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A structural model for the time-dependent recovery of mineral suspensions

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Abstract A thixotropic recovery model has been developed that is based on consideration of the microstructural interactions that occur between particles within a suspension particle network. The model is based on Smoluchowski coagulation rate theory, utilizing second order kinetics to describe the thixotropic recovery behavior. The model is applied to Na-montmorillonite-based coal tailings suspensions and is also shown to be applicable to brown coal and bauxite residue suspensions. The model describes all the recovery data well, especially at intermediate to large recovery times. The recovery of the montmorillonite

suspensions at short times was faster than predicted, indicating the existence of additional factors in early-time structure development. The discrepancy may have also been due to the highly anisotropic nature of the clay platelets. The recovery rate constant, K_r , increases with increasing solids concentration (for constant surface chemical conditions) as would be expected from the basis of the model.

Key words Thixotropy · Montmorillonite · Recovery · Structural model · Clay · Coal tailings · Bauxite residue · Brown coal suspensions

Introduction

The classical definition of thixotropy is as a time-dependent, isothermal, and reversible breakdown of a particulate structure in a suspension under shear, followed by structural reformation at rest (Bauer and Collins 1960; Mewis 1979). The term “thixotropy” was first used by Freundlich and Bircumshaw (1926) to describe the time dependent behavior of aluminum hydroxide gels where the transition on agitation was from a solid-like to a liquid-like state. The term was later extended to include materials that exhibited a less dramatic change in consistency.

For most materials of practical interest, the classical definition of thixotropy does not apply, in that either or both the degree of breakdown on shear is more than the degree of recovery on resting and/or the rates of the two processes are different. Such behavior has been reported

for *bauxite* residue (Nguyen and Boger 1985b) and brown coal suspensions (Boger et al. 1987). The accepted definition of thixotropy can be likened to pseudoplasticity, with a “reversible” breakdown of some kind of structure in the suspension during shear. The only real difference between the two phenomena is one of time scales: in thixotropy the time scales of either or both the breakdown and recovery processes are such that they can be experimentally measured.

In materials of practical importance, thixotropy manifests itself as follows. On shearing after a period of rest, the inherent structure in a thixotropic material will break down. After some time of shearing, a point is reached where an equilibrium is established between the rate of structure destruction and reformation. At this point, an equilibrium, broken-down state exists and further shear results in no further changes in the rheology. On rest, after shearing to equilibrium, the

suspension network structure re-builds. In some cases the breakdown recovery cycle is completely reversible; however a notable exception is the behavior of bauxite residue where the strength of the initial undisturbed material is not regained on resting after shear, even after months (Nguyen and Boger 1985b).

The breakdown of a thixotropic substance is generally measured by the decay in the shear stress with time at a constant shear rate in a rheometer. The most common geometry for this purpose is the cone and plate geometry which is characterized by a constant shear rate throughout the sample (Bird et al. 1960). In the case of a concentric cylinder geometry, for a thixotropic material the shear rate at the bob surface may not be constant (Nguyen and Boger 1987a; Zhang and Nguyen 1994) so there is no controllable constant parameter.

A relatively recent method for the measurement of breakdown rates was the measurement of the change in the yield stress of the suspension with time of agitation using the vane technique (Nguyen and Boger 1985b). The suitability of this method is limited to materials where the time scale of recovery or breakdown are much longer than the time scale of the measurement (minutes).

The material examined in the present study is a suspension of Na-montmorillonite clay-based coal tailings, for which the thixotropy was examined as a part of a project to using the interactions between surface chemistry and rheology to improve coal mining waste disposal (de Kretser et al. 1997). The thixotropy of Na-montmorillonite was first examined in the 1930s (Broughton and Squires 1936; Freundlich et al. 1932) and is classical in the sense that it occurs as a sol-gel transition and is reversible in terms of the magnitude of breakdown and recovery. It is also non-classical in terms of the differing rates of breakdown and recovery. The thixotropic behavior of Na-montmorillonite is complex, being affected by a number of factors relating to the particles and the suspending medium (de Kretser et al. 1997; Van Olphen 1956). One of the most significant factors affecting the rheological behavior is the ionic strength of the suspending medium (de Kretser et al. 1997; Rand et al. 1980; Van Olphen 1977).

The shear induced structural breakdown of Na-montmorillonite suspensions is very rapid, almost instantaneous, which makes characterization of the breakdown process very difficult. As a result, little is published on the subject in the literature. A method of characterizing thixotropy and breakdown was developed by Cheng (1973) using a cone and plate rheometer. The method was successfully applied to Na-montmorillonite (Cheng 1979); however, it was very time consuming and required large amounts of experimental flow data. Additionally, the maximum particle size of the coal tailings used in the present study was too large for the use of the cone and plate geometry for flow property measurement. The use of the concentric cylinder geo-

metry for measurement was also unsuitable due to the aforementioned shear rate calculation problems (Nguyen and Boger 1987a; Zhang and Nguyen 1994).

