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The rheological behaviour of $\text{Ca}(\text{OH})_2$ suspensions*)

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Abstract: The rheological behaviour of $\text{Ca}(\text{OH})_2$ suspensions is investigated, predominantly at a solid volume fraction of 0.25. The influence of standing without being subject to shear ("contact time") is distinguished from that of being sheared ("shearing time"). The results are interpreted on the basis of the "elastic floc" model of energy dissipation during flow, with a view to the problem whether, in addition to an energy dissipation term related to the viscous drag experienced by particles moving within flocs, there should be an independent energy dissipation term related to fluid movement in the flocs when they change volume or shape. It appears that this additional energy dissipation term is not necessary, if the increase in viscous friction, experienced by two particles which are close together, is taken into account.

Key words: $\text{Ca}(\text{OH})_2$ suspension, elastic floc model, energy dissipation

List of symbols

A	average distance between shear planes	$t_{1/2}$	time required for reaching 1/2 of the electric conductivity change, effected by dissolution of $\text{Ca}(\text{OH})_2$
A_1	average distance between shear planes for $\dot{\gamma} \rightarrow \infty$	u	angle between the direction of motion of an aggregate and the line connecting the centers of two other aggregates bordering a shear plane
a	radius of an aggregate	v_i	velocity of particle or aggregate i
c	radius of sphere	w	angle between the direction, in which two spheres move towards each other, and the line connecting their centers
c_v	solid volume fraction	$\dot{\gamma}$	shear rate
E	energy dissipation per unit of volume and time	δ	increase in distance between the centers of two equal spheres
f	average frictional coefficient (= quotient between actual friction and friction as calculated for an isolated sphere)	Δ	square root of the average area which can be assigned to an aggregate bordering a shear plane, in this plane
f_i	frictional coefficient of particle or aggregate i	δ_i	distance over which aggregate i is entrained by one of its neighbours
f'	frictional coefficient describing the work required for moving two spheres towards or away from each other	δ_0	distance over which an aggregate bordering a shear plane is displaced
l	fraction of distance traveled by an aggregate, over which it entrains its directly contacting neighbours (average value)	ε	energy dissipation during movement of two spheres towards each other
n	number of links between an aggregate within a domain, and an aggregate bordering a shear plane	ε_i	energy dissipation accompanying the movement of aggregate i
q	average number of directly contacting neighbours of a particle or aggregate in a floc	η	plastic viscosity (of Bingham fluid)
r	distance between centers of two spheres or aggregates	η_0	viscosity of suspension medium
r_0	initial distance between centers of two spheres	τ	shear stress
s	r/c	τ_0	Bingham yield value (constant term in a linear τ vs $\dot{\gamma}$ relation)
t_c	time during which $\text{Ca}(\text{OH})_2$ is in contact with water, without being sheared		
t_r	time during which a shear is applied		
t_i	time during which the movement of an aggregate bordering a shear plane occurs, on encountering another aggregate		

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1. Introduction

The aim of the present work was to investigate, whether the "elastic floc" model developed by Hunter et al. [1–3] and van de Ven and Hunter [4] can

account for the rheology of concentrated coagulated suspensions.

According to this model, energy dissipation during flow occurs only to an insignificant extent through formation and subsequent breaking of bonds between the suspended particles; the energy dissipation is caused in the main by [4]:

- a) energy required to stretch bonds between primary particles;
- b) energy required to overcome the viscous drag experienced by particles moving within flocs;
- c) energy required for the internal movement of liquid within the flocs when they change shape and/or volume.

It appears to the present authors, that the third energy term should in reality already be comprized in the second. For the work, required to move an object through a liquid as calculated, e.g., for isolated spheres by the Stokes equation, includes the work for displacing part of the surrounding liquid. Thus, one object of the present investigation was to check whether this third term is really necessary, or whether the rheological properties of suspensions may be calculated without this term (but including in the estimation of the second term the influence of surrounding particles on the friction experienced by a particle moving in a floc).

