Rheology of cementitious suspensions containing weighting agents.

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ABSTRACT
The use of manganese tetra-oxide as a weighting agent in suspensions for oil well cementing profoundly alters the time dependent rheological development. By measuring the thickening time as a function of mixing time in an atmospheric consistometer we have monitored the behaviour of the suspensions towards setting. The viscosity of the suspensions is also measured as a function of the shear rate. Furthermore, we have investigated if the Quemada model[1] can be used to describe the rheological behaviour of the suspensions.

INTRODUCTION

Manganese tetraoxide is used in drilling fluids and well cements as a weighting agent. It has a specific gravity of approximately 4.8. This is slightly higher than the 4.2 of Barite, which is the most common used weighting agent. Manganese tetraoxide is commonly used in cements and in drilling fluids when it is important to avoid larger particles in the fluids.
In this work we have investigated the properties of these manganese tetraoxide particles and looked at their influence on the behaviour of cement suspensions.

EXPERIMENTAL CONDITIONS

Sample preparation

All samples were mixed in accordance with API[2]. Three series of tests were conducted. One a neat cement suspension consisting of only Class G cement (Norcem A/S, Brevik) and distilled water. In the other two the cement was partly replaced by manganese tetraoxide, Mn_3O_4. The manganese tetraoxide was delivered by Elkem ASA and under the trading name Micromax. Technical data are given in Table 1.

Table 1. Technical data for Micromax given by Elkem ASA

Physical data:	
Average particle size	0.4μm
Surface area	2-4 m^2/g
Specific gravity	4.8
Specifications:	
Specific gravity	4.75-4.95
Mn content	67-70%
Fe content	Max 4.5%
CaO content	Max 0.4%
Chemical analysis:	
Major elements	Typical values
Mn	69 %
Fe	2 %
Minor elements	< 1%
Na	<0.1%
K	<0.1%
Solubility in water	Insoluble/slightly sol.

In one of the two samples made of cement and Micromax the water/cement-ratio (w/c-ratio by weight) was kept the same as that of the neat cement suspension. This increases the solid volume fraction of

the suspension. In the other sample, the solid fraction of the suspension was kept the same as that of the neat cement suspension. This increases the w/c-ratio of the suspension

In addition we also made two samples consisting of only Micromax. In one the Micromax was mixed with distilled water, in the other the Micromax was mixed with cement filtrate. This was done so that we could monitor the effect the dissolved ions from the cement have on the Micromax particles.

The cement filtrate was made from a 2:1 mixture by weight of distilled water and cement. The suspension was left to settle. The water was then filtrated through a 0.05µm filter before use. This gives a fluid saturated with ions dissolved from the cement particles, in which any remaining particles are to small to be measured in the Acoustosizer.

All our experiments were carried out at a temperature of 25±1 ºC.

Zeta-potential measurements

The zeta-potential was measured by use of an AcoustoSizer from Colloidal Dynamics, Warwick, RI, USA. This apparatus was also used to measure the pH and the conductivity of the suspensions and the average particle size and particle size distribution of the suspended particles. The fit error of the log normal particle size distribution model used by the AcoustoSizer was for all our measurements less than 11%.

Consistometer testing

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 mNm, which can be related to the Bc-units (Bearden units of consistency) used by API[2]. The time to reach 30Bc is considered as the time available for pumping and placing the cement slurry in the well.

Viscosity measurements

The rheological properties of the slurries were measured using a Chan 35 viscometer, in accordance with API[2]. This is a concentric rotational viscometer.

Rheological modelling

For rheological modelling we used the model proposed by Quemada[1] in 1998.

