Ultrasound for characterizing Cement dispersions.

Plasticizer efficiency, particle size, zeta potential.

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Abstract.

This paper 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. Electroacoustics provides data on ζ-potential. Neither method requires sample dilution.

We describe a procedure for preparing reproducible cement slurry samples using a high shear blender followed by high power sonication. This procedure allows us to start monitoring cement hydration almost immediately (1 minute) after mixing the cement powder with water. Electroacoustically measured ζ-potential reflects changes on the cement particles surfaces during hydration. It starts as negative and then becomes positive during initiation period. Length of this initiation period depends on application of sonication. Addition of small amounts of water reverses ζ-potential sign with further recovery.

Various sample handling setups offer the possibility of versatile characterization including time evolution of the sample and characterizing the role of a super-plasticizer.

We show how the ζ-potential changes with the addition of different super-plasticizers. It is possible to determine optimum dose of this additive.

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 a concentrated cement dispersion, without diluting it. This feature of ultrasound based techniques is critical for cement because of long-lasting hydration process. 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 ζ-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.

We used the same instruments on several occasions working with various cement samples submitted by our customers. In order to achieve goals formulated in these studies we have developed methodology of handling cement samples at the extremely high concentration of 72% by weight. We have learned how to prepare stable and reproducible samples. We have also learned how to run super-plasticizer titration. This paper presents our experience.

It is methodological.

It is not about evolution of the particular cement slurry chemistry or particular super-plasticizer chemistry.

It is about the ways of monitoring cement evolution with sufficient precision and reproducibility.

These are the goals that we pursue in this paper:

1. The first is time dependence study. It determines 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 gradually change 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. With this paper we want to describe some universal aspects of this characterization procedure, which are unique for cement slurries. These are justifications of writing this paper.

Materials and samples preparation

We used two different cement powders that we received from one of our customers. We were informed that there are some differences in chemical composition of the powders. The nature of these differences was not relevant to this paper, which is dedicated to the description of the method, but not the peculiar features of the particular cement.

We refer to these cement samples as “cement A” and “cement B”.

We also received three different plasticizers. The chemical nature of these substances is also not relevant here. We use them 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 and 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 after mixing and then sonication is applied to the sample in the chamber while it is being circulated with the external peristaltic pump.

We performed a special test for verifying role of sonication, which is described in details in the sections Results and Discussion.

Plasticizer solution was prepared by adding 0.5 g of substance to 100 ml of distilled water. This allows reducing water addition.

Instrumentation.

We use Dispersion Technology Inc., Acoustophor DT-1201. This instrument has a set of different sensors that are connected to the same electronics. This 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, 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

These sensors can be used separately or in any combination.

The Acoustic and Electroacoustic are unique. The following two sub-sections present some details of their basic function and underlying science. More information is available on the web site www.dispersion.com and book [4].

Acoustics

The Acoustic sensor of the DT-1201 measures ultrasound attenuation and sound speed. It has been designed for wide range of applications from very low to very high attenuating liquids. Water, alcohols are an examples of low attenuating liquids. Paints, ceramic slurries, cement slurries are examples of high attenuating liquids. The dynamic range of the instrument is specified as 0.01 to 20 dB/cm/MHz for multiple frequencies from 1 to 100 MHz. The precision of attenuation measurement is 0.01 dB/cm/MHz.

There is no restriction on sound speed range. Precision of the sound speed measurement is 0.1 m/sec.

This acoustic sensor works on the “transmission” principle. A piezo-electric transducer converts an input electrical tone burst to an ultrasound pulse of a certain frequency and intensity I_{in} and launches it into the sample. The intensity of this pulse decreases as it passes through the sample due to the interaction with the fluid. A second piezo-electric transducer converts this weakened acoustic pulse with intensity I_{out} back to an electric pulse and sends it to the electronics for comparison with the initial input pulse. The sensor performs this measurement at multiple frequencies, but also at multiple gaps. The distance between transmitter and receiver changes in steps, typically from 0.3 to 20 mm. The default number of steps is 21 and the default number of frequencies is 18. The software allows changes of these parameters for optimizing measurement for particular sample. Default setup allows instrument to function within above mentioned specification ranges.

The total loss and time delay from the input to output transducer for each frequency and each gap can be considered the “raw data” from which further interpretation is made.

