CHARACTERIZING CEMENT DISPERSIONS USING ACOUSTICS

This application note presents a methodology for studying concentrated cement slurry at 72 wt% using ultrasound. Two different ultrasound based technique are involved – acoustics and electroacoustics. Acoustics yields information on particle size and electroacoustics provides data on ζ (zeta) potential. Neither method requires sample dilution. Various sample handling setups offer the possibility of versatile characterization including time evolution of the sample and characterizing the role of a super-plasticizer. The results show that the zeta potential changes with the addition of different super-plasticizers. It is possible to determine the optimum dose of this additive by following the procedures described below.

Introduction

Several authors well known in the field of cement science published papers describing studies of various cement dispersions using ultrasound [1,2,3]. The main advantage of using an ultrasound based technique is the ability to characterize concentrated cement dispersion without dilution. This feature of ultrasound based techniques is critical for cement because of long-lasting hydration processes. The properties of the cement particles in water change over several hours. This time evolution depends strongly on particle concentration. The ability to study this process at concentrations that are similar to the industrial situation is very valuable.

Two different methods have been used in above mentioned papers. The first method is *acoustics* – the measurement of sound speed and attenuation at ultrasound frequencies. A study at NIST [1] presents clear evidence that the attenuation frequency spectra changes during cement hydration and in fact can be used as a fingerprint of this process. The second method is *electroacoustics* [4], which is usually applied for characterizing the zeta potential in concentrated dispersions. Authors of the papers [2,3] applied this method successfully for monitoring the interaction between super-plasticizer and cement. All of these groups used instruments designed and manufactured by Dispersion Technology Inc., currently supported by HORIBA Instruments in North America.

The same instruments were used on several occasions working with various cement samples submitted to the applications lab. Methodologies for handling cement samples at extremely high concentrations (i.e. 72 wt%) have been developed in order to achieve stable, reproducible preparations and to run super-plasticizer titrations. The focus is not evolution of the particular cement slurry chemistry or particular super-plasticizer chemistry, but about ways of monitoring cement evolution with sufficient precision and reproducibility.

These are the goals of the study described in this application note:

1. The first is a time dependence study which determines the condition when sample becomes almost stable.
2. Verification of the measurement reproducibility
3. Verification of sonication importance
4. Verification of the water addition role – effect of dilution
5. Testing various instrument setups with the same sample
6. Testing conductivity evolution
7. Sensitivity to super-plasticizer chemistry
8. Ability to determine optimum dose of super-plasticizer
9. Particle sizing in cement slurry

Cement slurries are very complex non-equilibrium systems that change gradually with time. They require special effort in sample handling and meaningful measurements. Every new group that uses ultrasound for characterizing these systems follows the same path of the method development. This application note describes some universal aspects of this characterization procedure which are unique for cement slurries.

Materials and Sample Preparations

The two cement powders received from customers used in this study are differentiated by variations in chemical composition. The nature of these differences is not relevant to this study which is dedicated to the description of the method, as opposed to peculiar features of the particular cement. These cement samples are labeled as "cement A" and "cement B". The chemical nature of the three plasticizers used in the study is also not relevant here. They are used just to show that this method is suitable for determining the better super-plasticizer and its optimum dose. We refer to these plasticizers as "plasticizer D", "plasticizer H", and "plasticizer G".

All cement samples were prepared at concentrations of 72% by weight. A relatively large sample volume of 200 ml was prepared in order to use an external peristaltic pump for sample circulation and mixing. In order to achieve these numbers we mixed 283 g of cement with 110.09 g of distilled water, assuming a density for the cement particles of 3.16 g/cm^3.

Comparison of various plasticizers would require having reproducible samples with the same properties. A combination of mixing in a high speed blender for one minute followed by high power sonication for fifteen minutes yields samples with a reproducible ζ-potential value. After mixing the sample is poured directly into the DT-1201 measuring chamber followed by sonication in the chamber while it is being circulated with the external peristaltic pump. The role of sonication is described in details in the Results and Discussion section. Plasticizer solution was prepared by adding 0.5 g of substance to 100 ml of distilled water. This allows reducing water addition.

Instrumentation

The Dispersion Technology Acoustophor DT-1201 was used for all measurements reported in this study. This instrument has a set of different sensors that are connected to the same electronics. These sensors can be used separately or in any combination. The sensor set includes:

1. Acoustic sensor for measuring attenuation and sound speed, which are the raw data for particle sizing and rheology
2. Electroacoustic sensor for measuring Colloid Vibration Current (CVI), which is the raw data for zeta potential calculation.
3. Conductivity probe
4. pH probe
5. Temperature probe
6. Burettes for changing the chemical composition of the sample

Experimental Setups

The DT-1201 is very flexible in terms of sample handling. The system is built as a set of sensors, which are connected to a single electronics unit. These sensors can work in any combination or completely separately. The necessity of mixing and sonication brings additional issues for designing the best sample handling setup for this application. Four different setups were used in this study, each having advantages and disadvantages. They are illustrated below by photos with short text descriptions.

