Pergamon

Cement and Concrete Research 30 (2000) 1767–1772

CEMENT AND CONCRETE RESEARCH

The effect of the cement zeta potential and slurry conductivity on the consistency of oilwell cement slurries

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Received 22 July 1999; accepted 29 August 2000

Abstract

The effect of time and input of different amounts of mixing energy on the zeta potential and particle size of an oilwell cement slurry have been studied using an AcoustoSizer. It has been shown that the zeta potential development seems to control the consistency of cement slurries in the early time of hydration. Furthermore, conductivity measurements along with pH and a special particle size distribution measurement has indicated the precipitation of solid fine grain material within the liquid phase at the time the consistency starts to increase. This is at the time the cement slowly starts to thicken and long before the cement sets and starts to solidify. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Particle size distribution; Adsorption; Cement paste; oilwell cement; Electroacoustics

1. Introduction

The pumping and placement of the cement slurry in primary oilwell cementing takes place during a period when the chemical reactions in the slurry are rather slow. This is the so-called induction period and is characterised as a period with constant and rather low heat production in a time vs. reaction heat diagram [1]. The induction period starts a few minutes after the addition of water and can last for several hours depending on type of cement, additives and temperature. During pumping the slurry is exposed to a continuous input of mixing energy. This energy input has an influence on the morphology of the cement and on the speed of the chemical reactions taking place. To simulate the input of various amounts of mixing energy to the cement slurry we have used an atmospheric consistometer [2]. The consistometer acts as a rather slow rotating mixer equipped with a temperature control. The consistometer is used to measure the time when a cement slurry is pumpable. An empirical value of 30 Bearden units of Consistency (Bc) is adopted as the value when the cement is no longer pumpable (Bearden units are arbitrary values, closely related to poise units). The energy input is meant to simulate the energy input from pumping in a real oilwell operation.

To monitor the zeta potential of the slurry we have used an AcoustoSizer. This is an instrument that enables measurement of the zeta potential and size distribution of the cement particles in a non-diluted slurry. The zeta potential of a particle is defined as the electrostatic potential in the slipping plane or the surface of shear, relative to the potential in the bulk solution [3]. It is expected that the zeta potential has an influence on the rate of coagulation [4] of the particles in the cement slurries and thus the pumpability of the slurries. The AcoustoSizer is equipped for measurement of the conductivity and the pH of the bulk fluid. The conductivity and pH are measured to yield information about the processes determining the zeta potential development of the slurries.

2. Sample preparation and experimental methods

2.1. Sample preparation

The sample preparations were done in accordance with specifications from the API [2]. For the initial high-speed mixing a Waring Blendor with the original propeller blade was used. The volume of each sample was 600 ml with a W/

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PII: S0008-8846(00)00417-8

C ratio of 0.44 by weight. All samples were mixed using cement and distilled water; no other additives were used. All tests were carried out at 20 ± 2°C and 50 ± 2°C, respectively. The input of mixing energy during the high-speed mixing was 5.5 kJ/kg [5–7]. For all our tests we have used a Class G oilwell cement produced by Norcem [7].

2.2. Consistency measurements

After the high-speed mixing the samples were placed in an atmospheric consistometer [2] and stirred at 150 rpm for different lengths of time. This was done in order to simulate different inputs of shear energy before the measurements were done. For the present work the atmospheric consistometer was equipped with a new inductive load cell named Q11/500 and made by Hottinger Baldwin Messtechnik in Germany. This enabled us to log the torque exerted on the paddle continuously.

2.3. Zeta potential measurements

For zeta potential and particle size measurements we have used an AcoustoSizer [8]. This is an apparatus that is able to measure the zeta potential of particles in suspensions containing more than 40% solids by volume. The particle content in our slurries was 41.5% by volume.

The basis for the measurements with the AcoustoSizer is the electrokinetic sonic amplitude or ESA effect, i.e. charged particles exposed to an alternating electric field in a solution generates sound waves. From the detected sound waves the AcoustoSizer determines the dynamic mobility of the particles. This is done over a range of frequencies from 0.3 to 11.2 MHz, giving a dynamic mobility distribution of particles in the size range from 0.1 to 10 μm. Based on a modified form of the Smoluchowski equation [8], the dynamic mobility distribution and a log normal particle size distribution model the AcoustoSizer calculates the zeta potential and particle size distribution of the slurry.

