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**Reprinted from Materials and Structures/Matériaux et Constructions, Vol. 35, 541-549,  
November 2002.**

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# Acoustophoretic characterization of cement suspensions

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Paper received: March 6, 2001; Paper accepted: October 31, 2001

## A B S T R A C T

Acoustophoresis has been used to study the evolution of the surface potential of hydrating cement suspensions because it is potentially capable of measuring zeta potentials of cement suspensions at concentrations high enough not to modify ion/particle interactions, which is not the case for most other methods. Measurements were performed using cement with and without addition of high-range water reducing admixture (HRWRA). In this paper it will be shown that quantitative determination of the potential is rendered difficult by the large size of cement particles as well as by ongoing hydration reactions. Other benefits of the technique will be discussed.

## R É S U M É

L'acoustophorèse a été utilisée pour étudier l'évolution du potentiel de surface de suspensions de pâtes de ciment, durant leur hydratation, parce que cette technique est potentiellement capable de mesurer le potentiel zéta d'une suspension de ciment à des concentrations suffisamment élevées pour ne pas modifier les interactions ion/particule, ce qui n'est pas le cas de la plupart des autres méthodes. Les mesures ont été faites, en présence ou non d'adjuvants à pouvoir réducteur d'eau élevé. Dans cet article, on démontre aussi que la détermination quantitative du potentiel est rendue difficile à cause de la large taille des particules ainsi que des réactions d'hydratation. D'autres avantages de cette technique sont également discutés.

## 1. INTRODUCTION

The use of small amounts of dispersing agents in concrete (< 1% of the cement mass) permits production of a highly flowable material with much less water, making the end product much more durable. It also facilitates efficient incorporation of waste or by-product materials as silica fume, fly-ash or slag, as a substitute for cement, which is an energy costly material [1].

The dispersing polymers, typically called either superplasticizers or high-range water reducing admixture (HRWRA), act by reducing the attractive interparticle force between cement particles. Until recently, all were polyanionic polymers. One of the most widely used is a sulfonated polycondensate of naphthalene and formaldehyde (SNFC) [2]. The latest generation contains a backbone with carboxylate functions and side chains of poly(ethylene-glycol-oxide) [3]. These induce

a steric repulsion expected to be much more effective than electrostatic repulsion in cement suspensions. Nevertheless, polymers of earlier generations remain competitive for many applications because of their lower cost. A side effect of most superplasticizers can be interference in the hydration reactions. Fernon *et al.* [4] demonstrated that SNFC could be incorporated into Afm phases, complicating the evaluation of superplasticizer performance [5].

The initial objective of this paper was to conduct a study of the zeta potential of cement suspensions, and its modification by SNFC. During this study, it appeared that information could be obtained about the cement hydration and the way it can be affected by SNFC. These results are reported in the light of developing a broader understanding of the behaviour of superplasticizers in cement suspensions.

Editorial Note

Dr. Chiara F. Ferraris is a RILEM Senior Member and works at NIST, a RILEM Titular Member.

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## 2. BACKGROUND

### 2.1 Zeta potential

A particle placed in a polar liquid (aqueous solution) will have an electrokinetic potential  $\psi_0$  due to a surface charge density  $\sigma_0$  (Fig. 1). Counterions will be adsorbed at the surface. The center of the plane formed by the center of the adsorbed counterions is called the Stern layer  $\psi_\delta$  (double layer). A third plane is defined as the zeta potential,  $\psi_\zeta$ . This plane defines the limit up to which the liquid molecules and ions are effectively bonded to the surface and unaffected by bulk motion of the liquid. The slip plane is often considered equivalent to the outer bound of the Stern layer. The direct measurement of the surface potential,  $\psi_0$ , is impossible because the surface is contaminated by the counterions adsorbed. The measurement of the Stern layer potential,  $\psi_\delta$ , is not possible because the degree of hydration at the surface is not known, therefore only the zeta potential,  $\psi_\zeta$ , can be measured [6]. Because of this, the interaction between charged particles is often calculated using zeta potential in place of Stern potential.

### 2.2 Reported zeta potential of cement

The zeta potential of cement particles is small. However, both positive [4, 7] and negative values can be found in the literature [4, 8, 9]. The addition of superplasticizers typically induces negative zeta potentials. For strong electrolytes, values are between  $-20$  mV and  $-30$  mV. For weaker electrolytes, as PEO containing copolymers, values can be as small as  $-5$  mV [9].

A common method for measuring zeta potential has been microelectrophoresis. It involves the determination of the velocity of particles under the influence of an electric potential. It requires very dilute suspensions (about 100–200 mg/L) because the velocity of individual particles needs to be timed. Such dilutions modify the ion/particle interactions of cement. In addition, the larger particles settle, which means that only the finer particles are measured.