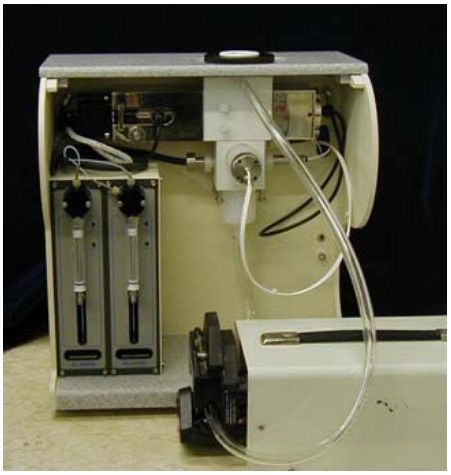

Figure 1: Setup 1 is based on the standard DT-1201 chassis, making all sensors available. The sonication probe goes on the top of the sample chamber. Mixing is performed with an external peristaltic pump. Two burettes open the possibility of automatic titrations. The sample volume is the largest for this setup, 200 mL. It has the disadvantage of requiring more involved cleaning. Both the zeta potential and conductivity probes could become contaminated if used without care.

Figure 2: Setup 2 is suitable for all probes except the acoustic sensor used for particle size analysis. The peristaltic pump performs the mixing. The sensor holder is designed so that the sample stream hits the face of the electroacoustic sensor in order to keep it clean. Sonication is possible in this configuration and the sample volume is 150 mL. The probes are easily accessed, but the disadvantage is that particle size analysis is not possible.

Figure 3: Setup 3 can be used with a sample that has already been prepared (mixed and sonicated) on the side in another vessel. It is stuiable for measuring zeta potential only and cleaning is very simple.

Figure 4: Setup 4 is the simplest configuration for measuring zeta potential. This setup was used at the end for measuring the effect of super-plasticizer on the cement zeta potential. There is no difference between data obtained from this configuration and that of Setup 3. The sample is prepared in a separate vessel just the same. A small amount of prepared sample is placed on the face of the electroacoustic sensor to perform the measurements.

Results and Discussion

Note that all results shown were first mixed for one minute in a high power blender and then placed into the measuring chamber of setup 1 or setup 2 for 15 minutes of sonication. Measurements were performed during the sonication period and after it.

Time Dependence Study: Verification of Measurement Reproducibility

The evolution of ζ-potential and conductivity during the sonication period for samples of both cements A and B was monitored. Figure 5 (red and green curves) shows how the ζ-potential of cement A changes with time. Two samples were measured using Setup 1. It can be seen that the initial ζ-potential is negative.

It then becomes positive due to the surface hydration after roughly five minutes and finally reaches a reproducible value after 15 minutes. Figure 6 shows the same experiment's results for cement B. Absolute values, negative and positive, are smaller for this cement compared to cement A.

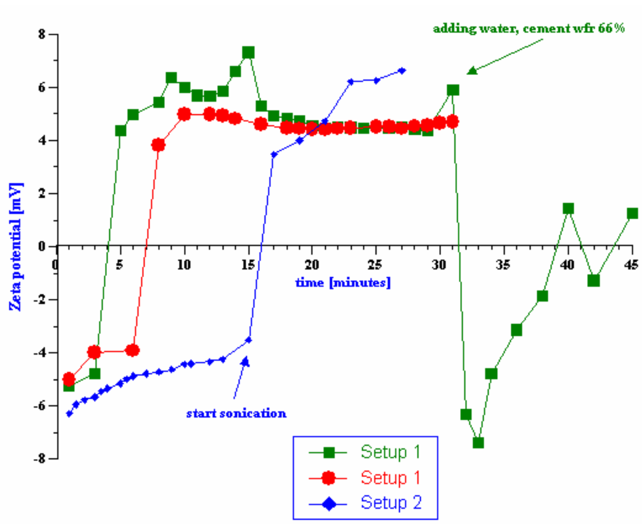

Figure 5: Green and red: zeta potential vs. time using Setup 1 for cement A. Blue: the effect of sonication for cement A using Setup 2.

