

# Some basic aspects of the interaction cement-superplasticizers

Yves F. Houst, Paul Bowen and Alain Siebold  
Swiss Federal Institute of Technology, Institute of Materials Science, Powder Technology  
Laboratory, MXD  
1015 LAUSANNE, Switzerland

**ABSTRACT.** Colloidal theories have been applied successfully to cement suspensions. Interparticle forces, important in the attractive networks formed by cement pastes, have been described and some of the limitations, often ignored until now, explored and discussed with reference to recent literature. How the complex pore solution met in cement pastes may be represented by a non integer charge, how electrostatic forces induced by superplasticizer adsorption and how the particle size distribution of cement particles can effect interparticle force calculations are discussed and demonstrated. Measurements of zeta potentials using multi frequency acoustophoretic analysis for ultra-fine cements are also presented.

**Keywords:** Adsorption, dispersion, interaction forces, modelling, rheology, superplasticizers.

**Y. F. Houst**, a chemist, is the Head of the Cement Group at the Powder Technology Laboratory (LTP), Swiss Federal Institute of Technology (EPFL), Lausanne, Switzerland. His current activities include transport mechanisms and durability aspects of cementitious materials, as well as the interaction of chemical admixtures with cement.

**P. Bowen** earned his Ph.D. from the University of Cambridge in physical chemistry. He has been a research associate at the LTP for 15 years. Current activities include powders synthesis, powder characterisation, powder dispersion and powder forming.

**A. Siebold**, is a post-doctoral chemist working at the LTP over the past year on the characterisation of model powder for cement admixture interactions.

## INTRODUCTION

Dispersion of agglomerated cement particles is a key point to improve the workability of concrete or to reduce the amount of mixing water. This is the role of superplasticizers or high range water reducers (HRWR). The development of new products, more efficient and tailored for specific applications, should be based on the knowledge of the mechanisms of their interaction with the cement. It is the aim of this article to present some basic aspects from the theoretical point of view and some new experimental techniques.

*Dispersion* or *London dispersion forces* play an important role in the properties of numerous materials and in particular in cement suspensions. The Lifshitz's theory was a major advance and founded our current understanding of these forces [1, 2]. In the last fifty years, it was successfully applied to various practical problems [2]. The dispersion forces are essentially attractive in suspensions of one type of particle (i.e. the same crystalline phase). The balance between these dispersion forces and repulsive forces from surface charge or adsorbed species governs the behaviour of particulate suspensions [3]. The DLVO theory takes into consideration the sum of these interparticle forces, and can be used to understand and predict suspension stability and rheology. This theory has been used to describe cementitious systems [4-6] despite the fact that cement suspensions are not really in the colloidal domain. These approaches have proven to be very useful in trying to understand the complex systems of cement suspensions with polymeric additives. However, the full complexity of such systems was generally not taken fully into consideration perhaps undermining some of the conclusions that may have been drawn from the approach. In more recent years attempts have been made to take into account the complexity of the ionic medium of cement suspensions, the effects of their broad particle size distributions and their interaction with superplasticizers [5, 6]. Steric repulsion, which plays a key role in superplasticizers of the latest generation, can be taken into account by applying de Gennes model, for instance [7]. The key parameters, which govern the steric repulsion, i.e. the adsorption layer thickness and its conformation at the solid liquid interface are often difficult to quantify.

This paper looks at the various assumptions generally used in calculating the interparticle forces for cementitious suspensions and discusses the avenues open for further improvement in the approach to help us towards a more quantitative assessment of cement suspension rheology. One obstacle often ignored is the correct measurement for the zeta potential of a cement suspension, highlighted by Lewis et al [4] and more thoroughly discussed by Flatt and Ferraris. These authors suggest that measurements of zeta potentials for ultra-fine cements multi frequency acoustophoretic analysis should give the most reliable results and some preliminary results are presented.

