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Compressive rheology of aggregated particulate suspensions

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Abstract

The measurement of the compressional rheological parameters for an aggregated particulate suspension is described. The parameters include the compressive yield stress and hindered settling function, describing the extent and rate of dewatering respectively. The variation of these parameters with shear rate and time of shear is also considered in the light of their sensitivity to low shear rates, with particular reference to the case of flocculated particulate suspensions. The latter is seen to be important in the future development of a comprehensive understanding of compressive rheology of aggregated particulate suspensions in industrial applications such as thickening, filtration and centrifugation.

Keywords : compressive rheology, permeability, yield stress, particulate suspension, shear

1. Introduction

Aggregated particulate suspensions are common to a wide range of industrial processing operations and the efficient removal and subsequent recovery of fluid (water) from these suspensions is an increasingly important problem. Typical processes include the thickening of mineral slurries for disposal to tailings dams or for paste backfill into mines, the filtration and centrifugation of biological wastes in the food, domestic waste water and dairy industries and the sedimentation or clarification of water for potable water production. Although not a comprehensive list, these processes in themselves represent a vast array of particulate materials and operational conditions.

Common to all of the above listed separation processes is the use of flocculants and coagulants to aggregate the fine particulates in the suspension and enhance the rate of dewatering. In gravity driven processes, this can manifest as an enhanced sedimentation rate and in the case of filtration and centrifugation, provide an improvement to the permeability of the particulate 'cake' formed during the process. In each case, the kinetic enhancement is usually at the expense of the ultimate solids that can be achieved in compression, although the reduction in ultimate solids is often small. In understanding this behaviour and the role of the flocculant, removal of water from the suspension can be divided into two operational modes, where the solids concentration is either above or below the gel point of the aggregated suspension, these conditions equating to networked and non-networked particulate conditions respectively. It is the behaviour of networked and un-networked suspensions of aggregated particles in both compression and a combination of compression and shear that is of interest here.

Compressional rheology involves the removal of a fluid (usually water) from a suspension and it is common to think of this process solely as a network failure problem. This provides a simple analogy to the measurement of the shear yield stress of a concentrated aggregated suspension (Nguyen and Boger, 1985), where the failure in shear is distinct from failure in compression, which is of interest here. Indeed, studies of coagulated suspensions show that up to a concentration approaching 40 v/v % solids, the ratio of the shear to compressive yield stress for a range of colloidal metal oxide suspensions is a constant (Zhou *et al.*, 2001). Given the wealth of information available on the shear yield stress behaviour of concentrated flocculated suspensions (Zhou *et al.*, 2001; Johnson *et al.*, 2000), this aspect of compressional rheology is well established, albeit with sparser data in the area of compression measurement.

However, the view of compressional rheology as simply a network failure issue is far too narrow and the kinetics of fluid removal from both networked and un-networked particulate suspensions also goes into a comprehensive definition of compressional rheology. This definition is based on the original work of Buscall and White, who established a continuum theory of compressional rheology for aggregated particulate suspensions (Buscall and White, 1987). The theory used two rheological parameters, namely the compressive yield stress (nominally the strength of the particulate network) and hindered settling factor (nominally

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the interphase drag or rate of fluid expression) as material property descriptors of particulate suspensions in compression. The two parameters have now been incorporated into a range of phenomenological device models, including thickeners, filters and centrifuges (Landman *et al.*, 1988; 1991; Stickland *et al.*, 2006; Usher and Scales, 2005; Stickland *et al.*, 2006). A recent review provides an overview of the development of the 'Buscall and White' compressional rheological parameters and both the comparison of these parameters to other descriptors and their utilisation in a range of applications involving fluid removal from suspensions (de Kretser *et al.*, 2003).

Although a macroscopic behavioural parameter set, compressional rheological parameters can be utilised in the same way as shear rheological parameters to infer microscopic trends associated with aggregate strength and network porosity. To this end, a large volume of high molecular weight polymeric flocculant is used annually in the dewatering of fine particulate aqueous slurries. The most common process involves the adsorption of a polymeric flocculant to the surface of fine particles in a stirred/mixed suspension or in a pipe at a low solids concentration. This produces an aggregated suspension of particles that nominally settle and dewater faster. A large amount of information is known about the inter-relationship between the applied shear, the type and concentration of flocculant and aggregate formation (Swift *et al.*, 2004; Heath *et al.*, 2006) but there is little quantification of the relationship between aggregate structure and dewatering. This type of information is critical to the selection of flocculants in dewatering devices such as thickeners and filters since it is not only the size and settling rate of aggregates that is important to the prediction of performance but also the response of these aggregates to shear and compressional forces.