In addition to the normal zeta potential, the AcoustoSizer calculates a special zeta potential using the Smoluchowski equation [8]. This calculation is based on a single average dynamic mobility measured at an electric field frequency of 0.3 MHz. At low frequencies it is difficult to assess particle size from the dynamic mobility but the special zeta potential can still be obtained. Thus, when the model used in the AcoustoSizer fails to converge and no information about particle size is obtained, this so-called Smoluchowski zeta potential can be used for monitoring the development.

In addition to the above-mentioned properties, the AcoustoSizer also measures the conductivity and the pH of the suspension. These measurements were used to gain additional information about the development of the slurries. For our measurements the AcoustoSizer was calibrated in accordance with the procedures given in the User's Manual [9].

3. Results and discussion

3.1. Consistometer measurements

Two series of experiments have been conducted; one at 20°C and the other at 50°C. The consistency curves are shown in Fig. 1. The curves are plotted as torque in m N m (10^{-3} N m) against time spent in the atmospheric consistometer. The curve to the right represents a slurry measured at 20°C and the curve to the left is measured at 50°C. The consistency measured at 20°C drops during the first 200 min from an initial value of approximately 26 down to 21 m N m (from 13 to 10.5 Bc). The input of mixing energy during the standard API conditioning of 20 min have been calculated to 0.41 kJ/kg. This is in agreement with the value of 0.48 kJ/kg found by Hodne et al. [7] for a neat Class G slurry at 20°C having a slightly lower W/C ratio of 0.38 by weight. The consistency value of 42.2 m N m (30 Bc) is reached after 575 min corresponding to an input of mixing energy of 12.7 kJ/kg from the consistometer.

The curve measured at 50°C shows a similar appearance to the curve measured at 20°C, but the decrease during the initial stable period is not so profound. The consistency shows a value of about 24 m N m (12 Bc) during the first 90 min. The input of mixing energy to the slurry during the first 20 min in the consistometer has been calculated to 0.39 kJ/kg, which is less than that at 20°C. As the consistometer is not sensitive enough to register any effect resulting from a reduction in the viscosity of the water due to a temperature increase, this reduced input of mixing energy could only be due to a change in the morphology of the cement particles. The value of 42.2 m N m (30 Bc) was reached after 140

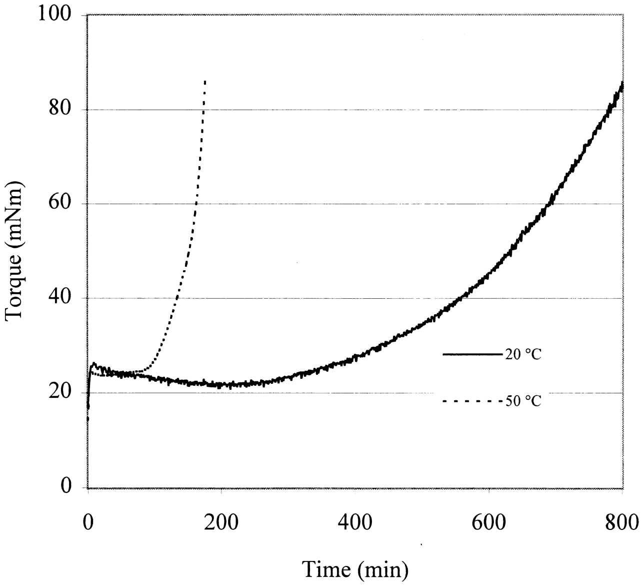

Fig. 1. Relation between time and torque measured at 20°C and 50°C in an atmospheric consistometer on a neat Class G slurry with a W/C ratio of 0.44 by weight.

min. The input of mixing energy from the consistometer during these 140 min has been calculated to 3.1 kJ/kg. This is almost a quarter of the amount of energy adsorbed before reaching 42.2 m N m (30 Bc) at 20°C. However, the time to reach 42.2 m N m (30 Bc) at 20°C is approximately four times as long. Therefore, the mixing energy input per unit time is similar for these two cases.

