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# Rheological Properties of High Temperature Oil Well Cement Slurries.

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## ABSTRACT

The design of a cement slurry for an oil well exposed to high temperatures have proved to be a challenge. Various additives are in use to prevent cement strength retrogression, and to maintain the needed rheological properties to work with the slurry. In the present study the rheological properties of selected high temperature slurries using different types of additives are measured. The effect of these additives onto the zeta-potential are also evaluated and collated with rheological data.

## INTRODUCTION

During the drilling of oil wells in areas where the later oil production temperature can exceed 120°C it is necessary to add silica to well cements to prevent strength retrogression. Addition of silica has yielded a change in time for the cement to cure in practical operations. A waiting time for cement to cure is extremely costly in oil well drilling and must therefore be minimised.

The current study outlines some of the initial tests performed to understand the rheological behaviour and early hydration of cements, which have been used in practical applications where the anticipated curing history was not observed. The stability of some of the sulphate minerals used to control thickening and early stages of cure in cements changes at 42°C[1]. Therefore, in the experiments all test were conducted at 25°C, 34°C and 49°C, to illustrate practical temperatures for cementing a 13 3/8" casing in a 17 ½" hole.

## EXPERIMENTAL CONDITIONS

### Sample preparation

All samples were mixed in accordance with API[2]. However, the prescribed conditioning time, prior to any measurements, of 20 minutes was increased to 30 minutes for all our samples.

Two series of tests were conducted. One using a Class G cement (Norcem A/S, Brevik) and water as a basis, in the other the cement was partly replaced by silica (quarts) flour. Silica flour is used to prevent compressive strength retrogression at high temperatures.

Silica flour has a rather low surface activity. A negative Smoluchowski zeta potential of -9.89mV was measured on a 19% by volume suspension of pure silica flour in water. The average particle size is expected to be slightly higher than that of the cement which when measured gave a d50 of 8.44μm.

The additives used came all as water based suspensions. A gas migration preventive, micro silica, or silica fume, was used. Micro silica is highly reactive. The particle size of the micro silica is small. A measurement on a sample containing 3.28% by volume gave a rather narrow particle size distribution with a d-50 of 0.45μm. The zeta potential measured

on the same sample was -156mV, which is rather high. It is expected to be due to chemicals added to the micro silica to create a stable suspension

Table 1. Sample composition.

| | **Sample 1a** | **Sample 2a** |
|---|---|---|
| Cement | 785g | 597g |
| Silica flour | | 209g |
| Water | 356g | 336g |
| W/C -ratio | 0.45 | 0.56 |
| Solid % by volume | 40.8 | 44.1 |
| | **Sample 1b** | **Sample 2b** |
| Cement | 763g | 583g |
| Silica flour | | 204g |
| Micro Silica | 53g | 41g |
| Water | 324g | 312g |
| W/C -ratio | 0.42 | 0.53 |
| Solid % by volume | 42.4 | 45.2 |
| | **Sample 1c** | **Sample 2c** |
| Cement | 778g | 592g |
| Silica flour | | 207g |
| Dispersant | 6.9g | 5.2g |
| Retarder | 19.3g | 14.7g |
| Water | 334g | 319g |
| W/C -ratio | 0.43 | 0.54 |
| Solid % by volume | 41.1 | 44.3 |
| | **Sample 1d** | **Sample 2d** |
| Cement | 757g | 580g |
| Silica flour | | 203g |
| Micro Silica | 52.6g | 40.3g |
| Dispersant | 6.7g | 5.1g |
| Retarder | 18.8g | 14.4g |
| Water | 303g | 296g |
| W/C -ratio | 0.40 | 0.51 |
| Solid % by volume | 42.7 | 45.5 |

As a retarder a synthetic acrylamide was used and as a dispersant a salt of sulphonic acid with slight retarding properties was used.

All the additives were mixed with distilled water before the cement or cement/silica flour was added. The amount of additives used in each sample was in proportion to the amount of cement used. Details of the samples are given in Table 1. All samples were made up to a specific gravity of 1.9. This density is used in parts of most oil well cementing operations.

The volume of each sample was 600 ml and the testing temperatures used were 25, 34 and 49°C respectively.

Consistency measurements

An atmospheric consistometer (Chandler Engineering, Tulsa, OK) was used to measure the thickening time of the slurries. The consistometer is a slow rotating mixer. The slurry container rotates with 150rpm and the torque exerted on an immersed and fixed paddle is measured. The torque is measured in Bc, Bearden units of consistency[2]. The time to reach 30Bc is considered as the time available for pumping and placing the cement slurry in the well. All the preparations of test samples and the consistometer tests were carried out within ±1°C of the set temperature.

