

Dewatering and Clays — The Importance of Controlling Dispersion ‘Up-Front’

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ABSTRACT

The shear rheology and dewatering behaviour of tailings containing clay can be dramatically improved by controlling the dispersion of the clays. Ideally clay dispersion would be controlled by preventing initial swelling and ensuring full cation exchange by the addition of excess Ca^{2+} ions, however this approach is not always practical in reality due to economic considerations and issues associated with the precipitation of calcium and other salts. This paper assesses the efficacy and practicality of partially controlling the dispersion such that the clays still exhibit swelling, but complete separation into individual dispersed clay particles is suppressed. The potential benefits to be gained through the prudent use of controlled dispersion, and the importance of dealing with clays at the front end of the process are highlighted.

1 INTRODUCTION

Many mineral deposits contain clays in the form of kaolinite, illite, montmorillonite and mixed layer illite/montmorillonite. These clays generally report to a tailings stream for dewatering and storage and are notoriously difficult to dewater. Upon addition to water (generally in the initial milling process), some clays hydrate and swell and in many cases, this leads to complete separation or break up of the layers composing the clay.

A key strategy in improving clay tailings dewatering is the control of clay swelling and suppression of particle dispersion through the addition of salts or cation exchange of the clay. However, the question arises as to whether suppressing separation and dispersion only is sufficient (partially controlled dispersion) or if complete suppression of clay swelling and break-up into individual platelets (controlled dispersion) is required. There are many partially swollen but not dispersed states between these two limits. To test this philosophy, dispersion testing was performed on a clay rich tailings sample from an Australian coal operation. This operation had a requirement to mechanically dewater coal tailings to 34% maximum moisture in a filter operation. Presenting the filter with a material pre-thickened to a high solids content was essential for the success of this process. The tailings contained a high proportion of clay (34% kaolinite, 33% mixed layer illite- smectite, 5% montmorillonite). Due to the high clay proportion, testing of controlled dispersion of the tailings was considered in order to maximise the thickener underflow solids concentration.

A clay rich sample, representative of the worst case in terms of mineralogy and a slurried run of mine tailings sample were provided for characterisation and determination of the dispersion properties.

2 CLAY DISPERSION

Clays exist as high aspect ratio crystalline stacks or tactoids consisting of many platelets with large face surface areas and small edge surface areas. The individual platelet faces have a net negative charge, which is balanced by the adsorption of exchangeable cations between adjacent platelets.

Upon wetting and hydration, the cations may be released to water and result in a surface of negative charge neutralised by an electrostatic double layer. These double layers force the platelets apart due to electrostatic double layer repulsion and complete platelet separation may occur. The dispersion of these charged

individual platelets is postulated (Van Olphen, 1977; Khandal and Tadros, 1988; de Kretser et al., 1997) to result in a randomly orientated, space-filling structured network often referred to as a card-house structure.

2.1 Controlled Dispersion

The dispersion of swelling clays can be controlled by suppressing the swelling via increasing the ionic strength of the aqueous medium to which the clays are added (Van Olphen, 1977; Norrish, 1954; Callaghan and Ottewill, 1974; de Kretser, 1997). As the ionic strength is increased, the electrical double layer is compressed, thereby reducing platelet repulsion and suppressing swelling. If a sufficiently high calcium ion concentration is simultaneously maintained, calcium ion exchange will occur with the exchangeable interlayer cations. As calcium is a divalent ion, the neutralising effects will be increased and platelet coagulation will occur at lower concentrations in addition to the promotion of space efficient face-face aggregation. The resultant suspension will have a reduced effective particle surface area, fewer interparticle interactions and a weaker network structure.

The concept of controlled dispersion is not new, however, implementation for tailings disposal is not widespread due to the belief that both clay swelling and complete platelet separation must be avoided, necessitating high calcium concentrations. The high calcium concentrations required for complete controlled dispersion are often not practical due to economic factors and the limited solubility of many available calcium sources leading to excessive scaling issues. However, it is our postulate that complete suppression of clay swelling and break up is not essential for improved dewatering performance and the research outlined herein shows that suppression of break up alone can lead to improved clay dewatering.