Doppler Electrophoretic Light Scattering Analyser (DELSA) loses accuracy at high electrolyte concentrations and requires low volume fractions. However, measurements can be done directly after water addition, which allowed Nachbaur [11] to demonstrate a significant dependence of the zeta potential of tricalcium silicate, a major phase in cement, on the solution content of calcium and sulphate ions.

Electro Sonic Amplitude (ESA) and acoustophoresis are two similar methods that present an important advantage for cement suspensions: they can measure suspensions with relatively high volume fractions of solids. Darwin *et al.* [10], who studied the effects of SNFC in cement suspensions using ESA, conducted one of the few detailed studies of such methods applied to cement suspensions.

In this paper, acoustophoresis is used to study the

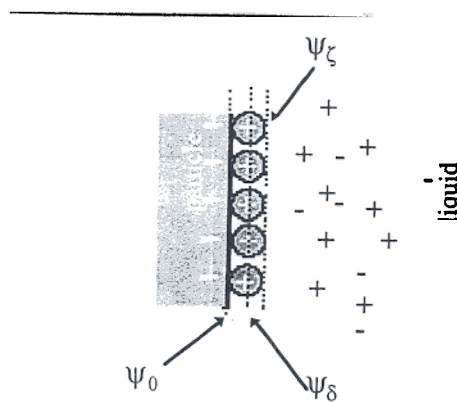


Fig. 1 – Schematic representation of the zeta potential

evolution of the surface potential of hydrating cement suspensions, whether or not in the presence of a HRWRA. Limitations linked to particle size distribution are developed in order to show how quantitative determination is rendered difficult due to ongoing hydration reactions. Results allow reinterpretation of unexplained results reported by Darwin *et al.* [10].

### 2.3 Principle of acoustophoresis

In acoustophoresis, a sound wave induces a periodic velocity difference between the continuous medium and the suspended particles, provided they do not have the same density. When particles are charged, a periodic electrical potential results. The amplitude of the macroscopic potential measured in the suspension is called the colloid vibration potential (CVP) and is linked to the zeta potential of the colloid particles. ESA systems are the reciprocal: a periodic electrical potential induces a sound wave.

A first generation system used a single wavelength, while more recent systems are capable of measuring over a broad span of wavelengths. Contributions to the calculation of zeta potential from ESA have improved the determination zeta potential by electroacoustic methods [12, 13]. Despite the advantages of the more recent systems, there is still interest in getting the most out of the monochromatic systems and Appendix A shows how the initial treatment [15] can be extended to account for particle size effects, while Appendix B addresses the effect of particle size distribution on the zeta potential.

The final result is that the zeta potential is proportional to a parameter termed Relative Acoustophoretic Mobility (RAM), but that the proportionality constant is subject to large uncertainties. For this reason we discuss the evolution of RAM, bearing in mind that it is linked to the zeta potential through a constant that depends on volume fraction, particle size distribution and the nature of both the solid and the continuous phases.

### 3. EXPERIMENTAL

#### 3.1 Materials

A Type I/II portland cement (ASTM C150<sup>1</sup>) from Lehigh Portland Cement Co. (Allentown, PA)<sup>2</sup> was used. Its chemical composition is given elsewhere [15]. Its specific gravity was  $3.15 \times 10^3 \text{ kg/m}^3$  and BET specific surface  $0.786 \text{ m}^2/\text{g}$  ( $\text{N}_2$  adsorption). The particle size distribution (Fig. 9) was measured in water by laser diffraction (Malvern Master Sizer E<sup>2</sup>), using ultrasonication to disperse particles.

An SNFC made by the W. R. Grace & Co. (DARACEM 19)<sup>2</sup> was used diluted to 20% dry extract by mass and used as HRWRA. Its average molecular mass was between 10'000 and 30'000. The solution was further diluted in water (about 20% by mass) to allow a more precise dosage.

#### 3.2 Relative acoustic mobility

Relative Acoustic Mobility (RAM) was measured at 23°C to 25°C by acoustophoresis (Penkem<sup>2</sup>, system 7000; Bedford Hills, USA). The suspensions were prepared by dispersing cement in demineralised water under vigorous agitation and sonification for 15 min (150 W, 20 kHz). Volume fractions of cement in the suspension were 2.1 %, 7.4 % and 19.4 %, referred to as 2.1 %v, 7.4 %v and 19.4 %v from here on. The suspension was then placed in the measuring cell, under magnetic stirring, and degassed for 5 min (the measuring cell was covered by a rubber seal linked to a vacuum of 3.5 kPa) to reduce attenuation by air bubbles. At the end of the measurements, the suspensions were centrifuged at 314 rad/s (3000 rpm) for 10 min and the supernatants were measured.

SNFC was added with a microdispenser, either progressively as a concentrated aqueous solution or shortly after the cement was put in contact with the solution. In the first case, referred to as progressive addition from here on, the volumes added are initially of 20  $\mu\text{L}$ . After each addition, the suspension is left to stabilise before an additional addition is performed. When there is little change in RAM, the volume of the addition is increased the following time.

