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Comparison of the rheologies of laterite and goethite suspensions

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Abstract

Comparisons in shear behaviour are made between aqueous suspensions of a laterite ore and aqueous suspensions of pure goethite (α-FeOOH), following prior papers in which the rheologies of the two mineral suspensions were characterized individually. Drawing comparisons is appropriate because the ore sample was about 65% goethite and it was originally thought that the pure goethite might serve as a model of the more complex laterite. Viscosity measurements of the two suspensions show that, at the same solids fraction, the goethite suspensions were more viscous by an order of magnitude, even though the goethite particles had much smaller aspect ratios. Similarly, yield stresses for the goethite suspensions were at least an order of magnitude higher. The most significant difference was in transient behaviour. Time-dependent effects were investigated by subjecting a fluid to a step change or a ramp sequence in shear rate, and measuring the resulting shear stress over time. In most cases, transient behaviour could not be detected in the goethite suspensions, whereas stresses in the laterite suspensions relaxed over periods of order 10 seconds. The disparate results indicate that a goethite suspension is a poor model of a laterite slurry.

Keywords **:** suspension, slurry, mineral, goethite, laterite, model fluid, flocculation, viscosity, yield stress, time dependence

1. Introduction

This paper follows two prior papers on the rheological behaviour of laterite and goethite suspensions. The first paper - Blakey and James (2003), denoted A hereafter - described the shear rheology of suspensions of a laterite ore from New Caledonia (a mixture of limonitic and saprolitic laterite ores provided by the International Nickel Co.). Laterites contain the worlds largest resources of nickel and cobalt, and, when processed to extract these metals hydrometallurgically, the ore is prepared in slurry form. Laterite slurries flocculate and their flow characteristics are complex, at least at the concentrations required for the extraction process. Because the major component of laterite is goethite, suspensions of pure goethite were investigated in order to understand flow behaviour with a simpler but similar material. The results of this work were reported in the second paper - Blakey and James (2003), denoted B. But the two fluids were not compared directly in the latter work, and that is the subject of the present paper.

In A, steady and unsteady shear measurements were reported for laterite suspensions having various concentrations. The research focused on time dependency because this aspect of viscometric behaviour had not been characterized before for lateriate slurries, even though time dependency had been observed and even though it is important industrially - in transport, mixing, heating, and in the choice of process equipment. The concentration range of the laterite slurries was 0.06 to 0.18 by volume, which covers the range of concentrations in the extraction process. Two types of unsteady measurements were carried out: first, a step down in shear rate, from 1000 s^{-1} to a desired lower steady rate; secondly, a three-ramp sequence in shear rate, specifically linear ramps from 1000 to 0 to 1000 and back to 0 s^{-1}. Data from these transient tests show that laterite slurries display both stress relaxation and yield behaviour. The values of yield stress were found to be consistent with values for similar ore slurries in the same concentration range. Relaxation behaviour was characterized in terms of a Maxwell-type relaxation time, which was found to be of order 10 seconds. This finding cannot be related to prior work, however, because the relaxation time has not been determined before. A constitutive model was sought for the laterite suspensions, and the Bingham-Maxwell equation was found to yield reasonably accurate curves for the ramp sequences. This model, the simplest one incorporating both a relaxation time and a yield stress, has been proposed and discussed before, as in Lataillade *et al.* (1980), but never before tested against actual data.

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In the second paper (B), the pure goethite particles (from Elementis Pigments Inc.) were synthetic and more uniform in size and shape than the natural goethite particles in the laterite suspensions. Like the laterite slurries, the goethite suspensions flocculated and in B it is shown that the degree of flocculation correlated with viscosity. Because of this observed relationship involving flocculation, the research on goethite focused on particle surface phenomena. To that end, the pH was varied and various amounts of sodium chloride concentration were added. It was found that the viscosity depended significantly on pH but not on ionic strength, at least not in the range of 0.001 to 0.1 M. The viscometric data in B show that these fluids possess yield behaviour, but, unlike the laterite systems, they exhibited almost no relaxation behaviour.