3.2. Zeta potential

In Fig. 2 the zeta potentials of the slurries as measured by the AcoustoSizer are shown. The zeta potential is plotted against time spent in the consistometer. Each point represents the value measured on an individual slurry. The curves are drawn as the average values at 20°C and 50°C, respectively. The first measurements were done after 20 min mixing in the consistometer. The zeta potentials are measured in mV and are found to be negative and lie between − 7 and − 3 mV throughout the measured interval from 20 to 120 min. The change in zeta potential from around − 6 mV towards zero was expected to be caused by the adsorption of mostly Ca^{2+}-ions present in the water of the slurry. When comparing the zeta potentials measured at 20°C and 50°C after 20 min in the consistometer, the absolute values of the potentials at 50°C are the highest (most negative). This could indicate that at this temperature there is a lower adsorption ratio of positive ions on to the cement particles. The decrease (towards zero) of the negative zeta potentials also indicates a development towards a positive zeta potential at later times. However, for these later times at 20°C the model used by the AcoustoSizer did not converge and a zeta potential could not be obtained. For information at these times we have to use the Smoluchowski zeta potential that still is measurable. The Smoluchowski zeta potential is shown in Fig. 3. For comparison the Smoluchowski zeta potentials are measured to be somewhat less negative than the zeta potentials shown in Fig. 2, approximately 1 to 2 mV less, but the trend with decreasing values towards zero is also shown in this case. After 380 min mixing in the consistometer the Smoluchowski zeta potential measured at 20°C reached a positive potential of approximately + 0.2 mV.

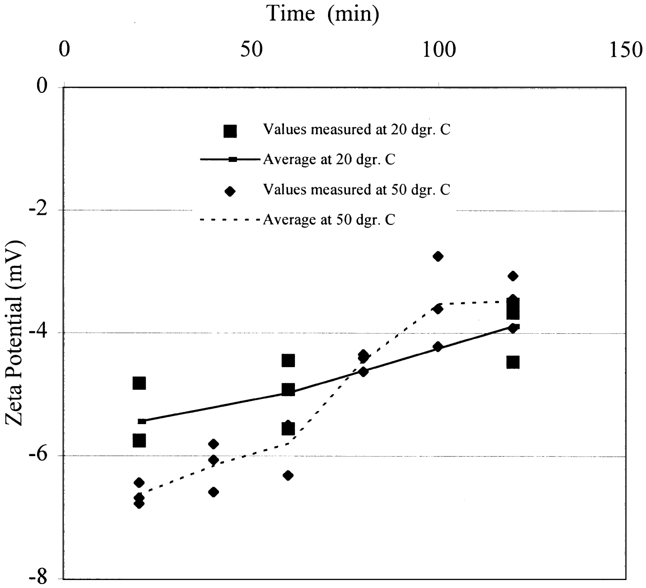

Fig. 2. Relation between time of agitation in an atmospheric consistometer and zeta potential of the cement particles as measured by an AcoustoSizer.

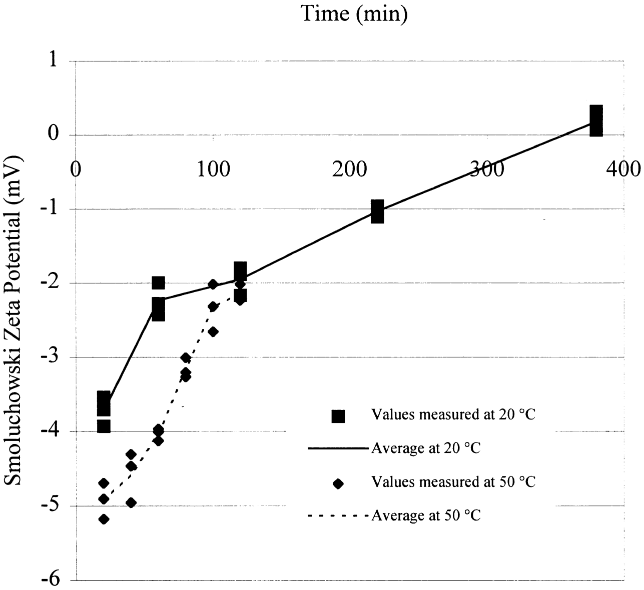

Fig. 3. Relation between time of agitation in an atmospheric consistometer and the measured Smoluchowski zeta potential of the cement particles.

