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ADSORPTION OF SUPERPLASTICIZERS ON MODEL POWDERS: TEMPERATURE DEPENDENCE, EFFECT ON ZETA POTENTIAL AND ROLE OF CHEMICAL STRUCTURE.

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ABSTRACT It has been shown that the adsorption of superplasticizers on MgO and Mg(OH)₂, at pH 12.1 and 11.3 respectively, can strongly vary with temperature according to the chemical nature of the superplasticizer. MgO and Mg(OH)₂ were chosen as model powders because their surfaces and zeta potentials are similar to cement. The two polymers studied, of similar molar mass, contain the same ionic groups but have different charge spacing. The influence of this structural difference on adsorption and zeta potential was studied.

Key-words: Admixtures, Adsorption, Superplasticizers, Temperature, Zeta Potential.

INTRODUCTION

In the early 1960's, the first synthetic, high performance water reducing admixtures for concrete were developed. These admixtures were based on sulfonated naphthalene-formaldehyde, and, some years later, melamine formaldehyde polycondensates. In the eighties and nineties, new types of polymers, which form the chemical basis of a novel class of high range water reducers (HRWR), also called superplasticizers, were introduced. At present mainly three types of anionic polymers (anionic polyelectrolytes) are used in modern superplasticizers: Sulfonated Naphthalene-Formaldehyde-Polycondensates (SFNC), Polycarboxylic Acid Polymers (PCA) and Polycarboxylic Ester-polymers (PCE).

Such admixtures are today a valuable help in the production of high performance concrete exhibiting high flow and excellent workability which develop high density and durability on setting.

The effect that these polymers induce in cement suspensions, which permits high water reduction for the same workability, is linked to a change in interparticle forces [Horn (1990), Israelachvili (1992)]. However, the exact way in which these polymers modify interparticle forces in cement suspensions, whether it is by electrostatic, steric or entropic effects or a combination of these, is still a debated matter [Aitcin et al (1994), Jolicoeur et al (1994)].

Our research aims to get new and additional information and knowledge about the mechanisms of the interaction of structurally different water-soluble polymers which are used or could be used as HRWRs. In this paper, we present results concerning the adsorption, at different temperatures, of a PCA and a PCE on model powders which bear many physical similarities to cement phases. We also look at the change in surface charge which these polymers induce on these model powders.

STRATEGY

When studying the effect of polymers on interparticle forces, it is important to know whether they adsorb on surfaces, and if so to what extent.

Because cement hydrates and its surface therefore changes with time, adsorption of HRWRs is commonly studied on inert model powders [Jolicoeur et al (1994), Nkinamubanzi (1994),

Chapuis (1990), Pierre et al (1988), Girod et al (1988), Daimon and Roy (1978)]. This is believed to provide information on the initial steps of the interaction between HRWRs and cement. Such studies, carried out by Nkinamubanzi (1994) and Pierre et al (1988) have shown for instance that the adsorption of PNS on TiO_2 is strongly dependent on the pH of the suspension. At pH 3, where TiO_2 bears a strong positive surface charge, the adsorption is maximum, while it becomes non-existent in the alkaline region where the surface charge of TiO_2 is negative. From this example, we see that electrostatic interactions between a HRWR and a surface can be a determining factor for its adsorption.

The model powder must therefore have both a zeta potential and a pH similar to that of a cement suspension if we intend to relate adsorption on the model powder to that on Portland cement. Nägele (1985) found this potential to be positive by a couple mV. On the other hand, 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 solution pH.

This brings a second condition for adsorption experiments. It is to have a pH similar to that of cement (about 12.5). This can be quite a problematic condition, since at such a pH most powders have a negative surface charge. To the best of our knowledge, no adsorption experiments have so far been carried at pH 12 with model powders positively charged under those conditions.

In this study, the powders used are MgO dead burnt and $\text{Mg}(\text{OH})_2$. Suspensions of MgO at pH 12 had positively charged surfaces since its Isoelectric Point (IEP) is at pH 12.4 [Parks (1964)]. $\text{Mg}(\text{OH})_2$ is expected to have an IEP at pH 12 [Parks (1964)], therefore we used suspensions at pH 11.3 to obtain slightly positively charged surfaces. The small pH difference is not expected to alter results significantly. Another major interest for these powders is their chemical similarity to the major cement phases C_3S , C_2S and C_3A . The Mg-O bond is much stronger than the Ca-O bond because of the smaller size of Mg (it is above Ca in the periodic table). By dead burning, the reactivity of this powder is further decreased, making it almost insoluble.