This is a model that tries to make account for inter-particle forces in suspensions. Due to these forces, the particles can form aggregates or structural units (SUs). These SUs also contain some of the suspending fluid and thus, the effective volume fraction (EVF) of the particles in the suspension is increased. This increases the viscosity of the suspension. The size and number of these SUs are expected to be shear-dependant. When sheared under a constant rate they are expected to become rather spherical and even of size and thus, obtain a rather mono disperse size distribution. When the shear-rate increases the size of the SUs will decrease and some of the locked up fluid is released. Thus, the EVF decreases and the viscosity is reduced.

The forming of SUs is also expected to influence the packing of the individual particles. For low shear-rates the forming of SUs reduces the limiting maximum packing obtainable. When the shear-rate is high enough to break down all the SUs into primary particles or irreducible aggregates a higher limiting maximum packing can be obtained.

Quemadas model is defined by Eq. 1:

$$\eta = \eta_\infty \left[\frac{1 + \left(\dot{\gamma}\dot{\gamma}_c^{-1}\right)^p}{\chi + \left(\dot{\gamma}\dot{\gamma}_c^{-1}\right)^p} \right]^2 \qquad (1)$$

Here η_∞ is the limiting steady state viscosity as $\dot{\gamma} \to \infty$. The term $\dot{\gamma}_c$ is a

characteristic shear rate and $\dot{\gamma}_c = t_c^{-1}$ where t_c is a characteristic time required for dimensional homogeneity. According to Quemada[1] the exponent p should be less than one and has often been found experimentally to be close to 0.5.

The term χ in Eq. 1 is called a structural index and is defined by Eq. 2:

$$\chi = \chi(\phi) = \frac{1 - \phi/\phi_0}{1 - \phi/\phi_\infty} \equiv \pm\left(\frac{\eta_\infty}{\eta_0}\right)^{\frac{1}{2}} \qquad (2)$$

The structural index depends on the limiting maximum packing, ϕ_∞ and ϕ_0, as $\dot{\gamma} \to \infty$ and $\dot{\gamma} \to 0$, respectively, defined by Eq. 3 and 4:

$$\phi_\infty = \frac{\phi_m}{1 + CS_\infty} \qquad (3)$$

$$\phi_0 = \frac{\phi_m}{1 + CS_0} \qquad (4)$$

Here C is a compactness factor and is directly related to φ, the mean compactness of SUs, through, $C = \varphi^{-1} - 1 = (1 - \varphi)/\varphi$ which is the fluid fraction divided by the mean compactness. Further, the mean compactness fraction $\varphi = \phi_A/\phi_{Aeff}$ where ϕ_A is the volume fraction of particles contained in all the SUs and ϕ_{Aeff} is the EVF of the SUs. (Note that the equation for mean compactness φ was misquoted in a previous work[3].) $S = \phi_A/\phi$ is a structural variable defined as the aggregated fraction and S_0 and S_∞ are the limiting values of S at very low and very high shear respectively.

This index χ in Eq. 2 also represents a relation between the asymptotic constant viscosities at high shear rates and low shear rates and for a shear thinning fluid the value of χ should lie between $0 < \chi < 1$.

For our data fitting we have used a simple spreadsheet and as a measure of the applicability of the model to our data sets, we have used the correlation coefficient R^2

RESULTS AND DISCUSSION

Zeta-potential measurements

In Table 2 the zeta-potential measurements carried out on suspensions of Micomax is shown. Two samples were made, both having a volume fraction of 0.067. This fraction gives the same water/Micromax fraction by volume as that of the cement/Micromax suspension reported in Table 3. One sample was mixed using distilled water as suspending fluid, for the other sample we used cement filtrate.

The zeta-potential of the Micromax particles when suspended in distilled water was measured to be negative and rather low in absolute value, –1.55 mV. When suspended in cement filtrate the zeta-potential of the Micromax particles changed to positive and it became slightly higher in absolute value, 6.9 mV. This is expected to be due to the adsorption of positive ions, mainly calcium ions, Ca^{2+}, on to the surface of the particles.