Solutions of lime and gypsum in 0.03 mol/L KOH were prepared to test the importance of electrolytes on the measured RAM. Solutions of KOH were first measured and then saturated with lime, gypsum or both. The saturated solutions were left to sediment and were then centrifuged before measuring the supernatant. All solutions were prepared with ultra-pure water boiled to avoid presence of  $\text{CO}_2$ .

#### 3.3 Calcium concentration

The concentration of calcium in the supernatant was measured using the atomic absorption (AA). A suspension (7.4 % volume of cement in water) was prepared and continuously stirred using a magnetic stirrer. At regular intervals, 1 mL of liquid was filtered and diluted 100 times. Two measurements were done: one of the aliquot as is, one of an aliquot after addition of HCl. The second measurement gives the total calcium concentration of divalent calcium, while the first gives only the amount of free divalent calcium (neither in an ion pair or a nuclei).

### 4. RESULTS

#### 4.1 Conductivity

Fig. 2 indicates that the conductivity of KOH solutions is mostly affected by the presence of lime. No clear increase of the conductivity is measured when gypsum is added.

All cement suspensions without SNFC exhibit a conductivity increase followed by an abrupt decrease,

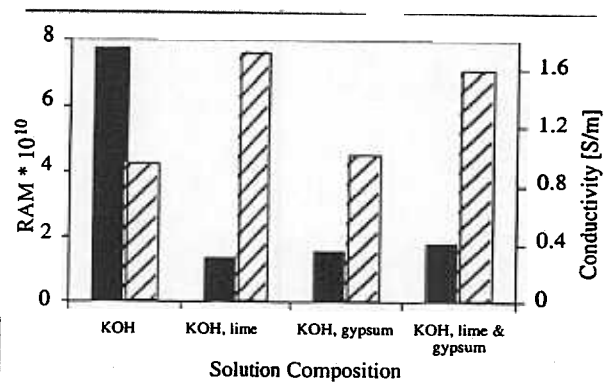


Fig. 2 – RAM (filled bars) and conductivity (dashed bars) of ionic solutions in 0.03 mol/L KOH. Three solutions are also saturated with respect to lime, gypsum or both.

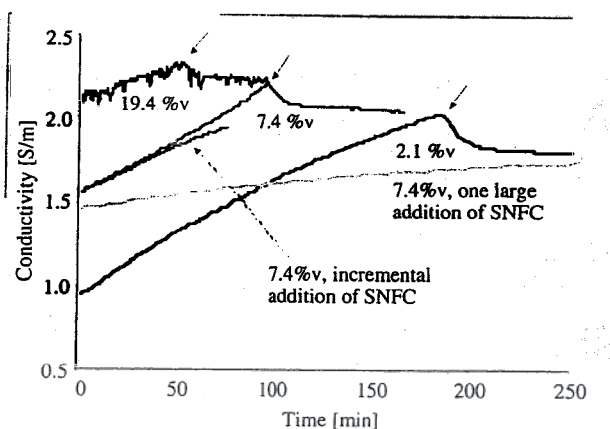


Fig. 3 – Conductivity of cement suspensions with cement volume fractions of 2.1 %, 7.4 % and 19.4 %. Also shown are two 7.4 %v suspensions to which SNFC was added either all at once after mixing or by increments. Continuous arrows indicate the conductivity peak.

(1) "Standard Specification for Portland Cement" ASTM C150 -95, Vol. 04.01.

(2) Brand names, names of manufacturers and equipment are identified in this report to adequately describe the experimental procedure. This does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material identified is necessarily the best available for the purpose.

and then a much slower decrease (Fig. 3). For  $C_3S$  suspensions, this was rationalized by the occurrence of a critical super-saturation at which massive precipitation of CH begins [17].

At the end of the experiments, the conductivity of the centrifuged suspensions (2.1 %v and 7.4 %v) was found to be essentially identical to that of the suspension (max 2.3 % difference). Addition of a small amount of SNFC did not change conductivity.

Progressive addition of SNFC to cement suspensions slowed the rate of conductivity increase with respect to the cement suspension without SNFC, as shown in Fig. 3. The same figure also indicates that if a large amount of SNFC is added at once (8.9 mg/m<sup>2</sup>, corresponding to the amount above which CVP did not change), then conductivity rise is extremely small. These results are not due to dilution by the concentrated solution of SNFC added (the error from neglecting dilution is given by the product  $\phi(1-\phi)$ , see Appendix A, and is only of 1.7 %).

With a large SNFC addition, no critical super-saturation could be identified, even at times much longer time than shown in Fig. 3 (two days). This might suggest that SNFC could take part in the nucleation of CH.