As the breakdown of the coal-clay tailings was essentially instantaneous, no evaluation of the breakdown rates was performed in this study. The breakdown of the structure appeared to be such that once any deformation occurred on the yielding of the gelled network, catastrophic collapse followed, resulting in a rapid loss of strength.

Recovery rates

Methods for the characterization of the recovery behavior of a thixotropic material are listed in the extensive reviews by Mewis (1979) and Bauer and Collins (1960). Of the methods described, the most relevant in the present case are the use of oscillatory flow measurements to monitor the increase in structure and monitoring the measurement of the yield stress with time of rest.

By monitoring the change in the storage modulus (G'), loss modulus (G'') or the shear modulus (G) with time of rest after shearing, the change from liquid-like behavior (low G') to solid-like behavior (high G') can be observed. The use of dynamic or oscillatory measurements for the characterization of the thixotropy of Na-montmorillonite has been performed by Khandal and Tadros (1988) and Sohm and Tadros (1989). Tadros later used dynamic measurements for gaining insights into particle interactions in concentrated suspensions of Latex (Tadros 1990). The advantage of dynamic methods is that the testing, provided the amplitude of the oscillations are small, is relatively non-destructive to the particle network.

The yield stress method involves simply measuring the yield stress of a sample at various times after the cessation of shear. The advantage of the method is that the yield stress is of direct industrial significance and is easier to interpret in terms of its relevance to real processes. The yield stress recovery method has been used by Leong (1988), Nguyen and Boger (1985b, 1987b), and Van Kessel and Blom (1998) for the determination of the recovery of brown coal, bauxite residue suspensions, and clay sediments respectively. A disadvantage of the method is that the testing is destructive, particularly in the case of the highly shear-sensitive Na-montmorillonite gels. Despite this, and due to the practical nature of the present investigation, the yield stress was used to characterize the recovery behavior of the suspensions studied.

In order to characterize effectively the recovery of the coal-clay tailings, the recovery behavior should be modeled with a mathematical expression so that calcu-

lation of the yield stress of the suspension can be completed for any time during the recovery process.

There is a dearth of recovery models available in the literature that use a real material parameter to characterize thixotropic recovery behavior. The main reason is that there has, until relatively recently, been no method of effectively quantifying the structure of a thixotropic material. The development of the vane yield stress measuring device and the improvements in the technology of dynamic flow property measurement have led to easy measurement of real material parameters enabling monitoring of the behavior of thixotropic substances with time of recovery.

The recovery behavior of the coal-clay tailings will be shown to be described by a mathematical model that is based on the postulate that changes in yield stress are due to changes in the concentration of particle bonds. In this sense, the model is an improvement over more empirical existing models, as it is built up from a consideration of microscopic particle interactions. The model was developed by Leong (1988) for the recovery of brown coal suspensions and the performance of the model in describing the recovery behavior of brown coal and bauxite residue suspensions will also be illustrated.

Theory: the recovery model

The model proposed by Leong (1988) was developed from a model used to describe the aging of cement paste as it set with time (Hattori and Izumi 1982a, b, c). The Hattori and Izumi model (Hattori and Izumi 1982a, b, c) was based on the assumption that the viscosity of the pastes was proportional to the concentration of the particle bonds. The formation of the particle bonds was a second order process based on Smoluchowski coagulation rate theory such that the decreasing number of discrete particles, n , is represented:

$$-\frac{dn}{dt} = 2K\kappa an^2 e^{-V_{\max}/kT} \quad (1)$$

where κ is the Debye Hückel parameter, a is the particle radius, k is the Poisson Boltzmann constant, T the temperature, and K is

$$K = \frac{4kT}{3\eta_m}$$

where η_m is the suspending fluid viscosity (in this case the viscosity of water).

To simplify, for constant temperature and surface chemical conditions, Eq. (1) reduces to

$$-\frac{dn}{dt} = k_r n^2 \quad (2)$$

where k_r is the coagulation rate constant, dependent upon temperature and surface chemical conditions.

The thixotropic recovery model was based on considerations of an ideal network of spheres. However, it will be shown to be broadly applicable to non-ideal networks of irregular shaped brown coal and bauxite residue suspensions and plate-like clay gels. A schematic of an ideal particle network is depicted in Fig. 1, with the particles being linked in a regular manner by attractive forces. In practice, even for spheres, such a regular network is unlikely to be encountered, however Figure 1 is depicted as such for illustrative purposes. If a shear stress, τ_{xy} , is applied to the network along a plane between two layers, the stress needed to shear the two layers will be directly proportional to the number of bonds per unit area and the strength of each bond. The stress, τ_{xy} , is equivalent to the yield stress, τ_y , of the material.

