A high volume of slimes which are separated out during the mining of heavy mineral sands has a high environmental impact and results in great capital as well as operational expenses. The presence of clay minerals drastically increases the slimes volume that needs to be catered for due to its low settling capability as well as swelling characteristics. By adding coagulants in the form of cations and organics, one can improve the settling rate of the minerals as well as the degree of solid bed compaction. The addition of flocculant, which is currently used in industry to improve settling rate, is detrimental to solid bed compaction. By combining the cations and flocculant one can dramatically improve the solid bed compaction. This combination, is however, detrimental to the settling rate of kaolinite rich slimes but improves the settling rate of smectite rich slimes. Organics can also be used to produce a clear supernatant and improve the settling rate.

**Classification and mineralogy of heavy minerals**

Heavy mineral deposits can be classified by the geographical location of their formation. South African heavy mineral deposits are classified in two classes: magmatic origin and beach deposits. The deposits belonging to the class of magmatic origin are situated inland whereas the beach deposits are located on the coastal regions of South Africa. The KZN sands operations, Hillendale and Port Durnfort, fall under the latter group (Bernstein, et al. 2008). The slimes fraction (-45 µm) of a heavy mineral deposit can amount to an average of up to thirty per cent of the orebody. Slimes are separated from the coarse fraction through the desliming cyclones followed by solid-liquid separation within the thickener. The mineralogy of this fraction is very important as it determines the settling characteristics as well as consolidation behaviour of the slimes tailings. The orebody under investigation consists of pockets with high smectite and kaolinite concentrations. The characteristics of these clay minerals such as small particle size and negative surface charge, have a detrimental effects on the settling rate and underflow behaviour of such ore bodies. Of these the negative surface charge contributes most to the negative settling properties. (van Olpen, 1977).

**Crystal structure of clay minerals**

Clay minerals belong to the phyllosilicate group, thus the sheet silicates. The structures of these sheets as well as the linkage between these sheets are used as the criteria for classification. These sheets can either be tetrahedral or octahedral. Tetrahedral sheets consist of two planes of oxygen atoms arranged in tetrahedral coordination around Si4+ cations and share basal oxygen atoms between adjacent tetrahedra (Figure 1). Octahedral sheets comprise of six oxygen or hydroxyl ions which share octahedral edges (Figure 2). This type of linking results in a net charge of -2 which is balanced by divalent cations or trivalent cations.
that bond to the sheet. This results in a reduction or completed neutralization of the negative charge (Horn and Strydom, 1998).

Clay minerals are defined as 1:1 or 2:1 clays. The 1:1 clay minerals consist of repetition of a single octahedral sheet linked with a single tetrahedral sheet. The linkage occurs through sharing of the apical oxygen between the octahedral and tetrahedral sheets. The enclosed ion of each tetrahedron is normally Si4+, but this can be replaced by Al3+ or Fe3+. Water cannot enter between these layers and these clays are termed non-swelling clays.

The 2:1 clay minerals consist of a single octahedral sheet which is bordered on both sides by a tetrahedral sheet in which the apical oxygen points towards the central octahedral sheet. This forms one layer which can be linked to a similar layer through interlayer cations. The fact that the interlayer cations can be replaced by other cations is important as it relates directly to the ease with which these clay minerals can be chemically altered (Horn and Strydom, 1998).

**Swelling of clay minerals**

Swelling clay minerals comprise of a 2:1 structure with the adjacent layers being held together with weak Van der Waals forces as well as strong columbic forces. Swelling of clay minerals is a two-phase process divided into crystalline swelling and osmotic swelling (Horn and Strydom, 1998).

Crystalline swelling results from the hydration of the exchangeable interlayer cations. This results in the widening of the spacing between the clay particle layers of up to 10–20 µ (McFarlane, et al., 2005b). The increase in volume will continue as more water layers are absorbed until a maximum displacement is reached. The addition of this water, which is chemically bound to the clay structure increases the total slimes volume. This leads not only to a tremendous capital expenditure due to the need for a larger slimes dam but also to a decrease in the density and stability of the slimes. Madsen and Müller-Vonmoos (1989) concluded that crystalline swelling can create pressures of up to 100 N/m².

Osmotic swelling follows crystalline swelling and is an indefinite process. Osmotic swelling can lead to pressures as high as 2 N/m² (Madsen and Müller-Vonmoos, 1989). This type of swelling occurs due to a large concentration gradient between the pore water and the electrostatically bonded ions.