The conductivity measured on the solution of Micromax in distilled water was rather low, 17.8 mS/m, and the measured pH was 7. Micromax is termed as insoluble/slightly soluble in water and thus such values could be expected. The distilled water in it self has a conductivity of less than 0.9 mS/m. The slightly higher conductivity of the suspension could thus, partly be caused by ions from impurities as Na or K, in the Micromax.

The pH and conductivity of the cement filtrate were measured to be 13 and 0.88 S/m before mixing with Micromax. When Micromax was suspended in the cement filtrate it did not influence the pH but it resulted in an increase of the measured conductivity of the suspension to 1.165 S/m,

which is above that of the cement filtrate. As the pH of the suspending fluid did not alter, the increase in conductivity must be caused by an increase of solute ions. The increase of pH from 7 to 13 experienced by the Micromax particles thus increases the amount of solute ions profoundly. It more than nullifies the reduction of conductivity expected as a result of the removal of calcium ions from the solution, ions, which are adsorbed on to the Micromax particles.

The change of suspending fluid from distilled water to cement filtrate also reduces the average particle size and narrows the particle size distribution.

Table 2. Measurements of zeta-potential, pH, conductivity, average particle size and particle size distribution of Micromax suspensions by use of an AcoustoSizer.

	Micromax in distilled water	Micromax in filtrated cement water
Solid volume fraction	0.067	0.067
Zeta-pot.	-1.55 mV	6.9 mV
Conduct.	17.8 mS/m	1.165 S/m
pH	7.1	13
d-50	0.953µm	0.563µm
d-16	0.441µm	0.341µm
d-84	2.06µm	0.928µm

The average particle size of the delivered Micromax, as given in Table 1, is 0.4µm. Our measurements indicated an average particle size, d-50, of 0.953µm for the Micromax particles when suspended in distilled water and 0.563µm when suspended in cement filtrate. The rather larger average particle size measured when the Micromax particles are suspended in distilled water indicates that the particles are partly flocculated. The reduction in average size and narrowing of particle size distribution when going from distilled water to cement filtrate as suspending fluid, is expected to be caused by a partial deflocculation of the particles. This again, is expected to be due to the increase of the repulsive forces between the particles, as the measured zeta-potential indicates.

In Table 3 a comparison is shown of values measured on a neat Class G suspension and a suspension where 10 % by volume of the cement is replaced by Micromax but where the w/c-ratio is kept constant at 0.44. This gives an increase in the solid volume fraction from 0.419 to 0.442.

Table 3. Measurements of zeta-potential, pH, conductivity, average particle size and particle size distribution of cementitious suspensions by use of an AcoustoSizer.

	Cement	Cement with 10% Micromax added
w/c-ratio	0.44	0.44
Solid volume fraction	0.419	0.442
Zeta-pot.	-10.7	-9.39
Conduct.	1.435 S/m	1.415 S/m
pH	13.3	13.4
d-50	9.48µm	4.05µm
d-16	3.8µm	1.86µm
d-84	23.6µm	8.84µm

The zeta-potential of the cement particles measured in the neat Class G suspension was –10.7 mV. The result of adding Micromax to the Class G suspension was a slight reduction of the average zeta-potential, down to –9.39 mV. This reduction of zeta-potential could be explained by the addition of Micromax particles becoming positively charged in the cement water. Further, there was a reduction in conductivity when Micromax was added, as shown in Table 3. As the volume of water is kept constant in the two suspensions the reduced conductivity also indicates a net removal of ions from the suspension on to the surface of the Micromax particles. The slight increase of pH from 13.3 to 13.4 indicates that there is an increase of OH^-

ions when Micromax is added. This increase should by it self result in an increase of the conductivity, but this contribution is more than outweighed by the adsorption of ions on to the Micromax particles.

From Table 3 it can also be seen that the average particle sizes measured are reduced and that the particle size distribution is narrowed when Micromax is added to the cement suspension. This is expected to be due to the addition of the relatively smaller Micromax particles to the suspension. In addition, the Micromax particles added, are expected to become more dispersed in this cement suspension than in the previous cement filtrate, as the amount of ions available for adsorption have increased.