In this respect, $\text{Ca}(\text{OH})_2$ suspensions in water offer special opportunities, because of the distinct but not too large solubility of the solid. $\text{Ca}(\text{OH})_2$ is soluble enough to employ the rate of its dissolution after diluting the suspension with water, as a measure for the degree of aggregation of the solid [5]; thus one of the parameters which influence the rheological behaviour of a suspension is accessible to independent check. On the other hand, the solubility is small enough (ionic strength about 0.06 M) to let the liquid phase retain the character of dilute electrolyte solution with a viscosity not largely different from that of water.

Nevertheless, the rheological behaviour of $\text{Ca}(\text{OH})_2$ suspensions has only seldom been investigated. Berens and Hoppe [6], though finding interesting time-dependent rheological properties, nevertheless do not give a clue for their understanding; moreover the results of their investigation are restricted in their general validity by the use of samples with a considerable impurity content.

We therefore thought it worthwhile to investigate suspensions of reasonably pure $\text{Ca}(\text{OH})_2$ by different methods, comprizing rheology, dissolution rate, sediment volume, electrokinetics and electron micro-

scopy. In order to prevent sedimentation during the rheological experiments, rather larger solid volume fractions (c_v) had to be employed than used by Hunter et al. [1–3] in the work, in which the model was developed.

Since it is known [5] that the properties of $\text{Ca}(\text{OH})_2$ suspensions are dependent on the time during which the systems are subjected to shear, we investigated the rheology by registering the torque experienced by the inner cylinder of a rotation viscometer, as a function of time at constant shear rate; values obtained for various shear rate at one particular shearing time were then combined into a torque-shear rate diagram. Of interest are primarily the diagrams obtained by extrapolation to shearing time zero (where the structure not yet broken down by shear is approached), and for long shearing times (where the final structure is approached).

2. Calculation of energy dissipation on the basis of the "elastic floc" model

The situation in a sheared suspension will be described here by the nomenclature employed, e.g. by Gratiano et al. [7]: the primary particles, which in our case are plate-like $\text{Ca}(\text{OH})_2$ crystals, are combined into "aggregates" (stock-like combinations of the primary particles, see fig. 2). The aggregates in turn combine into agglomerates. Under shear, the network structure existing in the unshared suspensions, is broken down into "domains", each consisting of an aggregate and occluded liquid. It will appear from the data that the aggregates are persistent during shear in $\text{Ca}(\text{OH})_2$ suspensions, so that the energy dissipation due to the stretching of bonds between primary particles can be neglected.

In the rather concentrated suspensions with which we are dealing here, the systems consist in the unshared state of one single floc. A shear imposed on such a system will not occur uniformly over the volume, but will be realized in shear planes dividing this floc into domains. The situation during shear is idealized by considering the shear planes in a Couette flow as cylindrical (with axis $\parallel$ the rotation axis); thus the domains are thought to be annuli. Part of such a sheared suspension is shown schematically in fig. 1; $x - x$ denotes shear planes, the average distance between them being A . In the domains, the aggregates remain in general surrounded by the same neighbouring aggregates; they are not at rest, however, because they are entrained when an aggregate of the same domain bordering a shear plane (such as 1 in fig. 1) is

displaced from its initial position in the domain, on passing an aggregate from a neighbouring domain (such as 2).

Fig. 1. Schematic representation of the situation in a sheared paste. In $\text{Ca}(\text{OH})_2$ suspensions in water, the circles in this figure correspond with stack-like aggregates of $\text{Ca}(\text{OH})_2$ crystals.

$x-x'$: shear planes, A : breadth of a domain, Δ : square root of average area, assigned to an aggregate bordering a shear plane, $\Delta \cos u$: average distance traveled by an aggregate bordering a shear plane, between two successive encounters with aggregates from a neighbouring domain.

For the meaning of the numerals, see text

If aggregate 1 during such an encounter is displaced over a distance δ_0 , it will entrain its direct neighbours over a distance $\delta_0 l$ ($0 < l < 1$); an aggregate which is n links away from aggregate 1 will be entrained over a distance $\delta_n = \delta_0 l^n$. Thus aggregate 3 in fig. 1, entrained by aggregate 1 through the intermediary of 4, will move over a distance $\delta_0 l^2$. When an aggregate moves, it entrains $(q - 1)$ direct neighbours, where q is the average number of direct neighbours within a domain; the neighbours will in turn each entrain $(q - 1)$ direct neighbours, etc.