The polymers used in this study (a PCA and a PCE) have the same ionic groups (carboxylate and sulfonate). However, the spacing of these groups is larger in the PCE, due to the inclusion of polyethylene glycol-ester (PEG-ester). This structural difference should allow us to get information concerning the importance of electrostatic interactions in the adsorption of such HRWRs.

EXPERIMENTAL

Powders

MgO dead burnt and $\text{Mg}(\text{OH})_2$ from Martin Marietta Magnesia Specialties Inc. (type: P-98 and MH-10 respectively; Baltimore, USA) were carefully sampled. Half the MgO was sieved. The fraction below 50 μm , sampled with a spinning riffler, was used in our experiments.

The particle size was determined by laser diffraction (Malvern Mastersizer; Malvern, GB). The BET specific surface was determined by adsorption of N_2 (Micromeritics Gemini III 2375; Norcross, USA). XRD showed the $\text{Mg}(\text{OH})_2$ contained a small amount of MgO, possibly formed at the surface by excess drying during the production. secondary phases were not observed in the MgO. Other powder characteristics are given in Table 1.

Table 1: Powder characteristics

	Mg(OH) ₂	MgO
Specific Surface Area	11.8 ± 0.1 m ² g ⁻¹	0.77 ± 0.03 m ² g ⁻¹
Median Volume Diameter	10.5 ± 0.2 μm	15.0 ± 0.5 μm

Polymers

The polymers used for this study are laboratory test products produced by Sika A.G. (Zürich, Switzerland). Information as to their composition is given in Table 2.

Table 2: Characteristics of the polymers used.

	PCA	PCE
Chemical type	Na-polycarboxylate-polysulfonate	Na-polycarboxylate-polysulfonate, PEG-ester containing
Number Average Molar Mass	11'500 ± 2'000 g mol ⁻¹	9'500 ± 1'500 g mol ⁻¹

Adsorption

Adsorption measurements were performed on suspensions of 10 g of MgO or 5 g of Mg(OH)₂ in 20 ml NaOH 0.01M (pH 12 ± 0.1), previously thermostated in rotary bath at 200 rpm (different masses were taken to achieve similar volume fractions). The superplasticizers were added as concentrated aqueous solutions with a microdispenser. This makes dilution minimal and avoids possible hydrolysis due to a long exposure in an alkaline solution). After 30 min in the rotary bath, the suspensions were centrifuged for 5 min at 3'000 rpm. Five ml of the supernatant, buffered with 25 μl of CH₃COOH (30% V/V), were filtered at 0.45 μm through a filter mounted on a dispensable syringe. The first 2 ml were discarded and the rest was analyzed by reverse phase chromatography with an HPLC 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 submitted to the same treatment.

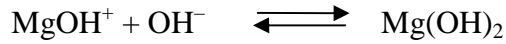
Zeta potential

Zeta potential was measured at 23-25° C by acoustophoresis (Penkem, system 7000; Bedford Hills, U.S.A.). Potentials were calculated from measured data using the method proposed by PenKem (Marlow et al 1988). The suspensions were prepared by dispersing 20 g of powder in 300 ml NaOH 0.01M under vigorous agitation and sonification for 15 min (150 W, 20 kHz). Prior to measuring, they were degassed for 5 min (≈20 torr). A slight vacuum was maintained in the measuring cell to avoid bubble formation which attenuates the signal. The superplasticizers were progressively added as concentrated aqueous solutions with a microdispenser.

RESULTS

Stability of powders

The pH of Mg(OH)₂ suspensions decreased from pH 12 to pH 11.3. This may be a result from the dissolution and/or precipitation of impurities not detected by XRD. Further pH decrease is hindered by the equilibrium:



The suspensions containing dead burnt MgO however remained at pH 12, indicating this powder to be essentially non reactive.

Adsorption

The adsorption isotherms on MgO at 25, 32 and 40 °C for superplasticizers PCA and PCE are reported in Figs 1 and 2 respectively. These figures show that the adsorption of the PCE increases sharply with temperature, while adsorption of the PCA is unaffected by it. Figures 3 and 4 give the adsorption isotherms of the same polymers on Mg(OH)₂. In this case, neither polymer is effected by temperature.