3 METHODOLOGY

A series of tests were conducted on a sample of clay taken from the coal seam associated with the mine and a run of mine tailings sample. The former sample had a substantially higher clay content. The tests conducted included:

- Jar tests to measure the settling and rheological (yield stress) characteristics of the samples to determine the optimum chemical regime to control the dispersion of clays.
- Gel point determination and transient batch settling tests to determine the dewatering properties of samples that have undergone controlled dispersion.

3.1 Sample Preparation

Coal tails samples were received in slurry form and were fully mixed using a mechanical stirrer. A clay rich sample was received and sent to HRL Laboratories for dry grinding to nominally -100 μm (ground clay sample) prior to sampling. Stock calcium solutions were prepared by dissolving a known amount of analytical grade dihydrate calcium chloride in milli-Q water. The ground clay sample was fully mixed and then added to the appropriate calcium solution to form a slurry at 4 wt%.

3.2 Particle Size Distribution

Particle size distribution measurements were conducted using a Coulter LS130 laser diffraction particle size analyser. This apparatus has a particle size measurement range of 1 μm to 900. The particle size of the samples was measured in the dispersed state.

3.3 Preliminary Equilibrium Settling Test

Preliminary equilibrium settling tests were conducted on a small scale to determine the appropriate calcium ion concentrations for more detailed analysis. Thirteen 100 g samples, denoted A1-A13, were prepared at 4% wt with initial calcium ion concentrations varying from 0 – 0.5 M. Equilibrium settling tests were used to qualitatively determine if clay break up would occur and the extent of clay swelling. For this preliminary work, mixing was carried out by shaking a closed vessel for 1 minute.

The final settled solids concentration can be found by measuring the final height of the settled solids and using:

$$\phi_i h_i = \phi_f h_f \quad (1)$$

Where ϕ is the volume fraction of the slurry and h is the height of the solids liquid interface. The subscripts i and f refer to initial and final states respectively.

3.4 Jar Tests

Initial mixing tests were conducted by adding the ground clay sample to the appropriate electrolyte solution contained in a 2000 ml beaker. Samples were mixed at 500 rpm, the speed required to suspend the heaviest particles, for a period of 5 minutes. A 1000 ml sub-sample was removed and allowed to settle in a 1000 ml measuring cylinder. The interface height was recorded until an equilibrium height was reached.

Further characterisation involved obtaining the gel point of a sample. The gel point (ϕ_g) is the critical solids concentration at which discrete flocs or particles come into contact forming a continuous network structure. Thus, the gel point is the maximum solids concentration that a suspension can attain through free settling alone with no compression or mechanical enhancement (e.g. rakes), which may increase the permeability.

3.5 Shear Yield Stress Measurement

Yield stress measurements were conducted using the vane-shear method (Nguyen and Boger, 1981, 1983, 1985). Many workers worldwide have adopted the vane-shear method and confirmed its applicability for numerous types of yield stress materials (Yoshimura, 1987; James et al., 1987; Avramidis and Turian, 1991; Liddel and Boger, 1996).

4 RESULTS

4.1 Particle Size Distribution

The run of mine tailings and ground clay samples display very similar particle size distributions with the ground clay sample being marginally smaller (see Figure 1). The two samples were measured using tap water as the background solution. Thus, it is likely that any swelling clays present in either sample have broken up.

The density of the tailings slurry was measured, at the as received solids concentration of 27.1% wt, as 1130 kg/m³. Therefore the solids particle density is 1740 kg/m³. The ground clay sample displayed a similar density of 1780 kg/m³.

Table 1 lists the particle size statistics for the tailings and ground clay sample.

Figure 1 shows the cumulative size distribution.