It is convenient to present these raw data in terms of an attenuation coefficient α_{exp} defined as

$$\alpha_{\exp}[dB/cm/MHz] = \frac{10}{f[MHz]L[cm]}\log\frac{I_{in}}{I_{out}} \tag{1}$$

where f is the frequency of the pulse, L the distance between transmitter and receiver. Decibel units are more widely accepted in Acoustics than *nepers*. Normalization by frequency is useful because the attenuation coefficient varies strongly with the frequency. This normalization allows better graphical presentation of this parameter within a wide frequency range.

Attenuation measurement at low frequency is affected by sound pulse diffraction. This occurs due to the large wavelength that reaches 1.5 mm at 1 MHz. The wavelength becomes comparable with distance between transducer and receiver at low frequency. There is a special procedure for calibrating out this diffraction effect, based on Stokes' law for water. Water is a Newtonian liquid and the attenuation should approach very small values under precision limit for frequencies below 10 MHz. The calibration procedure uses water measurement for calculating linear regression down to zero including only high frequency points that are not affected by diffraction. Then it calculates required corrections for low frequency water data. These corrections are saved as calibration constants for all frequencies. They are used then for measurements of other fluids and dispersions. This calibration is important only for low attenuating liquids.

Attenuation measurement is closely linked to the sound speed measurement. One needs to know sound speed for sampling pulses at the proper time. DTI acoustic sensor measures sound speed c using time of flight method. The instrument measures the delay time between emitting and receiving of the pulse t for a set of gaps. Sound speed is obtained from the linear regression $c = L/t$. It is usually done at a single frequency.

Measurement of a single attenuation frequency spectra and sound speed takes about five minutes.

The instrument is equipped with temperature measurement and temperature control. This allows measurement at fixed temperature above ambient maintained with precision 0.1 C. The instrument design requires the sample to be pumped through the chamber for maintaining fixed T. This determines the sample volume at 100 ml. Typical sample volume can be as little as 15 ml for samples that do not require stirring.

Electroacoustics

A photograph of the DT-1201 Electroacoustic sensor is shown in Figure 1. It is essential for this study that the probes can be used as deep in and, alternatively, as permanently mounted in the wall of the sample chamber. This will be discussed in details in the next section.

This sensor launches ultrasound pulses at 3 MHz frequency into the sample. Propagation of ultrasound through dispersed system generates electric signal, as predicted by Debye seventy years ago [5]. In either electrolyte solutions or dispersions, the effect is related to a coupling between electrodynamic and mechanical phenomena. For instance, the transmission of ultrasound through an electrolyte solution or dispersion generates a current, which is usually referred to as an Ion/Colloid Vibration Current. In the case of the DT-1201 sensor this ultrasound is generated with a piezo-electric transducer inside of the probe. It converts an electrical tone burst signal to a sound pulse that is then transmitted to the front face of the probe and into the colloid. This sound pulse generates electroacoustic signal in front of the probe, which is measured as a current between a central gold electrode and a surrounding annular electrode.

Experimental output of the electroacoustic measurement is Colloid Vibration Current (CVI) magnitude and phase. They are usually converted to the dynamic electrophoretic mobility and/or ζ-potential, which are considered as outputs of the electroacoustic technique. This conversion procedure requires a proper theory. Here is the simplest version, which is valid for sufficiently small particles with a thin Double Layer and negligible surface conductivity:

$$\frac{CVI_{\omega\to 0}}{\nabla P} = \frac{\varepsilon_m \varepsilon_0 \zeta \Phi K_s}{\eta K_m} \frac{(\rho_p - \rho_s)}{\rho_s} \qquad (2)$$

where $\boldsymbol{P}$ is pressure in the sound wave, $\boldsymbol{\varepsilon_m}$ and $\boldsymbol{\varepsilon_0}$ are dielectric permittivities of the media and vacuum, $\boldsymbol{\Phi}$ is volume fraction of the dispersed phase, $\boldsymbol{\eta}$ is dynamic viscosity, $\boldsymbol{\rho_p}$, $\boldsymbol{\rho_m}$ and $\boldsymbol{\rho_s}$ are densities of the particle, media and dispersion, $\boldsymbol{K_s}$ and $\boldsymbol{K_m}$ are conductivities of the system and media.

The second experimental parameter is the phase of electroacoustic signal. Calibration procedure with negatively charged silica Ludox assigns 180 degrees values to this phase for all negative particles. It is supposed to be close to 0 or 360 degrees for positive particles. This assumes that general electroacoustic theory is valid.

Experimental setups

Dispersion Technology instruments are flexible in terms of sample handling. They are 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.