## SPECIFICITY OF CEMENT SUSPENSIONS AND POSSIBLE SOLUTIONS

Portland cement is composed of roughly five mineralogical phases alite (impure  $C_3S$ ), belite (impure  $C_2S$ ),  $C_3A$  and  $C_4AF$ , and gypsum. These phases have different mechanical strengths and are not ground to the same degree when producing cement powder from a clinker. Different size fractions may therefore differ in composition, for example gypsum is concentrated in the fine fraction. The particle-size distribution (PSD) of cement is generally not taken into account in modelling of cement-superplasticizers interactions. It will be shown below how it can be taken into account. Cement particles are also often composed of two or

more phases with very different surface properties. Different portland cements, with close chemical composition can exhibit different behaviours with respect to the same superplasticizers which may be a consequence of this heterogeneous surface chemistry. Hence, it is often difficult to attribute specific behaviours to specific characteristics of the cements. Furthermore, hydration modifies cement particle surfaces over time. Part of superplasticizers can be trapped during hydration in organo-mineral phases (OMP), which is no longer available for plasticizing concrete [8]. Such difficulties in studying superplasticizers can partially be overcome by using non-reactive model powders. Recently MgO, which has surface properties at high pH close to that of cement (low positive charge), has been successfully used for adsorption and rheological studies [9, 10].

When cement is contacted with water, this latter dissolves numerous ions and the so-called pore solution becomes far from an ideal electrolyte. The ionic composition of the solution evolves with time and also depends on the cement type [5]. The interparticle interaction forces are strongly influenced by the ionic composition of the pore solution. It has also been shown recently how to take this parameter into consideration by using the Debye-Hückel approximation and a symmetrical and non-unit charge equivalent electrolyte [6].

Much discussion on superplasticizer performances is linked to adsorption measurements, which are most often performed by solution depletion. This assumes that the difference between the amount of polymer present in the aqueous phase before and after contact with cement is the amount adsorbed on the cement particle surfaces. What it really gives is an indication of the amount of polymer consumed both by OMP formation and adsorption. Solution depletion cannot distinguish between consumption and adsorption. Solution depletion data (consumption) cannot provide the concentration of superplasticizers adsorbed at the surface of cement particles. As this factor is a key element in the evaluation of interparticle forces it is difficult to interpret effects using data from solution depletion results alone, as long as saturation has not been reached – another reason for using model powders.

Adsorption of the first generations of superplasticizers was quickly recognised to induce a negative zeta potential (electric potential at a shear plane) on cement particles, larger in magnitude than that of the initial potential of cement. Zeta potentials were often measured in very dilute suspensions and far from the concentrated suspensions used in practice. Measurements performed using electroacoustic methods, which allow higher volume fractions, show that the induced charge or zeta potential is much lower than suggested by electrophoretic measurements [4] (-2 to -10 mV rather than -30 to -50 mV). The relatively large size of cement particles for this method creates an additional problem as the signal from acoustophoresis is a function of particle size and the applied frequency. For a 20 kHz frequency only particles less than 2 micrometers give an appreciable signal [11]. It has been shown that the background signal from the aqueous electrolyte can be larger than the signal produced by the cement particles themselves [12] at this single frequency. Using a finer cement fraction, as well as new commercially available apparatus with multiple frequencies extends the upper size limit to around 10 microns and should allow us to partially overcome this problem as illustrated later.

It is only recently that the issue of estimating the thickness of the adsorbed layer of superplasticizers has really begun to be addressed. This has been stimulated by the observation that polymers with side chains of poly(ethylene oxide) usually induce better dispersion with lower zeta potential. As a result, awareness of the importance of steric repulsion has grown. The measurements have been made predominantly by atomic force

microscopy (AFM) [13, 14]. Producing both suitable substrates and AFM probes for such studies is one of the challenges that will have to meet in the near future.

Cement particles, due to their large size, are more sensitive to shear forces than Brownian forces. For this reason, it is the maximum interparticle force that is the most relevant parameter to discuss with respect to the rheology of cement suspensions; rather than the interparticle potential most often used for evaluating the stability of colloidal particles (i.e. particles that do not sediment if well dispersed).

## THEORITICAL BACKGROUND

Theories of colloidal systems are particularly complex and are presented in many specialised books [2, 3]. Here we shall present some relevant expressions important for cement suspensions. The attractive dispersion force between two particles of radius  $a_1$  and  $a_2$  at a small separation distance (valid for the particle sizes typical for cement suspensions 0.5 to 50  $\mu\text{m}$ ) can be written [5]:

$$F_{(a_1, a_2, h)} \cong \frac{1}{12} A_{(h)} \left( \frac{\bar{a}}{h^2} \right) \quad (1)$$

Where:

$A_{(h)}$  is the retarded Hamaker constant (related to the dielectric properties of the material and the medium).