Consistometer measurements

Tree different suspensions were tested out in the atmospheric consistometer. Two of the samples were the same as those reported in Table 3. In the third sample the cement was also partly replaced by 10% by volume with Micromax, but in this sample the total volume fraction of solids was kept constant at 0.419. This resulted in an increase in w/c-ratio from 0.44 to 0.49.

In Fig. 1 the consistometer curves for the three different suspensions are plotted as the torque exerted on the stationary paddle against time. The torque exerted by the neat Class G suspension was the lowest throughout the whole measuring interval.

The effect of replacing 10% by volume of the cement with Micromax, keeping the total solid volume constant and increasing the w/c-ratio, was an increase of the torque throughout the whole measuring interval. As can be seen from the middle curve in Fig. 1, this also results in an earlier onset of the setting of the suspension. The onset of setting could be said to be indicated when the curves starts a more rapid increase.

When the cement was replaced by 10% by volume with Micromax and the w/c-ratio was kept constant and the solid volume fraction increases, the increase in torque was most profound, this can be seen from the uppermost curve in Fig. 1. The time before setting starts was also markedly reduced.

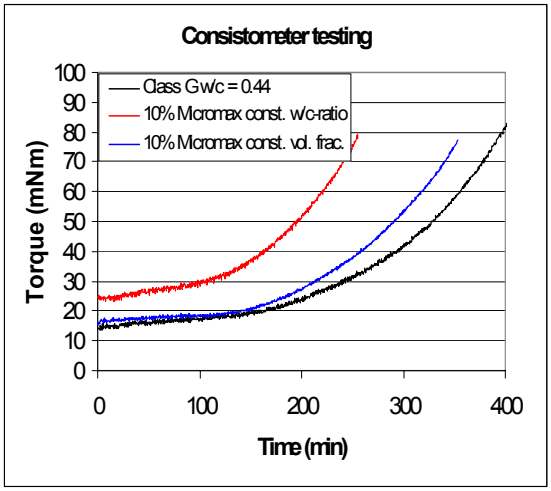

Figure 1. Torque measured as a function of time in an atmospheric consistometer.

Viscosity measurements

In Fig. 2 we have plotted the viscosity measured on the neat Class G suspension and the two suspensions containing 10% by volume of Micromax. The measured values are marked as points. The lines that are drawn in Fig. 2 represent values obtained from the rheological modelling.

All the three suspensions show a shear-thinning behaviour in the measured interval. The viscosity measured for the Class G was the lowest throughout the measured interval. It was reduced from 1.4 Pas at a shear-rate of $5.1s^{-1}$ to 82 mPas at a shear-rate of $511s^{-1}$. The suspension containing 10% by volume of Micromax and where the w/c-ratio was kept the same as that of the neat Class G suspension but the solid volume fraction increased, showed the highest values throughout the measured interval. This increase in viscosity when the solid volume fraction is increased is in agreement with earlier work[4] carried out on suspensions of cement and microsilica. The viscosity of the suspension was reduced from 3 Pas at a shear-rate of $5.1s^{-1}$ to 135 mPas at a shear-rate of $511s^{-1}$. For the suspension

containing 10% by volume of Micromax but where the solid volume fraction was kept constant with respect to that of the Class G suspension, the measured values were intermediate to those of the other two suspensions. This suspension also showed a slightly higher degree of shear thinning compared with that of the other two. For this suspension we measured the viscosity down to a shear-rate of $1.7s^{-1}$, which gave a viscosity of 4.5 Pas. Further, the measured viscosity was reduced from 2.1 Pas at a shear-rate of $5.1s^{-1}$ to 88 mPas at a shear-rate of $511s^{-1}$.