We have tested four different setups. Each of them has its advantages and disadvantages. They are illustrated below by photos with short text descriptions.

Setup 1 – Figure 2 .

This setup is based on the standard DT-1201 chassis. It makes 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 disadvantage of more complex cleaning. Zeta potential probe and conductivity could be contaminated. It is not easily accessible.

Setup 2 – Figure 3.

This setup is suitable for all probes but the Acoustic one. The peristaltic pump performs mixing. The sensor holder is design in a way that the sample stream hits the face of the electroacoustic sensor in order to keep it clean. Sonication is possible.

Sample volume is 150 ml.

Probes are easy accessible.

Disadvantage is that particle sizing is not possible.

Setup 3 – Figure 4.

This setup can be used with the sample that has been prepared, mixed and sonicated on the side, in another vessel.

It is suitable for measuring ζ-potential only. Cleaning is very simple.

Setup 4 – Figure 5.

This is the simplest way of measuring ζ-potential. We used it at the end for measuring effect of super-plasticizer on the cement ζ-potential. There is no difference with data from setup 3. It is very easy for cleaning.

Sample is prepared in the separate vessel. Just a small scoop of the sample is placed on the face of the electroacoustic sensor.

Results and Discussion

We will discuss results of the measurements following the list of goals formulated above.

Before doing this we would like to repeat again that each sample was mixed for one minute in high power blender. As the next step it was placed into the measuring chamber of setup 1 or setup 2 and sonicated for 15 minutes.

Measurements have been performed during the sonication period and after it.

Time dependence study. Verification of measurement reproducibility.

We monitored the evolution of ζ-potential and conductivity during the sonication period for samples of both cements A and B.

Figure 6 shows how the ζ-potential of the cement A changes with time. We measured two samples using Setup 1. It is seen that initial ζ-potential is negative. It becomes positive due to the surface hydration after roughly five minutes and then reaches reproducible value after 15 minutes.

Figure 7 shows same results for the cement B. Absolute values, negative and positive, are smaller for this cement comparing to the cement A.

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 additivies.

Verification of 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 we used Setup 2 with cement A. Instead of starting sonication immediately after placing the sample in the chamber we just used the peristaltic pump at the highest speed.

Figure 6 shows ζ-potential evolution in this case. It is seen that it remains negative for much longer time. Turning on sonication makes it immediately positive.

This test indicates that sonications speeds up very substantially the process of surface hydration. It is practically imperative to use it for preparing reproducible samples.

Verification of the water addition role – effect of dilution

In order to verify the effect of water dilution we added a small amount of water to one of the samples of "cement A" thirty minutes after it was prepared. The corresponding ζ-potential curve is shown in Figure 6. The water dilution reduced the weight fraction of the cement from 72% down to 66%.

It is seen 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. It raises 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, as shown in Figure 8.

Testing conductivity evolution

Figure 8 shows variation of conductivity for the cement A. It was measured together with ζ-potential using Setup 1. The conductivity increases substantially during initial period as the ζ-potential changes sign. It remains almost constant after that.

Addition of water does not affect conductivity much.

Sensitivity to super-plasticizer chemistry and dose

We tested the role of super-plasticizer using cement A. Sample remained continuously pumped through the chamber of Setup 2 even after sonication was turned off after 15 minutes.

Small amount of particular super-plasticizers were added to the mixing cement. Some time was required for this added chemical to be spread homogeneously through the mixing sample and adjust surface properties. We have allowed for 3 minutes waiting period. Only then we took a small portion of the mixing sample from the chamber and place it 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 cycle repeated.

The measured values of ζ-potential at different concentrations of all three tested super-plasticizers are shown in Figure 9.

It is seen that in all three cases the ζ-potential reverses sign at a specific concentration. This so-called "iso-electric point" 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 “iso-electric point” 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 10 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.

Conclusions.

Ultrasound based techniques – Electroacoustics and Acoustics, allows us 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 us in designing procedure of preparing reproducible and relatively stable cement dispersions. This procedure includes mixing in high power blender for 1 minute with following up 15 minutes sonication. Value of ζ-potential changes sign from negative to positive during this preparation procedure and reaches steady state value. It is possible to use such prepared reproducible samples for comparative studies of various super-plasticizers. Electroacoustic method of ζ-potential measurements reflects differences between different plasticizers and can be used for determining "iso-electric point" 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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Figure Titles

Figure 1. Picture of Electroacoustic ζ-potential probe of the Acoustophor DT-1201.