We start now from the hypothesis that the energy required to overcome this viscous drag experienced by particles moving within flocs is the only important energy dissipation term; ultimately we will check whether this hypothesis can be reconciled with the rheological data. On the basis of this hypothesis, the energy dissipation ε_i accompanying the movement of one aggregate i over distance δ_i is $6\pi\eta_0 a_i f_i V_i \delta_i$ (V_i is the velocity $\approx \delta_i/t_i$; t_i the time during which the movement takes place; f_i the frictional coefficient = 1

for an isolated sphere; a_i the radius of aggregate i ; η_0 the viscosity of the suspension medium). Thus:

$$\varepsilon_i = 6\pi\eta_0 a_i f_i \delta_i^2 / t_i \quad (1)$$

with t_i equal for all aggregates entrained on the encounter of two aggregates in a shear plane.

The total energy dissipation caused by the movement of one partner in such an encounter becomes:

$$\begin{aligned} \Sigma \varepsilon_i &= 6\pi\eta_0 a (f \delta_0^2 / t_1 + (q - 1) f \delta_0^2 l^2 / t_1 \\ &\quad + (q - 1)^2 f \delta_0^2 l^4 / t_1 + \dots) \\ &= \frac{6\pi\eta_0 a f \delta_0^2}{t_1} \cdot \frac{1}{1 - (q - 1)l^2}. \end{aligned} \quad (2)$$

Here the a_i and f_i are replaced by average values a and f , respectively.

The energy dissipation per unit of time and volume is then found by multiplying this expression by the number of aggregates bordering shear planes per unit of volume ($= 2/(A\Delta^2)$, if Δ^2 is the average area assigned to such an aggregate in a shear plane); and dividing the expression by the average time between two successive encounters between such aggregates ($= \Delta \cos u / (\dot{\gamma}A)$, where u is the angle between the main direction of motion and the connecting line between two aggregates bordering the shear plane, belonging to one domain; thus $\Delta \cos u$ is the average distance traveled by an aggregate between two successive encounters).

The time t_1 in expression (2) is of the order $a/(\dot{\gamma}A)$. Thus the energy dissipation per unit of volume and time becomes:

$$E = 12\pi\eta_0 f \frac{\delta_0^2 A}{\Delta^3 \cos u} \cdot \frac{\dot{\gamma}^2}{1 - (q - 1)l^2} \quad (3)$$

with $\overline{\cos u} = 0.637$.

In order to obtain a connection between E and rheological data, we remember that in stationary flow, $E = \tau \dot{\gamma}$. Thus:

$$\tau = 12\pi\eta_0 f \frac{\delta_0^2 A}{\Delta^3 \cos u} \cdot \frac{1}{1 - (q - 1)l^2} \cdot \dot{\gamma}. \quad (4)$$

This equation does not in general, in spite of its appearance, indicate Newtonian behaviour, because parameters like A and Δ may be functions of $\dot{\gamma}$.

3. Experimental

3.1 Materials

Ca(OH)_2 : pro analysi ex Merck. Three different batches were investigated, but experiments with batch 3 were restricted to electro-phoresis, electro-osmosis and sediment volume as affected by shearing. The main impurities were SO_4^{2-} and Na^+ ; no Cl^- could be detected. Thus the aqueous phase in a suspension with $c_v = 0.25$ contained:

	Batch 1	Batch 2
Ca^{2+}	$2.15 \cdot 10^{-2} \text{ M}$	$2.31 \cdot 10^{-2} \text{ M}$
Na^+	$0.28 \cdot 10^{-2} \text{ M}$	$0.20 \cdot 10^{-2} \text{ M}$
OH^-	$4.48 \cdot 10^{-2} \text{ M}$	$4.50 \cdot 10^{-2} \text{ M}$

BET N_2 adsorption
surface area $8.3 \text{ m}^2 \text{ g}^{-1}$ $5.6 \text{ m}^2 \text{ g}^{-1}$

SEM micrographs show conglomerates composed of flat plates arranged stack-wise (fig. 2).

Water: for the rheological experiments, deionized water was used; for the sediment volume and electrokinetic experiments (batch 3), twice distilled water was employed.

