

The influence of entrapped air on rheological properties of cement suspensions in early state of hydration

Helge Hodne¹, Vivian Falkeid¹ and Arild Saasen²

1-University of Stavanger, NO-4036 Stavanger, Norway

2-Statoil, NO-4035 Stavanger, Norway

ABSTRACT

Density measurements have revealed that air is still present in cement suspensions more than 20 minutes after the initial hydration and mixing when mixing in accordance with API procedures¹. The air is expected to be contained within aggregates of cement particles and thus contribute to an increased solid volume fraction of the suspension. By measuring the density of the suspensions and the rheological development during early times of hydration we have studied the effect of shear on the release of air from the suspensions. It has been shown that the release of air is shear rate dependent and results in a decrease in the measured viscosity.

INTRODUCTION

When concentrated cement suspensions used for oil well cementing are prepared for laboratory testing they are mixed in accordance with API procedures¹. This gives that after an initial high speed mixing lasting 50 seconds, the suspensions are mixed in an atmospheric consistometer, at a low speed, for an additional 20 minutes prior to any rheological measurements. Despite this thorough mixing, when the rheological measurements commence, a lack of stability in the measured values is observed. In some earlier work² it was shown that shearing for one minute at a shear rate of 1022s^{-1} prior to measurements at lower shear rate intervals, starting at a shear rate of 511s^{-1}

and going down, was needed to obtain stable readings at these lower shear rates. It was also observed through density measurements that during the shearing at 1022s^{-1} the density of the suspensions increased. This was found to be due to the release of air from the suspensions. The content of air found in the cement suspensions and its influence on the time and shear dependent rheological properties has been the object of this investigation.

EXPERIMENTAL CONDITIONS

Sample preparation

The preparation of the suspensions prior to rheological measurements was done in accordance with API¹. This preparation consist of an initial short period of high speed mixing in a Waring Blender, followed by 20 minutes of mixing at rather low speed, 150 rpm, in an atmospheric consistometer. The volume of each sample was approximately 600 ml and they were all prepared at a temperature of $25\pm 1^\circ\text{C}$. All samples were mixed using a Class G cement delivered by Norcem ASA. The Class G cement has been measured to have an almost log normal particle size distribution with a d50 of $12.6\mu\text{m}$, a d16 of $5.44\mu\text{m}$ and a d84 of $29.2\mu\text{m}$. This was measured on a suspension having a solid volume fraction of 0.42 and by using an AcoustoSizer from Colloidal Dynamics. The Blaine surface area of the Class G cement is given by the manufacturer to be $320\text{m}^2/\text{kg}$.

Density measurements of suspensions

To enable measurements of the amount of air still remaining in the suspensions a DMA 4500 densitometer from Anton Paar was used. This is an instrument that uses the oscillating u-tube principle for measurement. The accuracy is within $\pm 0.0001 \text{ g/cm}^3$. The density measurements with this instrument were carried out at $25 \pm 0.02^\circ\text{C}$. Prior to any sampling for density measurements the suspensions were mixed by hand until they appeared homogenous. This was done in order to reduce any effect of sedimentation³ in the suspensions.

Scanning electron microscopy

To what degree the cement particles in our suspensions form aggregates, was investigated by use a Low Temperature Scanning Electron Microscopy, LTSEM. For our experiments we used a SEM named Supra 35 VP delivered by Zeiss equipped with a LT cryogenic system from Polaron. Both the type of cement and mixing procedures followed those described under the subsection "Sample preparation". The suspension was quenched in liquid nitrogen before it was placed in the instrument. The instrument is able to keep the temperature of the sample at -190°C throughout the examination. At this temperature very little water sublimates from the surface of the sample and thus the vacuum needed for imaging can be obtained for a hydrated specimen without applying the drying procedure normally used with a standard SEM. The time spent for mixing and sample preparation prior to quenching in liquid nitrogen implies that the hydration of the cement was stopped after approximately 30 minutes.

Rheological measurements

To investigate how the amount of air remaining in the suspensions affect the viscosity of the suspensions a series of tests were performed in a rheometer. The rheological measurements were performed using a Physica UDS 200 rheometer fitted with a concentric

cylinder configuration, named Z3 DIN, having a smooth surface. The sample volume was approximately 8ml and all the samples were measured at a temperature of $25^\circ\text{C} \pm 0.5$.