$h$  is the separation distance between particle surfaces

$\bar{a} = \frac{2a_1 a_2}{a_1 + a_2}$  the harmonic average radius for particles of radius  $a_1$  and  $a_2$ .

Electrostatic forces between cement particles can be either repulsive between particles of identical charges or attractive between particle of opposite charge. As a negative charge is induced by adsorption of anionic superplasticizers, the resulting repulsive force can be written [5]:

$$F_{ES} \cong -2\pi\epsilon\epsilon_0\bar{a}\psi^2 \frac{\kappa e^{-\kappa(h-2L)}}{(1 + e^{-\kappa(h-2L)})} \quad (2)$$

Where:

$\epsilon_0$  is the permittivity of vacuum

$\psi$  is the electrostatic potential

$\epsilon$  is the relative dielectric constant of water

$\kappa^{-1}$  is the Debye length  $\sqrt{\frac{\epsilon\epsilon_0 k_B T}{2e^2 z_{eq}^2 n_{eq}^b}}$

$z_{eq}$  is the charge of the equivalent symmetric electrolyte

$n_{eq}^b$  is the bulk concentration of the equivalent symmetric electrolyte

$L$  is the distance from the particle surface used as the plane of origin for the electrostatic repulsion. This is often taken as the particle surface, but for charge induced by certain superplasticisers  $\psi$  may be nearer the polymer liquid interface rather than the particle surface.

By assuming that superplasticizers adsorb in a mushroom-like conformation, the steric force can be calculated by the de Gennes model [7]:

$$F_{Ste} = \bar{a} \frac{6\pi k_B T}{s^2} \left[ \left( \frac{2L}{h} \right)^{3/2} - 1 \right] \quad (3)$$

Where  $s$  is the distance between the centres of gravity of two neighbouring mushrooms.  $L$  is the maximum length extending into the solvent.

The total interaction force can be obtained by taking the sum of (1), (2) and (3). Since all these equations depend linearly on  $\bar{a}$ , it is possible to introduce an interparticle force parameter  $G_{(h)}$  given by:

$$G_{(h)} \cong F_{Disp} + F_{ES} + F_{Ster} \quad (4)$$

## SOME RESULTS

Modelling of the effects that superplasticizers have on rheological behaviour via the interparticle forces will now be presented. In general, the attractive forces found in cement suspensions create a rigid network, which prevents the cement from flowing without applying a certain shear force. The magnitude of this force, the yield stress, will depend on the interparticle forces and how these are modified by the presence of an adsorbed layer of superplasticizer. We would like to be able to predict this effect from a knowledge of the system parameters, particle size distribution, induced surface charge, adsorbed layer thickness and surface coverage. Such predictive theories would help in choosing dosage levels to maximize efficiency and minimize cost, when using superplasticizers.

The prediction of rheological properties with respect to interparticle forces for various ceramic systems has, in general, shown very good qualitative agreement but not a quantitative agreement [4, 15]. Various reasons have been evoked, one being that the interparticle forces are a function of particle size and hence size distribution and most calculations are limited to using some average diameter [4, 16]. When we consider a stable ceramic suspension, solids loadings towards the maximum packing fraction can be approached (65% volume solids) with the suspension remaining a fluid. For cement suspensions even with superplasticizers attractive non-flowing networks can be formed at much lower volume fractions around 48% solids loading (W/C ratio of 0.35). The reason behind this, is that the attractive forces between particles trap a certain fraction of the water, which in a stable ceramic suspension can lubricate the flow of ceramic particles past one another. So, a cement suspension is in fact like a cluster of agglomerates, which have a higher effective volume than the real solids volume present and in order to allow the cement suspension to flow this effective volume has to be decreased by breaking apart a certain fraction of the attractive particulate network.

A strategy has been developed to see what decrease in effective volume fraction of solids would be needed so that the attractive cement network begins to flow [18]. The decrease in effective volume fraction of solids will be directly related to the number and type of pairs of interacting particles – agglomerates – that could be broken apart by a given shear stress; as our doublets have a larger effective volume than the individual particles because of the liquid trapped between them as illustrated schematically in Figure 1(a). The dispersion of different

doublets with different individual particle sizes will not have the same effect on rheology, as each individual pair will have different effective to real volumes (Figure 1 (b)). The amount of volume lost per interacting particle pair,  $\Delta V_{k,l}$ , has been estimated using a truncated cone geometry, which is tangent to both spheres as shown in Figure 1(a).