The pressures resulting from swelling can be greater than the weak Van der Waals attraction forces. This swelling of clay minerals can result in the separation and rupture of the clay particles. According to McFarlane et al. (2005b) the now even smaller particles can worsen settling rates even more (< 0.1 m/h), and cause poor sediment solid loading (<10 wt %) as well as high yield stresses.

**The influence of cation addition on the swelling behaviour of clay minerals**

**Hydration of cations**

During dissolution of salts in water the salts ionize into cations and anions which hydrate in water to a certain degree. The swelling behaviour of the clay is affected by the cation exchange identity. According to Ferrage et al. (2005) the cation identity can be simplified in terms of the ionic potential of the cation. Ionic potential is defined as z/r, with r referring to the ionic radius and z to the cation valence. Higher ionic potential results in stronger interlayer hydration of the cation. One can therefore conclude that the hydration and therefore the swelling of the clay mineral can be influenced by changing the identity of the interlayer cation through ion exchange with the surrounding solution. In line with this Newman (1987) concluded that by replacing interlayer Cu2+ with K+ the interlayer space can readily be dehydrated. Cu2+ has an ionic potential of 2.7A-1 while K+ has an ionic potential of 0.72A-1.

**Hydration enthalpy**

Hydration enthalpy is the energy released or required from the surrounding environment to hydrate one mole of the interlayer cation (Richens, 1997). The hydration enthalpy is proportional to the ionic potential. It can therefore be concluded that a cation with a higher hydration enthalpy will lead to stronger interlayer cation hydration.

**Complex formation of cations**

Yamanaka and Brindley (1977) conducted an investigation on the metal hydroxide interlayer of montmorillonite by studying the complex formation of the transition metals, Ni2+, Cr3+ and Cu2+. This research concluded that the metal ions resulted in different numbers water molecules being absorbed during hydration. Ni2+ was found to be associated with 6 H2O molecules compared to the 14 H2O molecules associated with the hydration of Cu2+. Naturally the latter also showed a higher degree of swelling of the clay particles due to the higher degree of water adsorption.

**Cation exchange**

The process in which the cations present in the solution exchange places with cations which form part of the interlayer of the clay is known as cation exchange. The interlayer cations are mostly exchangeable cations such as Na+ and Ca2+. Exchange takes place due to the lowering of the energy resulting from the newly hydrated cation.

The permanent electrostatic charge and large specific area of smectite make the absorption of organic and inorganic cations possible (Schlegal, et al., 1999). The isomorphic exchange of cations within the smectite structure results in an electrostatic charge (Sposito, 1984). Cations will substitute one another within an exchange site if the hydration enthalpy of the sorbate is low enough to create a high enough driving force for absorption and if a great concentration gradient exists between the cation concentration in the clay and the background electrolyte concentration (Sposito, 1984). The degree of cation with for smectite then for kaolinite. The cation exchange capacity (CEC) is for smectite is 90 meq/100 g compared to kaolinite’s (CEC) of 5 meq/100 g (Ma, et al.).

Cation exchange between the solvent and clay surface is a quick process and can be completed within minutes (Schlegal, 1999). A study on cation absorption indicates that an increase in pH will lead to an increase in cation absorption (Schlegal, 1999). Under such conditions the outer sphere complexes which form near the basal plane of the smectite particle act as a transient cation buffer. From these sites cations can migrate further to edge sites (Schlegal, 1999). Inner sphere complex formation takes place on the octahedral edge sites. This migration of cations from the outer sphere to the inner sphere is a much slower process than the initial cation exchange and will reach equilibrium only after a few days.
The ability of the slimes to absorb cations is known as the slimes’ cation exchange capacity (CEC) and is measured as the number of centimoles of cations replaced per kilogram of slimes treated (Bland and Rolls, 1998). Research conducted by Mpofu (2004) showed that the addition of cations leads to sufficient dewatering with results in tremendous reduction in thickener underflow volume. This was proved by Ferrage et al. (2005). Ferrage et al. (2005) also concluded that K⁺ could reduce interlayer swelling to 12–13Å. This is more effective than using Na⁺ for collapsing the interlayer swelling.