If all particles are networked, then the concentration of particle bonds is proportional to the total number of individual particles per unit volume, n_0 . If some of the particles are initially segregated, then at time, t , we can define the concentration of *uninteracted* particles left, as n_t . As flocs or aggregates themselves are capable of interacting and growing, the concentration, n_t , will also include these entities. Hence, the number of particle bonds per unit volume existing at time, t , is proportional to $(n_0 - n_t)$, which can be expressed on a unit area basis as $(n_0 - n_t)^{2/3}$. Note that this reasoning holds for all particle shapes and sizes. Thus, as the yield stress at any time, t is proportional to the concentration of particle bonds per unit area, it can be expressed as

$$\tau_y(t) = H_m (n_0 - n(t))^{2/3} \quad (3)$$

where H_m is a proportionality constant.

In the equilibrium, fully broken down state, the presence of a yield stress indicates the existence of an inherent structure. In this fully broken down case, the yield stress may be represented as

$$\tau_{y0} = H_m (n_0 - n_e)^{2/3} \quad (4)$$

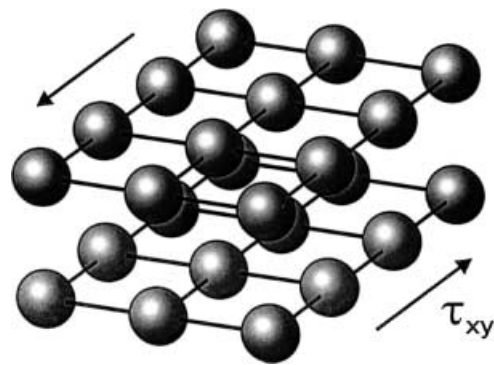


Fig. 1 Schematic of ideal particle network under shear along the plane between layers

Assuming that at infinite time the structure has fully rebuilt and the concentration of uninteracted particles, n_t , is zero, then Eq. (1) becomes

$$t_{y\infty} = H_m n_0^{2/3} \quad (5)$$

Integration of the second-order rate equation for the kinetics of bond formation during recovery (Eq. 2) with the boundary conditions, $t=0$, $n=n_e$, and $n=n_t$ for non-zero t , and incorporation into Eq. (3) leads to the following expression for the yield stress as a function of time:

$$\tau_y(t) = H_m n_0^{2/3} \left(1 - \frac{n_e/n_0}{1 + n_e k_r t} \right)^{2/3} \quad (6)$$

The parameters, n_0 , n_e , and H_m can be expressed using Eqs. (2) and (3) in terms of the yield stress as

$$\tau_y(t) = \tau_{y\infty} \left(1 - \frac{1 - \left(\frac{\tau_{y0}}{\tau_{y\infty}} \right)^{3/2}}{1 + K_r t} \right)^{2/3} \quad (7)$$

where $K_r (= n_e k_r)$ is a constant that is particular to the suspension being investigated and has the units of inverse time. The yield stress parameters can be determined experimentally and K_r evaluated. A limitation to the application of the model is the fact that the model approaches a limiting value of the yield stress only as $t \rightarrow \infty$. In real life this is not practical as a maximum yield stress is achieved at finite times. The discrepancy was found by Leong to produce errors in the model only at large recovery times (Leong 1988).

Nguyen-Boger model

Nguyen and Boger (1985b) developed a model based on first-order chemical reaction kinetics for structural reformation. The model can be expressed as

$$\tau_y(t) = \tau_{y\infty} - (\tau_{y\infty} - \tau_{y0}) e^{-k_{nb} t} \quad (8)$$

where $\tau_y(t)$, $\tau_{y\infty}$, and τ_{y0} are the yield stress at time t , the fully recovered state, and the equilibrium state respectively. k_{nb} is the recovery rate constant. The inverse of k_{nb} is a characteristic time of recovery. The model was used for the modeling of the recovery of bauxite residue suspensions (Nguyen and Boger 1985b, 1987b). The structure of Eq. (8) is exactly the same as that used for describing the recovery of clay sediments by Van Kessel and Blom (1998). A similar equation was used for the modeling of the recovery of Na-montmorillonite gels in the form of storage modulus data with recovery time (Khandal and Tadros 1988; Sohm and Tadros 1989). The form of the equation used by Khandal and Tadros (1988) was the same as the Nguyen-Boger model with the exception of the absence of the use of a zero time

value for the structural parameter. The Khandal-Tadros equation was

$$G'(t) = G'_\infty (1 - e^{-(t/t_g)}) \quad (9)$$

where $G'(t)$, G'_∞ , and t_g are the storage modulus at any time, t , the storage modulus at $t = \infty$, and the gelation time respectively. Note that the description of t_g as a gelation time has no fundamental significance in relation to other definitions of gelation times in the literature. The form of Eq. (9) is the same as that for Eq. (8) so only one equation need be fitted to check for validity of application.