Viscosity measurements

The viscosity of the slurries was measured using a Physica UDS 200 rheometer (Physica Meβtechnik GmbH, Stuttgart) fitted with a concentric cylinder configuration named Z3 DIN. The difference between this configuration and that given in API Spec 10[2] is that the Z3 has a smaller bob diameter, 25mm compared to the 34.49mm given by API. The gap between the rotor and the stator in the Z3 DIN configuration is 1.06mm. For all our measurements we used the shear rates and time intervals between consecutive measurements as specified by API[2]. All tests were done within ±0.5°C of the set temperature.

Zeta potential measurements

For zeta-potential and particle size measurements an AcoustoSizer (Colloidal Dynamics Inc., Warwick, RI) was used. This is an apparatus that is able to measure the mobility of particles in suspensions containing more than 40% solids by volume. The particle content in our slurries varied from 40.8 to 45.5%.

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 and the phase lag of the particles. This is done over a range of frequencies from 0.3 to 11.2 MHz, corresponding to particles in the size range from 0.1 to 10 μm. From the measured dynamic mobility distribution and the phase lag and by using Eq. 1[3] and a log normal particle size distribution model the AcoustoSizer calculates the zeta potential of the particles and the particle size distribution of the slurry.

$$\mu_d = \frac{2\varepsilon\xi}{3\eta} G\left(\frac{\omega a^2}{\nu}\right)\left(1 + f(\lambda,\omega)\right) \qquad (1)$$

In Eq. 1 $\mu_d$ is the dynamic mobility, ε is the permittivity of the liquid, ξ is the zeta potential, η is the dynamic viscosity of the liquid, the G factor is a function of ω, the frequency, a, the particle radius and ν, the kinematic viscosity of the liquid. G represents the effect of inertia forces on the dynamic mobility and at low frequencies G≈1. In the function f(λ,ω), λ is related to the double-layer conductance. For many colloids in water based suspensions the formula reduces to f = 0.5. Thus, for low frequencies and when the phase lag approaches zero the dynamic mobility equals the electrophoretic mobility measured in a DC field and Eq. 1 is reduced to Eq 2, which is called the Smoluchowski equation[4]. So, when the model in the AcoustoSizer based on Eq. 1 fails to converge a zeta potential can still be obtained using Eq. 2, this is called the Smoluchowski zeta potential.

$$\mu = \frac{\varepsilon\xi}{\eta} \qquad (2)$$

The measurements done in the AcoustoSizer had the following temperature ranges: 25±1°C, 34±2°C and 49±3°C.

RESULTS

Consistometer measurements

A typical set of Consistometer curves are shown in Fig. 1. In Fig. 1 is shown the testing of the samples containing cement and cement plus additives without silica flour at 25°C. The consistency of the slurry is shown as the development of torque as a function of time. A torque of 66.6mNm equals 30Bc and a torque of 204mNm equals 100Bc. The times to reach 30 and 100Bc are given for all samples in Table 2.

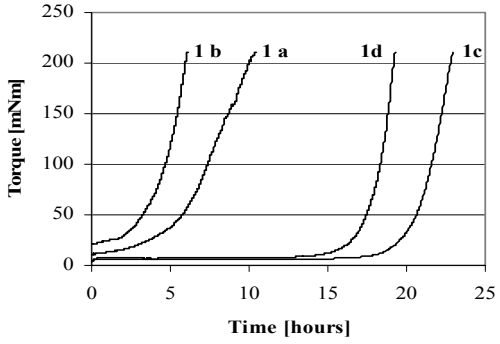


Figure 1. Atmospheric Consistometer testing of samples 1a-b-c-d at 25°C.

By adding micro silica to the cement slurries a reduction in thickening time is observed, as can be seen from Fig. 1 when samples 1a and 1b are compared. The effect is the same when retarder and dispersant is present, sample 1c-1d. The results for sample 1c are larger than those for 1d for all temperatures. From Table 2 it can be seen

that the reduction in thickening time when adding micro silica to the cement slurries holds for all temperatures.

For the samples where cement was partly replaced by silica flour the effect of adding micro silica is mixed. The results are shown in Table 2 for samples 2. When retarder and dispersant is not present, sample 2a-2b, there is a reduction in thickening time for all the investigated temperatures. When retarder and dispersant is present, sample 2c-2d, addition of micro silica gives an increased thickening time at 25°C. However, at 34 and 49°C the effect is a reduction in thickening time.