3.2 Apparatus and Procedures

Rheological measurements were performed in an Epprecht 15T-FC rotation viscometer (Contraves AG, Zürich) with rotating inner cylinder ($\varnothing$: 1.50 cm) and stationary outer cylinder (inner $\varnothing$: 1.90 cm); effective length 5.98 cm [8].

a)

b)

c)

Fig. 2. SEM of Ca(OH)_2 crystals.

a) Batch 1: untreated starting material.

b) Batch 2: untreated starting material.

c) Batch 2: $t_r = 50 \text{ min}$ at $\dot{\gamma} = 154.6 \text{ s}^{-1}$, after washing with acetone and drying.

In all micrographs the length of one side is $20 \mu\text{m}$.

Rheological measurements were generally performed in suspensions with $c_v = 0.25$. The suspensions were prepared in an Erweka KU 1 Kneading machine with stirrer R (Erweka-Apparatebau GmbH, Frankfurt/Main) by adding

$\text{Ca}(\text{OH})_2$ slowly to the water under continuous stirring. After mixing, stirring was continued for 15 minutes; the suspension was then divided over 150 ml glass vessels with screwed plastic covers. The samples were left standing until shortly prior to use for periods up to 168 hrs (contact time t_c). All operations up to this point were performed in a glove-box containing an atmosphere of nitrogen free of CO_2 .

About 30 min before use the sample in one of the vessels was homogenized by shaking and poured into the measuring system of the rheometer, where it was brought to temperature (20°C). The suspension was then homogenized by moving the inner cylinder by hand, and the rheometer was started.

Rheological measurements were performed by registering the torque vs. time at constant angular velocity of the inner cylinder [8]. During the measurements, nitrogen was led over the suspension.

Electroosmosis (batch 1 and 2) was performed in an U-tube type of apparatus [9] on samples with $c_v = 0.25$, which had been stored for about one week, and which were transferred to the electroosmosis apparatus without being diluted. In calculating ζ potentials, the "flat wall" von Smoluchowski equation [10] was employed ($1/\kappa$ in the solution being 1.16 nm). For batch 3, a suspension of 20 g $\text{Ca}(\text{OH})_2$ in 100 ml of water was used.

Electrophoresis was performed in a Smith and Lisse "double tube" cell [11] by diluting a suspension (20 g $\text{Ca}(\text{OH})_2$ in 100 ml of water) with distilled water in the ratio 1:100.

Sediment volumes were determined for 100 ml suspension in graduated cylinders of 100 and 250 ml, closed by rubber stoppers. Here 40 g $\text{Ca}(\text{OH})_2$ were dispersed in 200 ml H_2O , either by carefully stirring by hand or by stirring for 5.30 or 60 minutes at 3000 rpm, using a stirrer with eight blades (18×11 mm). The blades were placed two by two at one level perpendicular to the shaft; two successive levels were at a distance of 2.8 cm. The first and third level blades were placed vertically, but the second and fourth level blades were slightly twisted towards the vertical plane.

Dissolution rates were determined by pipetting 1 ml of a suspension, by means of a Gilson Pipetman pipette into 100 ml water (20°C), with continuous stirring (Grenier & Co compressed air stirring motor) at a velocity of 500–550 rpm. The rotation velocity was checked at frequent intervals by means of an Ono-Sokki HT-430 revolution counter. The conductivity of the aqueous suspension thus obtained was registered using a Philips PW 9512/01 conductivity cell, a Philips PR 9501 conductivity meter and a BBC Goerz Servogor 320 Transient Recorder. The time necessary for reaching 1/2 of the conductivity change, effected by the dissolution of $\text{Ca}(\text{OH})_2$, was taken as a measure for the dissolution rate ($t_{1/2}$). Adding the same amount of saturated $\text{Ca}(\text{OH})_2$ solution to the water resulted in only a very slight conductivity increase, which proves that the conductivity increase resulting from the addition of $\text{Ca}(\text{OH})_2$ suspension indeed is connected with the dissolution of the $\text{Ca}(\text{OH})_2$.