Flocculants and coagulants

Ionic concentration of the solvent

Slow settling rates are associated with low ionic concentrations. Low ionic concentrations result in a great repulsion force due to the uncompressed double layer which prevents flocculation. As the ionic concentration is increased the electric double layer is compressed as shown in Figure 1. Particles can now interact with each other and attraction forces start to dominate. The ionic concentration at which the particles start to attract each other is known as the critical coagulation concentration (CCC). Addai-Mensah (2007) concluded that the addition of hydrolysable ions Ca²⁺ and Mn²⁺ to smectite, could lead to the reduction of the zeta potential through adsorption of the cations by the clay minerals as discussed. This can be observed throughout the pH spectrum.

Coagulants and flocculants

Coagulant

The addition of coagulants is used to reduce the overall negative surface charge that surrounds each particle, as this renders particles colloidably stable. Coagulants enable the weak Van Der Waals Forces to dominate, which results in attraction between particles causing the colloidal clay rich suspension to settle out. This is a result of the coagulants neutralizing the surface charge of the clay.

Two different coagulation mechanisms are used in order to efficiently settle out slimes: inorganic salts and poly-electrolyte coagulation.

Inorganic salts

As previously explained, inorganic salts dissociate in the electrolyte into cations and anions. These ions are hydrolyzed to form different species (Ye et al., 2007). The species that form are determined by temperature and pH. This leads to the conclusion that the optimum coagulation would be determined by the species that form at that specific pH. The hydrolyzed cation that forms is adsorbed into the surface of the clay thereby reducing the negative surface charge. The most common ‘electrolyte’ coagulants are sodium chloride, ferric chloride and calcium chloride. Studies (Olivier, 2006) have concluded that the higher the cation valence the lower the cation concentration required to achieve the critical coagulant concentration. It was also noted that the higher the cation valence, the lower the required cation concentration required to achieve the critical coagulation concentration (CCC) and an improved clarity.

Organics

MacEwan (1948) showed that a large variety of polar organic molecules can be adsorbed by clay minerals. Organic ions have been found to enter into cationic exchange sites especially with smectite clay as proven by Geisking (1939). McAtee (1959) showed that primary amine organic molecules can replace the exchangeable cation in the clay interlayer which renders the clay hydrophilic. Grim (1968) stated that the amount of water absorbed by montmorillonite can be reduced by coating the basal surface with organic ions. The amount of water absorbed by clay minerals reduces as the chain length of the organic molecule increases. Organic materials may be present as molecules adsorbed on the surface of the clay-mineral or by intercalation between the silicate layers. Water, salts and especially polar organic molecules can enter between the unit layers of swelling clay minerals.
Other mechanisms encountered during flocculation are charge neutralization or compensation, polymer-particle surface complex formation and depletion flocculation (Gregory, 1987). A combination of these mechanisms can also occur. Charge neutralization or compensation is commonly encountered with non ionic polymers or high molecular weight polyelectrolyte.

**Flocculant type**
As discussed, clay rich slimes display a negative charge on the particle surface. This leads to the assumption that cationic flocculants would be the most effective. However studies performed on kimberlite slimes bearing smectite clay particles (O’Gordon and Kitcner, 1972) concluded that neutral flocculants had little effect, whereas cationic flocculants led to no flocculation at all.

Research also concluded that flocculant demand can be reduced if it is preceded by partial coagulation (O’Gordon and Kitchener, 1972). Flocculation test work indicated that divalent cations improve the effectiveness of anionic flocculants and that complete exchange of Na+ with Ca2+ could result in effective dewatering and flocculation using anionic PAM or polyethylene oxide (PEO) (O’Gordon and Kitchener, 1972). Scheiner and Smelly (1984) as well as Mekhamer and Assaad (1999) concluded that not only the surface charge but also the interlayer cations influence the effectiveness of PEO and anionic PAM. According to Mpofu (2003a) when one adds a hydrolysable metal ion, lower dosages of PEO could be used for dewatering of smectite particles than the dosages required for anionic PAM. The flocs that were produced by PEO also proved to be superior in terms of robustness, size and shear sensitivity.

Mpofu (2003a) used Ca2+, Mg2+, Ba2+ and Al3+ prior to PEO to achieve effective dewatering of smectite. Effective dewatering depends on the surface chemistry of the clays, the molecular structure of the flocculant and the flexibility and particle interaction during compression and moderate shear (Mpofu, 2003b). These factors need to be investigated in order to determine the long term behaviour of the slimes on the deposition site.