Figure 2. Experimental Setup 1.

Figure 3. Experimental Setup 2.

Figure 4. Experimental Setup 3.

Figure 5. Experimental Setup 4.

Figure 6. Evolution of ζ-potential in time (after 1 minute preliminary mixing in blender) for 3 different samples and 2 different experimental setups of cement A.

Figure 7. Evolution of ζ-potential in time (after 1 minute preliminary mixing in blender) for 2 different samples and 2 different experimental setups of cement B.

Figure 8. Evolution of ζ-potential and conductivity in time (after 1 minute preliminary mixing in blender) for one sample of cement A.

Figure 9. Values of ζ-potential for 3 different samples of cement A at different concentrations of super-plasticizers. Experimental setup 4. Measurements begin after 1 minute preliminary mixing in blender and 15 minutes sonication. Equilibration delay after each addition of super-plasticizer is 3 minutes.

Figure 10. Particle size distribution and attenuation frequency spectra (raw data) for both cements after reaching steady state due to preliminary mixing with following up 15 minutes sonication.

Figure 1

Figure 2

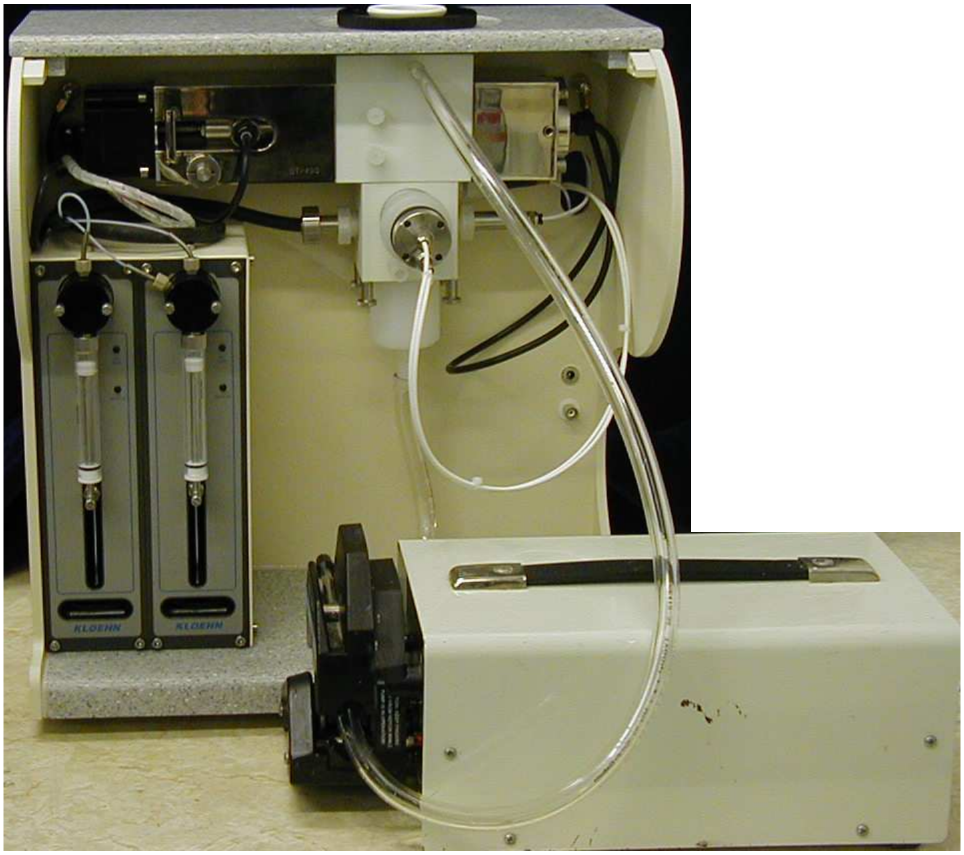


Figure 3

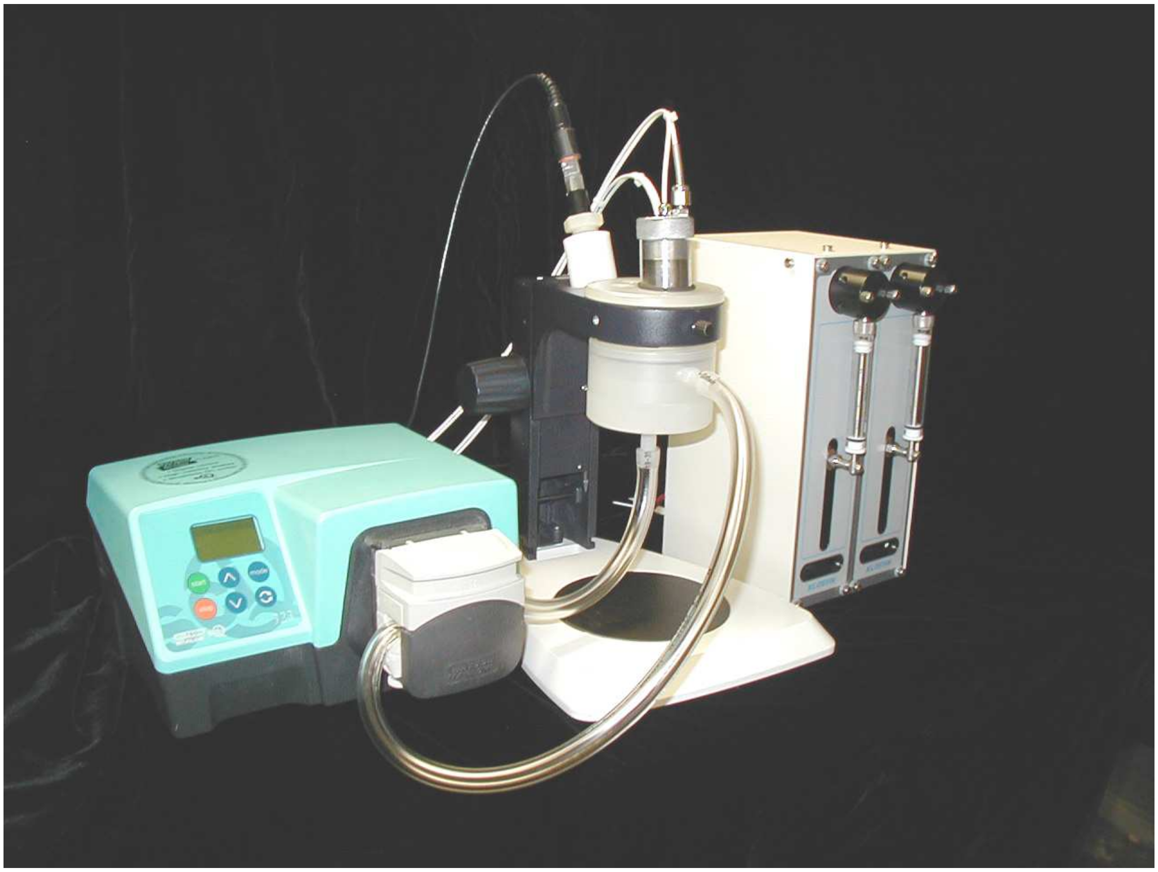


Figure 4

Figure 5

Figure 6

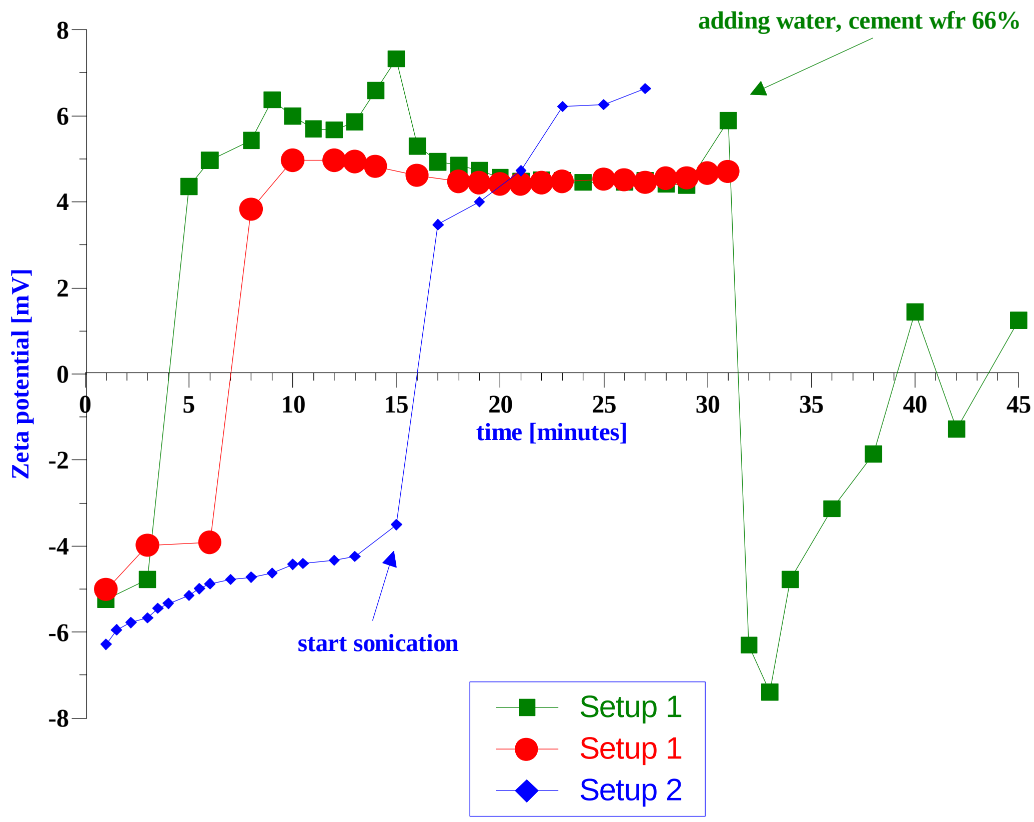

adding water, cement wfr 66%
start sonication
Zeta potential [mV]
time [minutes]
8
6
4
2
0
-2
-4
-6
-8
0
5
10
15
20
25
30
35
40
45
Setup 1
Setup 1
Setup 2

Figure 7

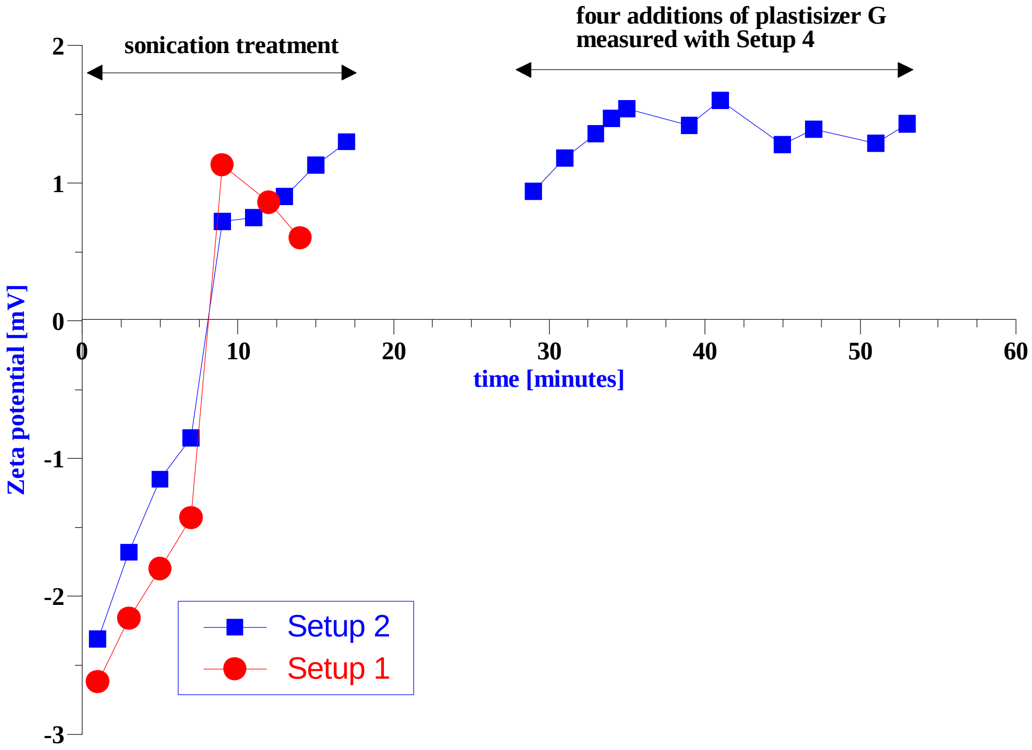

sonication treatment
four additions of plastisizer G
measured with Setup 4
Zeta potential [mV]
time [minutes]
2
1
0
-1
-2
-3
0
10
20
30
40
50
60
Setup 2
Setup 1