Samples were taken for the most part from suspensions which after standing for some time, had been homogenized by shaking but which had not otherwise been sheared. The influence of shearing on the dissolution rate was investigated by taking samples from a position at a depth about

halfway the effective gap of the viscometer, by lowering the tip of the pipette into it.

SEM: Samples for electronmicroscopy were either taken from dry starting-substances, or if taken from $\text{Ca}(\text{OH})_2$ suspensions, were washed with acetone and dried.

4. Results

Typical torque- $\dot{\gamma}$ diagrams, obtained by combining values obtained after one shearing time (t_r) for different $\dot{\gamma}$ values (fig. 3), are shown in fig. 4. The torque- $\dot{\gamma}$ diagrams show some spread which is not surprising in view of the fact that the curves as in fig. 3 relate to four different samples. These were prepared, to be sure, under identical conditions, but during the preparation of them one step, viz. the homogenization of the suspensions before the start of

Fig. 3. Typical torque vs. time graph for four samples (batch 1, $t_c = 74$ hours), at different shear rates: $x \dot{\gamma} = 14.8 \text{ s}^{-1}$, $\Delta \dot{\gamma} = 26.0 \text{ s}^{-1}$, $X \dot{\gamma} = 49.7 \text{ s}^{-1}$, $+ \dot{\gamma} = 87.8 \text{ s}^{-1}$, $O \dot{\gamma} = 154.6 \text{ s}^{-1}$

Fig. 4. Typical torque vs. $\dot{\gamma}$ graphs at equal t_r and t_c . Batch 2. $O t_r = 1 \text{ min}$, $t_c = 16.5 \text{ hr}$. (For this series, the "best fit" straight line is drawn.) $+ t_r = 1 \text{ min}$, $t_c = 47.5 \text{ hr}$, $X t_r = 1 \text{ min}$, $t_c = 160.5 \text{ hr}$

the rheological measurements, involves a partial demolition of the structure developed on standing causing inevitable differences between the samples.

The torque- $\dot{\gamma}$ diagrams such as fig. 4 were considered as parts of Bingham rheological curves: a straight line was fitted to the data by the least squares criterium, and from this line τ_0 and η were calculated. Although there is some arbitrariness in the assignment of a Bingham character to the torque- $\dot{\gamma}$ diagrams, the spread of the data does not permit of a more detailed conclusion with regard to the rheological character; and the quantities τ_0 and η thus calculated represent at least some important aspects of the rheological behaviour. The use of a Bingham equation does not, in the context of the present work, imply that the liquid really behaves as a Bingham liquid down to very low values of the shear rate; it implies only that the torque- $\dot{\gamma}$ relationship can within the accuracy of the measurements, be represented by a linear relation.

More fundamental is the consideration that combination of the torque values obtained for different $\dot{\gamma}$'s at one shearing time does not combine values obtained for the same degree of structure breakdown: subjecting a suspension for a time to one shear rate does not have the same effect as subjecting it for the same time to another shear rate. For this reason, quantitative calculations on the base of the "elastic floc" model are restricted to values obtained by extrapolating to $t_r \rightarrow 0$, or to values obtained at large shearing times (50 min).

A distinct difference is found between the rheological behaviour of suspensions of the $\text{Ca}(\text{OH})_2$ batches 1 and 2, batch 1 giving *ceteris paribus* a much "stiffer" suspension with less tendency towards sedimentation than batch 2. By other methods, the following differences were found between the two batches:

- The N_2 adsorption surface area of batch 1 is larger than that of batch 2;
- By SEM, batch 1 was seen to consist of aggregates with a more rounded shape, whereas those of batch 2 had a more angular character (compare fig. 2a and 2b);
- The aqueous phase in batch 1 was richer in Na^+ , poorer in Ca^{2+} , and richer in SO_4^{2-} than that in batch 2;
- The ζ potential of batch 1 as determined by electroosmosis was 10.3 mV, that of batch 2 was 19.0 mV.

These data taken together indicate that the primary crystals in batch 2 had a higher degree of ordering than those in batch 1, resulting for batch 2 in a larger

degree of adsorption of Ca^{2+} ions, which (together with the lower SO_4^{2-} concentration) leads to a larger ζ potential and hence to a larger repulsion between the aggregates. On development of the network structure during coagulation, the formation of bonds between the aggregate will be more restricted in direction, and thus q , the number of directly contacting neighbours in eq. (4) will be lower for batch 2 than for batch 1. However, in addition a difference in size distribution of the aggregates between the batches may play a role.