## 4.2 Background signal

Ions produce a signal, termed the Ion Vibration Potential (IVP) that must be deduced from that of the suspension, by taking a vector difference, to obtain the true CVP [14]. This corrected CVP multiplied by the conductivity of the continuous phase and divided by the pressure amplitude, gives the RAM. Because conductivity of the supernatant and the suspension were the same (see § 4.1) RAM could be determined using the suspension conductivity. Fig. 4 shows the CVP of cement suspensions and the IVP of their supernatants (2.1 %v and 7.4 %v were centrifuged at the end of the experiment, while as for 20 %v the suspension volume required was larger than the measuring, so a separate suspension was

prepared and its supernatant is representative of the initial rather than the final condition). In all cases the background signal is very important. In normal practice, the aqueous phase is measured first and an automatic background correction is then performed by the software. However, IVP is highly specific to the combination of cations and anions in the system [16] and since the ionic composition of cement suspensions evolves over time, such correction would only be of limited help.

The IVP from the KOH solutions we prepared (Fig. 2) indicates that the highest value of RAM is obtained in the KOH solution alone. All other values are substantially smaller and increase with the amount of dissolved calcium. Addition of gypsum has little effect on the value of lime alone. These results suggest that IVP will tend to increase during hydration. Only in the very first minutes of hydration might calcium concentrations be low enough to lead to a strong signal as found in the straight KOH solution.

## 4.3 Relative Acoustic Mobility (RAM)

Equations [A-4] and [A-6] indicate that the zeta potential of a particle is proportional the ratio (defined as RAM) of CVP over the product of conductivity and pressure. The proportionality factor is linked to particle size, particle size distribution, volume fraction, densities of the solid and liquid phase and viscosity of the continuous phase.

Fig. 5 shows that the RAM of suspensions without SNFC decreases initially followed by an increase. The minima (arrows with light lines) occur a little after half way point between mixing and the beginning of CH precipitation (arrows with dark lines). For the suspension containing a volume fraction of 19.4 %, the minimum probably occurs during sample preparation (about 20 min). At the end of these experiments, addition of a small amount of SNFC (40  $\mu$ L to 100  $\mu$ L) to the centrifuged supernatant resulted in an increase of RAM

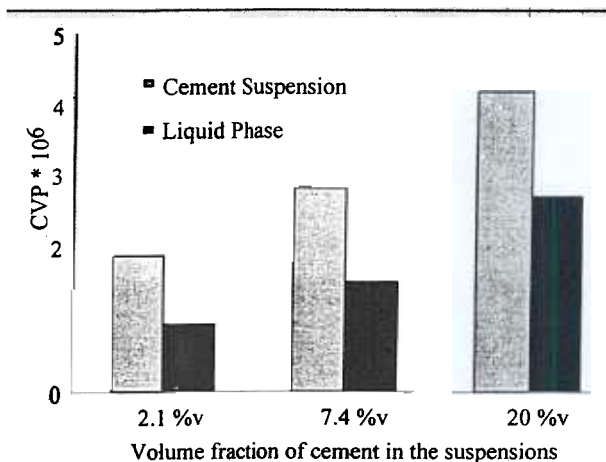


Fig. 4 – CVPs of cement suspensions and their liquid phases. There are no calculations of uncertainty because these are the results of only one measurement.

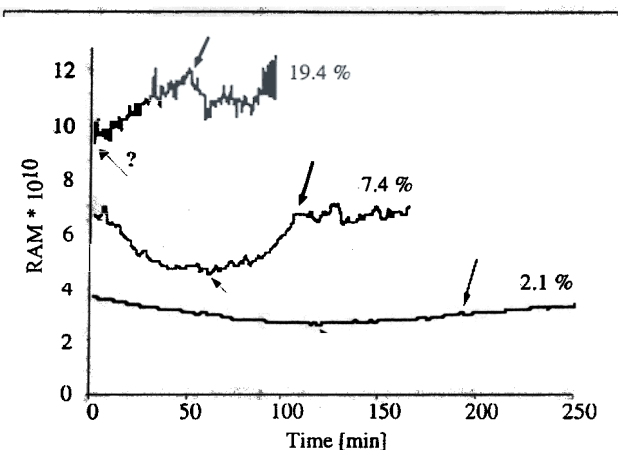


Fig. 5 – RAM evolution in cement suspensions without SNFC. Light arrows indicate where minimum occurs. Dark arrows show the time at which the conductivity peak was observed.



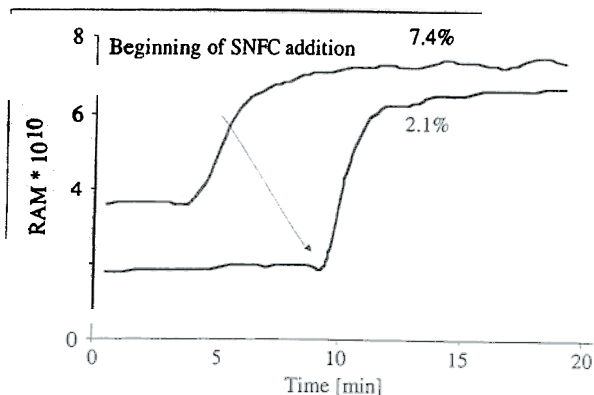


Fig. 6 – Evolution of the supernatant obtained from two suspensions (2.1 %v and 7.4 %v).