The absolute value of both the zeta potential and the Smoluchowski zeta potential are smaller at a temperature of 20°C than at 50°C. A stronger degree of coagulation could therefore be expected at 20°C. Since the mixing energy input per unit time is relatively similar in these two cases, the break-up forces from shear onto the coagulated structures should be equal. Furthermore, the increased kinetic energy of the water molecules at higher temperatures is anticipated to yield a destructive force on coagulated structures at higher temperatures. All these arguments indicate that the consistency should be higher in the slurry measured at 20°C than in the slurry measured at 50°C.

Initially the consistency is higher in the slurry measured at 20°C than in the slurry measured at 50°C, as shown in Fig. 1. However, the consistency values slowly decrease in the slurry measured at 20°C. The consistency values of the slurry measured at 50°C also decrease initially, albeit only a little. After some 60–70 min in the consistometer, the consistency of the slurry measured at 50°C becomes higher than that of the slurry measured at 20°C. All these changes that are observed within the first 60 min occur even though the zeta potential of the slurry measured at 20°C is less negative than that measured at 50°C. Furthermore, for both slurries the absolute value of the zeta potential decreases with time, implying a stronger degree of coagulation.

A possible explanation of these observations is that the smallest particles of the slurries are initially dispersed. The degree of dispersion is highest for the slurry measured at 50°C, yielding the lowest consistency of the two slurries. Since the absolute value of the zeta potential decreases with time for both slurries, a higher degree of coagulation of the finer solids to the larger solids should occur as the time is increased. Following the arguments above, this coagulation should be larger at 20°C than at 50°C, resulting in a more rapid removal of fines from the slurry measured at 20°C, and thereby a more pronounced reduction in consistency. This explanation fits well with the data shown in Fig. 1.

After approximately 60 min of mixing in the consistometer the slurry measured at 50°C has obtained the largest consistency, as shown in Fig. 1. At the same time the zeta potential of the slurry measured at 50°C becomes the least negative, which is evident from the data shown in Fig. 2. Some other mechanisms must be present than the mechanism described above. A coagulation of fine materials onto coarse material should lead to a decrease in consistency. An increase in consistency values is most likely to be a result of a combined coagulation of finer and coarser particles with precipitation of solids from the fluid.

3.3. Conductivity and pH

The conductivity and the pH of the slurries have been measured as a function of time spent in the consistometer. While the pH measured is due to the amount of hydrogen (H^+) and hydroxyl (OH^-) ions present in the water of the slurry, the measured conductivity is a result of a combination of the above-mentioned ions and other dissolved ions, mostly Ca^{2+}. The pH measured at 20°C, as shown in Fig. 5, shows a decrease during the time from 20 to 120 min followed by an increase in pH during the time from 120 to 380 min. The conductivity measured at the same temperature, shown in Fig. 4, shows an increase during the time from 20 to 60 min followed by a slight decrease throughout the rest of the measured interval from 60 to 380 min. These results indicates that in the interval from 20 to 120 min there is an increase in the amount of dissolved Ca^{2+} ions followed by a decrease after 120 min.

At 50°C the measured conductivity in Fig. 4 shows an increase during the time from 20 to 60 min followed by a decrease in the period from 60 to 120 min. The pH shows an increase throughout the whole measured interval from 20 to 120 min. Whether the increase in conductivity from 20 to 60 min is due to an increase in dissolved Ca^{2+} ions or an increase in dissolved OH^- ions could not be determined. However, the decrease in conductivity during the period from 60 to 120 min could only be due to a reduction in dissolved Ca^{2+} ions.

According to Castellan [10] it is expected on a general basis that an increase in temperature should lead to even higher ion conductivity. For ions other than H^+ and OH^- the increase in conductivity is mainly due to the reduction in the viscosity of the water. An average increase of about 2% per degree could be expected. For H^+ and OH^- ions the conductivity has larger temperature coefficients. Here the increase is about 14% for H^+ and about 16% for OH^- ions per degree. For these ions where the mechanism behind the conductivity is a proton jump, the conductivity is not so dependent on the viscosity of the water. In Fig. 4 it is shown that when the temperature of the slurries is increased from 20°C to 50°C the conductivity increases and the pH decreases, as shown in Fig. 5. The increase in conductivity is found to be about 1.8% per degree after 20 min, 1.5% per degree after 60 min and 0.9% after 120 min. The measured increase in conductivity is not as high as could be expected according to Castellan [10] and it is expected that this is mainly due to the measured decrease of the pH.

