

Rheological Properties of High Temperature Silica Oil Well Slurries.

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ABSTRACT

The storage of silica in water slurries used as an additive for cementing an oil well exposed to high temperatures have proved to be a challenge. A part of the challenge is the prevention of sedimentation of silica during storage and pumping, and to maintain the needed rheological properties to maintain a workable slurry. In the present study the rheological properties of different silica slurries have been measured. These slurries contain both amorphous and crystalline silica in various concentrations. The zeta-potential of these mixtures has been measured and is compared with the rheological data.

INTRODUCTION

When cementing oil wells in areas where high temperatures and high pressures are encountered in the wells, the addition of crystalline silica to prevent strength retrogression and amorphous silica to prevent gas migration of the cement, is much in use. The idea of having readily available and easy handled silica slurries of tailor made composition for use either as an additive to or as a full replacement for the cement has lately received a large interest.

In the current study we have looked into the challenge of making stable silica slurries. Furthermore, to improve the understanding of the behaviour of these slurries we have measured the rheological

properties and the zeta-potential or dynamic mobility of the slurries.

EXPERIMENTAL CONDITIONS

Sample preparation

Two types of silica were used, an amorphous micro silica, or silica fume, and a crystalline silica (quartz) flour.

Two of the samples, B1-32 and C1-31, consisted of amorphous micro silica and water. The number after the hyphen indicates the solids fraction by volume for each sample. These slurries were delivered as ready mixed slurries from two different suppliers. Into portions of these slurries were added crystalline silica flour, samples named B1-55 and C1-53. Sample A1-65 came from a third supplier as a ready mixed slurry containing both amorphous micro silica and crystalline silica flour. In addition it also contained 3.4% by volume of an acrylic copolymer based type of superplasticizer. Sample A1-55 is made from sample A1-65. The original sample was diluted with water to give a solid content of 55% by volume.

For all slurries, distilled water was used, and all measurements were done at a temperature of 25 °C.

Viscosity measurements

The rheological properties of the slurries were measured using a Physica UDS 200 rheometer (Physica Meßtechnik GmbH, Stuttgart) fitted with a concentric cylinder configuration named Z3 DIN. The

difference between this configuration and that given in API Spec 10¹ 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 shear rates and time intervals between consecutive measurements as specified by API¹. All tests were done within $\pm 0.5^\circ\text{C}$ of the set temperature.

Zeta potential measurements

For zeta-potential and particle size measurements an AcoustoSizer^{2,3} (Colloidal Dynamics Inc., Warwick, RI) was used. This is an apparatus that is able to measure the dynamic mobility of particles in concentrated suspensions. The particle content in our slurries varied from 22 to 65.3% by volume.

RESULTS

Viscosity measurements

For six different slurries we have measured the shear stress as a function of shear rate varying from 1.5 - to 1022 s⁻¹.

In Fig. 1 the measured shear stress against shear rate is shown for the two slurries consisting of amorphous silica, named B1-32 and C1-31. There is a marked difference between the two slurries. The slurry with the lowest solid content, named C1-31, has the highest shear stress for all the measured shear rates. The solid content in the slurries can be seen in Table 1. The C1-31 has a highly shear thinning behaviour, while the B1-32 sample show a slight shear thinning behaviour. For the higher shear rates the viscosity of the B1-32 sample approximates a constant value.

When crystalline silica was added to the slurries above, the result was a significant increase in the measured shear stress. This is shown in Fig. 2 for slurry B1-55 and C1-53. The viscosity increase was highest for the B1-55 slurry, but the C1-53 slurry still show the highest shear stress for all shear rates except at the highest shear rate of

1022s⁻¹ where the measured shear stress was lower than that of the B1-55 slurry. Both slurries show a region with a high degree of shear thinning at low shear rates.