Establishing a robust correlation between aggregate structure and dewatering behaviour using compressional rheological parameters is difficult as both parameters are non-linear functions of solids concentration and vary depending on the type of solid particles, flocculant type and concentration, aggregate formation conditions and post formation shear conditions. Based on this information, it is clearly not a straight-forward process to quantify the relationship between aggregate structure and compressional rheology since there is a wide range of variables to consider. This is even the case in apparently simple examples where for instance, it is decided to characterise a given particulate suspension using a specific flocculant at a fixed flocculant dose. For the case where both compressional rheological parameters are changing at once, the optimum fluid removal scenario is not obvious and the correct choice of flocculant and dose and aggregate formation process may indeed depend on the application and solids concentration range of operation. Our attempts to make these comparisons to date are best described as academic, especially if one considers the needs of operational personnel attempting to optimise process devices such as thickeners (Harbour *et al.*, 2004).

Recent work has shown that it is now possible to extract quantitative hindered settling function and compressive yield stress information across a range of solids concentrations from a combination of simple batch settling and filtration tests (Abd Aziz *et al.*, 2000; de Kretser *et al.*, 2001; Usher *et al.*, 2001; Lester *et al.*, 2005). Using these parameters as inputs to predictive models then allows quantification of dewatering in terms of throughput in industrial processes and by implication, quantification of the role of aggregate structure on dewatering. Current practice in our laboratories is to characterise dewatering performance through floc settling (via free settling and final sediment height measurements) and pressure filtration tests. Industrial practice typically uses only one of these tests and as such, the industrial tests provide data for only a small range of the total solids regime of relevance to dewatering and do not allow predictive modelling. The role of aggregate properties in controlling these processes is by inference, poorly established as a result.

In addition to the rather recent development of systematic and comprehensive characterisation techniques, anecdotal evidence is that the settling behaviour of flocculated aggregates is changed dramatically in the presence of shear. Observed effects include a strong dependence of the flocculant concentration and mode of aggregate formation on shear sensitivity and a shear sensitive transition from beneficial to detrimental dewatering behaviour. It is the latter observation that is of particular interest since it invokes the concept that there is a force balance between break-up and densification in flocculated aggregates. This observation has been reported for other aggregate systems (Mills *et al.*, 1991).

In terms of compressional rheology parameters, the anecdotal evidence implies that shear processes in compression can induce a change in aggregate material properties that are not simply a higher solids manifestation of the properties of the same material but those of a 'new' material. The analogy here is to shear history sensitivity in shear rheology measurements of particulate slurries, a notoriously difficult phenomenon to quantify. Indeed, the use of cross plots of shear rate and time is usually required to quantify the behaviour across a broad range of conditions. The same type of approach is required for characterising the compressional rheology of aggregated suspensions in shear.

Therefore, the key research question that arises from this analysis is whether quantitative compressional rheological analysis, when combined with process models, can establish the best aggregate formation route for a given process. As an example, the question arises in batch settling and thickening operations as to whether it is more fruitful to build a dense and robust aggregate through repeated breakage and reformation under high shear conditions (typical of the thickener feedwell) or build an open and weak aggregate that can subsequently be easily densified even when subjected to very low shear conditions. In fractal terms, one might expect the former scenario to produce aggregates that are highly fractal and of a fractal dimension well beyond the limit of reaction limited aggregation but well below that achieved through pelletization. In the case of pelletization, the fractal nature of the resultant aggregate is debateable (Walaszek and Ay, 2005). On the other hand, densification of weak aggregates may well produce aggregate densities more akin to pelletization. The obvious risk in the second case is that the initial aggregate will exhibit poor robustness in a process sense and be susceptible to shear disintegration. The continuous addition of binder in the pelletization process overcomes this issue but this option is not available to most dewatering operations, where only a single point of flocculant addition is available.