Table 2. Time in hours for samples to reach 30 and 100Bc (66.6 and 204 mNm) in the Atmospheric Consistometer.

| | 30Bc | | | 100Bc | | |
|---|---|---|---|---|---|---|
| Sample | 25°C | 34°C | 49°C | 25°C | 34°C | 49°C |
| 1a | 6.5 | 5.2 | 2.7 | 10.1 | 9.3 | 3.9 |
| 1b | 3.9 | 3.1 | 1.7 | 6.0 | 4.4 | 2.4 |
| 1c | 21.0 | 35.6 | 26.0 | 22.8 | 36.6 | 26.5 |
| 1d | 17.8 | 21.5 | 19.4 | 19.2 | 22.4 | 19.8 |
| | 30 Bc | | | 100Bc | | |
| Sample | 25°C | 34°C | 49°C | 25°C | 34°C | 49°C |
| 2a | 5.8 | 3.9 | 3.9 | 10.3 | 6.0 | 6.0 |
| 2b | 3.9 | 2.9 | 1.5 | 6.7 | 4.5 | 2.4 |
| 2c | 20.0 | 30.8 | 25.2 | 21.3 | 31.7 | 25.6 |
| 2d | 20.6 | 24.9 | 19.2 | 21.9 | 25.7 | 19.6 |

The effect on the thickening time when cement is partially replaced with silica flour is more complicated. Comparing sample 1a with 2a in Table 2 gives a decrease in time to reach 30Bc at 25 and 34°C and an increase at 49°C. The time to reach 100Bc is increased at 25 and 49°C and decreased at 34°C. The effect of micro silica on the cement/silica flour mixture compared to the effect on the cement, sample 1b and 2b, is a reduction in time to reach 30Bc for all temperatures. However, the time to reach 100Bc increases at 25 and 34°C while it is reduced at 49°C. When retarder and dispersant is present and no micro silica is added, sample 1c-2c, the effect of replacing some of the cement with silica flour is a reduction in thickening times for all temperatures. When micro silica is added together with retarder and diperser the replacement of cement with silica flour, sample 1d-2d, increases the thickening time at 25 and 34 °C and reduces the thickening time at 49°C.

Viscosity measurements

The rheological behaviour of the test samples could be divided into two distinct groups. The first group being the samples without retarder and dispersant. In this group the measured viscosity is the highest, with a shear thinning region at the lowest shear rates followed by a Newtonian region at the higher shear rates. This is shown in Figs. 2, 3 and 4, for sample 1a, 1b, 2a and 2b at 25, 34 and 49°C respectively.

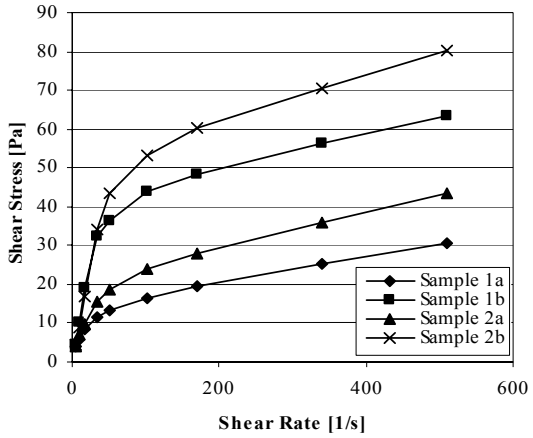


Figure 2. Shear stress as a function of shear rate measured at 25°C.

As can be seen from Figs. 2, 3 and 4, the general trend when some of the cement is replaced with silica flour, is an increase in shear stress; sample 1a-2a. Only at 49°C the measured shear stress of the two samples is similar.

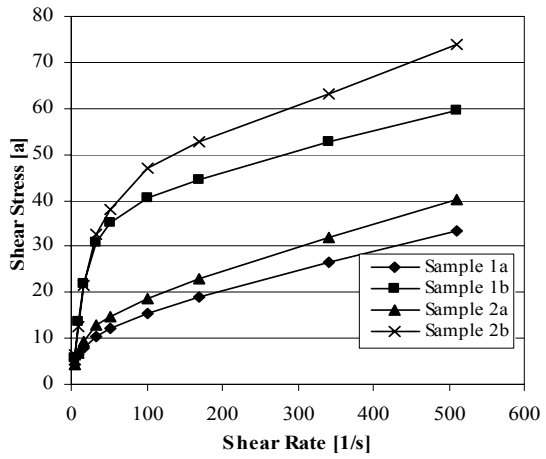


Figure 3. Shear stress as a function of shear rate measured at 34°C.