The two prior papers were submitted separately because the flow characteristics of the two suspensions were found to be significantly different and because the papers had different emphases, with A focusing on transient behaviour and B focusing on interfacial phenomena. Because each paper was considered to be independent, no effort was made to compare the two rheologies. But a proper comparison is warranted because both suspensions consisted of goethite-dominant materials and because it was originally hoped that a suspension of goethite might be a model of a laterite slurry. Hence this paper will explore similarities in rheological behaviour. The comparison, while valuable in its own right, will primarily serve as a case study of model systems, i.e., in this case, how well does the model system relate to the more complex system it represents?

Investigating the rheology of a complex fluid by using simpler fluid model is a reasonable approach and offers advantages; namely, characterizations of the microstructure and interfacial interactions are easier to carry out, and mathematical modeling of the rheology is generally simpler. This approach has been used by many investigators. Weiss and McClements (2000), for instance, studied an emulsion of purified hydrocarbon oil in water as a model fluid for a variety of complex emulsion-based materials, such as foods, cosmetics, petrochemicals and pharmaceuticals. Another group, Rodriguez Nino *et al.* (1996), investigated the viscoelastic properties of monostearin and monoolein films that were prepared as models of "complex, real food formulations". Also, Green and Boger (1997) studied the compressive yield stress of concentrated suspensions of zirconia and alumina, because they were considered to be models of the industrial suspensions found, for example, in ceramics manufacturing and mineral processing. In most studies, however, the results obtained for the model fluids were not related to those for the complex ones, and so it is not certain that a better understanding of the complex systems was in fact achieved. The purpose of this work, then, is to compare as directly as possible the rheology of a model system and its complex counterpart, specifically, to compare goethite suspensions with laterite slurries.

2. Flocculation

Before presenting data for the two fluids together, it may be useful to say more about flocculation and how the two fluids are similar in this way. When each is viewed through an optical microscope, one sees fuzzy lumps of various sizes, which are loosely connected. Such images have been presented in Fig. 2 of A and in Chapter 6 of Blakey (2002) for laterite, and for goethite in Fig. 5 of B and in Chapter 7 of Blakey. At a finer scale, aggregates can be seen in both fluids. Fig. 1 is an image, obtained by transmission electron microscopy, of laterite particles from a highly

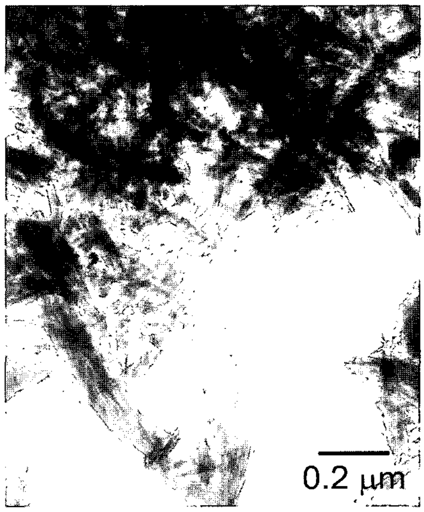

Fig. 1. A transmission electron micrograph of goethite particles in a laterite ore sample.

Fig. 2. A transmission electron micrograph of the pure synthetic goethite particles.

diluted suspension. The spindly particles seen there are goethite particles, and orientations of clusters of particles appear to be random. Measurements of particle size from such micrographs indicate that the average length of the goethite particles was about 0.3 μm and that the aspect ratio was about 15, similar to what Krause *et al.* (1998) found for another laterite ore obtained from the same geographical region. Fig. 2 is an electron micrograph of goethite particles, also from a highly diluted suspension. These particles are stubby by comparison their aspect ratio is close to three - and they are more uniform in size and shape. Here the individual particles are randomly oriented. Data presented in B support the view that the goethite particles aggregate because of both van der Waals forces and attractive electrostatic forces. Electrostatic attraction is possible because of the atomic structure at the surface of crystalline goethite; that is, it was found that the different facets of the crystal may have different charges, to the extent that some facets may be positively charged and some negatively charged. A study with small charged latex particles appears to confirm that different facets can have different charges. With positive charges in some regions and negative charges in others, it is possible for particles to join and form structures, such as those seen in the images.