With increasing shearing time t_r , τ_0 decreases whereas η increases. This is observed for both batches (fig. 5 and 6). The decrease in τ_0 is universally very pronounced, while the η increase is less so. The η increase expresses the fact that the torque decreases with increasing t_r , less rapidly at large $\dot{\gamma}$ values than at lower ones (fig. 3).

Fig. 5. τ_0 (+) and η (O) vs. t_r . Batch 1, $t_c = 45$ hr

Fig. 6. τ_0 (+) and η (O) vs. t_r . Batch 2, $t_c = 46$ hrs

Quite a large amount of attention was paid to the question, whether these effects were connected with changes in the $\text{Ca}(\text{OH})_2$ crystals or the degree of aggregation. By SEM, no changes in the aggregates on shearing could be detected (cf. fig. 2b and 2c); neither did the sediment volume change (see fig. 9 and 10; finally the sediment volume attained a value of 38–41 ml for all experiments). The influence of shearing on the dissolution rate lies within the uncertainty of the determination (table 1); the same obtains for the ζ potentials (table 2).

Table 1a. $t_{1/2}$ for various contact times, for batch 2, $t_r = 0$

t_c (hrs)	$t_{1/2}$ (sec)	Number of experiments	Standard deviation (sec)
16.5	1.915	14	0.119
23	1.888	14	0.175
40.5	1.972	15	0.109
46	2.036	15	0.164
64.5	2.075	15	0.226
71	2.018	15	0.136
89	2.026	12	0.159
95	2.033	15	0.102
160.5	2.130	15	0.315

Table 1b. $t_{1/2}$ for various shearing times, for batch 2

$t_c = 50 \text{ hr}, \dot{\gamma} = 36.9 \text{ s}^{-1}$ $t_c = 360 \text{ hr}, \dot{\gamma} = 11.9 \text{ s}^{-1}$		
t_r (min)	$t_{1/2}$ (sec)	$t_{1/2}$ (sec)
0	2.000	2.229
10	2.312	2.667
50	2.146	2.604

Table 2. ζ potentials (batch 3) after shearing at 3000 rpm

shearing time (min)	ζ (by electro- osmosis) (mV)	ζ (by electro- osmosis) (mV)
0	+12.8	+25.4
30	+13.4	+28.2

The fact that the ζ potentials determined by electro-osmosis differ from those determined by electrophoresis may be related to differences in the liquid media in both cases; however, similar differences have been reported by other authors as well [12]. In the context of the present paper it is primarily important that the ζ potential does not change with increasing t_r .

We conclude that shearing does not affect the degree of aggregate formation by the primary $\text{Ca}(\text{OH})_2$ crystals, and that the aggregates behave

during flow as unchanging units. The influence of shearing time on τ_0 indicates that the number of shear planes increases not only with increasing $\dot{\gamma}$ but also with increasing t_r . With an increasing number of shear planes (hence decreasing A in eq. (4)) these planes pass through regions with smaller values for Δ , which may temporarily withstand a shearing stress without being disrupted but which in the long run are broken down.

The influence of increasing t_c on τ_0 and η (fig. 7 and 8) can be stated with less precision than that of increasing t_r , owing to the spread of the data. Nevertheless there is a generally increasing tendency of τ_0 at $t_r \rightarrow 0$, with increasing t_c ; this is interpreted as indicating that the network structure changes on standing in the direction of increasing solidification, while parts of this structure are retained during the

Fig. 7a. τ_0 for $t_r \rightarrow 0$ vs. t_c : + batch 1, o batch 2 Fig. 7b. η for $t_r \rightarrow 0$ vs. t_c : + batch 1, o batch 2

Fig. 8a. τ_0 at $t_r = 50$ min vs. t_c : + batch 1, $\circ$ batch 2

Fig. 8b. η at $t_r = 50$ min vs. t_c : + batch 1, $\circ$ batch 2

homogenization necessary for introducing the samples in the rheometer, but not on shearing for a long time (see the values for $t_r = 50$ min, fig. 8). In spite of the network structure being broken down for the greater part during shearing, the difference between the two batches with regard to η remains. This agrees with the interpretation given to this difference as being due to the difference in ζ potentials (but it would agree also with an interpretation involving differences in aggregate size distribution): η is related to energy dissipation during flow in a structure which is as completely broken down as may be effected by increasing $\dot{\gamma}$, and thus is determined by A , q and b in eq. (4), whereas τ_0 is determined primarily by the value of A at low $\dot{\gamma}$ values.