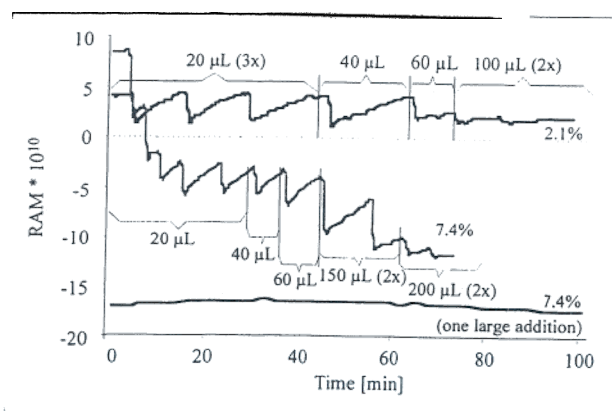


Fig. 7 – RAM of suspensions 2.1 %v 7.4 %v show sudden decreases upon SNFC addition. A 7.4 %v suspension to which the same total amount of SNFC was added shows stable behaviour.

(Fig. 6). This could be linked to the formation of complexes between Ca and SNFC.

The RAM of the suspension with SNFC added just after mixing was quite stable (Fig. 7). When SNFC is added progressively, RAM undergoes a sudden decrease and then progressively recovers (Fig. 7). The depth of these steps decrease as the total amount of SNFC already added increases until the suspension is unaffected by further additions. The amounts of added (given in µL of 20 % solutions of SNFC in Fig. 7) were gradually increased to maintain observable effects. The amount of SNFC beyond which substantial effects on the RAM were no longer detected, was used for the 7.4 % suspension to which SNFC was added in one step shortly after mixing.

#### 4.4 Evolution of calcium concentration

Fig. 8 shows the evolution of the calcium concentration and conductivity in a suspension with a volume fraction of 7.4 %. Two concentrations were measured: total amount of calcium and the free calcium. It is assumed that some calcium is not in the form of  $\text{Ca}^{++}$  but combined with other ions. Therefore, a direct measure-

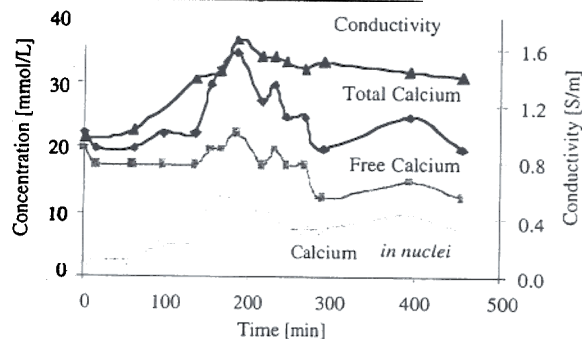


Fig. 8 – Calcium content and conductivity versus time of a suspension with 7.4 % cement by volume.

ment of the aliquot gives the free cations. A small amount of HCl was added to the aliquot and the measurement of the total amount of calcium was then possible, because the  $\text{CaOH}^+$  ion pair are dissociated and nuclei of hydrates are dissociated. It is only under the dissociated form  $\text{Ca}^{2+}$  that calcium is detected. The difference between the total calcium and the free divalent calcium gives the calcium in nuclei (calcium that is not free).

In the neat cement suspension, the evolution of calcium (free and total) is similar to that of conductivity. It increases to a maximum and then goes down sharply but eventually levels off.

## 5. DISCUSSION

### 5.1 Limitations linked to cement

Fig. 4 indicates that the signal of the liquid phase is of comparable magnitude to that of the suspension. Obtaining a precise value for the signal due to the cement particles alone is therefore a difficult task. The small signal of the particles can be the result of two things: a small surface potential and a large fraction of large particles.

The signal generated by large particles ( $> 1 \mu\text{m}$ ) decreases quickly with particle size increase (Appendix B, Fig. 9). Only lower frequencies could limit the extent of this problem. However, this device already measures at a relatively low frequency, so this is an intrinsic limitation of applying electroacoustic methods to portland cements. The only remaining possibility would be to grind the particles to the sub-micron range.

At high volume fractions, the cement signal might therefore become large enough with respect to the background to make the zeta potential determination conceivable. However, this would remain at best imprecise because of the complex effect of particle size distribution (Appendix B), which in addition evolves with time due to hydration.

### 5.2 Importance of electrolyte

The effect of volume fraction on the background signal of solutions is not trivial. On one hand, the

concentrations of ions constitutive of minerals that are close to saturation will be only slightly sensitive to the volume fraction of solids in the suspension. On the other hand, the most soluble phases ( $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , etc.) will undergo almost complete dissolution. So the higher the cement fraction, the higher will be the concentration of dissolved ions coming from these minerals.