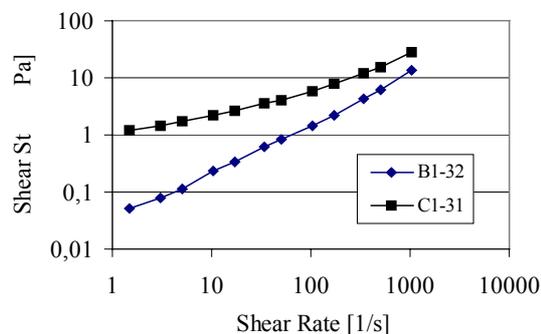


Figure 1. Shear stress as a function of shear rates for the amorphous silica slurries

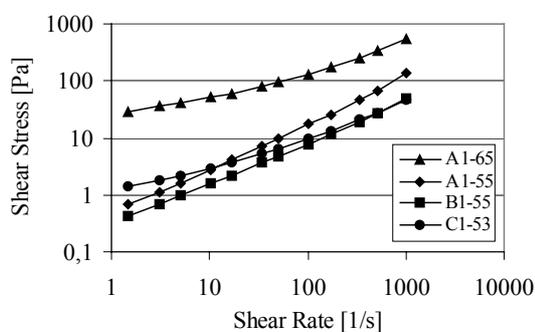


Figure 2. Shear stress as a function of shear rates for the mixed silica slurries

In Fig. 2 we have also plotted the shear stress measured on the slurry A1-65. This is a slurry with a very high solids content as can be seen from Table 3. The measured shear stress of the slurry is very high and the slurry viscosity curve shows a marked shear thinning behaviour. When the slurry was diluted with water to give a solid content of 55% by volume, curve labelled A1-55 in Fig. 2, the reduction in shear stress is profound; the largest reduction in shear stress being measured at the lowest shear rates. This slurry also shows a slightly shear thinning behaviour. For higher shear rates the viscosity curves fit well to Bingham plastic models. For the lower shear rates, less than 50s⁻¹, the viscosity curve model approximates the power law model for all the slurries.

Table 1. Input data and size and charge analysis from the AcoustoSizer for the amorphous silica slurries.

Sample:	B1-32	C1-31
Total volume fraction of solids	0.321	0.311
Volume fraction of amorphous silica	0.321	0.311
Zeta-potential [mV]	-49.1	-42.7
d50 [μm]	0.368	0.240
d16	0.333	0.217
d84	0.407	0.265

Table 2. Input data and size and charge analysis from the AcoustoSizer for the mixed silica slurries.

Sample:	B1-55	C1-53
Total volume fraction of solids	0.55	0.531
Volume fraction of amorphous silica	0.19	0.212
Volume fraction of crystalline silica	0.36	0.319
Zeta-potential [mV]	-	-33.5
d50 [μm]	-	0.373
d16	-	0.0286
d84	-	4.86

Table 3. Input data and size and charge analysis from the AcoustoSizer for the mixed silica slurries.

Sample:	A1-65	A1-55
Total volume fraction of solids	0.653	0.55
Volume fraction of amorphous silica	.134	0.113
Volume fraction of crystalline silica	0.484	0.408
Zeta-potential [mV]	-5.91	-
d50 [μm]	0.456	-
d16	0.29	-
d84	0.715	-

When comparing the two slurries having the same solids volume fraction, as shown in Fig. 2 for slurry A1-55 and B1-55, we see that the measured shear stress of A1-55 is higher for all shear rates.

Zeta potential measurements

In Fig. 3 the measured dynamic mobility of the two slurries, containing only amorphous silica, slurry B1-32 and C1-31, is shown as a function of frequency. The silica particles in the B1-32 slurry show the highest dynamic mobility (most negative). Based on these mobility spectra the zeta-potential for the amorphous silica particles was calculated³. From Table 1 it can be seen that the silica particles in slurry B1-32 have the highest zeta-potential.

The dynamic mobility of the slurries containing both amorphous and crystalline silica is shown in Fig. 4. When crystalline silica is added the result is a reduction of the dynamic mobility as can be seen when comparing the curves for slurries B1-55 and C1-53 in Fig. 4, with the curves for slurries B1-32 and C1-31 in Fig. 3. The reduction is largest for the B1-55 slurry.

In Fig. 4 it is also shown that slurry A1-65 has the lowest dynamic mobility. When water is added and thus, the solids fraction is reduced, an increase in dynamic mobility was observed as can be seen when comparing the dynamic mobility measured on slurry A1-65 with that of A1-55 in Fig. 4.

When comparing the curves for the two slurries in Fig. 4 that have the same volume fraction of solids, slurry A1-55 and B1-55, we see that the latter has the highest dynamic mobility.

