Energy dissipation during flow of coagulating concentrated suspensions

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ENERGY DISSIPATION DURING FLOW OF COAGULATING CONCENTRATED SUSPENSIONS

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Abstract
The energy dissipation during stationary flow is calculated for suspensions of such concentration that division into separate flocs and surrounding medium can be neglected (absence of sedimentation in the suspension at rest). This restriction removes some uncertainties in the "elastic floc" model [5]. The system is conceived as one giant floc when at rest, and to be divided by shear planes into domains when being sheared.

Experiments performed on aqueous suspensions of Ca(OH)$_2$ (solid volume fractions = 0.25) show that the energy dissipation can be accounted for by that connected with the work required for overcoming the viscous drag experienced by particles moving within the domains. The influence of the nearby presence of other particles on the viscous drag is taken into account, but no separate term for energy dissipation by fluid flow in the flocs is necessary.

Introduction
Analysis of rheological data for suspensions, with a view to obtain from them information on hydrodynamic or colloid chemical interaction between the suspended particles, is often performed by considering forces between the particles in the unsheared suspension (see e.g. [1]). During the last years, however, a different way of discussing rheological data has been developed [2-5], which starts from energy dissipation in stationary flow.

The essential point in the latter type of analysis is that, for stationary flow, the energy dissipation equals the work performed on the system. Thus, per unit of volume and time,

\[ E = \tau \times \dot{\gamma} \]  

(E = energy dissipation per unit of volume and time; \( \tau \) = shear stress; \( \dot{\gamma} \) = shear rate) irrespective of the type of flow (Newtonian or non-Newtonian). The analysis then proceeds by calculating E on the basis
of model considerations. The most important contributions to the energy dissipation, insofar as they are related to interaction between the suspended particles, appear to be:
1. Elastic energy required to stretch bonds between primary particles;
2. Energy required to overcome the viscous drag experienced by particles moving within flocs;
3. Energy required for the internal movement of liquid within the flocs when they change volume and/or shape.

Compared with those effects, the energy dissipation through the formation and subsequent breaking of bonds between the suspended particles is negligible. The model employed was named "elastic floc" model. Van de Ven and Hunter [5] described the rheological behaviour of the suspensions studied by them by a Bingham type of equation, which leads, with (1), to:

$$\eta = \tau_B \times \dot{\gamma} + \eta_{PL} \times \dot{\gamma}^2$$

(\(\tau_B\) = yield value; \(\eta_{PL}\) = plastic viscosity). The second term on the right side was totally ascribed to energy dissipation by non-interacting flocs, whereas the first was ascribed to the energy dissipation within the flocs. The theory was developed for relatively dilute coagulating suspensions (\(c_F < 0.2\)) where discrete flocs can be discerned in a continuous liquid. The assumption that the energy dissipation \(\eta_{PL} \times \dot{\gamma}^2\) is due solely to energy dissipation by "non-interacting" flocs led these authors to estimate an important parameter in the calculations, viz. the solid volume fraction within the flocs, by applying either the Einstein equation [6]

$$\eta_{PL} = \eta_0 (1 + 2.5 \, c_F)$$

or the Krieger equation [7]

$$\eta_{PL} = \eta_o (1 - c_F/c_{max})^{-2.5 \, c_{max}}$$

(\(c_F\) = volume fraction of flocs; \(c_{max}\) = maximum solid volume fraction which permits flow).

Several points in this chain of reasoning are debatable, however. Thus, the assumption of a clear-cut division between energy dissipation by non-interacting flocs (\(\eta_{PL} \times \dot{\gamma}^2\)) and within flocs (\(\tau_B \times \dot{\gamma}\)) involves the assumption, that energy dissipation by particles within flocs does not contribute terms proportional to a larger power of \(\dot{\gamma}\) than the first one. In addition, the inclusion of a separate term for energy dissipation by the movement of liquid within the flocs (the third term in the above enumeration) is not logical: this energy dissipation should be comprised in the second term. Thus, for an isolated spherical particle moving in an infinite liquid, the work required for the motion as calculated from the Stokes equation includes the work needed for displacing part of the surrounding medium.