Table 1 Particle size distribution summary for coal tailings (where d_{10} is the particle size, in μm , below which 10% of the sample volume is attributable)

	Mean	d_{10}	d_{25}	d_{50}	d_{75}	d_{90}
Tailings	42	3	7	20	52	111
Ground clay	30	2	5	16	44	80

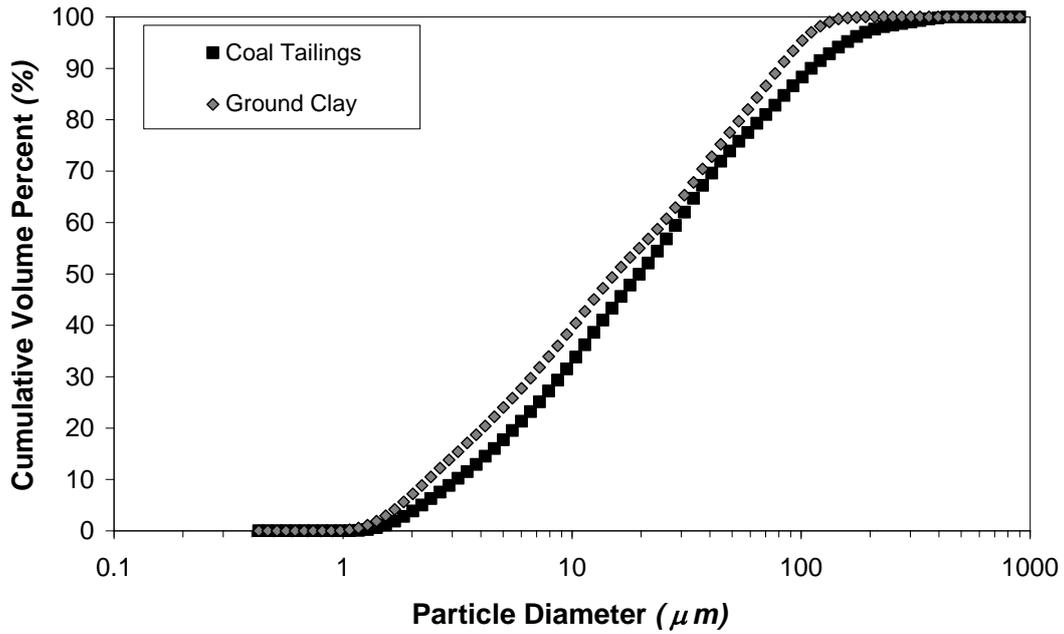


Figure 1 Particle size distribution for coal tailings and ground clay samples. Cumulative volume percent vs. particle diameter (μm)

4.2 Preliminary Equilibrium Settling Tests

Thirteen preliminary equilibrium batch settling tests were completed with initial calcium ion concentrations varying from 0 M to 0.5 M, as shown in Table 2.

Table 2 Preliminary equilibrium batch settling results for samples A1-13

Sample No.	[CaCl ₂] (M)	Final Height (mm)	Final Solids (wt %)	Final Solids (vol %)
A1	0	NA	NA	NA
A2	0.001	24.39	11.9	7.0
A3	0.002	11.90	23.1	14.4
A4	0.003	10.99	24.8	15.6
A5	0.005	10.83	25.1	15.8
A6	0.01	10.80	25.2	15.9
A7	0.02	10.60	25.6	16.2
A8	0.03	9.84	27.3	17.4
A9	0.04	9.37	28.5	18.3
A10	0.05	8.19	32.0	20.9
A11	0.1	7.33	35.2	23.4
A12	0.2	6.01	41.5	28.5
A13	0.5	5.33	45.8	32.2

Figure 2 shows the relationship between the equilibrium calcium ion concentration (i.e. the residual calcium ion concentration in the supernatant at the completion of the settling test) and the equilibrium settled solids weight fraction and the calcium uptake. It can be seen that there is a step change in the sediment concentration between 0.001 to 0.002 M Ca^{2+} . It should be noted that the 0.001 M sample took several weeks to settle and the 0.002 M reached equilibrium overnight, indicating that 0.002 M CaCl_2 represents the minimum equilibrium calcium ion concentration required for suppression of clay break up. Further additions of CaCl_2 do not appear to increase the final settled solids concentration until approximately 0.01 M, where both swelling and break up are suppressed. Thereafter the sediment concentration increases with calcium ion concentration according to a log – linear relationship.