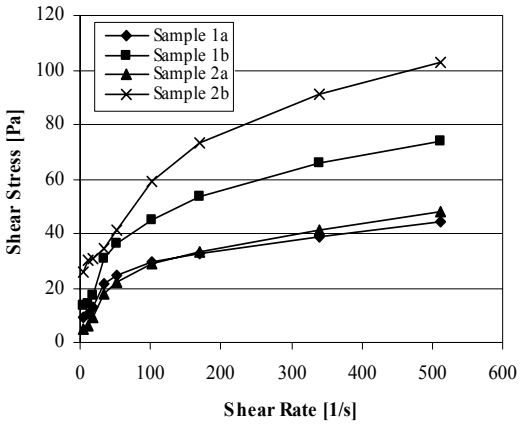


Figure 4. Shear stress as a function of shear rate measured at 49°C.

It can also be seen that the effect of adding micro silica to the two samples gives a marked increase in measured shear stress for both samples at all temperatures. The dominant effect of increase in temperature for sample 1a, 1b, 2a and 2b is an increase in measured shear stress. Only for sample 1a when temperature is increased from 25 to 34°C the measured shear stress is the same.

In the second group, the slurries with retarder and dispersant added a Newtonian behaviour with a rather low viscosity for all shear rates was measured. The measured viscosities are shown in Table 3.

From the data in Table 3 it can be seen that addition of micro silica gives a reduction in viscosity at all temperatures. This is contrary to the effect when micro silica was added to the samples without retarder and dispersant. The effect of replacing some of the cement with silica flour, sample 1c compared to sample 2c, is somewhat mixed. At 25 and 34°C the viscosity is increased.

Table 3. Viscosity in mPas of samples showing a Newtonian behaviour.

| Sample | 25°C | 34°C | 49°C |
|---|---|---|---|
| 1c | 27.3 | 22.4 | 66.5 |
| 1d | 21.9 | 20.4 | 14.2 |
| 2c | 32.4 | 30.1 | 17.8 |
| 2d | 19.0 | 28.4 | 14.7 |

The rather high viscosity measured on sample 1c at 49°C is expected to be due to an instable suspension and thus, the effect of replacing cement with silica flour at this temperature remains uncertain. The effect of replacing cement with silica flour when micro silica is present, sample 1d compared to sample 2d, is a decrease in viscosity at 25°C and an increase at 34 and 49°C. The effect of increasing the temperature on sample 1d and 2c is a reduction in viscosity. For sample 1c the effect is a decrease in viscosity when temperature is increased from 25 to 34°C followed by an increase in viscosity when temperature is increased from 34 to 49°C. For sample 2d the effect of increasing the temperature is the opposite, an increase in viscosity when temperature is increased from 25 to 34°C and a decrease in viscosity when temperature is increased from 34 to 49°C.

Zeta Potential measurements

The measured zeta potentials of the slurries are shown in Table 4. For many of the measurements the model for calculating the zeta potential did not converge. Thus in Table 4 the Smoluchowski zeta potentials are listed as they indicate the development of the particle charges.

Table 4. Zeta potentials of samples.

| | Zeta potential [mV] | | | Smoluchowski Zeta potential | | |
|---|---|---|---|---|---|---|
| Sample | 25°C | 34°C | 49°C | 25°C | 34°C | 49°C |
| 1a | -6.1 | -6.7 | -11.2 | -4.5 | -5.0 | -6.9 |
| 1b | -5.0 | -* | - | -3.6 | -4.6 | -5.9 |
| 1c | - | - | - | -31.7 | -32.0 | -36.2 |
| 1d | - | - | - | -32.1 | -33.3 | -42.8 |
| | Zeta potential [mV] | | | Smoluchowski Zeta potential | | |
| Sample | 25°C | 34°C | 49°C | 25°C | 34°C | 49°C |
| 2a | -6.1 | -4.5 | -6.7 | -3.4 | -3.4 | -4.12 |
| 2b | -2.7 | -2.3 | - | -1.9 | -1.9 | -4.1 |
| 2c | - | - | - | -32.8 | -33.6 | -42.4 |
| 2d | - | - | - | -32.1 | -33.1 | -42.2 |

*No data as the model did not converge.