RESULTS AND DISCUSSION

Viscosity measurements

For all our viscosity measurements the suspensions were mixed using a w/c weight ratio of 0.44 giving a solid volume fraction of 0.41. The viscosities obtained are shown in Fig. 1 and 2. Here each curve drawn represents the average of two measurements carried out on two different suspensions. All measurements started approximately 25 minutes after the first contact between water and cement. The viscosities were measured at constant shear rates for a period of 10 minutes. Six different shear rates were used and the respective shear rates are used as legends in the figures.

All our measurements indicate a shear thinning behaviour as the viscosity is found to decrease with increasing shear rates. The initial viscosities measured after 10 seconds of shearing is found to decrease from a value of 329mPas at a shear rate of 51.1s^{-1} to 59mPas at a shear rate of 1022s^{-1} .

From Fig. 1 and 2 it can also be seen that there is a decrease in the measured viscosities as a function of time at the various constant shear rates. Only at a shear rate of 1022s^{-1} , as shown in Fig. 2, the initial decrease in viscosity is followed by an increase. At this shear rate the minimum value in viscosity of 48.3mPas was reached after approximately 190 second of constant shear.

Several factors are expected to influence the development of the viscosities. In the early stage it is expected that the shearing will break down aggregated cement particles into smaller aggregates or single grains. The break down of the cement aggregates will release entrapped air. Entrapped air that initially contributed to an increased solid volume fraction and thus, the release of air will lead to a decrease in solid volume and viscosity. Also the degree of

dispersion of the solids will increase and contribute to a reduction in the measured viscosity⁴. Both effects are expected to increase with increasing shear rates.

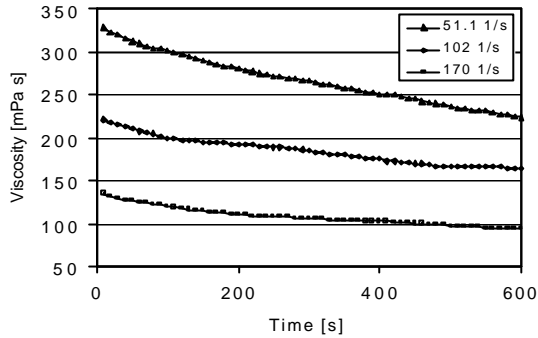


Figure 1. Viscosities of neat Class G cement suspensions as a function of time.

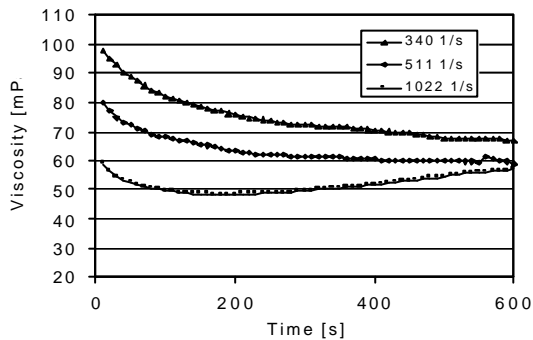


Figure 2. Viscosities of neat Class G cement suspensions as a function of time.

In Fig. 3 a LTSEM picture of a hydrated cement suspension is shown. The suspension was mixed in accordance with API¹ prior to quenching in liquid nitrogen. Thus it had been hydrated for approximately 30 minutes and it corresponds to a suspension prior to the viscosity measurement. From the picture it can be seen that the suspension consists of aggregates of hydrated cement grains of variable size. The biggest aggregates shown in the picture are on the order of 10 μ m or less in diameter. Corr et al.⁵ showed that when adding air entraining agents to a cement suspension

some of the aggregates formed internal air-filled voids. Whether the air in our suspensions was kept in voids formed within the aggregates or just filled up space between the particles forming the aggregates could not be confirmed using our sample preparation technique.