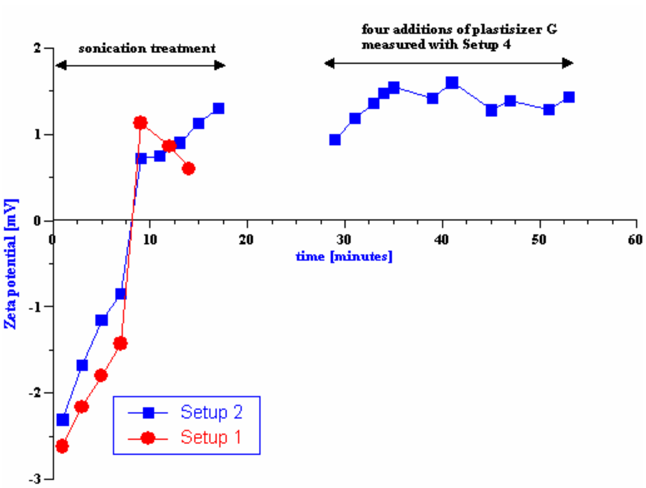

Figure 6: Zeta potential vs. time for cement B using Setup 1 and Setup 2.

The main conclusion is that the surface of the cement particles reaches an almost stable condition after 15 minutes of sonication. These samples could be used for comparative studies with different chemical additives.

Verification of the Importance of Sonication

One might posit that sonication is not important and that high power mixing is sufficient for stabilizing the surface chemistry of the cement particles. In order to verify the importance of sonication Setup 2 was used with cement A. The peristaltic pump at the highest speed was only used instead of starting sonication immediately after placing the sample in the chamber. Figure 5 (blue curve) shows zeta potential evolution during this study.

It is seen that zeta potential remains negative for a much longer time compared to turning on sonication where it immediately becomes positive. This test indicates that sonication substantially speeds up the process of surface hydration. It appears imperative to use sonication for preparing reproducible samples.

Verification of the Water Addition Role: Effect of Dilution

In order to verify the effect of water dilution a small amount of water was added to one of the samples of cement A 30 minutes after it was prepared. The corresponding ζ-potential curve is shown in Figure 7 (red curve). The water dilution reduced the weight fraction of the cement from 72% down to 66%.

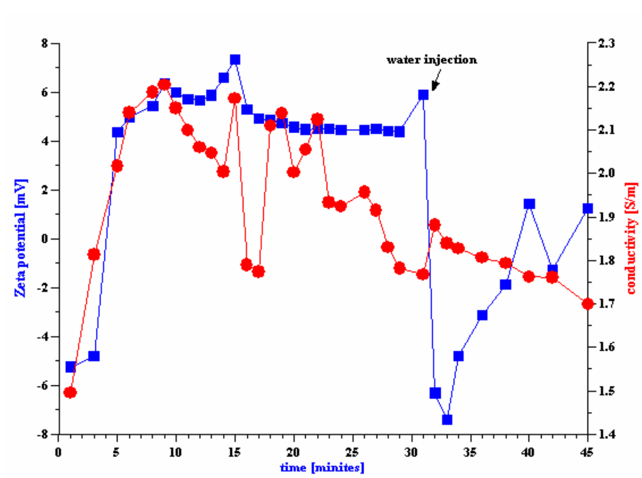

Figure 7: Blue curve: zeta potential vs. time dilution study. Red curve: conductivity vs. time for cement A using Setup 1.

Figure 7 shows that the ζ-potential has not only changed value, it has changed sign. Then, with time it slowly recovers back to positive values but with a much smaller magnitude. This test indicates that dilution of the concentrated cement sample changes ζ-potential dramatically. These results raise questions on the relevance of the data collected with traditional light based ζ-potential instruments that work at extreme dilution. It is interesting that addition of water does not affect conductivity much.

Testing Conductivity Evolution

Figure 7 (blue curve) shows the variation of conductivity for the cement A. Conductivity was measured together with zeta potential using Setup 1. The conductivity increases substantially during initial period as the zeta potential changes sign. It remains almost constant after that. Addition of water does not affect conductivity significantly.

Sensitivity to Chemistry and Dose of Super-plasticizer

The role of super-plasticizer was tested using cement A continuously pumped through the chamber of Setup 2 even after sonication was turned off after 15 minutes. A small amount of a particular super-plasticizers was then added to the mixing cement. Some time was required for this added chemical to spread homogeneously through the mixing chamber and adjust surface properties. After a 3 minutes waiting period a small portion of the mixing sample from the chamber was placed on the top of the Electroacoustic probe as shown on Setup 4 for ζ-potential measurement. After the ζ-potential measurement was finished, this portion of the sample was returned back to the chamber. Then a new incremental injection of super-plasticizer was made and the cycle was repeated. The measured values of ζ-potential at different concentrations of all three tested super-plasticizers are shown in Figure 8.