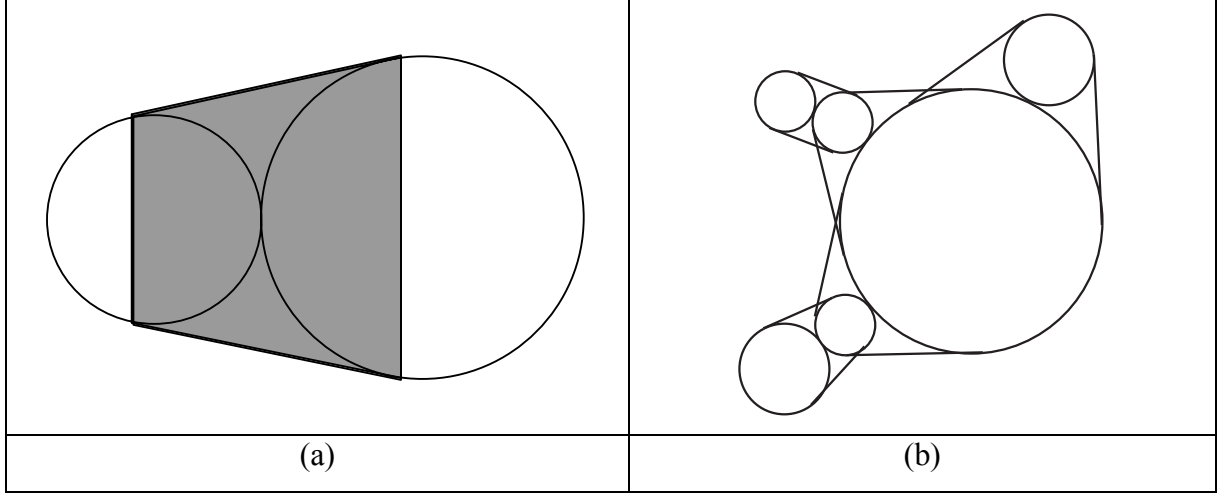


Figure 1. (a) Truncated cone used to determine the effective volume change due to a doublet (b) different pairs of doublets illustrating the different effective volumes for different pairs.

This volume is given for two unequal spheres by:

$$\Delta V_{k,l} = \frac{2\pi}{3} \hat{a}^2 (4\hat{a} - \bar{a}) \quad (5)$$

Using a particle packing model to create a microstructural picture of the interacting particles, which takes into account the broad particle size distribution, a maximum interparticle force can be calculated [18]:

$$G = \frac{F}{\bar{a}} = \frac{F_{vdW} + F_{ES} + F_{Ste}}{\bar{a}} = \frac{A_{eff}(h)}{12h^2} - 2\pi\epsilon\epsilon_0\psi^2 \frac{\kappa e^{-\kappa(h-2L)}}{(1 + e^{-\kappa(h-2L)})} - \frac{6\pi k_B T}{s^2} \left[ \left( \frac{2L}{h} \right)^{5/3} - 1 \right] \quad (6)$$

This is illustrated in Figure 2 for a model MgO powder with the key parameters being the adsorbed layer thickness and induced surface charge linked with the superplasticiser adsorption. Positive values indicate repulsion and negative values attraction. In absence of electrostatic repulsion this maximum is reached for separations of about twice the maximum length of the layer extending from the surface into the solvent. When electrostatic effects come into play, the point of maximum repulsion is beyond this distance. There is a clear steric effect which can be significantly complemented by electrostatic repulsion, provided one can place the potential at the outer bound of the adsorbed layer [6].