The aim of this work is to appraise techniques that can be used to provide a quantitative assessment of the relationship between compressional rheology and aggregate structure, both in the presence and absence of shear. This requires that we can measure the compressional rheological parameters accurately under a range of conditions and further, that aggregate size and density can also be quantified. The shear sensitivity of flocculated aggregates makes this assessment particularly difficult. Despite this fact, we report herein a number of aggregation states that have been examined for a given dose of polymer flocculant at fixed aggregate formation conditions. It is acknowledged that this in itself represents only one point in a large matrix of possible tests but it is hoped that it will at least demonstrate the importance of comprehensive quantification of rheological parameters if our knowledge of these phenomena is to be enhanced.

2. Experimental methods

An industrial calcite sample (Omyacarb-10) was chosen for this work with an average size of 10 microns. The flocculant was a high molecular weight polyacrylamide-acrylate copolymer (AN934SH) from SNF. All water for flocculant makeup was from a Milli-Q system. A 0.1% by weight polymer solution was made up by adding dry polymer powder to the vortex of a stirred solution followed by high speed mixing for one hour. The solution was then mixed on an end over end mixer for twelve hours. The solution was then rested for a further twelve hours prior to use. All polymer solutions were used 24-48 hours after make up. Suspensions were diluted in tap water. The particulate suspensions were flocculated in a linear pipe reactor of length 1.8 m and 12.5 mm internal diameter at a flow rate of 6.1 litres min^{-1} giving a residence time of 2.2 seconds (Swift *et al.*, 2004). The flocculated output of the pipe reactor was fed directly to a measuring cylinder. A shear rate of 875 s^{-1} was calculated for the flocculation event based on a mean energy dissipation.

The compressional rheological behaviour of suspensions was measured using a combination of sedimentation and filtration techniques since there is no single technique that covers the required broad particle concentration range. Filtration was used to establish suspension compressive and hindered settling behaviour in the 10-300 kPa pressure range using an automated filter technique (de Kretser *et al.*, 2001), using the rig shown in Fig. 1. Low solids hindered settling information was determined from sedimentation

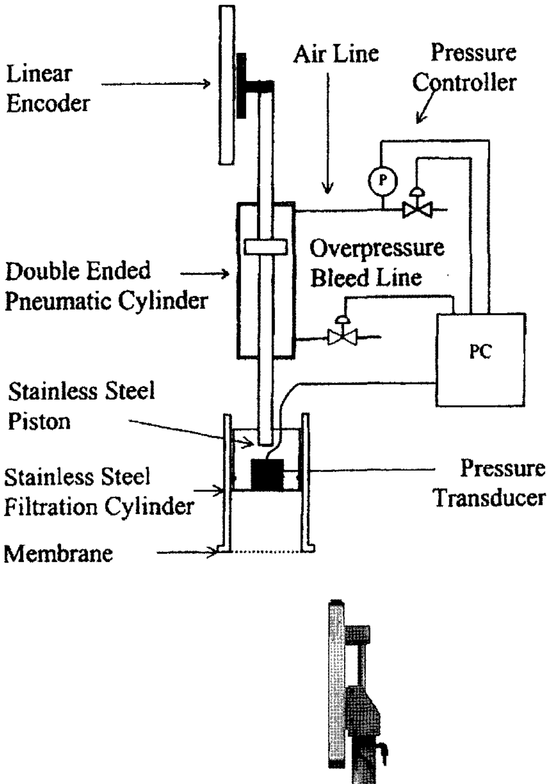

Fig. 1. Pneumatic piston driven pressure filtration apparatus.

tests in a 500 cm^3 measuring cylinder. The height of the settling interface was recorded for a period of two hours and the data, along with information on the initial solids concentration was analysed, using an analytical technique for the extraction of hindered settling function data (Lester *et al.*, 2005). The analysis also used the filtration data. Using a combination of sedimentation and filtration, a comprehensive compressional rheological characterisation was completed. This is now a generic approach for analysis of the compresional rheology of aggregated particulate suspensions.

Settling data was also obtained in the presence of shear using a couette shear cell in which an inner Perspex cylinder was rotated in a 12 cm diameter settling cylinder. Calculations showed the shear rate to be in the range 0-10 s^{-1} for a rotation rate of 0-10 rpm. Analysis of the data used the same method as for the un-sheared case in the 500 cm^3 cylinder. Additional data was obtained using a fluidised cell without mechanical shear. Data was obtained for a range of flocculant addition rates from 0-60 grams of flocculant per tonne of solid (0-60 g/g of solid). Flocculation was performed at a solids concentration of 10 w/w %.