The fact that on both powders adsorption of the PCA is not effected by temperature can be assumed to be due to a large adsorption enthalpy ΔH_{ads} . Indeed, over small temperature ranges, both enthalpy ΔH_{ads} and entropy ΔS_{ads} can be regarded as constant and the adsorption free energy ΔG_{ads} is therefore mainly effected by the $-T\Delta S_{\text{ads}}$ term, as $\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}$.

Understanding the behavior of the PCE is a more challenging task. However, we can gain some insight using similar considerations regarding its adsorption free energy. The PCE polymer is similar to the PCA but has ionic groups which are further apart, due to the insertion in this polymer of PEG-ester segments which act as charge spacers. This anionic polymer will therefore have weaker electrostatic interactions with the positively charged surface and consequently a smaller heat of adsorption ΔH_{ads} than the PCA. Although this could explain a temperature dependent adsorption, it does not account for an increase as a function of temperature. Indeed, because of the decrease in configuration entropy linked with adsorption ΔS_{ads} is expected to be positive and adsorption to decrease with temperature. However, it could be that the PCE polymer would remain on the surface but be linked to it by less anchor points. This would then allow larger amounts of polymers to adsorb on the surface. Over a larger temperature range, these polymers would be expected to desorb. The reason why adsorption remains unchanged with temperature on the Mg(OH)₂ could be due to a larger ΔH_{ads} interaction with this powder.

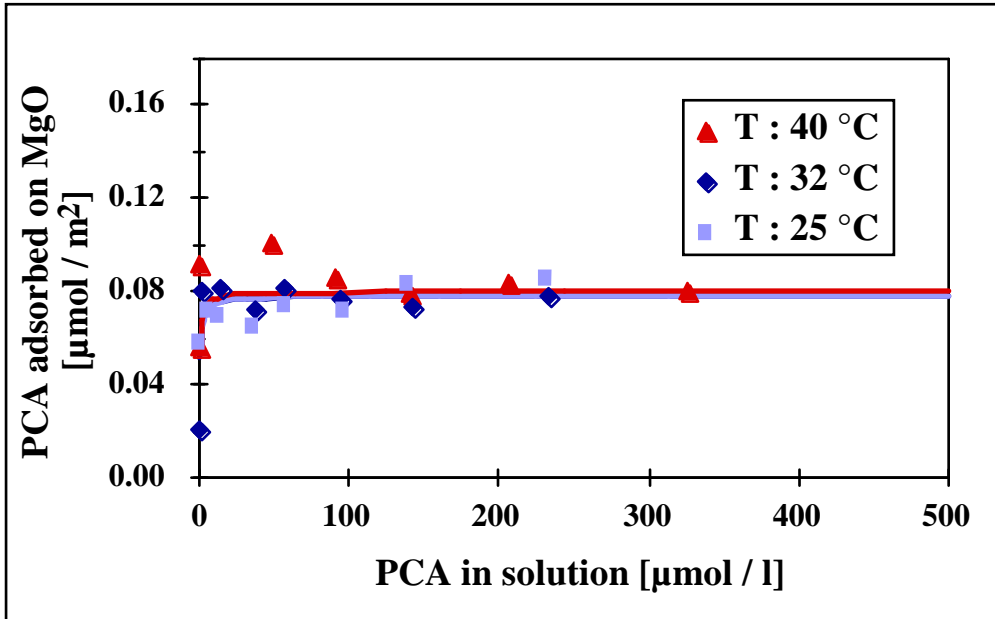


Figure 1 Adsorption isotherms of PCA on magnesium oxide at 25, 32 and 40°C.