These interparticle forces can then be used with the effective volume freed on agglomerate disruption to predict a yield stress for the attractive network as proposed recently by Flatt et al. [18]. A simpler method would be to take the average coordination number, the average

interparticle interaction force, using the mean harmonic diameter  $\langle \bar{a} \rangle$ , then use the number of interactions per unit volume to calculate the force necessary to break the network (similar to the approach proposed by Kapur et al. [17]). This has been done for a gamma alumina suspension [19] and the average coordination number resulting from a numerical particle packing model using measured PSDs [20] gave very coherent results. Similar coordination numbers to those from the models of Goto, and Iwata & Homma, cited by Kapur et al [17]. It would be interesting to take this approach further and perhaps use analytical models related to the particle size distribution to provide an average coordination number and harmonic average diameter.

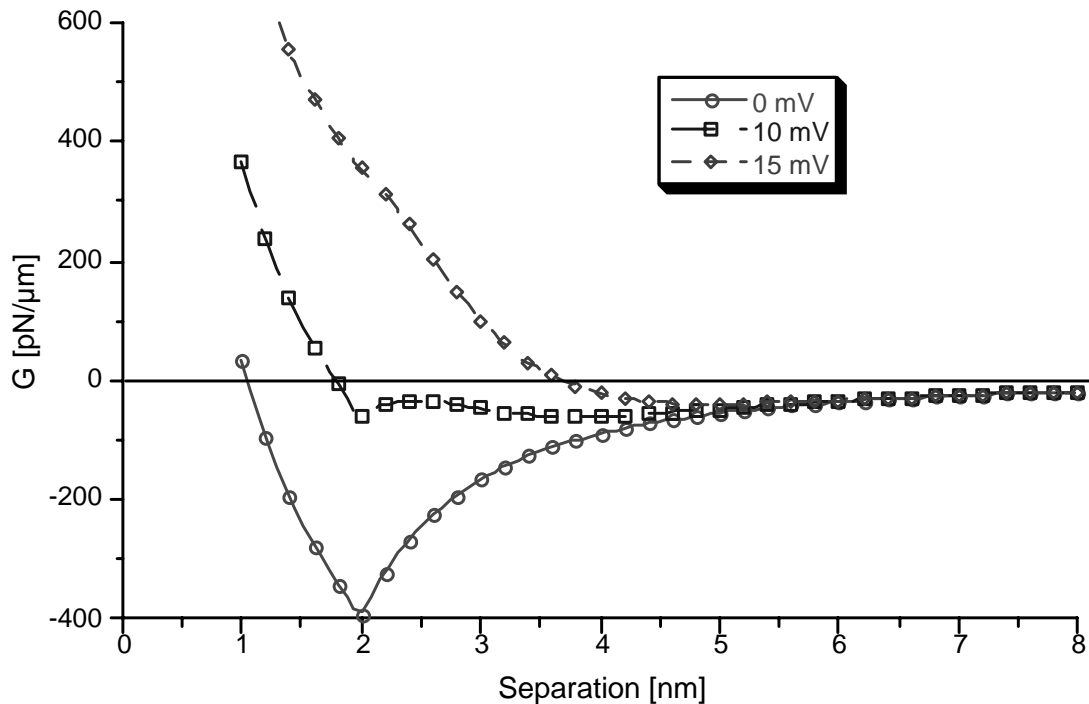


Figure 2. Normalised interparticle force as a function of separation, for three different potentials. Positive values indicate repulsion and negative values attraction. Adsorbed layer is 1 nm. Computed for MgO particles, in the equivalent symmetric electrolyte representation of a cement suspension.

## FUTURE PROSPECTS

Future prospects would be to further investigate the various parameters, which are still uncertain to some degree, in the evaluation of the interparticle forces and need to be more accurately established such as more reliable zeta potential measurements, maximum allowable effective volume fraction increase due to a non dispersed doublet, the adsorbed polymer layer thickness, the plane of origin for electrostatic forces (placed at the surface of the adsorbed layer for the above calculations, but placed half way to the surface by Lewis et al. [4]), hydrodynamic forces which are expected to oppose dispersion, better Hamaker constants for

the different cement phases (calculations done presently with MgO data, the fact that cement particles are multiphase and non spherical).