In view of these uncertainties, it appeared to the present authors of interest to investigate whether the "elastic floc" model can describe the rheology of a coagulating suspension of such concentration that
separation into discrete flocs and a surrounding homogeneous liquid cannot occur (or might be neglected). This removes (diminishes) the uncertainties about the solid volume fraction in the surroundings of the suspended particles. Moreover, a check is obtained whether the assumption that all energy dissipation terms proportional to $\gamma^2$ may be ascribed to non-interacting flocs, is reasonable. As a solid, Ca(OH)$_2$ was chosen because its distinct solubility in water permits an independent check of one important parameter: the degree of dispersion of the solid, by measuring the dissolution rate of Ca(OH)$_2$ after diluting the suspension with an excess of water [8].

In spite of their many industrial applications, not much attention has been paid hitherto to the rheology of aqueous Ca(OH)$_2$ suspensions; the most extensive investigation to date [9] is restricted to samples with a considerable impurity content. In the present investigation, Ca(OH)$_2$ ex Merck ("pro analysi") was employed. By SEM, this was seen to consist of aggregates (figure 1) of the flat primary Ca(OH)$_2$ crystals which, however, remain intact on being dispersed in water (see later).

**Figure 1** SEM of Ca(OH)$_2$. (One side of the figure corresponds with 20 $\mu$m).

**Experimental procedures [10]**

Pastes consisting of Ca(OH)$_2$ and water, of $c_v = 0.25$, were prepared by intensive kneading (using an Erweka KU1 kneading machine with stirrer R, Erweka-Apparatebau GmbH, Frankfurt/Main). After mixing, stirring was continued for 15 minutes; the suspension was then stored in a glove-box containing an atmosphere free of CO$_2$. 
About 30 minutes before use the suspension was homogenized by shaking and introduced into a rheometer (Epprecht 15T-FC, Contraves AG, Zürich), where it was brought to temperature (20°C). The suspension was then homogenized again by moving the inner cylinder of the viscosimeter by hand, and the inner cylinder was rotated at a constant angular velocity for 50 minutes. During this time, the torque experienced by the inner cylinder was registered [11]. The torque values read at one shearing time (tᵣ) for different angular velocities of the inner cylinder, were combined into torque vs. Υ curves. For every angular velocity, a new suspension sample was employed in order to eliminate the influence (if any) of a sample's previous history. Of interest in the present investigation are primarily values obtained at long shearing times (tᵣ = 50 min), referring to the suspension in stationary flow; in addition values obtained by extrapolating tᵣ to 0 will be mentioned, because they refer to the structure at the start of shearing. Changes in the degree of dispersion of the Ca(OH)₂ during preparation of the sample, standing without being sheared, and shearing were investigated by comparing SEM, sediment volume, electroosmosis and Ca(OH)₂ dissolution rate of untreated starting material (SEM only) and material extracted from the suspensions. The dissolution rates were determined by pipetting 1 ml of a suspension into 100 ml of water (20°C), with continuous stirring; the geometry of the apparatus and the stirrer speed (500-550 rpm) were kept constant. The electrical conductivity of the dilute 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 to reach 1/2 of the conductivity change effected by the dissolution of Ca(OH)₂, was taken as a measure for the dissolution rate ("t₁/₂"). All methods employed agreed in that shearing does not disrupt the aggregates of Ca(OH)₂ crystals found in the untreated material. These aggregates contain only a very small amount of voids, as evidenced by measurement of the specific volume of the Ca(OH)₂ samples in a pyknometer.