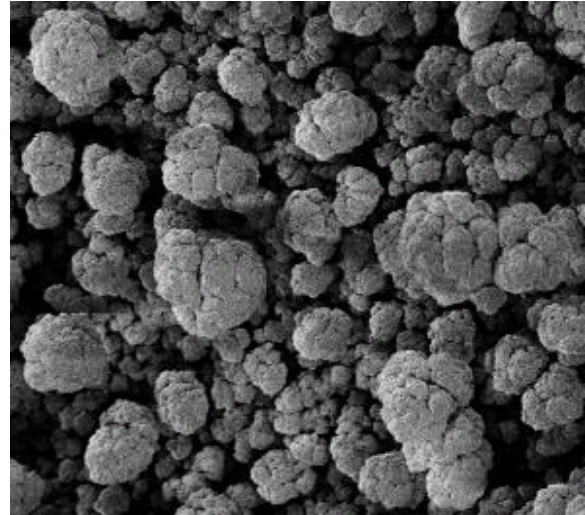


Figure 3. LTSEM picture of hydrated Class G cement suspension. Height x width of picture is 44 x 48 μ m.

To enable a verification of the amount of entrapped air the specific densities of the respective suspensions were measured both prior to and after the viscosity measurements. The results are shown in Table 1. As can be seen from the table the shearing was found to increase the densities of all the suspensions. Although the number of suspensions founding the basis for Table 1 could be said to be too scarce to draw any decisive conclusions it could be argued that there is a tendency of increasing volume reduction with increasing shear rates. The volume reduction of 3.1% measured at a shear rate of 1022s⁻¹ is in agreement with earlier measurements by Hodne et al.² who measured a 2% volume decrease after 2 minutes of constant shear at 1022s⁻¹. This was also measured on a neat Class G cement suspension with the same w/c ratio.

Table 1. Average specific densities of the suspensions measured prior to and after 600 seconds at constant shear.

Shear rate:	Specific density prior to shearing	Specific density after shearing	Volume reduction
1022s ⁻¹	1.885*	1.944*	3.1%*
511s ⁻¹	1.891	1.914	1.2%
340s ⁻¹	1.888*	1.900*	0.6%*
170s ⁻¹	1.892*	1.920*	1.5%*
102s ⁻¹	1.895	1.909	0.7%
51.1s ⁻¹	1.909	1.911	0.1%

*Based on only one measurement

Another factor that was found to influence the viscosity measurements at later times was an observed tendency for the suspensions to sediment in the measuring cup. Although not quantified the degree of sedimentation was found to increase with decreasing shear rates. Only at a shear rate of 1022s⁻¹ no sedimentation was observed. While the increased dispersion and break down of aggregates and release of entrapped air could explain the decrease in viscosity at the early stages, this sedimentation could explain the decrease in viscosity measured for all the suspensions except the last one, at later times.

For the suspension sheared at 1022s⁻¹ and where there is an increase in viscosity after 190 seconds still another factor could be expected to influence the development. When the aggregates are dispersed into smaller aggregates or particles and entrapped air is released new and un-hydrated surfaces are exposed to water. The water reacts chemically and binds to the cement particles and thus the solid volume will start to increase resulting in an increase in viscosity. The solid volume increase due to chemically bound water has in some earlier work² been found to be approximately 2.4% after 22 minutes of hydration. Also, at this high shear rate collisions between particles are expected to be frequent, this could result in the formation of new aggregates, aggregates that would lock up some of the fluid resulting in

an increase in solid volume and an increase viscosity.

All the factors mentioned above are expected to contribute to the time dependent development of the viscosities of the cement suspensions and thus, the measured values are expected to represent their sum.

CONCLUSION

It has been shown that the cement particles in a hydrated and mixed suspension form aggregates of various sizes. It has also been shown that these aggregates still contain air after more than 20 minutes of continuous mixing. When sheared in a viscometer the air is released and this release contributes to a reduction in the viscosity.

REFERENCES

1. American Petroleum Institute, RP 10B-2/ISO 10426-2, Recommended Practice for Testing Well Cements, First Edition, July 2005.
2. Hodne, H., Galta, S. and Saasen, A. (2006), "Rheological modelling of cementitious materials using the Quemada modell", Submitted for publication.
3. Log, P.A. and Saasen, A., "Sedimentation behaviour during rheological evaluation of oil well cement slurries", *Matr. Eng.*, **8**, (1) pp. 34-41
4. Barnes, H.A., Hutton, J.F., and Walters, K. (1989), "An Introduction to Rheology", Elsevier, Amsterdam, pp. 115-139.
5. Corr, D.J., Lebourgeois, J., Monteiro, P.J.M., Bastacky, S.J. and Gartner, E.M. (2002), "Air void morphology in fresh cement pastes", *Cem. Concr. Res.*, **32**, (7) pp. 1025-1031