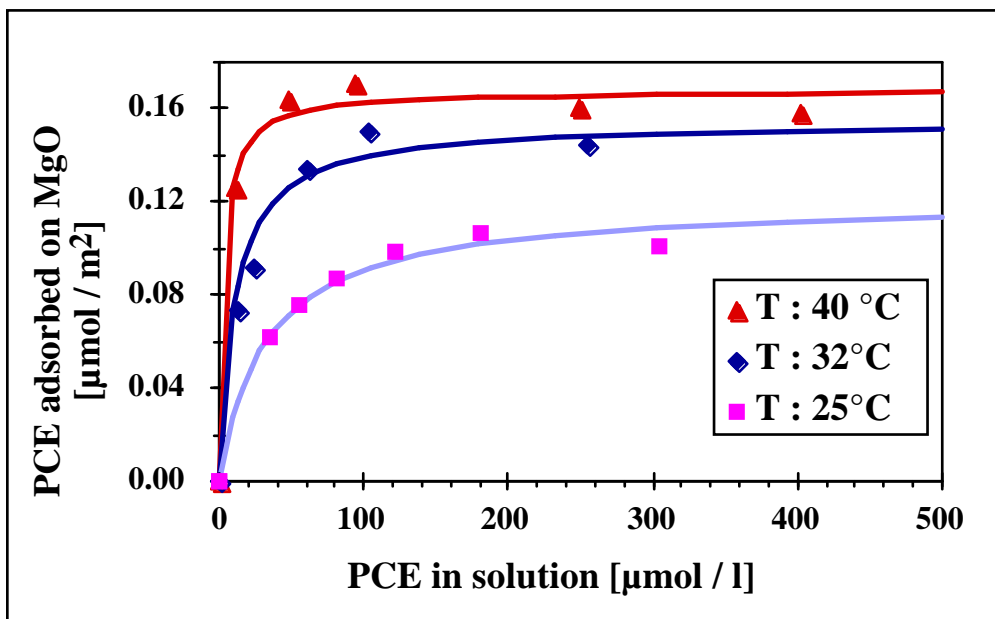


Figure 2 Adsorption isotherms of PCE on magnesium oxide at 25, 32 and 40°C.

Another possible consequence of the PCE having a smaller ΔG_{ads} than the PCA, would be to allow competitive adsorption of hydroxyl groups OH^- . These would be more easily desorbed by rises in temperature, allowing a higher surface coverage, especially on MgO. Adsorption on the $\text{Mg}(\text{OH})_2$ might not be influenced by temperature because of the pH difference (12 and 11.3), which corresponds to a five fold concentration difference in OH^- .

On the other hand, it is known that PEO polymers, which are similar to our PCE, have increased polymer-polymer interactions with temperature rises over similar ranges (Claesson et al. 1986). This might lead to multiple layer adsorption (Klein 1997) on the MgO. This may not occur on the $\text{Mg}(\text{OH})_2$ either because of different surface interactions, the pH difference or a larger

porosity. We can point out that the interaction energy increase between PEO polymers is believed to be linked to the loss of a solvation layer (Israelachvili 1996). This in turn would lead to smaller surface occupation of the adsorbed polymers and would allow increased adsorption.

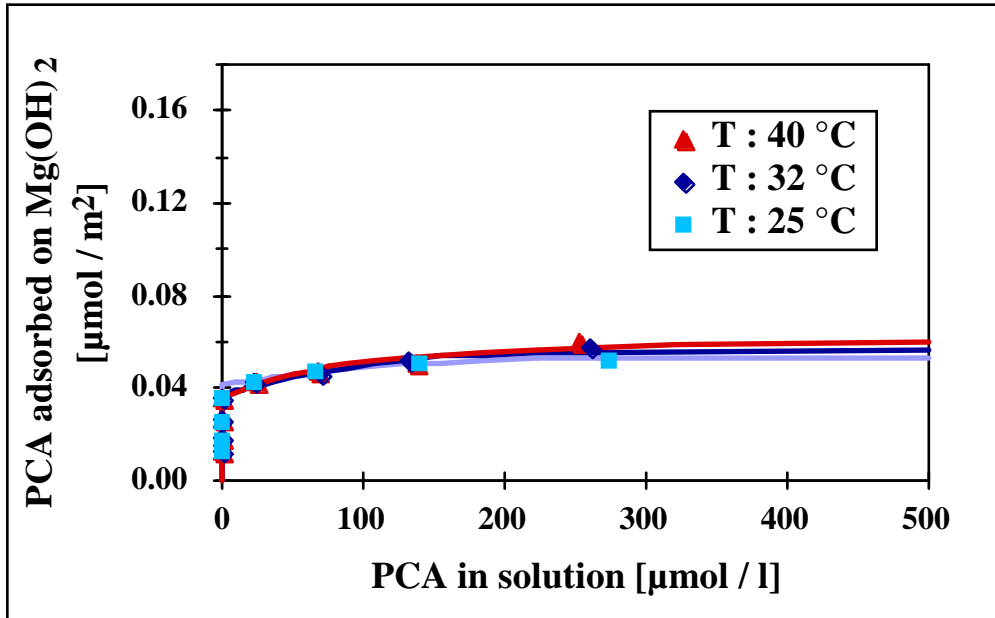


Figure 3 Adsorption isotherms of PCA on magnesium hydroxide at 25, 32 and 40°C.