Results
Contrary to results obtained for suspensions which show no rheologically measurable tendency to coagulation [11], in the case at hand the introduction of the sample into the rheometer is a crucial step because it invariably entails destruction of the coagulation structure developed in the suspension during standing. Whereas the torque vs. time graphs generally had a smooth character, the torque vs. Υ graphs showed more scatter than those obtained for non-coagulating suspensions [11]. Figure 2 shows some typical results. The scatter necessitated statistical treatment; it was more pronounced for values obtained for tᵣ > 0 than for tᵣ = 50 min (correlation coefficients for the torque vs. Υ graphs ranged from 0.73 upwards for tᵣ > 0, and from 0.91 upwards for tᵣ = 50 min).

In table 1, equations are mentioned which summarize the results for two different samples of Ca(OH)₂. For shortness' sake, the data are summarized by Bingham type equations, but no other implications are
Figure 2  Typical torque vs. $\dot{\gamma}$ graphs. $+$ $t_r$ = 0;  $\circ$ $t_r$ = 50 min.

Table 1  Summary of experimental data for two Ca(OH)$_2$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$t_r$ (min)</th>
<th>$\tau_B$ (g.cm$^{-1}$s$^{-2}$)</th>
<th>$\eta$ (g.cm$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0</td>
<td>111.68x(1+1.4270x10$^{-3}$xt$_c$)</td>
<td>0.3354x(1+8.7656x10$^{-4}$xt$_c$)</td>
</tr>
<tr>
<td>I</td>
<td>50</td>
<td>79.72x(1-7.9591x10$^{-4}$xt$_c$)</td>
<td>0.4353x(1+1.7202x10$^{-3}$xt$_c$)</td>
</tr>
<tr>
<td>II</td>
<td>0</td>
<td>124.40x(1+1.5220x10$^{-3}$xt$_c$)</td>
<td>0.3827x(1+1.7344x10$^{-4}$xt$_c$)</td>
</tr>
<tr>
<td>II</td>
<td>50</td>
<td>65.26x(1+2.5990x10$^{-4}$xt$_c$)</td>
<td>0.5493x(1+1.4424x10$^{-3}$xt$_c$)</td>
</tr>
</tbody>
</table>

$t_c$: contact time (hrs), i.e. the time that Ca(OH)$_2$ and water are in contact without being sheared.
intended by the use of $\tau_B$ and $\eta_{pl}$ than that the data can, within their accuracy and within the $\dot{\gamma}$ range investigated, be represented reasonably well by a linear relation between $\tau$ and $\dot{\gamma}$.

In spite of some uncertainty due to the scatter mentioned, it can be seen that one prediction of the Van de Ven and Hunter model is not fulfilled: viz. the statement that energy dissipation terms proportional to $\dot{\gamma}^2$ are restricted to energy dissipation by non-interacting flocs. For if this would be true, the shear stress necessary for flow should be independent of $\dot{\gamma}$ in the case at hand, where the whole suspension in the unsheared state must be conceived as one single giant floc (cf. the absence of sedimentation).

General tendencies observed are:
1. With increasing $t_r$, $\tau_B$ decreases whereas $\eta_{pl}$ increases. The former effect is more pronounced than the latter.
2. Increasing contact time $t_c$ (i.e. the time during which Ca(OH)$_2$ and water are in contact before being sheared) results in an increasing $\tau_B$ for $t_r \rightarrow 0$; but the effect is not very pronounced and is not apparent at $t_r = 50$ min.

These findings, together with the more pronounced scatter of the torque vs. $\dot{\gamma}$ graphs at $t_r = 0$, indicate that after introduction of the sample into the rheometer (but before shearing) there are present some remnants of the structure developed on standing, but that these entities are destroyed by shear.