Figure 8

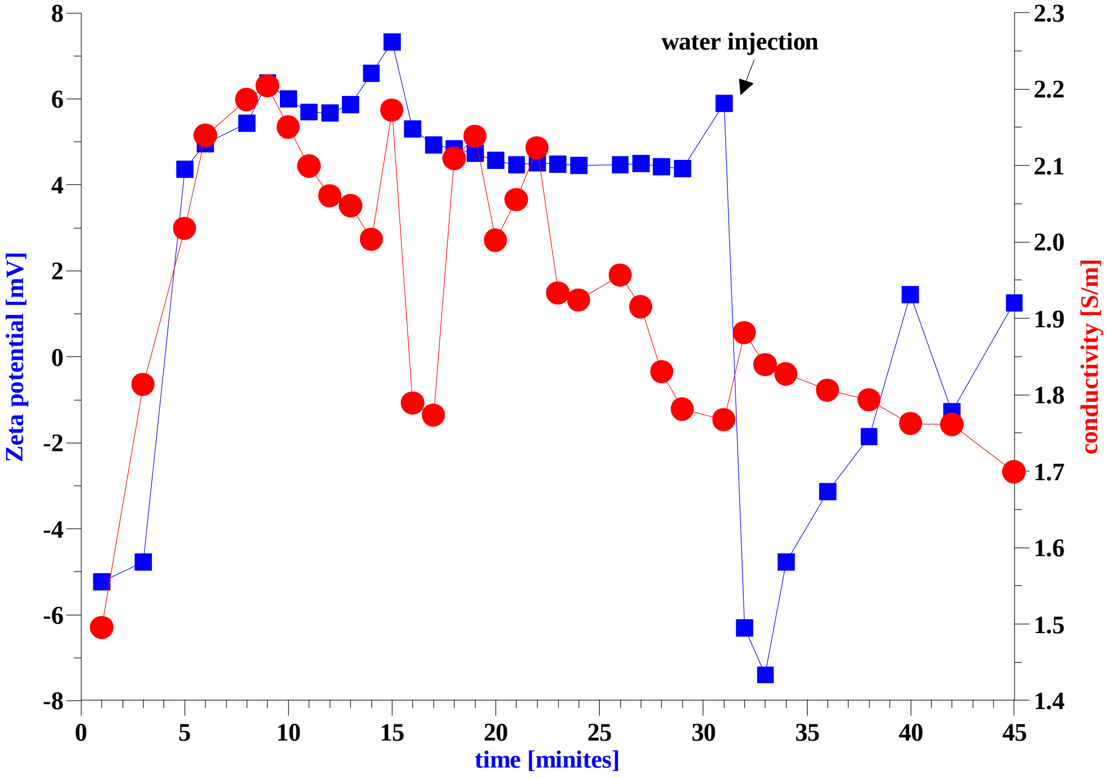

water injection
Zeta potential [mV]
8
6
4
2
0
-2
-4
-6
-8
conductivity [S/m]
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
0
5
10
15
20
25
30
35
40
45
time [minites]