For equilibrium calcium ion concentrations less than 0.0045 M, no calcium uptake was observed, i.e. no ion exchange. Here the equilibrium calcium ion concentration was within experimental error of the original calcium ion concentration. For concentrations greater than 0.0045 M a measurable calcium ion uptake was observed. This represents a level where calcium-sodium ion exchange occurs and clay break up is suppressed.

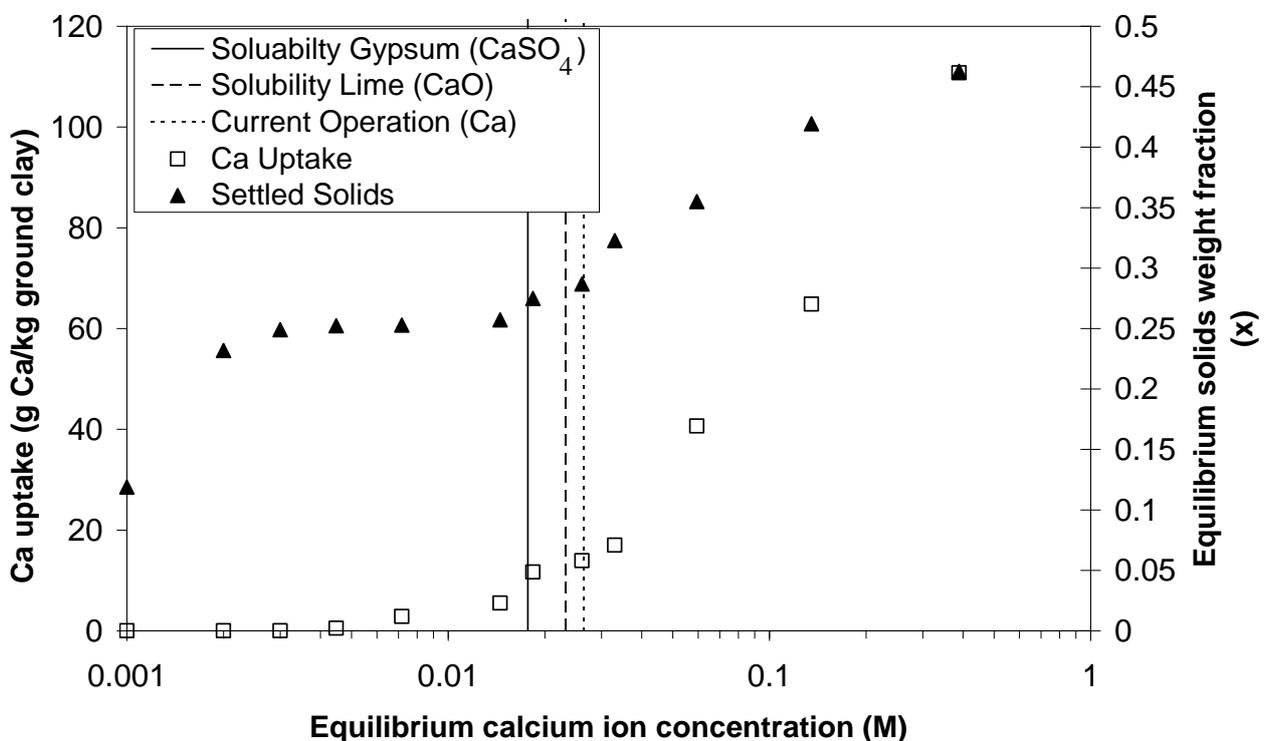


Figure 2 Calcium ion concentration versus equilibrium settled solids weight fraction (x) for ground clay samples 1-13

Two common sources of calcium are gypsum and lime and their solubility limits are shown in Figure 2. Throughout the study $2\text{H}_2\text{O}.\text{CaCl}_2$ was used as a calcium source due to its very high solubility (970 g/L, 6.6 M), however, dihydrate calcium chloride is not generally used in industry due to problems associated with chlorides and economic considerations. Gypsum is the more favoured calcium source due to pH issues associated with the addition of lime. However, scaling issues necessitate that concentrations are kept well below the solubility limit.