\begin{figure}[h]
\centering
\begin{tikzpicture}
\begin{axis}[
    xlabel=$t_{1/2}$ (sec),
    ylabel=$t_r$ (min),
    xmin=10, xmax=50,
    ymin=1, ymax=3,
    xtick={10,20,30,40,50},
    ytick={1,2,3},
    legend style={at={(0.5,1.15)},anchor=north},
]
\addplot[only marks,mark=o] table [x index=0, y index=1] {data1.dat};
\addplot[only marks,mark=x] table [x index=0, y index=1] {data2.dat};
\legend{$\dot{\gamma} = 11.9 \, s^{-1}$, $\dot{\gamma} = 36.9 \, s^{-1}$}
\end{axis}
\end{tikzpicture}
\caption{$t_{1/2}$ vs. $t_r$. $\circ \, \dot{\gamma} = 11.9 \, s^{-1}$; $\times \, \dot{\gamma} = 36.9 \, s^{-1}$}
\end{figure}
It appeared, from a comparison of dissolution rate (figure 3), sediment volume and SEM data that these remnants are not the aggregates formed by primary Ca(OH)$_2$ crystals in a stockwise arrangement (figure 1). On the contrary, these aggregates appear to persist during shear. What is changing during shear involves combinations of such aggregates rather than the aggregates themselves.

In order to account for the energy dissipation in stationary flow (t$_n$ → ∞), which appears to conform to equation (2), we employ the following model: At rest, the system consists of one single floc. When such a system is subjected to shear, the shear will not be realized homogeneously throughout the volume, but be restricted to "shear planes" developing in the main parallel to the direction of shear, though locally deviations from this direction will occur. In the "domains" between those shear planes, a coagulation structure is present similar to that in the original system (though the domains themselves are not necessarily unchanged relicts of the unsheared system: it is not necessary that the shear planes remain situated at the same positions during the shear time t$_p$). During shear, within the domains some movement to and fro of the aggregates is possible, but in the main an aggregate remains surrounded by the same neighbours.

Compared with more dilute suspensions, the theoretical treatment can be considerably simplified for our systems, since non-interacting flocs are absent. In addition, when the aggregates persist during shear the primary Ca(OH)$_2$ crystals in them do not move towards each other, thus no energy dissipation occurs through the stretching of bonds between them. It is true that some energy dissipation may occur through the stretching of bonds between the aggregates, but this will be only a weak effect because the Van der Waals attraction between the aggregates is relatively weak (because of the retardation [12]).

Thus, among the energy dissipation effects taken into consideration by Van de Ven and Hunter, there remain only that connected with the viscous drag experienced by aggregates moving within the domains, and possibly that caused by the movement of liquid within the domains. Thus it should be possible to check, whether inclusion of the second energy dissipation term is really necessary.

In order to do so, we calculate the energy dissipation connected with the former effect, and consider whether it can account for the total energy dissipation as found from the rheological data.

Aggregates will be set into motion towards their surroundings by encounters between aggregates in the shear planes. These encounters will primarily move the aggregates bordering a shear plane, but the presence of a coagulation structure in a domain causes an entrainment of other aggregates. If a certain aggregate i moves over a distance δ$_i$, it will entrain its immediate neighbours over a distance $\lambda$δ$_i$ (0 < $\lambda$ < 1). The number of entrained neighbours is q-1 (where q = the average number of neighbours in an aggregate in the coagulation structure).

The energy dissipation $\varepsilon_i$ accompanying the movement of aggregate i itself (without that connected with the motion of entrained neighbours) will be
\[ \epsilon_i = 6\pi \eta_0 a_i f_i \delta_i^2 / t_1 \]

where \( f_i = \) the frictional coefficient (= 1 for an individual sphere), \( a_i = \) the radius of aggregate \( i \), \( \eta_0 = \) the viscosity of the suspension medium (water in the case at hand), \( t_1, \) the time during which the movement takes place, is 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:

\[ \Sigma \epsilon_i = 6\pi \eta_0 a (f_0^2 / t_1 + (q-1)f_0^2 / t_1 + \ldots) \]

where I refers to the aggregate bordering a shear plane, II to neighbours in the first remove, III to neighbours in the second remove, etc. Average values for \( a, q, f \) and \( \lambda \) are used. Equation (5) can be represented as a geometrical series:

\[ \Sigma \epsilon_i = \frac{6\pi \eta_0 a f_0^2}{t_1} \times \frac{1}{1-(q-1)\lambda^2} \]