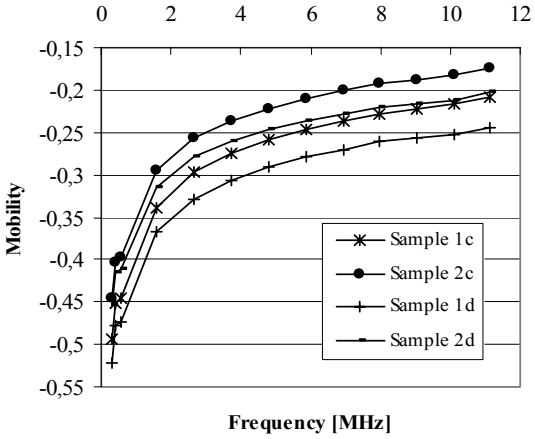


Figure 5. Mobility [$\cdot 10^{-8}$ $m^2$/Vs] measured as a function of frequency at 25°C.

For the slurries with retarder and dispersant added we have also plotted the measured dynamic mobility in Figs. 5, 6 and 7 at 25, 34 and 49°C respectively.

The zeta potential of the Class G cement, sample 1a, is rather low, namely -6.1 mV at 25°C. This is in accordance with earlier measurements on neat Class G cement slurries[5]. When the cement is partially replaced by silica flour, sample 2a, there is no change in zeta potential.

The effect of adding micro silica to the two slurries above, samples 1b and 2b, is a small reduction of the zeta potential.

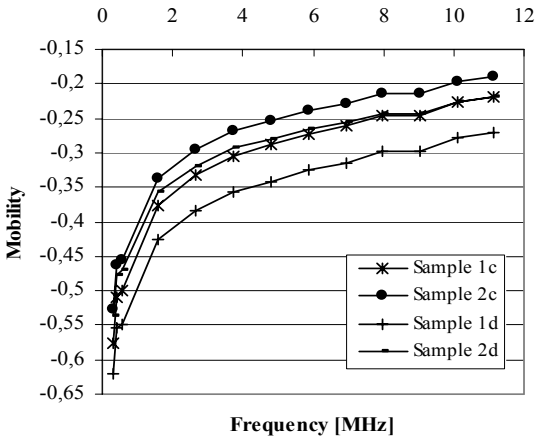


Figure 6. Mobility [$\cdot 10^{-8}$ $m^2$/Vs] measured as a function of frequency at 34°C.

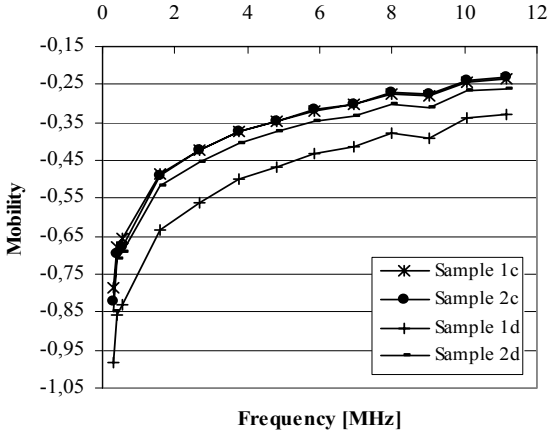


Figure 7. Mobility [$\cdot 10^{-8}$ $m^2$/Vs] measured as a function of frequency at 49°C.

The addition of retarder and dispersant gives a significant increase in the Smoluchowski zeta potential for all samples. However, as the Smoluchowski zeta potential is calculated based on the mobility measured at 0.3MHz only, it does not always give a correct indication of the total development. In comparing data from Table 4 with data in Figs. 5, 6 and 7 it can be seen that when micro silica is added to the sample with only cement, sample 1c-1d, the Smoluchowski zeta potential indicate an increase which corresponds to the increase in the measured dynamic mobility. But, when comparing data for the samples with silica flour, sample 2c-2d, they differ. Here the Smoluchowski zeta potential is reduced

when micro silica is added, while the measured dynamic mobility of the samples show an increase.

From Figs.5, 6 and 7 it can be seen that when retarder and dispersant are present the particles in the cement slurry have a higher dynamic mobility than the particles in the cement/silica flour slurry for all frequencies. The effect of adding micro silica is an increase in dynamic mobility for both samples. This effect is the opposite of the effect registered when micro silica was added to the samples without retarder and dispersant.

