasticizer are also given in figure 8 as an example. The same trends can be observed.
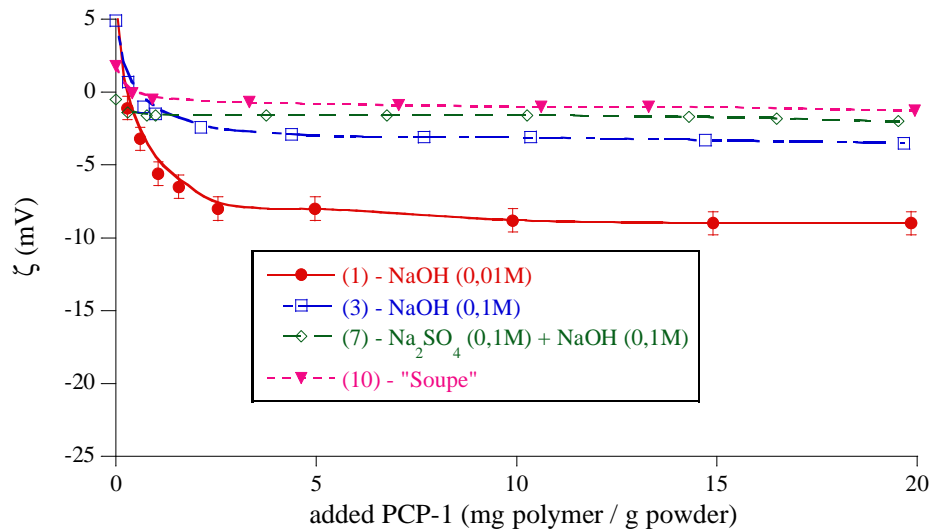
Figure 8 - ζ potential of MgO P98-C as a function of added PCP-1 in different ionic solutions.

Table 3 - Zeta potential of MgO P98-C in different electrolytes and Debye length (1/κ).

Composition of 1 liter of solution	ζ potential (mV)		1/κ (nm)	
(pH adjusted by NaOH)	pH 11	pH 13	pH 11	pH 13
100 mmol NaCl	+3.8	-1.3	1.0	0.7
100 mmol NaCl + 10 mmol CaCl$_2$	+8	+5	0.8	0.6
100 mmol NaCl + 100 mmol Na$_2$SO$_4$	+0.5	-3	0.5	0.4

5 Conclusions

The adsorption curves of polycarboxylates superplasticizers measured at pH≈12 on MgO have generally the same trend: a linear section followed by a non-linear section ending in a plateau. Electroacoustic measurements show that ζ potential decreases as a function of added SP amount to a similar plateau value. This confirms that ζ potential is linked to the adsorption of SPs and we saw that the |ζ| was proportional to the amount of adsorbed carboxylate groups.

When Ca^{2+} ions are added to an MgO suspension, the ζ potential increases to more positive values and remains positive at pH 13. SO_4^{2-} ions also affect the zeta potential but in this case towards a less positive or a more negative value. This shows that both Ca^{2+} and SO_4^{2-} ions interact with the MgO surfaces. This is important for a better

understanding of the adsorption of SPs. Further work is planned for a typical polycarboxylate SP to investigate the effect of ions on surface charge, adsorption and consequently the behavior of cementitious systems.

Acknowledgements

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