The energy dissipation per unit of volume and time is obtained by multiplying \( \Sigma \epsilon_i \) by the number of aggregates involved in an encounter in a shear plane, per unit of volume and time. In order to estimate this, we assign to each aggregate bordering a shear plane, an area \( A_\Delta \) in this plane; thus, if \( \Delta = \) the average distance between shear planes, and \( N_A = \) the number of aggregates bordering a shear plane per unit of volume, \( N_A \times A_\Delta \Delta / 2 \) is one unit of volume. Thus:

\[ N_A = 2/(A \Delta^2) \]

The distance traveled by an aggregate between two successive encounters will be \( \Delta \cos u \) (\( u = \) the angle between the main direction of motion and the line connecting two aggregates bordering a shear plane); while \( \dot{\gamma} A \) is the mutual velocity of aggregates in a shear plane, belonging to different domains. Thus, the number of aggregates involved in an encounter in a shear plane per unit of volume and time becomes:

\[ N_A \times \frac{\dot{\gamma} A}{\Delta \cos u} = \frac{2\dot{\gamma}}{\Delta^3 \cos u} \]

The time \( t_1 \) in equation (6) is of the order \( a/(\dot{\gamma} A) \). Thus:

\[ E = 12\pi \eta_0 f \frac{\delta A}{\Delta^3 \cos u} \times \frac{1}{1-(q-1)\lambda^2} \times \dot{\gamma}^2 \]
and the rheological equation becomes (cf. equation (1)):

\[ \tau = 12\pi n_0 f \frac{\delta^2 A}{\Delta^3 \cos u} \times \frac{1}{1-(q-1)\xi^2} \times \dot{\gamma} \]  

(10)

Though this formula, by its form, suggests Newtonian behaviour, this will be true only if parameters like \( \delta_0 \), \( A \) and \( \Delta \) would be independent of \( \dot{\gamma} \). The general tendencies of the observations can be interpreted as follows: The Bingham behaviour of the pastes is connected with the appearance of an increasing number of shear planes (hence a decrease of \( A \)) with increasing \( \dot{\gamma} \) (hence increasing shear stress). Regions which withstand a low shear stress may break down under a larger one. During standing without being sheared the coagulation structure changes in the direction of increasing solidification; part of this change is retained during the introduction of the samples into the rheometer, but not on shearing for a long time. Continued shearing is accompanied by the development of additional shear planes, because regions which can temporarily withstand a shearing stress may break down in the long run; this explains the decrease of \( \tau_0 \) with increasing shearing time. The simultaneous tendency of \( \eta_{\text{pl}} \) to increase is thought to be connected with a loosening of the structure, accompanied by an increase of \( \xi \).

In order to check whether equation (10) can quantitatively describe the rheology of the suspensions, we must look for reasonable values for the parameters. Assuming a random structure in the vicinity of a shearing plane, we introduce

\[ \cos u = \int_0^{\pi/2} \cos u \, du = \frac{\pi}{2} \approx 0.637 \]

The parameter \( q \) is estimated by considering an infinite network of equal-sized spheres, arranged e.g. in a diamond type lattice then a number of the spheres is successively removed such as to leave a coherent structure. The regularity imposed by the initial structure of course is artificial, it is, however, tempered by regarding a number of unit cells. For such structures the average number of directly contacting neighbours was calculated; the result is only insignificantly dependent on the type of initial coordination (tetrahedral or octahedral) and on the particular spheres removed from the starting structure in order to obtain a given solid volume fraction (figure 4). For \( c_v = 0.25 \), one thus obtains \( q \approx 3.2 \); the uncertainty in this estimate is predominantly caused by the fact that the aggregates in the real systems are not equal-sized.

A further restraint is imposed on this formula by the requirement that \( (q-1)\xi^2 \) must be \(<1\) in order to prevent an infinite amount of energy dissipation to be occasioned by one encounter between aggregates in a shear plane; with \( q = 3.2 \) this leads to \( \xi < 0.674 \).