Prior to this study, it was recommended that this operation add gypsum to improve dewatering performance. This study was implemented to fine tune the Ca^{2+} concentration required. For the run of mine tailings sample (collected after the commencement of gypsum addition), process water elemental analysis shows calcium ion levels at 0.026 M, which is greater than the solubility of gypsum. Long-term operation under these conditions would cause scaling issues. Operating at 0.0045 M Ca, the minimum concentration at which ion exchange was observed, represents a quarter of the solubility limit of gypsum (2.4 g/L, 0.017 M). A suitable

residual calcium ion concentration of 0.007 M was recommended, which is 40% of the solubility limit of gypsum and above the minimum required for ion exchange.

The photograph in Figure 3 shows the equilibrium batch settling experiments for samples A1 – A13 (A1 on left to A13 on right) after 45 days settling. A direct comparison of the final equilibrium heights is possible as each sample contains the same solids and solids mass fraction. The step change between samples with 0.001 M (A1) and 0.002 M (A2) CaCl_2 is seen as a difference in the supernatant clarity, shown more clearly in Figure 4. From these results it is apparent 0.002 M CaCl_2 represents the minimum calcium ion concentration required to prevent the clays from breaking up. Increasing the calcium ion concentration to 0.5 M decreases the equilibrium height and thus the degree of clay swelling. For further testing, four initial calcium ion concentrations were chosen that span the range of interest found in this preliminary exercise, namely 0.002, 0.01, 0.1 and 0.5 M.