3. Viscometry

The instrumentation and procedures by which the rheological data were obtained are described in A and B and in more detail in Blakey (2002). The rheometer was a Haake RV30 viscometer with a Couette fixture, an instrument capable of generating step changes and ramp sequences in shear rate, in addition to normal steady shear rates. This rheometer cannot measure G' or G", the usual properties to characterize the dynamic response of a fluid. But these properties are not the most relevant ones for these suspensions anyway. In the first place, relaxation time scales were found to be of order 10 seconds; thus the associated frequency is of order 0.1 s^{-1}, which is a regime where dynamic measurements are impossible or difficult because the stresses are so low. Secondly, dynamic measurements are made about the rest state, which is not a state associated with transport. That is, it is more appropriate to make measurements at shear rates relevant to transport processes, i.e., in the range of 100 to 1000 s^{-1}. This was the range in A and B. And finally, the particles in these suspensions settled, and it was found that the rate of settling decreased with increasing shear rate. Hence our step and ramp tests were carried out well away from the rest state. In fact both types of tests were started at the maximum available shear rate of 1000 s^{-1}. In this way, settling was minimized. Moreover, its influence was straightforwardly taken into account in the test protocol of A. Settling was also the reason a Couette fixture was used in the rheometer.

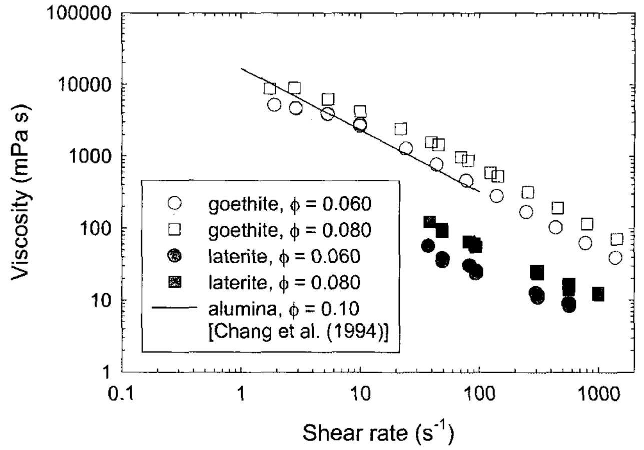

Fig. 3. The viscosity of laterite and goethite suspensions, at the same solid volume fractions. The data of Chang *et al.* (1994) for alumina are included for comparison.

With cone-and-plate fixtures, a particle-free zone quickly forms on top of the fluid, next to the cone, so that the shear rate in the sample is no longer uniform. With a Couette fixture, the stress is measured on a surface perpendicular to the direction of gravity, and so the influence of gravity is much less.

4. Viscosity

Steady-state viscosity measurements are presented in A for laterite and in B for goethite. The only two solid volume fractions in common were 0.06 and 0.08, and the data for those concentrations are presented together in Fig. 3. Plotted along with our results are the data of Chang *et al.* (1994) for an alumina suspension with a solid volume fraction of 0.1, the closest fluid in the literature to our two. Our data are consistent with their data, both quantitatively and qualitatively, which is reassuring. Perhaps the most notable feature of the graph is that the viscosity of a goethite suspension is about ten times that of a laterite suspension at the same concentration. This finding may be unexpected in view of the higher aspect ratio for laterite particles, but that expectation is based on particle hydrodynamics, which plays only a minor role in these dilute suspensions. Shear-thinning behaviour appears to be the same for the two types of fluid. Shear thinning is normally more pronounced as the aspect ratio increases, but for these flocculated systems it likely depends on the breakdown of floc structures.