3. Results and discussion

Calcium carbonate samples were flocculated in a pipe reactor under controlled conditions, with the main variable being the dose of flocculant utilised. This had the effect of increasing the size and free settling rate of the flocs with increasing dose, as shown by the settling data in Fig. 2. Compressive and hindered settling data for these flocculated calcium carbonate suspensions at a range of flocculant doses are shown in Figs. 3 and 4 respectively. The hindered settling function is observed to be both a strong function of solids concentration and improves (goes to lower values) with increasing flocculant dose. This is consistent with observations that the settling behaviour of aggregates generally improves with increasing flocculant dose, assuming flocculation conditions (mixing and time) are held constant. The compressive yield stress of the material (Fig. 3) is observed to also be a strong function of solids concentration but shows only a weak response to flocculant dose. The compressive yield stress data is a

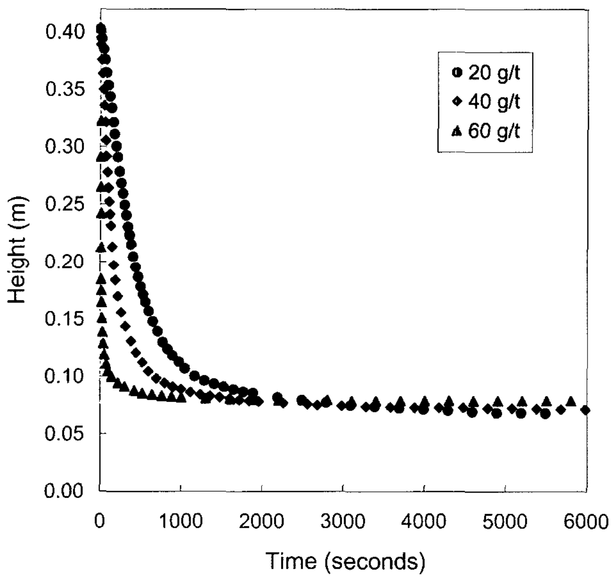

Fig. 2. Transient settling data for a calcium carbonate sample as a function of flocculant dose.

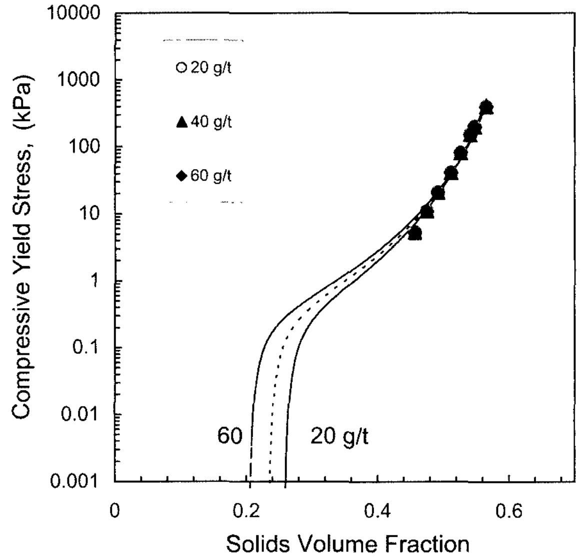

Fig. 3. Compressive yield stress versus solids volume fraction for a calcium carbonate sample as a function of flocculant dose.

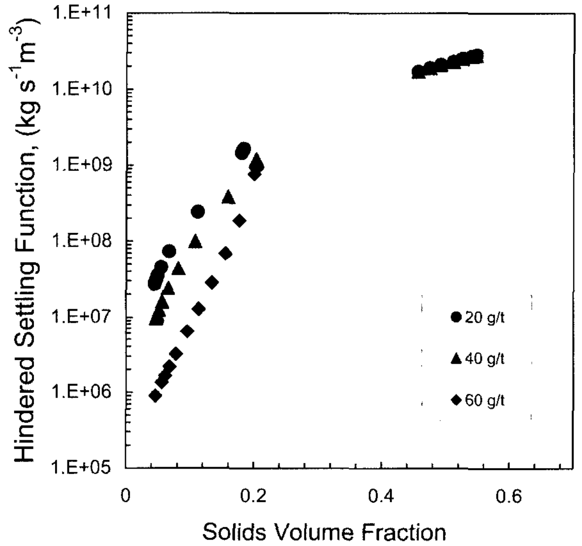

Fig. 4. Hindered settling function versus solids volume fraction for a calcium carbonate sample as a function of flocculant dose.

combination of experimental data from filtration testing (solid points) and a fitted curve that utilises the final settled height in sedimentation.