DISCUSSION

The slurries consisting of only amorphous silica, slurry B1-32 and C1-31 have a very different rheological behaviour. From Fig. 1 we see that the slurry, B1-32, having the highest solids content has the lowest viscosity. This is expected partly to be due the content of bigger particles in the

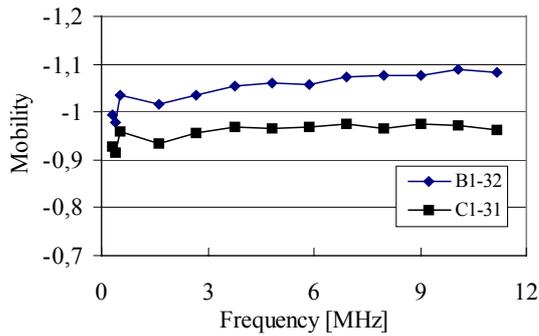


Figure 3. Mobility [$\cdot 10^{-8} \text{m}^2/\text{Vs}$] measured as a function of frequency for the amorphous silica slurries

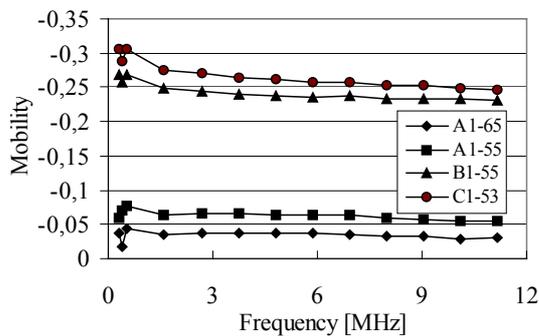


Figure 4. Mobility [$\cdot 10^{-8} \text{m}^2/\text{Vs}$] measured as a function of frequency for the mixed silica slurries

B1-32 slurry⁴ and partly that the particles have a higher zeta potential.

Both these properties can be seen from Table 1. A difference in zeta potential could be expected as the amorphous silica used in the two slurries has different origin. This is in accordance with Taylor⁵ who reported a considerable variation in composition and properties of amorphous silica from different sources.

Another difference between the two slurries was also noticed. While the particles in the C1-31 slurry readily settled the particles in the B1-32 slurry stayed suspended for several weeks. This is expected to be due to the difference in the measured zeta potential of the two slurries. The absolute values of the zeta potentials lies in a region where a transition from an unstable to stable suspension is expected⁶

and thus, only the particles in the B1-32 slurry, with the highest zeta potential form a relatively stable suspension.

The effect of adding silica flour to the two slurries is an increase in the viscosity. This is expected to be mainly due to the increase of the solids fraction of the two slurries. The fact that there is a reduced difference in viscosity between the two slurries, B1-55 and C1-53, is thought to be mainly due to the addition of larger amounts of crystalline silica to the B1-55 slurry than to the C1-53 slurry. This can be seen in Table 2.

The effect of increasing the content of crystalline silica is confirmed when comparing the two slurries, A1-55 and B1-55 in Fig. 2. The slurries have the same solids content, 55% by volume, but A1-55 has the highest content of crystalline silica and has the highest viscosity.

The measured dynamic mobility is an average measurement for the whole suspension and the effect of adding crystalline silica is a reduction of the measured dynamic mobility. This is expected to be partly due to the addition of the crystalline silica particles having a surface with a rather low activity compared to that of the amorphous silica and partly the total increase of the solids fraction. The increase of the solids fraction hinders the free movement of the particles.

It was also observed that the particles no longer stayed suspended in the slurries and that sedimentation started after a relatively short period of stand still. This was observed in a parallel experiment. This experiment showed that it was difficult to make a stable slurry with the desired composition of amorphous and crystalline silica.

When the solids content is as high as 65.3% by volume, as in slurry A1-65, the slurry behaves like a shear thinning paste with a very high initial viscosity. The measured dynamic mobility is very low. This is again expected to be due to the high total solids fraction in the slurry, the high

crystalline silica fraction and the hindrance of free movement of the particles. Therefore, when the solids fraction was reduced by the addition of water, slurry A1-55, we saw that the result was a viscosity decrease and an increase in dynamic mobility.

CONCLUSION

The rheological properties of a series of silica in water slurries have been investigated. As expected, an increase in solids content gave generally an increase in viscosity and a decrease in dynamic mobility.

When the particle size of the amorphous silica is decreased, still having a constant solids volume fraction, an increase in viscosity was observed. Further, an increase in dynamic mobility resulted in a viscosity decrease.

Replacing the amorphous silica with crystalline silica gave an increase in viscosity and a decrease in dynamic mobility. It also resulted in creating slurries that readily sediments.

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