5. Yield stresses

Mineral slurries have usually been characterized in terms of yield stress, as opposed to viscosity, partly because yield behaviour is usually observed and partly because yield stress is the crucial fluid property in the handling of tailings

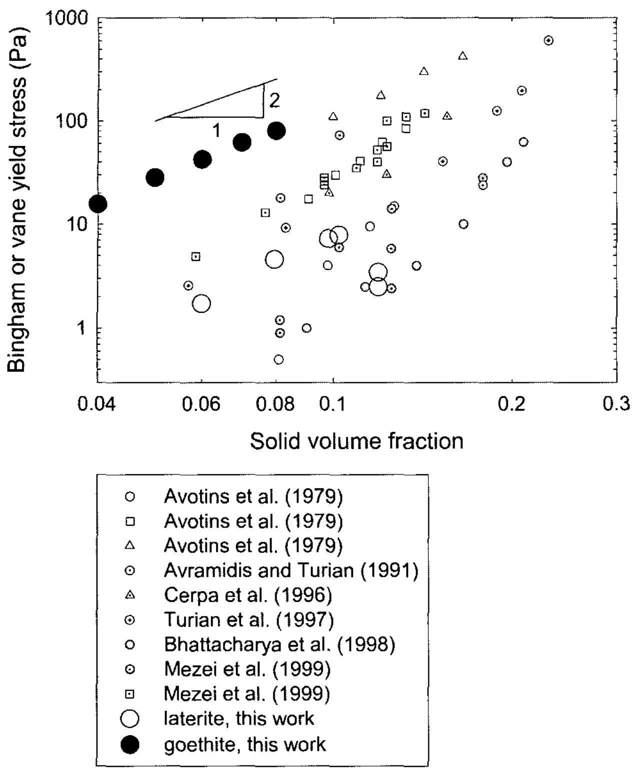

Fig. 4. Yield stresses for laterite and goethite suspensions, in the context of prior values for other goethite-dominant mineral suspensions.

pastes. In these pastes, the concentration of solids is generally around 0.5 by volume, a range where yield behaviour is expected and a range much above the present one. Nevertheless, yield behaviour was observed in our laterite and goethite systems, even for solid volume fractions below 0.1. The yield stresses of the two systems are compared in Fig. 4, and, to put these data in context, they are plotted along with all relevant yield stress values from the literature. Our laterite values fall in the middle of the previous laterite data, even though the dependence on concentration is peculiar.

As explained in A, yield stresses for the laterite suspensions were determined from fits of the Bingham-Maxwell equation to ramp data (the equation contains the yield stress τ_y and will written out later), while goethite values were found by extrapolation of shear stress data to zero shear rate, as described in B. The different methods of obtaining the yield stress do not account for the large difference in values in Fig. 4; in fact, the two sets of values appear to be unrelated. In addition to differing by more than an order of magnitude, the yield stress for the laterite suspensions was detectable only over a narrow range in concentration, while the stress for the goethite suspensions increases approximately with the square of the solid volume fraction, which is the normal pattern for mineral slurries. While our two sets of data are consistent with prior data, the differences between the two sets are so significant that one fluid does not appear to be related to the other.

6. Time dependence

Some of the investigators whose data are plotted in Fig. 4 noted transient effects in their rheological measurements, and some describe the effects in detail. But none clearly described how they obtained their reported steady-state values when transients effects were present. Knowledge of transient effects is crucial in design when the characteristic time of the fluid exceeds the characteristic time of the flow. For example, when a fluid experiences high shear rates in a pump and then lower rates downstream, or when the shear rate in a pipeline increases because of a reduction in pipe size, transient effects determine flow resistance for some distance downstream and so must be taken into account. This is particularly true for the present laterite suspensions, first because their characteristic times were found in A to be of order 10 seconds, while changes in shear rate in a pipeline typically occur in less than a second, and secondly because the fluids are significantly shear-thinning. Hence, when there is a change in shear rate, the long memory time causes the transition zone to extend many diameters downstream.