When the temperature increases the cement based slurries show an increase in mobility for all temperatures. This is also true for the cement/silica flour based slurries where dispersant and retarder are added, sample 2c and 2d. Sample 2a and 2b on the other hand show a slight reduction when temperature is raised from 25 to 34°C. When the temperature is increased from 34 to 49°C an increase is also shown for these samples.

## DISCUSSION

When cement is partly replaced with silica flour in our slurries it results in a general reduction of thickening time, an increase in viscosity and a reduction in zeta potential and dynamic mobility. The decrease of thickening time and increase in viscosity is expected to be mainly due to the increase in solid content as can be seen from Table 1. The measured zeta potential and dynamic mobility is an average measurement of the whole suspension. Thus, the reduction in zeta potential and dynamic mobility is expected to be due to the partial replacement of rather chemically reactive cement particles with rather inert silica flour particles.

The effect of adding micro silica to the samples without retarder and dispersant is a decrease of thickening time, an increase of viscosity and a decrease of zeta potential. The micro silica particles added comes as a suspension. A suspension stabilized by a dispersant giving the micro silica particles their high negative surface charge. It is expected that the micro silica particles add to the surface of the less reactive particles present. When micro silica is added there is also an increase of solid content. These two effects are expected to cause the reduced thickening times and the increased viscosity. The amount of dispersant added with the micro silica suspension seems to be too small to have any effect. The reduction of the zeta potential, confirm the reduction of repulsive surface forces and thus, an increased viscosity.

When retarder and dispersant are present the effect of adding micro silica also gives a reduction of the thickening time. The effects on the viscosity and the zeta potential and dynamic mobility are the opposite of those observed above, namely a decrease of viscosity and an increase of zeta potential and dynamic mobility. The decrease of the thickening time is again expected to be due to the high reactivity of the micro silica. The increase of the zeta potential and dynamic mobility confirms the increase in repulsive forces between the particles and thus the reduction in viscosity. Although the adding of micro silica gives a higher solid content the chemicals present outweighs this effect on the viscosity.

The effects of increasing temperature on the slurries without retarder and dispersant show a decrease in thickening time an increase in viscosity and a general increase in mobility. The increase in thickening time and viscosity with increasing temperature is expected to be due to the increasing speed of the chemical reactions taking place. The interpretation of the influence of increasing temperature on the zeta potential and dynamic mobility is more mixed. Both the permittivity and viscosity of the water in the suspension goes into the calculations as can be seen in Eq. 1. Both parameters are reduced with increasing temperature, the

viscosity more than the permittivity. The result is an increase of the zeta potential and dynamic mobility with increasing temperature. When compensating the measured values for the decrease in permittivity and viscosity of the water, there is a net increase in zeta potential and dynamic mobility and thus, the increase of the surface activity is confirmed.

Samples with retarder and dispersant show an increase in thickening time with increasing temperature. The increase is more profound at 34 than at 49°C. The general trend is a reduction in viscosity and an increase in mobility. The reduction in the measured viscosity with increasing temperature is expected to be mainly due to the reduction of the water viscosity. The increase in zeta potential and dynamic mobility measure when temperature is increased from 25 to 34°C is due to the reduction in permittivity and viscosity of the water. No real increase in surface charge is measured. When temperature is increased from 34 to 49°C the increase in zeta potential and dynamic mobility is larger than that due to the reduction of the permittivity and viscosity of the water. Some of the measured increase in zeta potential and dynamic mobility is therefore anticipated to be a real increase in surface charge. The reason for the increase in thickening time measured when temperature is increased from 25 to 34°C is not known. Since there are no change in the surface charge, no changes in chemical activity is expected, which would yield a small decrease in the thickening time. This is in contradiction to the observations. The further decrease in thickening time when temperature is increased from 34 to 49°C indicate the existence of a reduction in the zeta potential and dynamic mobility, which again is opposite to the observations. The combined observations may indicate a precipitation of small crystals, perhaps ettringite, in the liquid between the particles.

## CONCLUSION

When cement is partly replaced by silica flour, and the water content is adjusted to maintain the same slurry density, a reduction in thickening time is observed. At the same time the slurry viscosity is increased and the zeta potential is reduced.

For dispersant and retarder free slurries the addition of liquid micro silica leads to a decreased thickening time and an increase in viscosity. The zeta potential and dynamic mobility is decreased. If the investigated retarder and dispersant are present the viscosity is reduced by addition of liquid micro silica, while the zeta potential and dynamic mobility is increased.

Contradicting results from mobility measurements and thickening time measurements indicate precipitations of small crystals in the liquid solution.

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