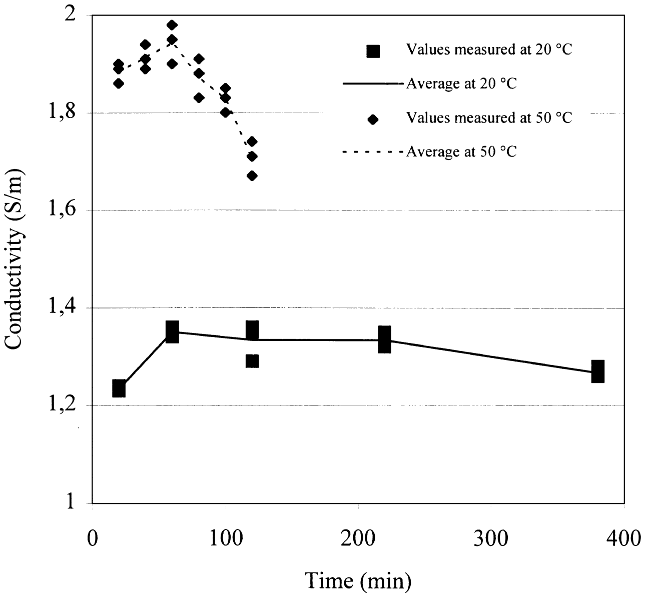

Fig. 4. Relation between time of agitation in an atmospheric consistometer and the measured conductivity of the slurries.

The decrease in the conductivity with time observed for the slurry measured at 50°C starts at the same time as the consistency of the slurry starts to increase. Therefore, it is possible that dissolved Ca^{2+} ions start to precipitate either as C-S-H gel, or even more likely, small calcium silicate hydrate and calcium hydroxide crystals within the fluid. Such a precipitation would increase the consistency of the slurry, still leaving the slurry in a fluid state.

The similar decrease in conductivity for the slurry measured at 20°C seems to start between 60 and 200 min although a decrease is not very pronounced before 220 min, as shown in Fig. 4. As being the case for the slurry measured at 50°C, this time at approximately 220 min, is the time when the consistency of the slurry starts to increase. The increase in consistency at 20°C, however, is very slow, as shown in Fig. 1. Thus, it seems plausible that the rate of decrease in conductivity reflects the reactivity of the cement at the time when the cement slurry consistency starts to increase.

3.4. Particle size

The AcoustoSizer particle size distribution was measured as a function of time or input of mixing energy, as shown in Fig. 6. In this figure the lines represents the average values measured for the d-16, d-50 and d-84 in μm at 20°C and 50°C. The real particle size distribution is not measured. The data shown in Fig. 6 is a particle size distribution fitted to a particular model from the acoustical data obtained at different frequencies. Thus, our particle size distribution illustrates a change in morphology resulting from coagulation of the finer material, dissolution of solids and precipitation of new fine-grained solids in the slurry, excluding the coarser particles from the cement slurry. Therefore, the AcoustoSizer particle size distribution is expected to be qualitatively correct for the finer part of the cement grains.

The AcoustoSizer particle sizes measured at 20°C increased with time and shows a maximum after 60 min in the consistometer with a following decrease after 120 min. According to Yang et al. [4], cement particles in a neat suspension coagulates due to the high ionic strength. Here the measured increase in particle size could be caused by an increased coagulation of the cement particles taking place due to a less negative zeta potential, which support the proposed hypothesis given in the previous paragraphs about the consistency behaviour shown in Fig. 1. It is not clear if the decrease in particle size from 60 to 120 min is a result of a slow breakdown of the coagulated particles due to the input of mixing energy combined with a precipitation of small particles or if it is due to experimental errors. The latter is more plausible since the consistency of the slurry measured at 20°C does not start to increase noticeably before approximately 220 min. However, a later precipitation of very fine solid material in the fluid is expected to happen. This expectation is based on one single AcoustoSizer particle size measurement done after 650 min of mixing in the consistometer. The measured values after this long time of mixing were 0.32 μm for the d-50 particles, 0.29 μm for the d-16 and 0.36 μm for the d-84, which are much smaller than the values measured initially.