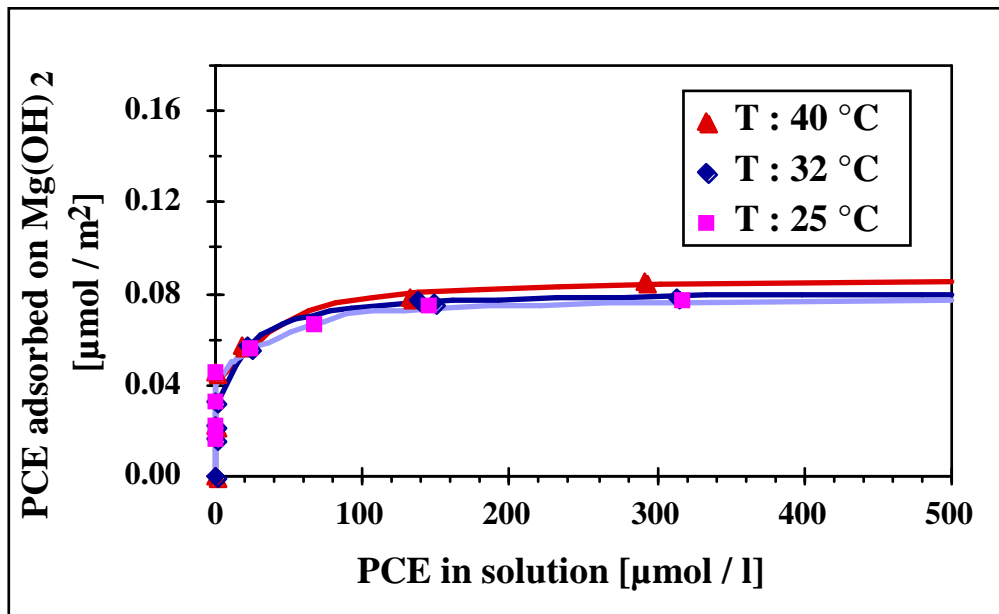


Figure 4 Adsorption isotherms of PCE on magnesium hydroxide at 25, 32 and 40°C.

Zeta potential

In Figs 5 and 6, we have reported the change in zeta potential (related to the surface charge) that the PCA and the PCE induce on MgO and Mg(OH)₂, respectively. In both cases, the PCA induces a larger negative zeta potential. This means that the larger adsorption of the PCE is not sufficient to overbalance the greater charge of the PCA. It is possible to compare absolute molar

concentrations of these polymers because they have similar molar mass and similar mass distributions.

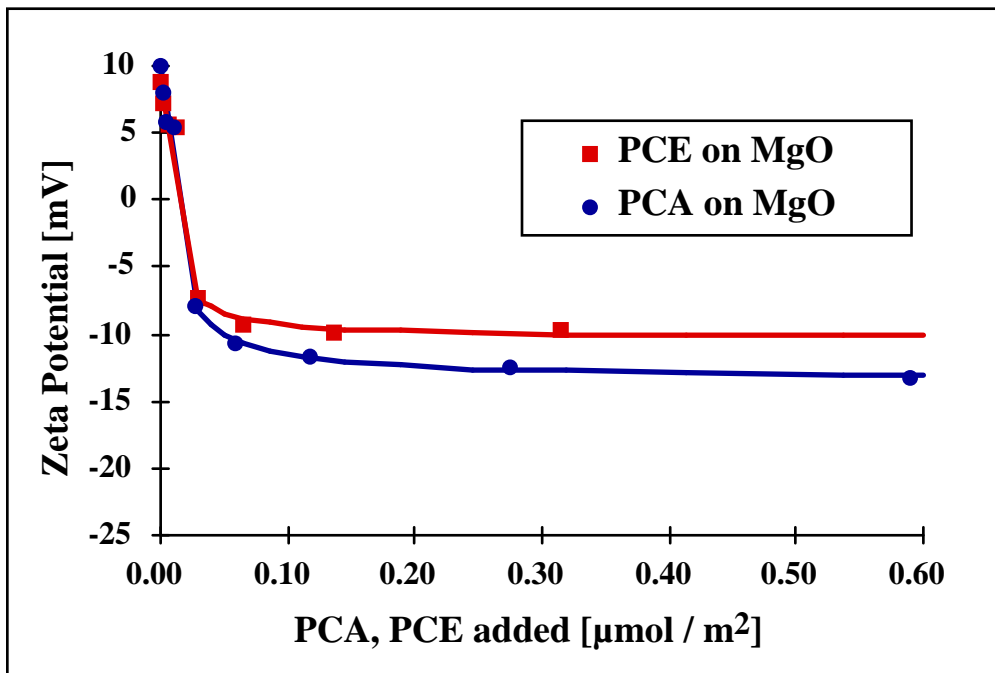


Figure 5 Zeta potential measured on magnesium oxide. The amount of superplasticizer added is given with respect to the surface of the powder in the suspension.