Materials and experimental techniques

Coal tailings slurry properties

The tailings samples were taken from a synthetically prepared 6.1 wt% solids stock suspension created from as-mined clay and finely ground coal dispersed in water. The suspension solids were approximately 64 wt% clay. The suspending liquor had a conductivity of 1.679 mS cm⁻¹, a pH of 9.0, and a dissolved calcium ion concentration of only 6.483 × 10⁻⁵ mol l⁻¹, indicating the clay to be in the sodium ion exchanged state. The average solids density was 2200 kg m⁻³. Concentration of the suspension was completed in a centrifuge with subsequent dilutions being performed using the supernatant in order to determine the properties at a range of solids concentrations.

Recovery rate measurement technique used

A special recovery rate measurement technique was employed in the project in order to overcome the difficulties of the shear sensitivity of the samples. It was desired to characterize the thixotropy in terms of the yield stress and measurements were carried out using a Haake viscometer utilizing the vane configuration developed by Nguyen and Boger (1985a). Previous measurements of recovery behavior utilizing the yield stress involved using a sample of large enough surface area to allow repeated vane measurements at a range of increasing times of recovery on a fresh section of sample each time. However, limitations in the amount of coal tailings available meant that only small testing samples could be used. Due to the shear sensitivity of the simulated tailings, after each yield stress measurement the sample had to be sheared back to the equilibrium state before another measurement at some other time of recovery could be made.

Initial experiments revealed that the recovery rates at very short times were quite rapid and that noticeable recovery was occurring during the time taken for the sample to be transferred to the vane rheometer. The solution to this problem was actually to use the vane rotated at speeds of around 100 rpm to shear the sample to the equilibrium state. The equilibrium state could be detected by the point at which the scale reading on the Haake viscometer's operating console remained constant with time of shear.

Performing experiments in this fashion also had the advantage of eliminating another difficulty associated with working with the coal tailings. Due to the shear sensitivity of the gelled tailings' structure, even the disturbance produced by lowering the vane into the sample produced noticeable breakdown, particularly in the latter stages of the gelation process. The effect of lowering the vane into the sample on the development of structure is illustrated in Fig. 2 for a 19.6 vol.% solids (35 wt%) tailings sample. The true recovery curve is shown and it is observed that the data obtained

from measurements where the vane was lowered into the sample after recovery (circled) are substantially lower than the “true” results. If the vane, after being lowered into the sample after recovery, was left immersed for a time and the yield stress measured later, the results are observed to approach the true recovery curve (indicated by the arrow).

The results indicate that the levels of structure built up at longer recovery times are very weak, which is also reflected in the corresponding decrease in the rate of change of structure at longer times. Thus, after initial shearing was completed, the vane was left immersed in the sample during recovery. The sample was then tested at a designated time after the cessation of shear.

Hence, the recovery measurement technique employed in this project involved immersion of the vane in the sample, rotating the vane at 100 rpm until the torque registered on the Haake viscometer ceased to change with time, measurement of the yield stress at the equilibrium state, τ_{y0} ($t=0$), and then leaving the sample for the desired recovery time and re-measuring the yield stress. By repeating the procedure a number of times on the same sample and each time waiting for a different time of recovery, a curve of yield stress vs time of recovery could be constructed as in Fig. 2. The yield stress eventually recovers to what is termed an infinite time value ($\tau_{y\infty}$), although quite clearly it occurs at a finite time. Results for the recovery of the simulated tailings at a variety of solids concentrations are presented in the next section.

Results and discussion

Applicability of model to coal-clay waste

Recovery rates. The data for the recovery of the simulated tailings suspensions were collected at four solids concentrations, 13.2 vol.%, 16.5 vol.%, 19.6 vol.%, and 21.4 vol.% solids (25.1, 30.3, 35.0, and 37.5 wt%). A fifth solids concentration, 23.3 vol.% solids (40.1 wt%) was also investigated; however, no thixotropy could be measured. The yield stress of this suspension was found to be time-independent (on the time scale of measurement) at 860 Pa. The recovery

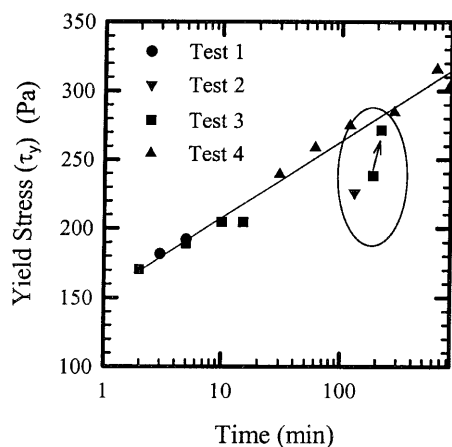


Fig. 2 Example of yield stress vs time recovery data for the Na-montmorillonite-based suspension showing the effect of vane insertion into the sample and subsequent recovery

behavior for the samples studied is presented in Fig. 3. From Fig. 3 it is observed that the recovery rates decrease as the time of recovery becomes large and the time scale of recovery is of the order of hours (compared with breakdown times of the order of seconds).