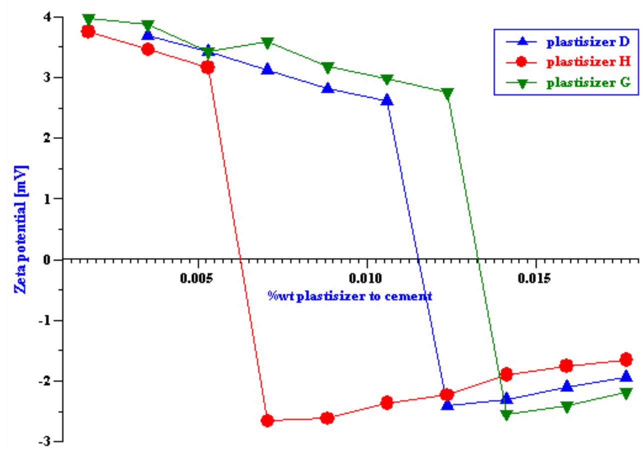

Figure 8: Zeta potential of three super-plasticizers at different concentrations.

It is seen that in all three cases the ζ-potential reverses sign at a specific concentration. This so-called iso-electric point (IEP) depends on the nature of super-plasticizer, and varies by a factor of three times from the most efficient plasticizer H to the least efficient plasticizer G. The concentration of super-plasticizer at the IEP is essentially the optimum dose for that particular additive.

Particle Sizing in Cement Slurry

We have measured particle size distributions of both cements after they reached steady state. Figure 9 shows the attenuation spectra for both cement slurries as well as the corresponding particle size distribution.

It is interesting that these cements have very different ζ-potentials, but practically identical particle size distributions.

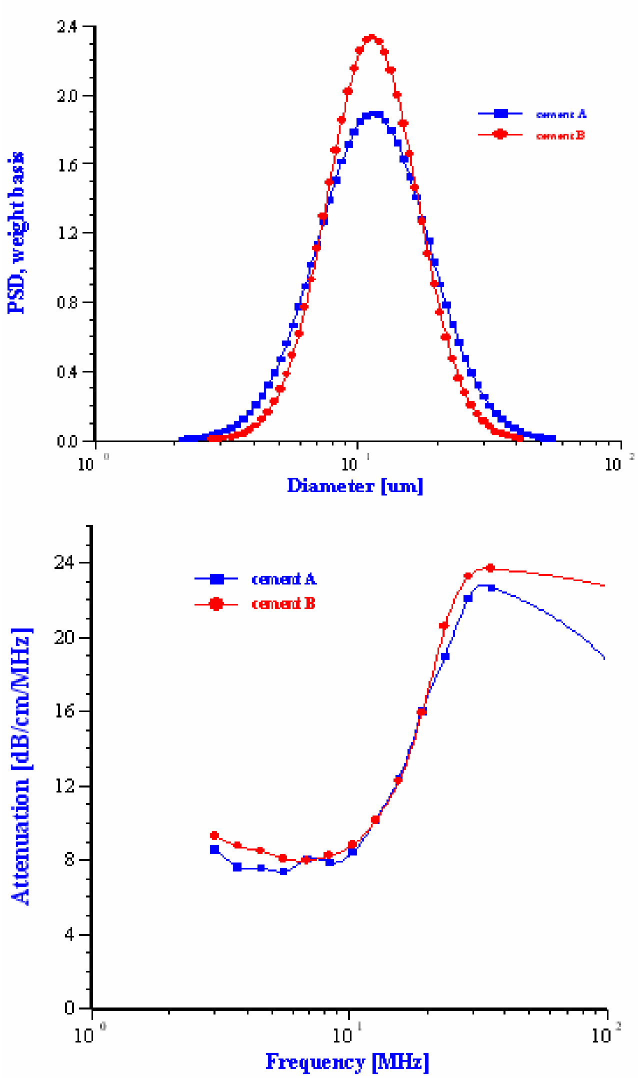

Figure 9: Above: the particle size distributions of cement A and cement B. Below: the attenuation spectra for cement A and cement B.

Conclusions

The ultrasound based techniques of electroacoustics and acoustics were used to characterize concentrated cement dispersion at 72%wt with no dilution. Electroacoustics yields information on cement particles ζ-potential. It is suitable for characterizing this parameter during early stages of cement hydration. Monitoring how this parameter evolves helps in designing procedures for preparing reproducible and relatively stable cement dispersions. This procedure includes mixing in a high power blender for 1 minute followed by up to 15 minutes of sonication. The value of ζ-potential changes sign from negative to positive during this preparation procedure and reaches a steady state value. It is possible to use such prepared reproducible samples for comparative studies of various super-plasticizers. The electroacoustic method of ζ-potential measurements reflects differences between different plasticizers and can be used for determining IEP and optimum dose of these additives. The second ultrasound based technique – acoustics - yields information on particles size distribution in the concentrated cement dispersions.

References

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