An estimate of the compressive yield stress at solids concentrations close to the gel point (concentration at which the aggregates first form a percolating network that can transmit stress) can be obtained from finding the solids concentration of a networked bed of particles in the limit of zero bed height. Alternatively, a value of the compressive yield stress near the gel point can be obtained from estimation of the solids pressure based on the average solids concentration in the settled aggregate bed. The latter method extracts data in-situ, without further manipulation of the aggregate structure and is the preferred methodology. A curve is then fitted to the batch settling point and the filtration data. The functional form chosen has been shown to be representative of a wide range of flocculated materials, the details of which are given elsewhere (Usher and Scales, 2005). If anything, the compressive yield stress moves to lower solids (to the left) as flocculant dose increases. This is consistent with the concept that the role of the flocculant is to strengthen the aggregate and that improvements in aggregate strength (at constant aggregate density) will manifest as an increase in the compressive yield stress at a given solids concentration.

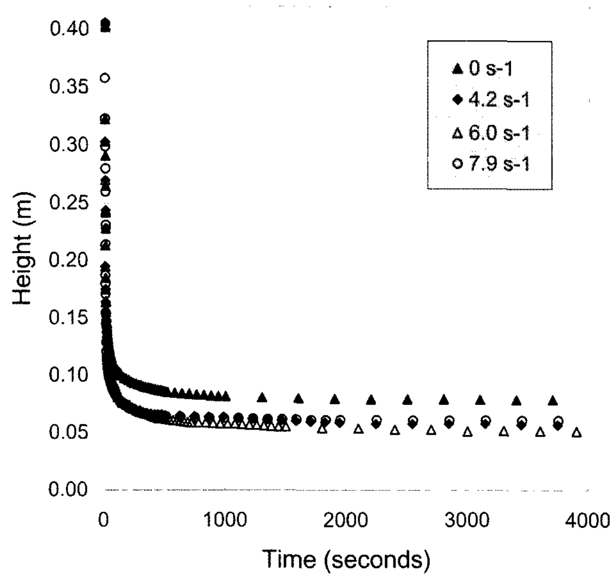

Fig. 5. Transient settling data for a flocculated calcium carbonate sample as a function of post formation shear rate. Flocculant dose was 60 g/t.

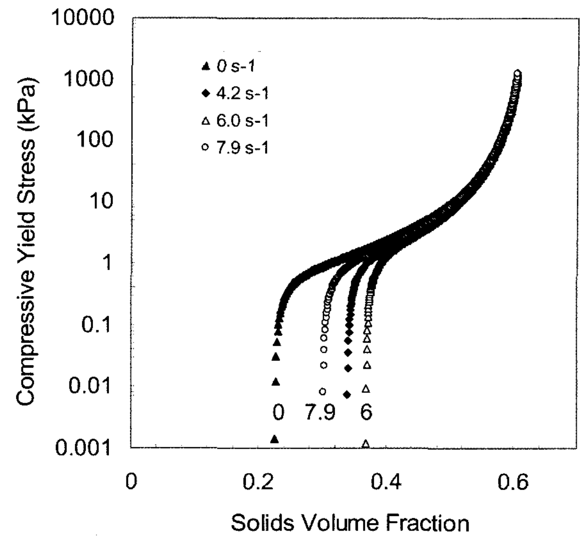

Fig. 6. Compressive yield stress versus volume fraction solids for a flocculated calcium carbonate sample as a function of post formation shear rate. Flocculant dose was 60 g/t.

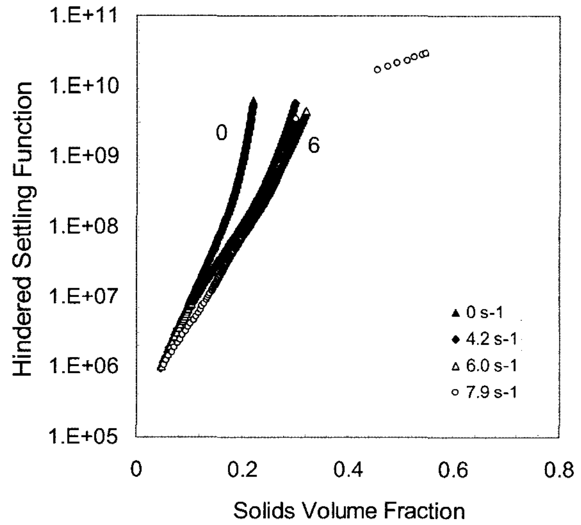

Fig. 7. Hindered settling function versus solids volume fraction for a flocculated calcium carbonate sample as a function of post formation shear rate. Flocculant dose was 60 g/t.