Results of fitting. In order to evaluate the applicability of the above equations, the parameters $\tau_{y\infty}$ and τ_{y0} need to be determined. τ_{y0} was determined directly from the initial yield stress at the cessation of shear. Values of $\tau_{y\infty}$ were determined via a method similar to that used by Khandal and Tadros (1988) for the determination of G'_{∞} . The method used involved plotting of $1/\tau_y$ vs $1/t$ and extrapolating back to the intercept on the $1/\tau_y$ axis so that the value of $\tau_{y\infty}$ could be found. Khandal and Tadros (1988) found that the plots were linear; however, in the present case the plots were found to be non-linear. To perform the extrapolation, a polynomial was fitted to the lower portion of the curves and the intercept calculated from the fitted equation. Examples of the fitting of the data are presented in Fig. 4 for 19.6 and 16.5 vol.% solids (35.0 and 30.3 wt%) tailings suspensions.

For each sample a number of combinations of second- or third-order polynomial and different numbers of data points fitted were trialled. For each sample the variance in the determined values for $\tau_{y\infty}$ with fitting conditions was no more than around 5% and the value used subsequently lay in the middle of the data spread. Values determined for the parameters, $\tau_{y\infty}$ and τ_{y0} , are listed in Table 1.

Fitting of the Nguyen-Boger model. To evaluate the applicability of the Nguyen-Boger model, the yield stress versus time data must be linear on a plot of $\log(\tau_{y\infty} - \tau_y(t))$ vs t . The model was found to be inapplicable for all of the four solids concentrations studied. An example of the poor fit of the equation is presented in Fig. 5 for a

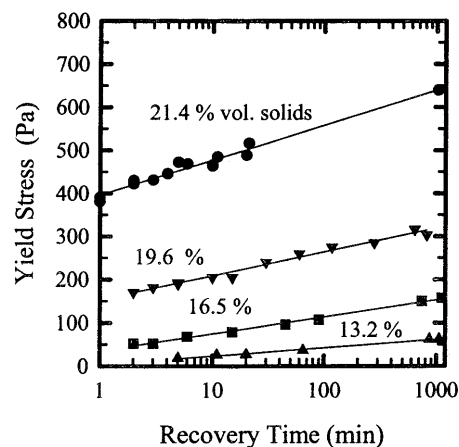


Fig. 3 Summary of the recovery data for the Na-montmorillonite-based suspensions tested. Volume percent solids concentrations are indicated

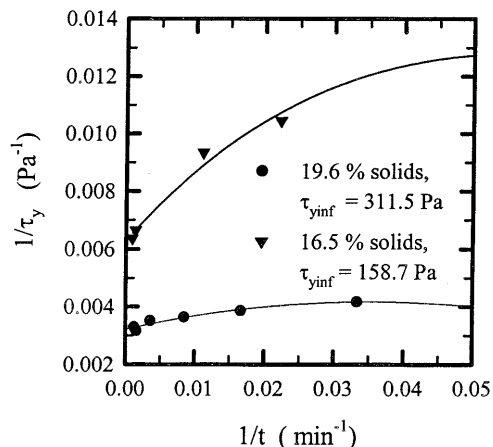


Fig. 4 Examples of $\tau_{y\infty}$ determination for Na-montmorillonite suspensions at the solids concentrations indicated

19.6 vol.% solids (35.0 wt%) simulated tailings suspension. There is quite clearly no linear relationship that describes the data.

Fitting of the Leong model. The Leong model will be obeyed if a plot of $(1 - (\tau_{y0}/\tau_{y\infty})^{3/2}) / (1 - (\tau_y(t)/\tau_{y\infty})^{3/2})$ vs t is linear. The slope of the plot will be the parameter K_r . It was found that the data at large times of recovery which were close to $\tau_{y\infty}$ caused great error in the fitting of the model. The error was due to the breakdown in the model that occurs as a result of the assumption that the yield stress approaches a limiting value only at infinite time. Ignoring large time data, the fit of the model is quite good for all solids concentrations. The fit of the model to the data is indicated in Fig. 6. Scatter is observed in the results at 21.4 vol.% solids (37.5 wt%) which is a result of the difficulties in obtaining reliable data at high solids concentration due to problems such as air bubble entrapment within the sample. Overall, the theory describes the recovery behavior well and the fitting parameters are listed in Table 2.

The sensitivity of the Leong model fit to variation in the determined $\tau_{y\infty}$ values was investigated. Using $\tau_{y\infty}$ values that varied by as much as 5% resulted in little change in the r^2 values for the model fit. The best r^2 values were obtained using the $\tau_{y\infty}$ values in Table 1, vindicating their choice. In all cases the r^2 values for fitting of the Leong model were well above those for fitting of the Nguyen-Boger model.