A prior study which showed transient effects, but for a different material, is that by Kanai and Amari (1986) for a suspension of maghemite in mineral oil. Their results, of shear stress response to steps down in shear rate, are plotted in Fig. 4 of their 1986 paper. The weight concentration of the mineral was 33%, which translates to a solid volume fraction of about 0.1 and therefore makes the fluid comparable with the present suspensions. As seen in their figure, for a small step down in shear rate, e.g. from 300 to 100 s^{-1}, the stress drops immediately to its new value; but when the step is large, e.g. 300 to 10 s^{-1}, the time to reach the new steady state stress can take many minutes. Long-term memory like this of a former stress can affect the performance of a transport system.

The study of time dependence in our prior papers shows that transient effects were significant for laterite suspensions but not for goethite suspensions. Step tests in shear rate, similar to those done by Kanai and Amari, were carried out for both sets of suspensions, and comparisons of the responses are now made in two ways. First, results for suspensions at the same solids volume fraction are contrasted in Fig. 5, with lines representing the data. The common concentration is 0.06 and the shear rate changed from 1000 to 100 s^{-1}. The plot shows no transient effect for either fluid. But the initial shear stress levels are so different that one wonders whether the basis of comparison is the most suitable one. An equally appropriate basis, perhaps, is that the two suspensions have the same initial stress, say at 1000 s^{-1}. A number of such comparisons

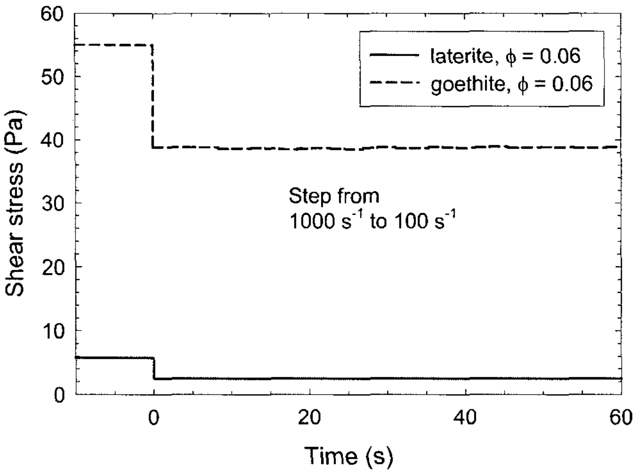

Fig. 5. Shear stress histories following a step down in shear rate from 1000 to 100 s^{-1}, for a laterite and goethite suspension each having the same solid volume fraction of 0.06.

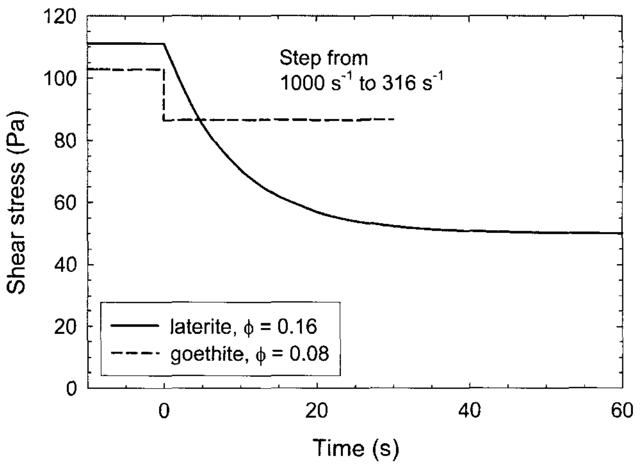

Fig. 6. Shear stress histories following a step down in shear rate from 1000 to 316 s^{-1}, for a laterite and goethite suspension each having about the same initial shear stress.