Fig. 9. Sediment volumes as a function of time. Batch 3, initial $c_v = 0.082$, inner diameter of graduated cylinder = 35 mm.

$\circ$ not stirred, $\times$ stirred for 5 min at 3000 rpm, + stirred for 30 min at 3000 rpm

Fig. 10. Sediment volume as a function of time. Batch 3, initial $c_v = 0.082$, inner diameter of graduated cylinder = 25 mm.

$\circ$ not stirred, $\times$ stirred for 5 min at 3000 rpm, + stirred for 30 min at 3000 rpm

5. Application of the energy dissipation equation based on the "Elastic floc" model

The question raised in the introduction is, whether the energy dissipation calculation on the basis of van de Ven and Hunter's elastic floc model include an explicit term for movement of liquid within flocs or not. In order to check this, we calculate values for A and f under various circumstances, and see whether we can arrive at reasonable values without invoking an additional energy term like c , (see Introduction).

We first consider η . If no other change in the structure occurs with increasing shear rate except the creation of new shear planes, the energy dissipation per unit of volume and time ($\tau\dot{\gamma}$) would approach $\eta\dot{\gamma}^2$ for $\dot{\gamma} \rightarrow \infty$. Thus, for $t_r \rightarrow 0$ and batch 2, η/η_0 is about 40 (fig. 7b) and this should be equal to:

$$\frac{\eta}{\eta_0} = 12\pi f \left(\frac{\delta_0}{\Delta} \right)^2 \cdot \frac{A_1}{\Delta} \cdot \frac{1}{\cos u} \cdot \frac{1}{1 - (q - 1)l^2} \quad (5)$$

with A_1 the average distance between shear planes for $\dot{\gamma} \rightarrow \infty$. In the case of rather loose networks, such as are present for $c_v = 0.25$, a reasonable assumption would be $A_1/\Delta = 1$; $\Delta \approx 5a$, while $\delta_0 \approx a$.

We now consider two cases:

- $(q - 1)l^2 \ll 1$, which is equivalent to the assumption that most of the energy dissipation occurs through the motion of aggregates bordering the shear planes;
- $(q - 1)l^2 < 1$, but not $\ll 1$, say $(q - 1)l^2 \approx 0.6$. In this case, the greater part of the energy dissipation occurs through the motion of aggregates within the domains.

These alternatives can be distinguished by the value for f , required for making eq. (5) agree with the experimental datum $\eta/\eta_0 \approx 40$. For case a), we obtain $f \approx 17$; for case b): $f \approx 7$.

An independent estimate of f can be obtained as follows:

If two equal spheres (radius c) at a distance r move away from each other, they have their individual frictional factor $6\pi\eta c$ increased because of their interaction by a factor $(6s^2 - 11s)/(6s^2 - 20s + 16)$, where $s = r/c$ [13–15]; when they move in a direction perpendicular to the line connecting their centers, their frictional factors do not significantly differ from $6\pi\eta c$ [16].