Table 1 $\tau_{y\infty}$ and τ_{y0} for the coal tailings suspensions studied

Solids %	21.4	19.6	16.5	13.2
τ_{y0} (Pa)	309.9	121.2	26.1	3.1
$\tau_{y\infty}$ (Pa)	641.0	311.5	158.7	62.1

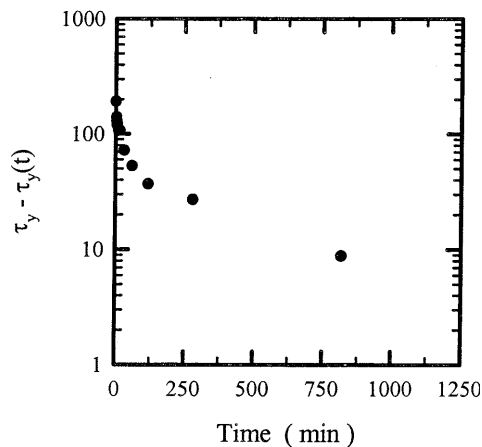


Fig. 5 Example of non-suitability of the Nguyen-Boger recovery model for modeling the recovery behavior of the Na-montmorillonite-based suspensions. Data for a 19.6 vol.% solids suspension are presented

Fitting parameters and discussion of results. Table 2 shows that the time constant, K_r , increases with increasing solids concentration indicating more rapid structure build up with the increase in the number of interacting particles in the system. The rate of increase in K_r with solids concentration is very high above 20 vol.% solids (35 wt%), as illustrated in Fig. 7. This is as expected, given it was assumed that the rate of structure recovery was a function of the concentration of particles available to interact (Eq. 2).

The findings in Table 2 and Fig. 7 are more significant if they are combined with the attempts to measure time dependency in the yield stress at 23.3 vol.% solids (40.1 wt%). At 23.3 vol.% solids, the degree of breakdown and rates of recovery of structure were too small and fast respectively to enable any time dependency to

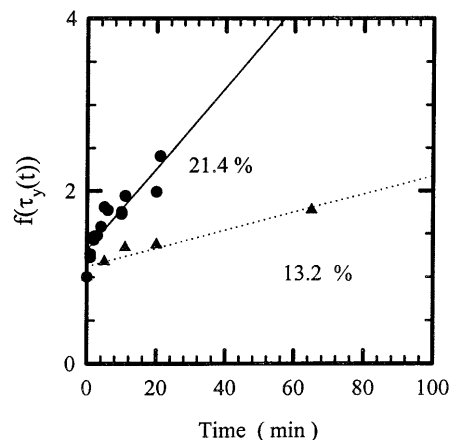


Fig. 6 Examples of the suitability of the Leong recovery model for modeling the recovery behavior of the Na-montmorillonite-based suspensions. Solids concentrations are indicated

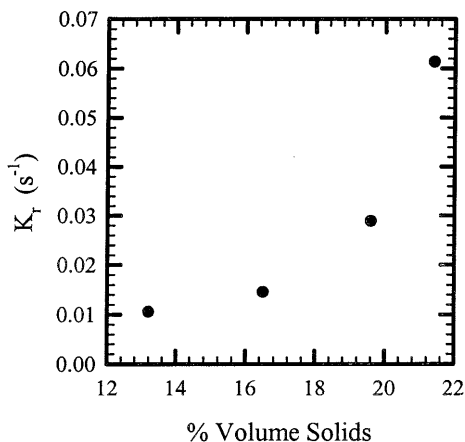
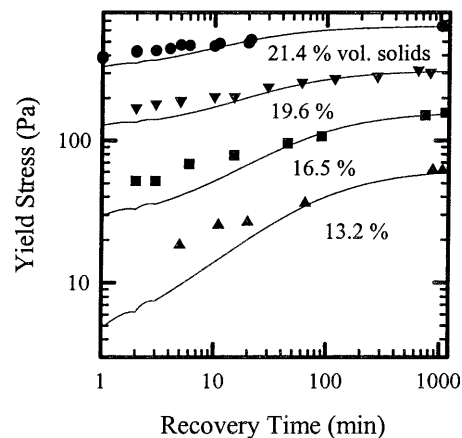
Table 2 Fitting parameters for the Leong model

Solids conc. %	Coal-clay waste	
	$K_r(S^{-1})$	r^2
21.4	0.0613	0.747
19.6	0.0289	0.971
16.5	0.0146	0.999
13.2	0.0106	0.916

be detected. It is apparent that there exists a concentration where, on the time scales of observation, there is a high enough concentration of particles that, on shear, the rate of structure breakage is equaled by the rate of reformation and no lasting structure change occurs.

The experimental and predicted recovery behavior are compared in Fig. 8. It is clear that the Leong model predicts the limiting behavior of the recovered yield stress very well at all solids concentrations investigated. It is observed that there are discrepancies between the model predictions and the real recovery behavior at short times, particularly below 10 min. It appears that for the clay-based suspensions, the second-order recovery kinetics of Smoluchowski-type coagulation, whilst predicting a more rapid structure build up than the first-order Nguyen-Boger model, fail to capture the early-time recovery behavior. It appears there is an additional component to the structural recovery behavior at early time, which may also be linked to the highly anisotropic nature of the shape and charge distribution on clay platelets.