Figure 9

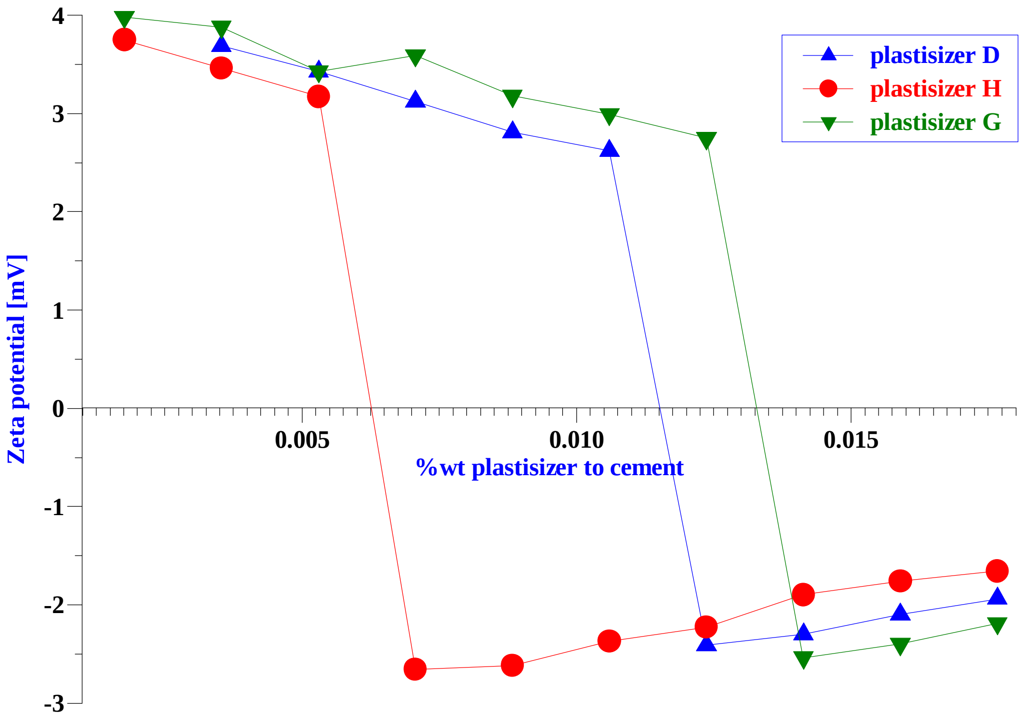
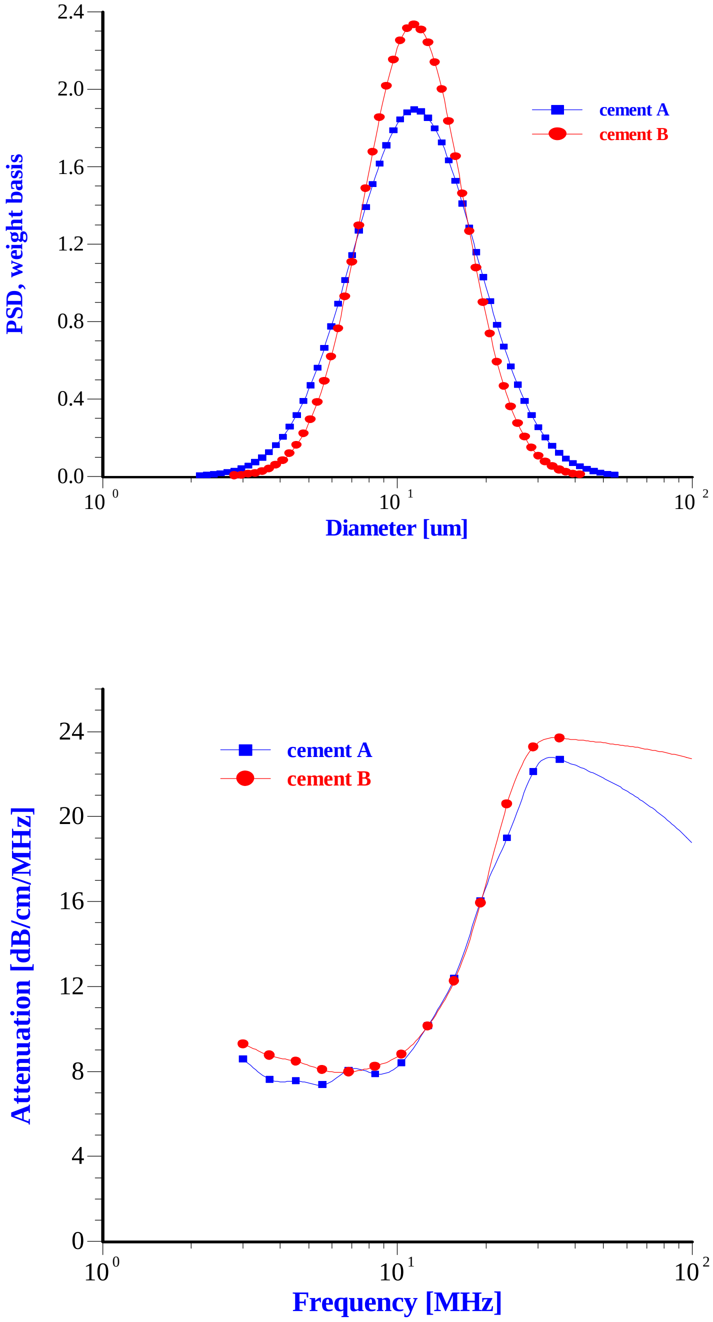

4
3
2
1
0
-1
-2
-3
Zeta potential [mV]
0.005
0.010
0.015
%wt plastisizer to cement
plastisizer D
plastisizer H
plastisizer G

Figure 10


PSD, weight basis
2.4
2.0
1.6
1.2
0.8
0.4
0.0
10^0
10^1
10^2
Diameter [um]
cement A
cement B
Attenuation [dB/cm/MHz]
24
20
16
12
8
4
0
10^0
10^1
10^2
Frequency [MHz]
cement A
cement B