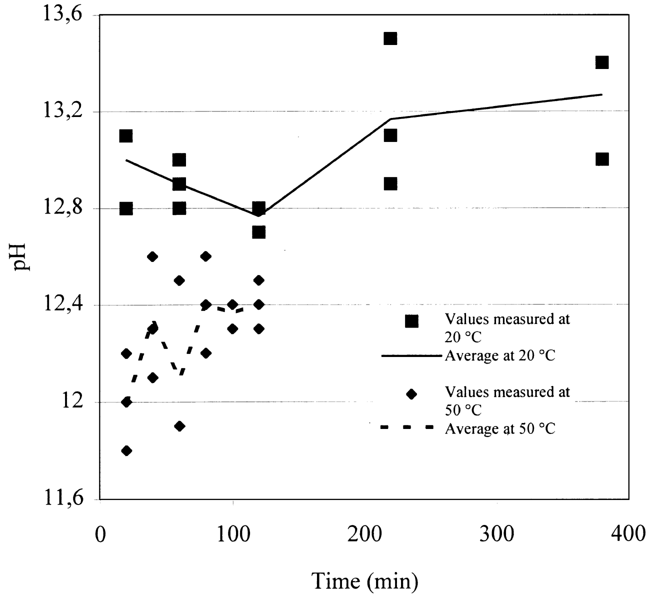

Fig. 5. Relation between time of agitation in an atmospheric consistometer and the measured pH of the slurries.

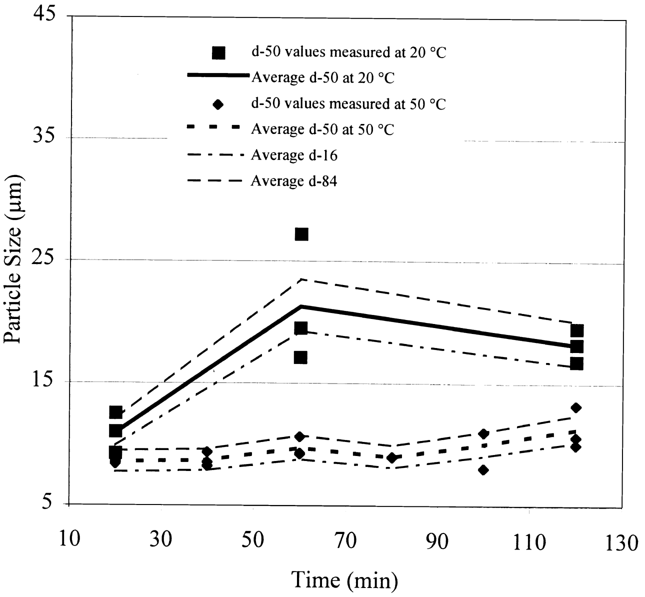

Fig. 6. Relation between time of agitation in an atmospheric consistometer and the measured particle size distribution of the slurries.

The measured particle size distribution at 50°C is almost constant throughout the measured interval, indicating that any further coagulation is hindered by the input of mixing energy. As the measured average AcoustoSizer particle sizes at 20°C are larger than those measured at 50°C, it is expected that the finer cement particles coagulates more readily at 20°C as indicated in previous paragraphs. The fact that the width of the particle size distribution and spread in data are larger at 20°C could also indicate a higher degree of coagulation at this temperature. The consistency of the slurry measured at 50°C started to increase after around 60–70 min mixing in the consistometer. This is expected to be a result of a combined coagulation of both finer and coarser particles with a simultaneous precipitation of new fine solid material.

4. Conclusions

A series of experiments have been conducted to measure the development of the consistency of cement slurries along with the zeta potential, Smoluchowski zeta potential, conductivity, pH and a special AcoustoSizer particle size distribution of the cement slurries.

The absolute value of the zeta potential after a short time of mixing is higher when the temperature is 50°C than when it is 20°C. This results in a better dispersed slurry at 50°C and thus a lower consistency than observed at 20°C. The reduction in the absolute value of the zeta potential with time indicates that the finer grains of a cement coagulate more easily onto coarser grains at lower temperatures than at higher temperatures, leaving a slurry with decreased consistency values.

Measurement values of the conductivity fits very well with consistency measurement data for the cement slurries. At the time when the consistency of a cement slurry starts to increase the conductivity starts to decrease. The conductivity decrease rate seems to reflect the reactivity of the cement slurry.

The data and conclusions from the zeta potential analysis and the conductivity measurement analysis are also supported by data from the pH measurements and measurements of a special AcoustoSizer particle size distribution.

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