There is clearly further scope for investigation of the recovery kinetics of clay-based suspensions using the Leong model, ideally using a model clay system such as a purified bentonite or a synthetic Laponite. There was

**Fig. 7** Recovery rate constant, K_r , as a function of solids concentration for the Na-montmorillonite-based suspensions**Fig. 8** Comparison of the experimental and Leong model predicted recovery data for the Na-montmorillonite-based suspensions at the solids concentrations indicated. The lines represent the calculated data

no scope for investigation of the effect of temperature on the recovery kinetics in the current work; however validation of the basis of the model requires such deeper investigation into the nature of the rate constant, K_r .

Applicability of model to other thixotropic materials

To illustrate the wide variety of suspensions to which the Leong model is applicable, results of fitting the model to brown coal and bauxite residue recovery data are presented. In each case the values of $\tau_{y\infty}$ were determined as described previously. The bauxite residue data are from Nguyen (1983) and the brown coal data from Leong (1988). The bauxite residue is a highly caustic (pH = 12–13) suspension of primarily iron oxide and alumino-silicate minerals with a particle size of 1–200 μm and average solids density of 3000 kg m^{-3} . The brown coal suspensions had a solids density of 1430 kg m^{-3} and variable surface chemical properties depending on the origins of the coal. The pHs for the brown coal suspensions ranged from 3.6 to 5.0. Note that the Nguyen-Boger recovery model was found to describe adequately the recovery data of the bauxite residue suspensions (Nguyen and Boger 1985b), but was not found to be suitable for the brown coal data (Leong 1988). The experimental data and the fitted Leong recovery model are presented in Figs. 9 and 10 for the brown coal and bauxite residue suspensions respectively.

In all cases, except for the bauxite residue III, the agreement between the experimentally observed and the calculated recovery behavior was very good. A possible reason for the poor fit of the model to the bauxite residue III data is that not enough recovery data at large times were available to obtain a good fit or estimate of the infinite time recovered yield stress, $\tau_{y\infty}$. Note that the

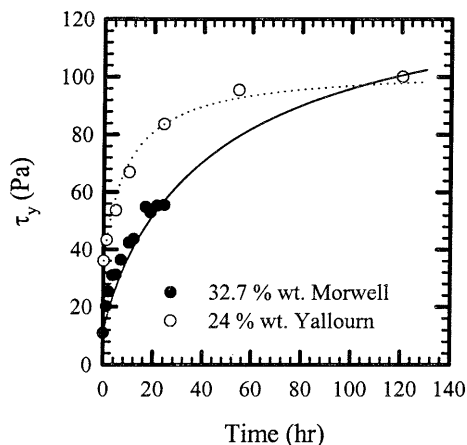


Fig. 9 Comparison of the experimental and Leong model predicted recovery data for the Brown Coal suspensions

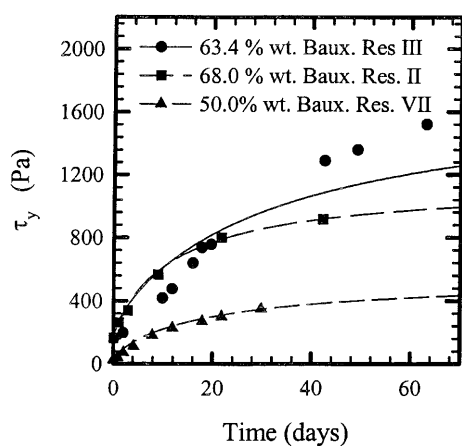


Fig. 10 Comparison of the experimental and Leong model predicted recovery data for the three bauxite residue samples investigated

short term recovery behavior is more effectively described by the model for these materials, lending additional support to the belief that it is the highly anisotropic nature of the clay platelets present in coal tailings that contributes to the observed more rapid short time structure build up. The fitting parameter, k_r , and the regression coefficient, r^2 , for the brown coal and

Table 3 Model fitting data for brown coal and bauxite residue suspensions

Sample	K_r (hr^{-1})	r^2	$\tau_{y\infty}$ (Pa)	wt% solids
Yallourn brown coal	0.0814	0.9901	103.1	24.0
Morwell brown coal	0.0159	0.9862	128.2	32.7
Bauxite residue II	2.317×10^{-3}	0.9977	1144	68.0
Bauxite residue III	8.417×10^{-4}	0.9309	1760	62.4
Bauxite residue VII	1.367×10^{-3}	0.9915	550	50.5

bauxite residue suspensions along with their solids concentrations are presented in Table 3. It is observed that, unlike the clay-based suspensions, k_r shows no trend with solids concentration. Unlike the clay results, however, the brown coal and bauxite residue suspensions are not all of similar surface chemical conditions or particle size distributions (Leong 1988; Nguyen 1983). As a result the expected trend of increasing recovery rate constant with increasing solids concentration is not observed.