Thus, the work necessary for moving a sphere in time t_1 in a direction making an angle w with the line connecting its center with that of another sphere, such that the mutual distance between the centers increases from r_0 to $r_0 + \delta$, becomes:

$$\varepsilon = 6\pi\eta_0 c \left[\frac{\delta}{t_1} \cos w \int_{r_0}^{r_0+\delta} \frac{6s^2 - 11s}{6s^2 - 20s + 16} \cos w dr + \frac{\delta}{t_1} \sin w \int_{r_0}^{r_0+\delta} \sin w dr \right]. \quad (6)$$

On averaging over all angles, we obtain:

$$\varepsilon = 6\pi\eta_0 c \frac{\delta}{t_1} \left[\delta + \frac{1}{6} c \ln \frac{r_0 + \delta - 2c}{r_0 - 2c} + \frac{1}{3} c \ln \frac{r_0 + \delta - \frac{4}{3}c}{r_0 - \frac{4}{3}c} \right]. \quad (7)$$

Thus f' , the frictional coefficient describing the work required for moving two spheres towards or away from each other, becomes:

$$f' = 1 + \frac{1}{6} \frac{c}{\delta} \ln \frac{r_0 + \delta - 2c}{r_0 - 2c} + \frac{1}{3} \frac{c}{\delta} \ln \frac{r_0 + \delta - \frac{4}{3}c}{r_0 - \frac{4}{3}c}. \quad (8)$$

f' significantly surpasses 1 only for the case of spheres which are either very close to each other at the start or at the end of the motion. For the comparison with experimental data, this consideration implies that only the motion towards directly contacting neighbours significantly contributes to f . Thus, for an aggregate in a floc we may assume:

$$f \approx 1 + (f' - 1)q. \quad (9)$$

At $c_v = 0.25$, q will be only slightly larger than 2. Thus, values for f' of the order of 8 would be required, if $(q - 1)l^2 \ll 1$. In this case however, δ/a in eq. (8) would be about 1, because the energy dissipation in this case occurs predominantly through aggregates in a shear plane. Rather unrealistic values for $r_0 - 2a$ (about $10^{-12} a$) would be required to obtain $f' \approx 8$; it is known that the idealization of regarding two contacting bodies of arbitrary shape, as far as coagulation behaviour is concerned, as two perfectly smooth spheres breaks down when the mutual distance between the surfaces becomes less than $70 \text{ \AA}$ [17]. This rules out alternative a).

On the other hand, alternative b) makes both the value required for f' lower, and decreases δ/a , since in this case, most of the energy dissipation occurs through the motion of aggregates which move over a

distance smaller than δ_0 . Thus, $f = 7$ can be obtained, at $q \approx 2$, by $f' = 4$, which can be obtained from (8) through $\delta/a = 0.1$ and $r_0/a = 2.02$. These values appear to be reasonable.

For $t_r = 50$ min, η/η_0 is about 60 (fig. 8b). If the effect of increasing t_r is attributed to a decrease of both A_1 and of Δ , with again $A_1/\Delta = 1$ for $\dot{\gamma} \rightarrow \infty$, the difference between the viscosities at $t_r \rightarrow 0$ and at $t_r = 50$ min can be accounted for by assuming $\delta_0/\Delta = 0.2$ and 0.25 for these cases.

Next we will check whether we obtain acceptable values for A/Δ at lower values of $\dot{\gamma}$, if we keep to the assumption that $A_1/\Delta \rightarrow 1$ for $\dot{\gamma} \rightarrow \infty$. In a typical experiment (batch 2, $t_c = 16.5$ hr, $t_r \rightarrow 0$), for which $\tau_0 = 107.41 \text{ g cm}^{-1} \text{ s}^{-2}$ and $\eta = 52.5 \text{ cP}$, we obtain $A/\Delta \approx 20$ at $\dot{\gamma} = 10 \text{ s}^{-1}$. This value also appears to be reasonable.

A limited amount of data has been obtained at $c_v = 0.30$ (fig. 11). In comparison with the values obtained at $c_v = 0.25$, τ_0 has not changed significantly but η differs by a factor of about 30. This difference should be ascribed primarily to an increased value of q ; f' should not differ very much. However, A_1/Δ may for stiffer pastes significantly surpass 1.

Fig. 11. Torque vs. $\dot{\gamma}$ for $c_v = 0.30$ (+) and $c_v = 0.25$ (o). Batch 2, $t_c = 23$ hr, $t_r = 1$ min

The considerations in this discussion are not intended to yield definite values for the parameters concerned. They are meant only to show that the rheological properties of $\text{Ca}(\text{OH})_2$ suspensions can be accounted for on the basis of the elastic floc model with

reasonable values for the parameters, without introduction of an additional term for flow movement inside the flocs.

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