A more difficult parameter to estimate is \( f \). Van de Ven and Hunter assumed \( f \approx 1 \), referring to work by Gluckman c.s. [13]; however, Gluckman's calculations refer to particles which remain at rest with
regard to each other. When the particles move towards each other (as is supposed both by Van de Ven and Hunter, and in the present investigation), \( f \) may appreciably surpass 1 [14]. In order to obtain an estimate for \( f \), we neglect the difference between \( f \) and 1 when two particles move parallel to the plane dividing their separation distance halfway perpendicularly [15], while we use for two particles moving in the direction of their centers Honig's c.s. approximate expression [16]:

\[
f = \frac{6s^2 - 11s}{6s^2 - 20s + 16}
\]

with \( s = r/a \); \( r \) = the distance between the centers. Thus we find for the work necessary for moving two equal spheres (radius \( c \)) from a mutual distance \( r_o \) to \( r_o + d \) in time \( t \), in a direction making an angle \( \omega \) with the line connecting their centers:

\[
\varepsilon = 6\pi n_0 c \times \left[ \frac{d}{t} \cos \omega x \right] \frac{r_o + d}{r_o} \left( \frac{6s^2 - 11s}{6s^2 - 20s + 16} \cos \omega dr + \frac{d}{t} \sin \omega x \right) \frac{r_o + d}{r_o} \sin \omega dr
\]

which leads, on averaging over all angles \( \omega \), to:

\[
f' = 1 + c \ln \frac{r_o + d - 2c}{r_o - 2c} + \frac{c}{3d} \ln \frac{r_o + d - \frac{4}{3}c}{r_o - \frac{4}{3}c}
\]

This differs appreciably from 1 only, if the two spheres are very close to each other either at the start or at the end of the motion. Thus, the predominant contribution to \( f \) for an aggregate in a floc comes from
its directly contacting neighbours:

\[ f \approx 1 + (f' - 1) \times q \]  \hspace{1cm} (14)

What kind of estimate should be introduced for \( f' \), depends on the extent to which we may treat the aggregates as perfectly smooth spheres. \( f' \) is determined primarily by \( r_0/c \) and by \( d/c \) only if \( r_0/c \) is very close to 2; but such values of \( r_0/c \) are prevented by the irregular shape of the aggregates. \( r_0/c \) values of 2.1 seem to be realistic (which means that the fluid motion occurring on separation of two directly contacting aggregates can be compared with that occurring between spheres held apart for about 5\% of their diameter). Then \( f' \) becomes about 3 (see figure 5), and \( f \) becomes 7-8.

![Graph showing the relationship between \( f' \) and \( r_0/c \)](image)

**Figure 5** \( f' \), the frictional coefficient describing the work necessary for increasing the distance between the centers of two equal-sized spheres from \( r_0 \) to \( r_0 + d \), as calculated by equation (13).
- 1 \( d/c = 0.001 \)
- 2 \( d/c = 0.01 \)
- 3 \( d/c = 0.1 \)

A reasonable supposition with regard to \( \delta_0 \) would be to take it equal to \( a \) (an aggregate bordering a shear plane must be displaced over about half its diameter in order to let an encountering aggregate pass), while from steric model considerations one would arrive at \( \Delta \approx 5a \).

In order to compare equation (10) with experiments, we neglect the influence of \( t_0 \) on the values obtained at \( t_0 = 50 \) min and take an average of all experiments. Thus, we find for sample 1: \( \tau_B = 75.1 \text{ g cm}^{-1} \text{s}^{-2} \)
(σ = 10.4 g cm⁻¹ s⁻²), \( n_{PL} = 0.49 \text{ g cm}^{-1} \text{s}^{-1} \) (σ = 0.14 g cm⁻¹ s⁻¹); for sample II: \( \tau_B = 66.4 \text{ g cm}^{-1} \text{s}^{-2} \) (σ = 4.1 g cm⁻¹ s⁻²), \( n_{PL} = 0.60 \text{ g cm}^{-1} \text{s}^{-1} \) (σ = 0.05 g cm⁻¹ s⁻¹).