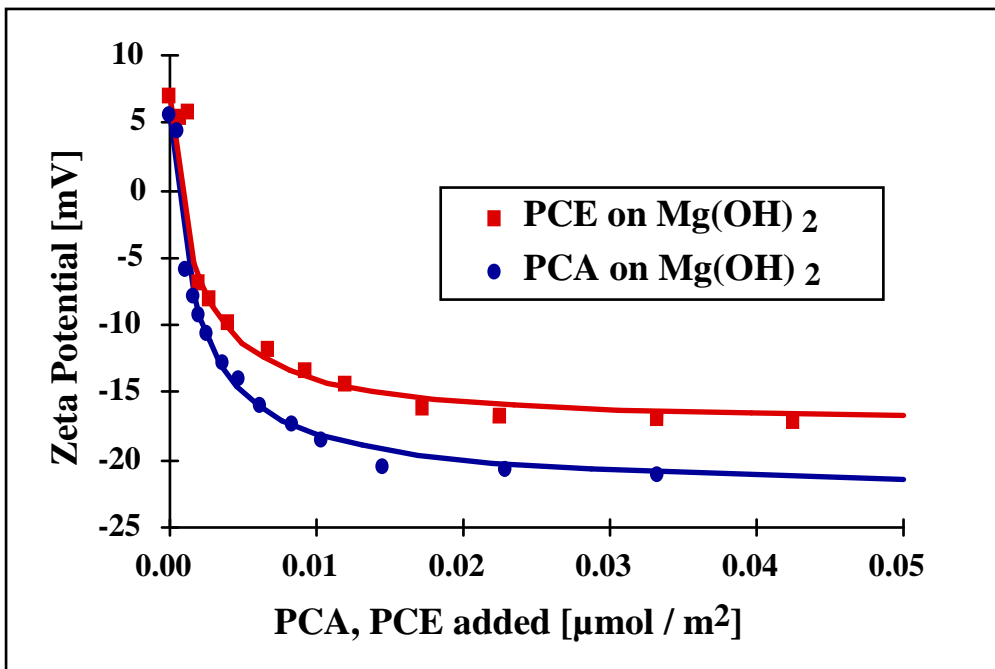


Figure 6 Zeta potential measured on magnesium hydroxide. The amount of superplasticizer added is given with respect to the surface of the powder in the suspension.

We also see especially in Fig 6, that the adsorption continues after the surface has acquired a negative charge. This might be due to either a non electrostatic interaction involved in the adsorption process, or to an inhomogeneity in the surface charge distribution. Hoogeveen et al

(1996) in their study of the adsorption of cationic polyelectrolytes on oxides (TiO_2 and SiO_2) find the latter possibility the most likely in explaining a similar result with TiO_2 .

CONCLUSIONS

The adsorption of the PCA polymer (a polycarboxylate, polysulfonate) on MgO does not depend on temperature, while it does for the PCE polymer (a polycarboxylate, polysulfonate, polyethylene glycol-ester containing). This may result from the PCA having a stronger interaction with the MgO surface, due to its larger number of ionic groups. On the $\text{Mg}(\text{OH})_2$ no temperature dependence is observed. This can be due to the differences between the surfaces of both powders. More PCE than PCA can be adsorbed on either surface. However, the extra amount of adsorbed PCE is not sufficient to induce a larger negative zeta potential than the PCA.

When considering the dispersion effect of these polymers, we must therefore expect that the electrostatic effect of the PCA will be greater than for the PCE. However, due to its greater adsorption, the PCE will probably have a more important effect through steric repulsion or by entropic exclusion.

Rheological measurements must now be carried out to determine which of these polymers is the most efficient water reducer. From such measurements and with the above conclusions it may be possible to find out which effect is the most important. This knowledge will be an important help in the design and production of new even more efficient superplasticizers.

The strong temperature dependence for the adsorption of the PCE has shown that this factor could be a dominant issue concerning the use of some superplasticizers. Consequences on the rheology have still to be studied.

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