Fig. 2 indicated that the signal of the KOH solutions is stronger when saturated with respect to lime, gypsum or both. However, for these three solutions, the signal increases with calcium concentration. Because Fig. 8 indicates that the calcium concentration is already high at the beginning, we can focus on the effect of increasing calcium concentration on the signal.

### 5.3 Suspensions without SNFC

Fig. 3 shows that the conductivity of the suspensions without SNFC goes through a maximum attributed to the nucleation of calcium hydroxide. After this, the rapid decrease is explained by the precipitation of CH until a steady state between dissolution and precipitation is reached [17].

Interestingly, RAM values decrease at first and then increase to reach a plateau value at the time conductivity reaches its peak value. In the case of the 19.4 %v suspension, the minimum is not observed, probably because it occurred during the ultrasonication preceding the measurement.

The change in background signal alone cannot account for the change in the trend of RAM evolution. Furthermore, the minimum occurs between the beginning of the experiment and the peak in conductivity, corresponding to the moment at which Damidot *et al.* [17] speculate that there is a transition between two types of C-S-H (calcium silicate hydrate). They call these  $\beta$ -C-S-H and  $\gamma$ -C-S-H. The former is expected to contain lower amounts of calcium and have a lower surface potential. Above calcium concentrations of about 20 mmol/L of total calcium, the  $\gamma$ -C-S-H becomes more stable. At higher concentrations, super-saturation finally allows the precipitation of calcium hydroxide to begin and both calcium concentrations conductivity drop quickly. The exact calcium concentration at which the transition occurs depends also on the presence of other ions in the aqueous phase [11].

These observations suggest that the change in the direction of RAM evolution over time might be linked to this C-S-H phase change. It would then level off to a constant value when the CH precipitation begins and a steady state is reached between dissolution and precipitation. This remains speculative and that measurements with pure calcium silicate phases would be necessary to confirm these ideas. Using many frequencies would allow the contribution from precipitating phases to be evaluated.

These results indicate that the method is not appropriate for determining absolute values of zeta potentials of cement particles. However, it seems to offer possibilities to bring additional data and insight to cement hydration studies.

### 5.4 Suspensions with SNFC

When a large amount of SNFC is added, no singularity is observed either in conductivity (Fig. 3), RAM (Fig. 7). RAM remains essentially constant, while conductivity evolves towards a plateau.

When a SNFC is added in increments, the RAM undergoes a sudden decrease, followed by a recovery (Fig. 7). Conductivity is only modified over the long term and does not undergo sudden variations (Fig. 3). The sudden RAM decrease is attributed to a fast adsorption of the SNFC onto the particles. Why this is followed by an increase is not clear. It could originate from an initially heterogeneous adsorption of SNFC tending to redistribute more evenly. This would primarily involve small oligomers since the larger polymers have a strong affinity for cement particles. Another possibility is that the particles with only partial SNFC coverage agglomerate through bridging flocculation, leading to signal loss because of the size of the agglomerates.

Fig. 6 suggests another possible interpretation. It shows that when SNFC is added to the liquid phase of a SNFC-free suspension, the RAM increases. This is not linked to the polymer alone, since further additions are without effect. The process could therefore be due to the formation of micelles between the added SNFC and the cations available in the solution. The time scale of this process is shorter than that of the RAM recovery. However, in the case of the cement suspension, it is probably also coupled with the dissolution. So, the ongoing dissolution seems to be providing species that decrease the magnitude of the surface potential induced by SNFC adsorption. This probably accounts for rapid loss of workability of cement pastes containing these polymers at low dosages. At higher dosages, the dissolution is hindered by the high surface coverage, so the workability loss is slower.

In addition, the formation of a positively-charged complex between SNFC and calcium allows an interpretation of unexplained results in an ESA study of cement and SNFC interactions [10]. These authors had found that, for low cement volume fractions, SNFC addition caused an increase in the apparent zeta potential, while they expected a decrease as observed at larger volume fractions. A competition between the formation of this complex in the aqueous phase and adsorption onto particles explains why at low cement dosages the signal increases and why at high cement dosages it decreases. Though the ionic concentrations increase with solids fraction, they do not increase as much as the cement specific surface does. For this reason, when the volume fraction of solids is low, the signal generated by such complexes should be large with respect to the signal generated by particles with adsorbed polymers. On the other hand, when the volume fraction is high, the signal generated by the particles becomes much more important than the signal generated by those compounds formed in the liquid phase.