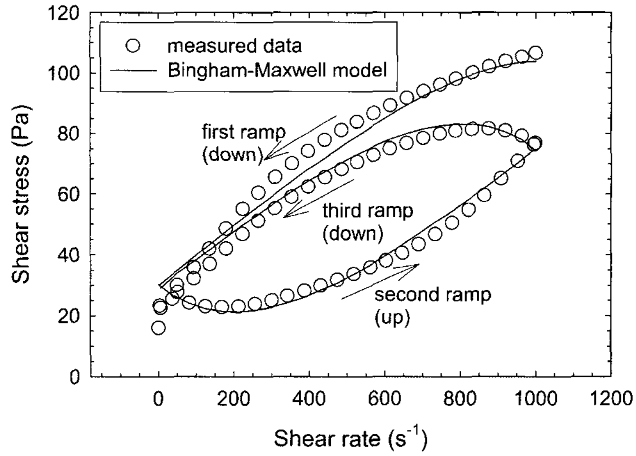

Fig. 7. Shear stress response to a three-stage ramp sequence in shear rate, for a laterite suspension with a solid volume fraction of 0.16. The curves are solutions of the Bingham-Maxwell equation, with parameters chosen to obtain best fits of the curves to the data.

could be made from the data available, but the most similar initial stresses were found to be those when the goethite concentration was 0.08 and the laterite concentration was 0.16. The comparison is presented in Fig. 6. As the figure shows, the initial stresses were not equal but they were close enough for the present purpose and, on this basis, there is a clear difference in the two systems, i.e., the plot indicates time dependency for the laterite suspension but not for the goethite one. This transient behaviour, for the laterite suspensions only, was more firmly established by the other type of unsteady test, the ramp sequence.

Ramp tests were conducted for laterite suspensions ranging in concentration from 0.06 to 0.18, and a typical set of results is presented in Fig. 7. The plot shows the three-stage sequence described earlier in which the shear rate was initially steady at 1000 s^{-1}, declined to zero, then went up to 1000 s^{-1}, and finally down again to zero. The time for each stage was two minutes, so that the ramp sequence took six minutes in all; this time period was used because it was found to be optimal for exposing the transient nature of the fluids. Also shown in Fig. 7 are curves from the Maxwell-Bingham equation. This equation gives shear stress as a function of time and shear rate,

$$\lambda\frac{\partial\tau}{\partial t}+\tau=\tau_y+\eta_B\dot{\gamma}$$

and it incorporates three fluid properties: the yield stress τ_y, the relaxation time λ, and the Bingham viscosity η_B. This equation was solved analytically for the specified ramp sequence, and the three parameters in the equation - τ_y, λ and η_B - were chosen to obtain best fits of the analytical curves to the data. The figure shows that this equation, the simplest one combining a yield stress and a relaxation time, fits the data reasonably well, and similar fits were obtained at other concentrations. The values of τ_y obtained in this way are the ones which appear in Fig. 4. The values of λ obtained in this way are plotted in Fig. 8, along with values for the goethite suspensions. Since no transient effects were detectable for the latter fluids - at least none below two seconds which is the limit of the present instrument - the relaxation times for these fluids were taken to be zero and plotted as such. The graph indicates that relaxation times for the two systems are not actually inconsistent. However, not much should be read into this because consistency is easily achieved when the values are zero, and the region of overlap is small. In hindsight, it would have been worthwhile to check transient effects for goethite suspensions having concentrations higher than 0.08, but the viscosity at 0.08 was already well above the