Under shear, the response of the hindered settling and compressibility behaviour is quite different. Fig. 5 shows the transient settling data for calcium carbonate suspensions flocculated at a fixed flocculant dose of 60 g/t in the presence of varying levels of shear. The data was obtained from batch sedimentation tests in a couette shear cell. The shear rates calculated assume a Newtonian response of the suspension although, as settling proceeds, this will be less accurate. Figs. 6 and 7 show how the varying levels of shear influence the compressive and hindered settling parameters for a fixed flocculant dose. It just so happens that most of the observed changes are at concentrations less than the gel point and this approximation is unlikely to cause significant error. The hindered settling behaviour is observed to improve dramatically in the presence of low levels of shear but not show a high sensitivity to the magnitude of the shear in the range considered. Higher shear rates (i.e. 100 s^{-1}) are known to be detrimental to the hindered settling behaviour. The compressive yield stress behaviour is more sensitive to shear and the data shows an improvement in the gel point and compressive yield stress at low shear followed by a transition at a shear rate of around 6 s^{-1}. Higher shear rates produced results consistent with the un-sheared case. The data at higher solids, from filtration testing, was found to be insensitive to the relatively low levels of shear applied in these tests and as such, only one set of filtration data is shown.

Understanding this behaviour for a wide range of flocculant types and concentrations is clearly a complex task but the data shown is consistent with the early work of Mills *et al.* (1991), whereby aggregate densification was observed at low shear and break-up at high initial shear rates. They observed that further densification was possible at higher shear rates but only after densification at lower shear rates first. This data has implications for the role of shear in a range of dewatering operations and further complicates our view of the role of forces in controlling aggregate properties. The data shows that the propensity of an aggregate to increase in density and by inference, cause an improvement in the key hindered settling function and compressive yield stress dewatering parameters will be a function of not only the aggregate formation conditions but the relationship between flocculant concentration, post formation shear rate and time. This represents a subtle balance of forces and the data presented is an indication that the techniques employed here can discriminate the aggregate changes in terms of measurable macroscopic parameters of relevance to real industrial processes. None the less, as discussed in the introduction, quantification of all of the shear behaviour would require a cross plot of hindered settling function, shear rate and time and additionally, a cross plot of compressive yield stress, shear rate and time. This is currently an experimentally arduous task.

Subsequent work on the shear enhancement of the hindered settling function of flocculated aggregates at low solids concentration, in which an aggregated bed of particles was fluidised, showed that the improvements in compressional rheological parameters for a flocculated calcite suspension can be improved even further than indicated in Figs. 6 and 7, especially at low solids concentration. The data is very sensitive none the less to the aggregate formation conditions (not just the flocculant dose) and initial data indicates that aggregates that experience a wide range of shear rates (especially high shear rates) during formation, tend to produce a more shear robust aggregate. These aggregates tend to be more robust in shear and are less susceptible to subsequent low shear densification. Data was obtained for the same material at the same flocculant dose, manufactured in a stirred reaction cell and in a pipe reactor (where the shear rate is both lower and less variable). Of note was that there was a vast difference in the susceptibility of the aggregates to post formation shear and the implication for processing in low solids concentration environments such as a thickener is clear, namely that the compressional rheological characteristics of weak open aggregates can be substantially manipulated to the benefits of the process if the initial aggregate is not robust to shear.

4. Conclusions

The compressional rheological characteristics of aggregated suspensions can now be measured routinely for a broad range of conditions and the relationship of different approaches to the measurement of compressional rheological parameters has been reviewed (de Kretser *et al.*, 2003). The characterisation in the presence of shear is still under development but initial experiments indicate that manipulation of aggregate structure using shear processes, whilst in compression, can dramatically change the kinetics and extent of fluid removal from concentrated aggregated suspensions. However, the benefits appear to be limited to non robust aggregates and in these systems, there is a clear differentiation between levels of shear that cause aggregate break-up as distinct from rearrangement. For the flocculant type, concentration and formation conditions considered here, the shear rate transition between densification and break-up was observed to be at a shear rate of approximately 6 s^{-1}.

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