Conclusions

A model to describe the recovery behavior of thixotropic suspensions at rest after shearing to equilibrium has been presented. The model has the advantage that it was developed from suspension micro-structural considerations and has been shown to be applicable to a variety of suspensions with a wide range of chemical properties and particle shapes and sizes. The model was applied to the recovery behavior of a number of mineral suspension systems and in each case described the data well. The rapid early time recovery behavior of the clay-based coal tailings was faster than described by the model, possibly due to the highly anisotropic nature of the clay platelets present.

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References

- Bauer WH, Collins EA (1960) Thixotropy and dilatancy. In: Eirich FR (ed) Rheology theory and applications. Academic, NY, vol 4, pp 423–459
- Bird RB, Stewart WE, Lightfoot EN (1960) Transport phenomena. Wiley, NY
- Boger DV, Leong YK, Christie GB, Mainwaring DE (1987) Impact of material properties on the flow behaviour and energy consumption in coal slurry pipelines. In: Chemeca '87, Melbourne, Australia, I Chem E (Aust), pp 1–10
- Broughton G, Squires L (1936) The gelation of bentonite suspensions. J Phys Chem 40:1041–1053
- Cheng DCH (1973) Rheol Acta 12:228
- Cheng DCH (1979) Measurement techniques for thixotropic properties. In: Paper to Joint British, Italian and Netherlands, Society of Rheology, Amsterdam, British Society of Rheology
- de Kretser RG, Scales PJ, Boger D (1997) Improving clay-based tailings disposal:

- a case study on coal tailings. *AIChE J* 43:1894–1903
- Freundlich VH, Bircumshaw LL (1926) Über das Thixotropie Verhalten von Aluminiumhydroxydgelen. *Kolloid Z* 40:19–22
- Freundlich H, Schmidt O, Lindau G (1932) Über die Thixotropie on Bentonit-Suspensionen. *Kolloidchem Beih* 36:43–81
- Hattori K, Izumi K (1982a) A rheological expression of coagulation rate theory. 1. Time dependent viscosity of unagitated suspensions. *J Disp Sci Tech* 3:129–145
- Hattori K, Izumi K (1982b) A rheological expression of coagulation rate theory. 2. Combined effects of shear rate and coagulation rate on viscosity. *J Disp Sci Tech* 3:147–167
- Hattori K, Izumi K (1982c) A rheological expression of coagulation rate theory. 3. Calculation of hysteresis and theoretical summary. *J Disp Sci Tech* 3:169–193
- Khandal RK, Tadros TF (1988) Application of viscoelastic measurement to the investigation of the swelling of Na montmorillonite suspensions. *J Colloid Interface Sci* 125:122–128
- Leong YK (1988) Rheology of modified and unmodified Victorian brown coal suspensions. PhD Thesis, Melbourne University
- Mewis J (1979) Thixotropy – a general review. *J Non-Newtonian Fluid Mech* 6:1–20
- Nguyen QD (1983) Rheology of concentrated bauxite residue suspensions. PhD Thesis, Monash University
- Nguyen QD, Boger D (1985a) Direct yield stress measurement with the vane technique. *J Rheol* 29:335–347
- Nguyen QD, Boger D (1985b) Thixotropic behaviour of concentrated bauxite residue suspensions. *Rheol Acta* 24:427–437
- Nguyen QD, Boger D (1987a) Characterisation of yield stress fluids with concentric cylinder viscometers. *Rheol Acta* 26:508–515
- Nguyen QD, Boger D (1987b) The rheology of concentrated bauxite residue suspensions – a complete story. In: *Proceedings of the International Conference Bauxite Tailings*, Kingston, Jamaica, pp 53–65
- Rand B, Peckenc E, Goodwin JW, Smith RW (1980) Investigations into the existence of edge-face coagulated structures in Na-montmorillonite suspensions. *J Chem Soc Faraday Trans 1* 76:225–235
- Sohm R, Tadros TF (1989) Viscoelastic properties of sodium montmorillonite (Gelwhite H) suspensions. *J Colloid Interface Sci* 132:62–71
- Tadros TF (1990) Use of viscoelastic measurements in studying interactions in concentrated dispersions. *Langmuir* 6:28–35
- Van Kessel T, Blom B (1998) Rheology of cohesive sediments: comparison between a natural and an artificial mud. *J Hydraul Res* 36:591–612
- Van Olphen H (1956) Forces between suspended bentonite particles. *Clays Clay Miner* 4:204–224
- Van Olphen H (1977) *Introduction to clay colloid chemistry*, 2nd edn. Wiley, NY
- Zhang X, Nguyen QD (1994) Characterisation of thixotropic yield stress fluids with concentric cylinder viscometry. In: Halley PJ, Mackay M (eds) *Proceedings of 7th National Conference on Rheology*, Brisbane, Australia, pp 239–242