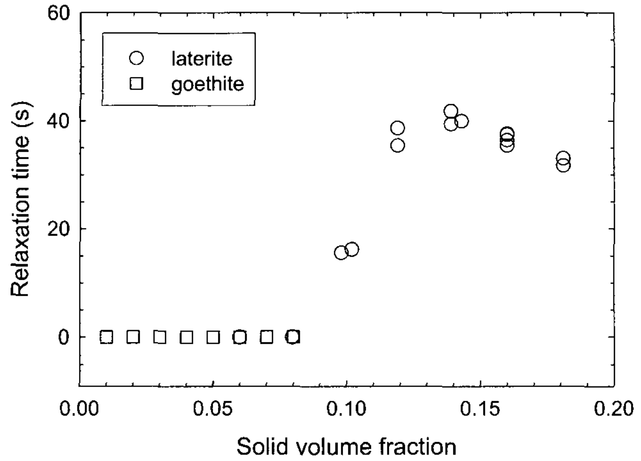

Fig. 8. Relaxation times for laterite and goethite suspensions.

viscosity range of the companion laterite suspensions and so higher concentrations were not considered.

7. Conclusions

The comparisons in this work show distinct differences in the rheology of laterite and goethite suspensions. At the same solids volume concentration, the goethite suspensions are much more viscous and have much higher yield stresses, despite the goethite particles having smaller aspect ratios. The most positive statement one can make is that the two systems appear to be qualitatively similar, in Fig. 3, in their steady viscous behaviour. But no similarities appear when it comes to stress relaxation. That is, there is essentially no transient behaviour in the goethite suspensions, on the basis either of the same solid fraction or at the same stress level, while the laterite suspensions are markedly viscoelastic, with relaxation times of order 10 seconds.

At the beginning, it was stated that the primary objective was to judge the suitability of goethite suspensions as model fluids for laterite slurries. From the summary in the paragraph above, the answer seems to be that goethite does not provide a good model because of both qualitative and quantitative differences. The simpler, better-defined goethite system was useful, however, for understanding some aspects of flocculation. Because the goethite particles were pure and approximately uniform in size and shape, tests on these particles were straightforward to perform and interpret, which would not have been the case with the diverse particles in the laterite slurries. While the simpler system may help one to understand some physical aspects of the complex system, such as flocculation, it cannot be used to simulate it.

The comparisons in this work have been based almost entirely on the same solid volume fraction, which seems the most logical approach. The only other possible basis is the same volume fraction of goethite particles. Since the laterite sample was about 65% wt. goethite, this basis would cause a reduction in solid volume fraction values for laterite by about 35%. This reduction would bring the two sets of data in Fig. 4 closer together, for example, but yield stresses would continue to differ significantly, by almost an order of magnitude. Even with this different basis, the conclusions would not change.

8. Remaining questions

While this work shows that pure goethite is hardly a substitute for laterite, vis-à-vis rheology, other questions need to be answered, and some of these are actually more fundamental. Perhaps the most important one is a physical explanation of the high viscosities at low solids content. The explanation does not lie in hydrodynamic effects because solid volume fractions are of order 0.1 and aspect ratios are no more than 15.

The large resistance has been shown to be related to particle aggregation, through the correlation of viscosity with flocculation (in paper B), but it is not known how flocculation *per se* causes so much flow resistance. Perhaps each floc traps considerable water, enough that there is minimal free water between flocs and then the suspension is effectively a highly-concentrated one. In this way, the virtual solid volume fraction approaches the maximum packing fraction, and then, as is well known, the viscosity may be orders of magnitude above that for the suspending fluid. Such structures may be broken by shear, releasing water and thereby reducing the viscosity. Certainly the shear-thinning behaviour can be explained in this way. But a proper explanation requires a fundamental study of floc structure under shear.

A final concern pertains to yield stresses for the laterite slurries. The pattern for the goethite suspensions follows the usual strong dependence on volume fraction. But yield behaviour for the laterite occurred only for a limited range in volume fraction. This dependence is unlike any other for a goethite-dominated material, as Fig. 4 shows, and defies explanation. This question too deserves investigation and the answer may depend on the method used to determine the steady-state value of the yield stress.

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