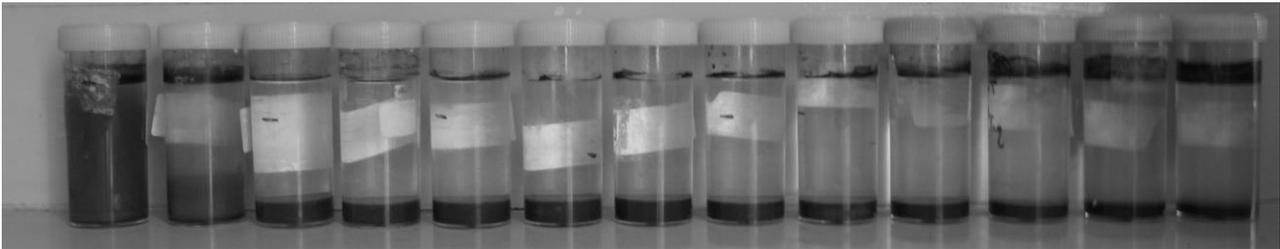


Figure 3 Equilibrium batch settling test for samples A1 - A13

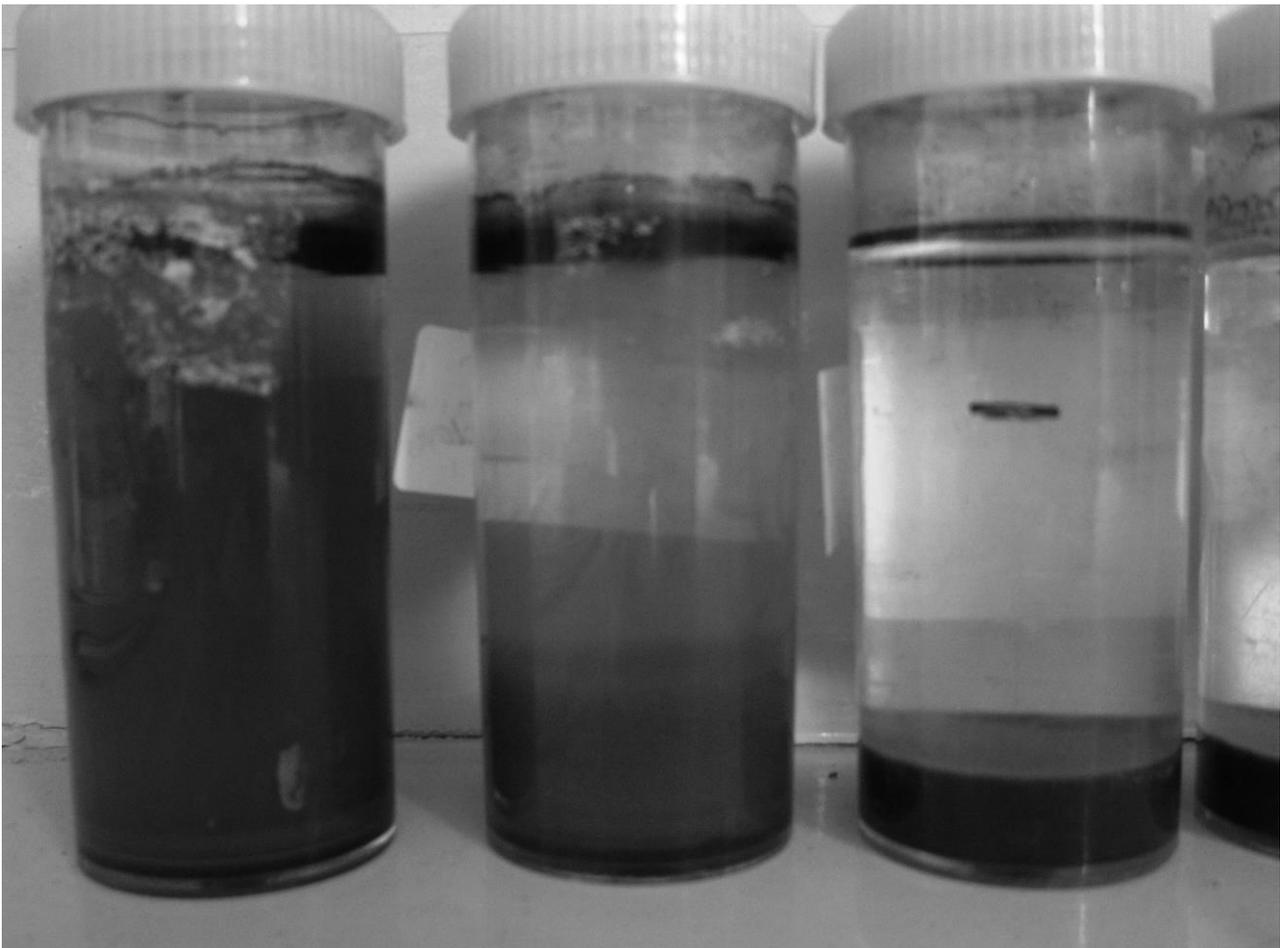


Figure 4 Equilibrium batch settling test for samples A1 – A3 (0, 0.001 and 0.002 M)

4.3 Jar Tests

Using the calcium ion concentrations selected in the preliminary equilibrium batch settling results, four samples were prepared for transient batch settling experiments. Initial calcium ion concentrations used were 0.002 M, 0.01 M, 0.1 M and 0.5 M.

As each sample was prepared at the same weight fraction of ground clay (4 wt%) and settling was conducted in identical cylinders from the same initial heights, direct comparisons of the height versus time curves are possible. Figure 5 displays the height versus time curves for the four calcium ion concentrations examined. The height versus time curves for the four samples are quite similar. Each sample has a similar linear settling region (0.97- 2.1 m/hr) and the three highest concentration CaCl₂ samples have similar final settling heights (0.012 – 0.015 m).