On the basis of the model, we expect a nearly total breakdown of the structure at large \( \dot{\gamma} \) values, which means that \( A/A \) will approach unity. If no other changes in the structure occur with increasing \( \dot{\gamma} \) other than the creation of new shear planes, \( E \) in this case should approach to \( n_{PL} \times \dot{\gamma}^2 \), which means that

\[
\frac{n_{PL}}{n_0} = 12 \pi \times f \times \left( \frac{\delta \phi}{\Lambda} \right)^2 \times \frac{A_1}{\Lambda} \times \frac{1}{\cos \theta} \times \frac{1}{1-(q-1)\ell^2} \tag{15}
\]

where \( A_1 \) = the distance between shear planes at large \( \dot{\gamma} \) values; \( A_1/\Lambda = 1 \). With the estimated values for the parameters \( f, \delta \phi, \Lambda \) and \( \cos \theta \), we can obtain agreement with the experimental values if \( (q-1)\ell^2 \approx 6 \) (sample I) or 0.7 (sample II). Both agree with \( \ell \approx 0.5 \).

The next question to be asked is, whether the result is compatible with acceptable values for \( A/\Delta \) at lower \( \dot{\gamma} \) values. The lowest \( \dot{\gamma} \) value employed was 33 s⁻¹ for sample I; here we would find \( A/\Delta = 6.2 \).

While these are certainly reasonable values, it should be stressed that for some of the parameters rather debatable values had to be introduced. Our conclusion at present therefore must be limited to the statement that, with acceptable values for the parameters mentioned the energy dissipation during flow can be accounted for without invoking an independent term for energy dissipation by fluid flow in the flocs.

References
10. A more extended description of this investigation will appear in Rheologica Acta.
Notations

- **A** average distance between shear planes
- **A_1** the same for \( \dot{\gamma} \to \infty \)
- **a** radius of an aggregate composed of Ca(OH)\(_2\) crystals piled stack-wise
- **a_i** radius of aggregate \( i \)
- **c** radius of one of a pair of equal-sized spheres
- **C_F** solid volume fraction of flocs
- **c_{max}** maximum floc solid volume fraction at which flow is possible
- **c'** solid volume fraction
- **d** distance over which one of a pair of equal-sized spheres is removed from its partner
- **E** energy dissipation per unit of volume and time
- **f'** average frictional coefficient for aggregates in a floc
- **f** frictional coefficient describing the work necessary for moving two equal-sized spheres from a distance \( r_0 \) to \( r_0 + d \)
- **f_i** frictional coefficient for aggregate \( i \)
- **\lambda'** fraction of the distance traveled by an aggregate, over which it entails its directly connected neighbours
- **N_A** number of aggregates bordering a shear plane, per unit of volume
- **q** average number of directly connected neighbours of an aggregate in a floc
- **r** distance between centers of equal-sized spheres
- **r_0** r at the start of the motion
- **r/a or r/c**
- **t** time necessary for reaching \( \frac{1}{2} \) of the conductivity effect caused by dissolution of Ca(OH)\(_2\) on diluting the suspension
- **t_0** time during which an encounter between aggregates in a shear plane takes place
- **t_c** time during which Ca(OH)\(_2\) and water are in contact before the suspension is sheared
- **t_r** time during which the suspension is sheared
- **u'** angle between the direction of motion of an aggregate and the line connecting the centers of two other aggregates bordering a shear plane
- **w** angle between the direction, in which two spheres move towards each other, and the line connecting their centers
- **\dot{\gamma}** shear rate
- **\Delta** square root of the average area which can be assigned to an aggregate bordering a shear plane, in this plane
- **\delta_0** distance over which an aggregate in a shear plane moves during an encounter
- **\varepsilon_i** energy dissipated by aggregate \( i \)
- **\varepsilon** work required when two spheres move towards each other
- **n_p** viscosity of the suspension medium
- **n_pL** plastic viscosity
- **\sigma** standard deviation
- **\tau** shear stress
- **\tau_B** constant in Bingham type equation