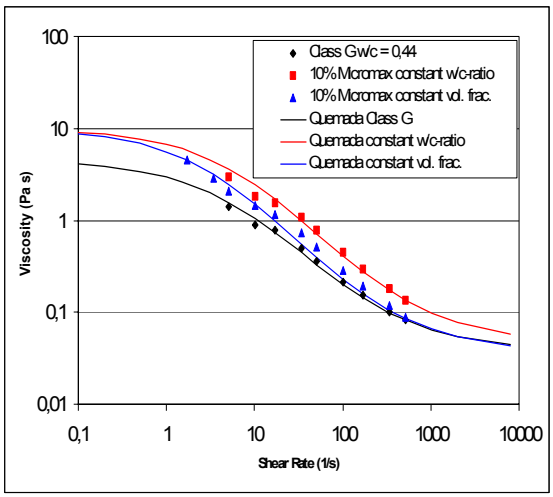

Figure 2. Viscosity measured as a function of shear rate.

The successive increasing in viscosity measured when Micromax was added was also confirmed by the consistometer readings, when the torque measured in Fig. 1 is taken as an expression of the viscosity of the suspensions.

It could also be expected that the increase in viscosity when adding Micromax could be due to the positive Micromax particles adhering to the negative cement particles and thus forming more and larger SUs. But this was not confirmed by the particle size measurements shown in Table 3.

Rheological modelling

The parameters chosen for the rheological modelling are listed in Table 4. In addition the correlation coefficient, R^2 is shown. The value of 0.63 used for maximum particle fraction, ϕ_m, was chosen in accordance with Quemada[1] who reports that ϕ_m often is observed close to the value of Random Close Pack, $\phi_{RCP} = 0.637$. The values for $\phi_{A\infty}$ and ϕ_{A0} are the limiting values of ϕ_A, being the volume fraction of particles contained in all the SUs at very high and low shear. In the present study the best fit was given when these values were kept almost constant at 0.13 and 0.30 respectively. Only for the Class G and Micromax suspension with constant w/c ratio the value for of $\phi_{A\infty}$ was increased to 0.14.

Table 4. Selected parameters used for the Quemada model calculations.

	Class G	10% Micromax constant volume fraction	10% Micromax constant w/c-ratio
p	0.7	0.7	0.7
$\dot{\gamma}_c$	200 s^{-1}	217s^{-1}	357 s^{-1}
ϕ_m	0.63	0.63	0.63
ϕ	0.419	0.419	0.442
$\phi_{A\infty}$	0.13	0.13	0.14
ϕ_{A0}	0.3	0.3	0.3
φ	0.575	0.579	0.624
R^2	0.9884	0.99	0.9854

For the exponent p of Eq. 1 a value of 0.7 could be used for all three suspensions. For the characteristic shear-rate $\dot{\gamma}_c$, an increasing value was used, an increase that followed the increasing viscosities of the suspensions. The mean compactness factor φ was also increased with increasing suspension viscosity.

The viscosity data obtained using the parameter from Table 4 are shown as curves in Fig. 2. These calculated curves also indicate that the measured data represents a shear-thinning region. In addition they indicate an upper and lower plateau with regards to the viscosity of the suspensions.
The middle curve describing the behaviour of the suspension containing Micomax and cement and where the solid volume fraction was kept the same as that of the Class G suspension also confirms that this suspension has a higher degree of shear thinning than the other two suspensions.

In future work the establishing of suitable measuring methods for the measuring of $\phi_{A\infty}$ and ϕ_{A0} will play an important part.

CONCLUSION

We have found that the effect of adding Micromax to a cement suspension is an increase in viscosity of the suspension.

The adding of Micromax also reduces the setting time of the cement.

When the Micromax particles are mixed with cement, the surface charge of the particles changes sign and becomes positive.

The rheological model proposed by Quemada[1] can be used to describe the rheological behaviour of suspensions of cement and Micromax.

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