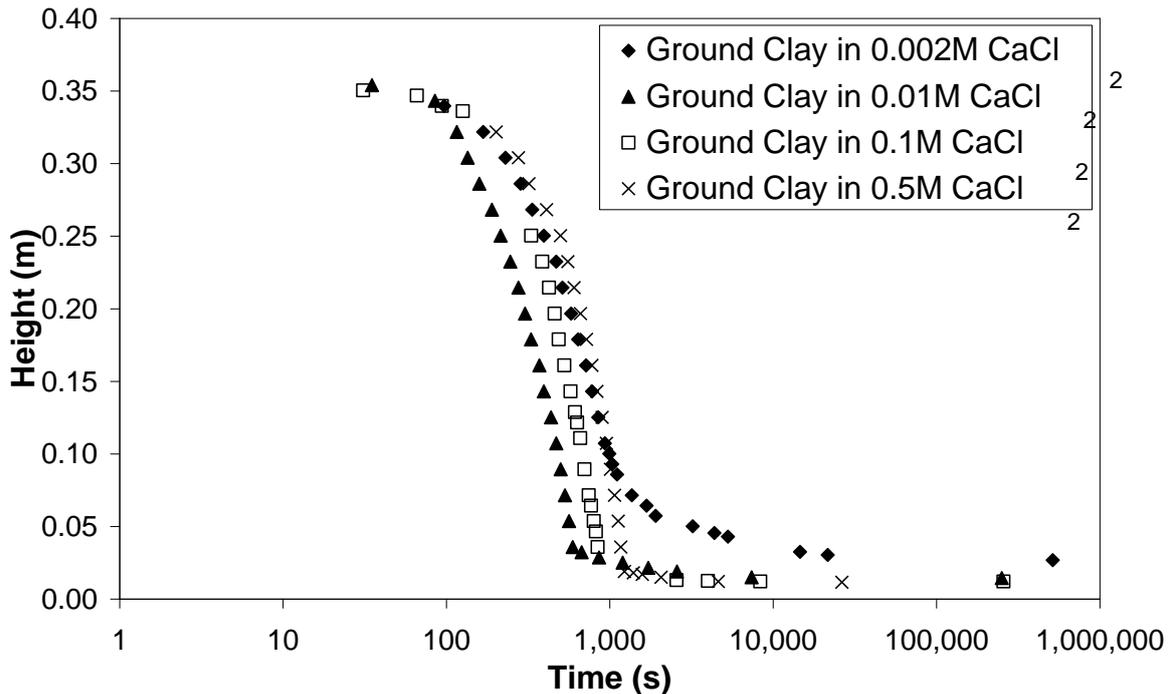


Figure 5 Transient batch settling results for ground clay in varying concentrations of CaCl₂

Although the final settled heights of the three highest concentration CaCl₂ samples appear similar, the settled solids concentrations are actually quite different, see Table 3. This apparent discrepancy is due to the low initial solids of the settling samples. The low initial solids translate to large changes in settled solids concentration for small changes in final heights (approximately 5 wt% for 1 mm). The higher initial concentrations used for the gel point test nullify this effect and therefore the gel point provides a more accurate representation of the trends. The 0.002 M CaCl₂ sample has a considerably higher final settling height, approximately double that of the other three, at 0.027 m. Thus there is a benefit, with respect to equilibrium settling solids, in have a starting calcium ion concentration of more than 0.002 M (but not more than 0.1 M), though there is minimal improvement in the settling rate.

Table 3 Settled solids results for all samples

Sample	Settled Solids (wt%)
Ground clay in 0.002M CaCl ₂	43.8
Ground clay in 0.01M CaCl ₂	69.7
Ground clay in 0.1M CaCl ₂	79.2
Ground clay in 0.5M CaCl ₂	80.3

The gel points for the tailings sample and the ground clay sample at four ionic strengths are shown in Table 4. The run of mine tailings sample had a gel point (21.1 wt%) ranking between the ground clay samples with initial calcium concentrations of 0.01 M and 0.1 M. This was not unexpected as gypsum addition was being conducted on site at the time of sample collection, and the measured on site Ca^{2+} concentration of 0.026 M is consistent with an expected gel point of between 17.6 and 26.5 wt%. Increasing the calcium ion concentration increased the gel point where the ground clay in 0.5 M calcium had a gel point of 38.5 wt% approximately 1.8 times that of the coal tails sample and almost 3 times the ground clay sample in 0.002M CaCl_2 . It is clear that the gel point behaviour of the tailings was dominated by clay swelling and break up, which is not surprising for a sample with approximately 72 wt% clays.