## 6. CONCLUSION

Measuring the zeta potential of cement dispersed in aqueous media presents many problems. Most methods of measurement require high dilutions, which are not representative of practical cement concentrations. In addition, some methods only measure sub-micron particles. Acoustophoresis allows investigations at higher solid concentrations. Nevertheless, the relatively large size of cement particles causes a significant loss of signal. Mathematical corrections for the effect of particle size distribution are limited by the accuracy with which the fraction of small particles can be determined. Therefore, it would be better to grind the cement fine enough to get a good signal from most of the particles, and not only from the lower 10 % to 20 %. However, this would probably also change the ratio of exposed phases and might also lead to misinterpretation.

Despite these limitations, the method leads to an evolution of RAM that is compatible with some interpretations of the hydration of the main component of cement (tricalcium silicate). To further use this method for cement hydration interpretation, measurements with pure phases need to be performed.

The addition of SNFC to the suspension induces a negative charge on the cement particles as expected. Interestingly, at low additions, this rapid change is followed by a slow decrease of this potential, attributed to a complexation of the adsorbed layer by dissolving ions. If this happens on the adsorbed polymers that have many sulfonate groups oriented towards the solution, it might be one of the reasons for the rapid workability loss in cementitious systems observed at low additions.

In conclusion, acoustophoresis is a promising method to improve our understanding of the interaction between cement and HRWRA in the cement hydration process. Its advantage over common other methods are to be able to measure concentrated suspensions closer to typical cement loadings. Nevertheless, further studies are needed before the method can be sufficiently well understood to assess its usefulness in routine analysis.

## ACKNOWLEDGMENTS

Dr. Paul Bowen (LTP, EPFL, Switzerland), Prof. Lennart Bergström (YKI, Stockholm, Sweden), Dr. Denis Damidot (LLCR, Lyon, France) and Dr. Vince Hackley (NIST, Gaithersburg, USA) are greatly thanked for their constructive remarks in discussing the findings of this study. Carlos Morais (LTP, EPFL, Switzerland) is thanked for assistance with some complementary measurements.

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## APPENDIX A. CVP dependence on particle size (monodisperse powder)

Marlow *et al.* [14] explained the link between zeta potential and CVP. First, they recognize that the velocity difference,  $v$ , between the fluid and particle, using the Stokes limit (valid in suspensions containing up to a volume fraction of 10 % of solid), is given by:

$$v = \frac{2a^2}{9\eta}(\rho_p - \rho_f)(2\pi fU) \sin\left(\frac{2\pi x}{\lambda} - 2\pi ft + \pi\right) \quad A-$$

Where:  $a$  is the particle radius,  $\eta$  is fluid viscosity,  $\rho_p$  and  $\rho_f$  are respectively the density of the particle and of the fluid,  $\lambda$  is the acoustic wave length,  $f$  is the frequency of the acoustic wave,  $x$  is the position of the particle center at time  $t$  and  $U$  is the velocity amplitude of the fluid.

The system measures the amplitude of a macroscopic potential between two electrodes separated by half a wavelength. Assuming all ion mobilities are equal, they can consider the macroscopic potential difference along the direction of propagation of the sound wave to be proportional to the number of dipoles (particles) and to their dipole moment.

$$\frac{d\phi_m}{dx} = \frac{Nm}{\epsilon_0 D} \quad A-2$$

Where:  $\phi_m$  is the macroscopic electric potential,  $N$  is the number of dipoles,  $m$  is the dipole moment,  $\epsilon_0$  is the dielectric permittivity of a vacuum and  $D$  is the relative permittivity of the fluid.

Enderby [18] gives an expression for the dipole moment:

$$m = (4\pi\epsilon_0 D) \frac{3}{2} \frac{\epsilon_0 D \zeta f(\chi a)}{\lambda_0} v a$$

Where:  $\zeta$  is the zeta potential of the particle,  $f(\chi a)$  is identical to the Henry correction factor [14] as  $\chi a \rightarrow 0$ ,  $f(\chi a) \rightarrow 2/3$ ; as  $\chi a \rightarrow \infty$ ,  $f(\chi a) \rightarrow 1$ ,  $\lambda_0$  is the specific volume conductivity of the continuous phase.

Equation [A-3] is substituted into the [A-2]. By integration over half a wavelength ( $\lambda/2$ ), a periodic function is obtained. The amplitude of this function is called the colloid vibration potential (CVP).

$$\Delta\Phi_{\lambda/2} = CVP \sin(-2\pi ft) \quad A-4$$

$$CVP = \frac{2P\phi}{\lambda_0} \left( \frac{\rho_p - \rho_f}{\rho_f} \right) \frac{\epsilon_0 D \zeta f(\chi a)}{\eta}$$

Where:  $\phi$  is the volume fraction of the solid in the suspension and  $P$  is the pressure amplitude.