We have very recently made measurements on fine cements (98% < 10  $\mu\text{m}$ ) using a Colloidal Dynamics Acoustosizer II instrument which measures zeta potentials for particles up to 10  $\mu\text{m}$  in diameter. The results are shown in Figure 3 as a function of added superplasticizer (SP). The cement alone measurement was on the same time scale as for the superplasticizer additions and therefore shows how the cement alone changes over the 90 minute period taken for the experiments. The zeta potential decreases on addition of both polycarbonate-polysulfonate (PCPS) and a polynaphthalene sulfonate from  $-10$  to  $-13$  and  $-15$  mV respectively, although small would have an effect on the rheological behavior of the cement as illustrated in Figure 3. Efforts to make measurements on an old generation single frequency instrument (Pen Kem 7000) gave very low signals and very low values of zeta potential (around  $-1$  mV) even for the PNS at 1% mass addition where  $-15$  mV is observed in Figure 3.

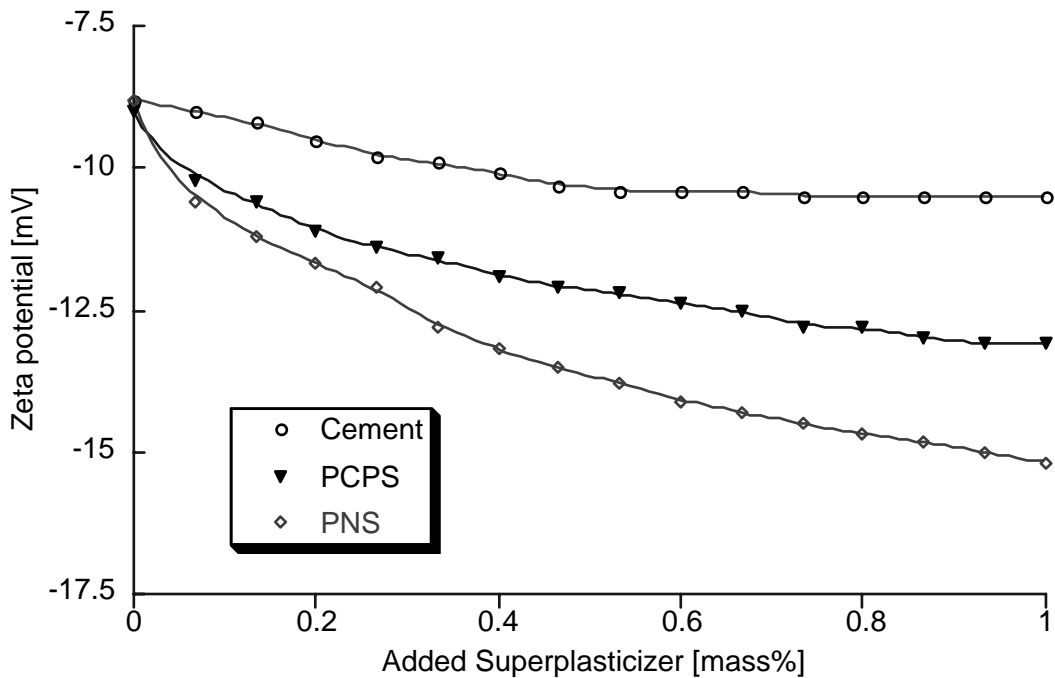


Figure 3. Zeta potentials using the Colloidal Dynamics Acoustosizer II for fine cement (98% < 10  $\mu\text{m}$ ) as a function of added superplasticiser . PNS: sodium polynaphthalene sulfonate PCPS): sodium polycarbonate-polysulfonate

## CONCLUSION

It has been shown how colloidal theories can be applied to the very complex system of cement suspensions, thought cement particles are not in the range of colloids. The interparticle forces, electrostatic, steric and dispersion, that act on cement particles were all found to scale on the harmonic diameter,  $\bar{a} = \frac{2a_1a_2}{a_1 + a_2}$ , for un-equal spheres. Several parameters in the calculation of the interparticle force calculation have been reviewed and the importance of a small charge induced by superplasticiser adsorption shown to be important.



The particle size distribution can be taken into account by using a particle packing model which provides the harmonic diameter distribution of randomly packed cement particle size distribution. The possibility of taking into account the particle size distribution is an important step forward as it has often been cited as one of the stumbling blocks limiting the use of interparticle interaction energies for quantitative assessment of concentrated suspension rheology. Novel developments of relatively new experimental techniques, like acoustophoresis, permit the measurement of zeta potentials for fine grained cement and will help in the quest towards the quantification of the effect of superplasticizers on the rheology of cement suspensions.

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