Table 4 Gel point results for all samples

Sample	Gel Point (wt%)
Coal Tailings	21.1
Ground clay in 0.002M CaCl_2	13.1
Ground clay in 0.01M CaCl_2	17.6
Ground clay in 0.1M CaCl_2	26.5
Ground clay in 0.5M CaCl_2	38.3

4.4 Shear Yield Stress

The yield stresses versus solids behaviour of three samples was examined; the run of mine tailings and the ground clay samples in 0.002 and 0.5 M CaCl_2 . Each of samples displayed an exponential increase in yield stress with solids mass fraction. The yield stress versus solids mass fraction curves are shown in Figure 6.

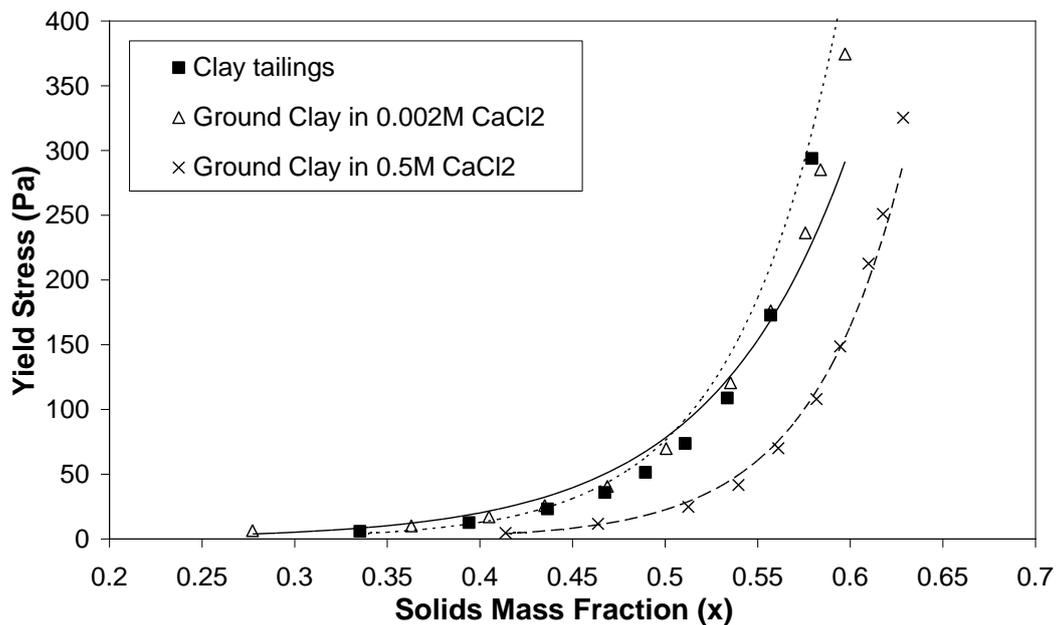


Figure 6 Shear yield stress (τ_y) vs solids mass fraction (x) for samples treated with different levels of Ca^{2+} (lines are exponential model data fits)

The tailings sample and the ground clay sample in 0.002 M CaCl_2 displayed similar yield stress versus solids characteristics, while the ground clay sample in 0.5 M CaCl_2 showed a clear difference and displayed the lowest yield stress for any given solids mass fraction within the range tested. The increased calcium ion concentration reduces the swelling of the clays and thus causes a lower yield stress at any given solids concentration. Therefore, increasing the calcium concentration above the minimum Ca^{2+} concentration

required to suppress swelling of 0.002 M will lead to a decrease in the yield stress but complete suppression of swelling is required to achieve a significant extra effect.

5 CONCLUSION

This work shows that the settling and consolidation behaviour of clay rich tailings can be significantly improved by application of Ca^{2+} at less than the fully exchanged capacity of the clay whereby break up of the clay structure is suppressed. Clearly this would require a holistic approach to the addition of calcium at the initial point of ore wetting as distinct from addition of calcium or other additives within the tailings treatment section of the plant alone, as the break up of clays into individual platelets is largely irreversible.

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