A major limitation of this equation lies in the Stokes limit for the relative motion of particles submitted to a

sound wave. Temkin [19] has developed a more reliable expression. It is given by:

$$v = U_0 A_s \sin(kx - \omega t + \varphi_{(a)}) \quad A-5$$

Where:

$$\tan(\varphi_{(a)}) = \frac{\beta_2}{\alpha} \quad \text{sgn}(\sin(\varphi_{(a)})) = \text{sgn}(\beta_2) \quad A_{(a)} = \frac{(\beta_2 - \beta_1)}{\sqrt{\alpha^2 + \beta_2^2}}$$

$$\alpha = 1 + y \quad \beta_1 = \frac{2}{3}y^2 + y \quad \beta_2 = \omega \tau_d \left(1 + \frac{1}{2}\delta\right) + y$$

$$y = \sqrt{\frac{\omega a^2}{2\nu_0}} \quad \delta = \frac{\rho_f}{\rho_p} \quad \tau_d = \frac{2}{9} \frac{a^2}{\eta/\rho_p}$$

Substituting Equations [A-3] and [A-5] into [A-2] and integrating leads to the following definition of the macroscopic potential between the electrodes:

$$\Delta\Phi_{\lambda/2} = CVP \sin(-2\pi ft + \varphi_{(a)}) \quad A-6$$

$$CVP = \frac{9\pi P \epsilon_0 D \zeta \phi f(\chi a)}{\lambda_0 a^2 \omega \rho_f} A_{(a)}$$

For small particles [A-6] is equivalent to [A-4], where the only dependence on particle size is through the  $f(\chi a)$  term. For  $\chi a \gg 1$  and  $\lambda_0/2\pi\epsilon_0\phi \gg 1$ , as in cement suspensions, this term can however be taken as unity [14].

The ratio between the CVP predicted by [A-6] and [A-4] is equivalent to that of the relative velocities in [A-5] and [A-1]. It is a measure of the signal loss due to increasing particle size. For cement particles in water, values in Fig. 9 indicate that the Stokes limit may only be assumed for sub-micron particles. Equation [A-6] indicate that the phase shift also depends on particle size. The consequence on polydisperse systems and is dealt with in Annex B.

An additional correction accounts for the particle interactions at high volume fraction [14]. It consists in multiplying CVP by the cell correction factor given by  $(1-\phi)$ .

## APPENDIX B. CVP and particle size distribution (polydisperse powder)

The expression [A-6] for CVP indicates that both the amplitude and phase shift depend on particle size. In addition, the amplitude is proportional to the volume fraction of particles. Let us assume that the movement of particles of one size does not affect the movement of particles of another to calculate the signal from each for size category. We can write:

$$\phi_a = \phi'_a \phi \quad B-1$$

Where:  $\phi'_a$  is the volume fraction of particles of size  $a$  in the powder and  $\phi$  is the volume fraction of powder in

suspension.

The difference between two consecutive values in the cumulative size distribution function in a cumulative distribution (ex: Fig. 9), gives  $\phi'_a$ . We use:

$$\phi'_{a[i+1:j]} = \frac{V_{a[i+1:j]}}{V_{tot}} \cong \frac{V_{i+1} - V_i}{V_{tot}} \quad \text{B-2}$$

$$a_{[i+1:j]} = \frac{a_{i+1} + a_i}{2}$$

Where:  $a_{[i+1:j]}$  is the average radius of particles in the interval  $[i+1;j]$ ,  $V_i$  is the cumulative volume of particles with radius smaller than  $a_i$  and  $V_{tot}$  is the total volume of particles in suspension.

A summation of the contributions of all particle sizes allows to identify the maximum signal and the phase shift at which it occurs. By comparing the new amplitude to the one predicted by [A-4], we find how much smaller the measured signal is than if all particles were within the Stokes limit as is assumed in the software provided with the instrument.

In Fig. 9, the particle size distribution of the cement (diamonds) and its cumulated normalized signal (squares) are plotted against particle size. For our

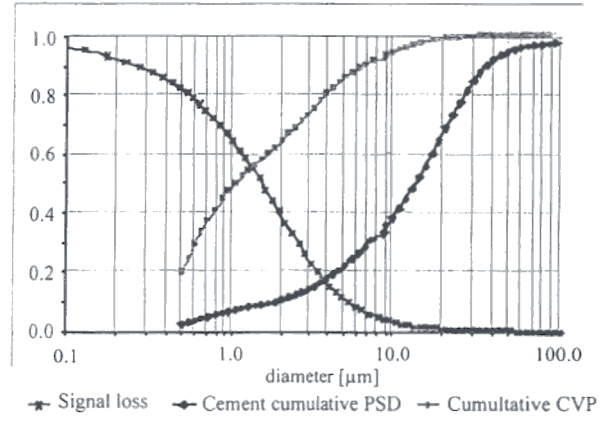


Fig. 9 – Ratio of Stokes velocity to velocity predicted by Temkin [19]. This ratio is the same as the one between values of CVP. Cement PSD and its cumulative CVP are also indicated.

cement, about 60 % of the signal turns out to be generated by the 10 % smallest particles. Because obtaining a precise size distribution in the small size fraction is complicated, the use of this method to predict the zeta potential of cement particles is limited.