Flocculation is generally detrimental to final consolidation of the sediment (Wills, 2007).

**Experimental**

The aim of the test work was to determine the effect of cations on the settling rate of kaolinite and smectite rich samples from the Port Durnford orebody. The cations for also combined with flocculant enhanced settling in order to measure the effect on the flocculant induced settling.

**Sample preparation**

Samples were taken from three different material types which form part of the Port Durnford orebody. T2, T5 and T6. The type of ore has been classified on the basis of colour and slimes content. The samples were numbered as follows T2 PD71/42, with T2 referring to the type of material, PD to the orebody, 71 to the drill hole and 42 to the depth in metres.

**Natural settling**

A base case natural settling test on all the samples was performed in order to highlight the problem areas of material type and depths. Once the problematic areas were flagged, XRD analysis was used to determine the mineralogical composition responsible for the poor settling behaviour. For this study all XRD analysis was done using quantitative X-ray diffraction analysis at the University of Pretoria. A PANalytical X’Pert pro powder diffractometer with X’Celerator detector and variable divergence and receiving slits with Fe filtered Co-Kα radiation were used. Quantification was performed using the Rietveld method (Autoqan Program). Table I states the base case conditions used for settling tests. Even though for processing considerations the -45 µm fraction is regarded as the slimes fraction, this limit is moved to -75 µm for test work. This assumption is supported by the fact that de-sliming cyclones are only 99% effective.

**Coagulant settling**

The most problematic base case settling sample was subsequently subjected to coagulation settling using cations as coagulants. The cation spectrum was tested at 0.01M concentration and included KCl, NaCl, MgCl2, CaCl2, AlCl3. CaCl2 proved to be the best coagulant and was tested further for its CCC. The hydrolysable salt, 25 g of dry sample and distilled water were added and stirred at 500 rpm for 10 minutes. The rest of the conditions remained the same as in the base case (Table I).

**Flocculant and coagulant settling**

The best hydrolysable salt was subsequently combined with the best flocculant for settling tests. The coagulant (cations), flocculant, distilled water and 25g of sample were mixed and then stirred at 500 rpm for 10 minutes.

The settling rates of flocculant, cations and the combination of flocculant and cation were compared. Furthermore the consolidation behaviour and clarity of supernatant were noted for the different tests.

**Organics**

The effect of organics as a coagulant on the settling properties was also investigated on both T2 and T6 samples –of which T6 proved to be the most problematic in the natural settling test. The following organics were evaluated: pentanoic acid, formic acid, oxalic acid, citric acid and...
methanol. Tests were performed at a concentration of 0.3 M in order to select the most promising organic in terms of improved settling, solid bed compaction and clear supernatant. The organic with the best results was then tested further at concentrations of 0.05, 0.1 and 0.2 M to determine the optimum concentration.

**Results and discussion**

**Natural settling**

Figures 3 and 4 show that T6 and T5 had no solid liquid interface after 24 hours. The natural settling of the different T2 samples shown in Figure 5 flagged the most problematic area in the type 2 sample as T2 PD71J/42. Due to the fact that little to no natural settling occurred in T5 and T6, there was not a single most problematic zone that could be selected. T5 PD0055J/28 and T6 PD0053J/39 were therefore selected for further test work.

XRD analysis was performed on the samples. Table II indicates the composition of the -75 µm for the T2 and T6 problem areas. All T5 samples showed at least 60% smectite in the -75 µm size fraction.

The high smectite content of T5 and T6 explains the poor natural settling ability of these two samples as smectite is a swelling clay that is known to be detrimental to the settling rate (Addai-Mensah, 2007).

**Coagulant settling**

**Cations**

Figure 6 shows the settling results for the T2 sample with the addition of Na+, K+, Ca2+, Mg2+ and Al3+ species. Ca2+ is shown to be the cation resulting in the most significant improvement in the settling rate, followed by Na+, then Mg2+, Al3+ and K+ in order of slower settling rate. The most compacted bed was achieved with Ca2+, then Mg2+, Na+, Al3+ and lastly K+.

![Figure 3. Results for natural settling tests after 24 hours for various T6 samples](image)

![Figure 4. Results for natural settling tests after 24 hours for a T5 material](image)

![Figure 5. Natural settling for various T2 samples](image)

![Figure 6. Coagulant settling test results for sample T2](image)

![Table II XRD analysis for type 2 and type 6 samples](table)

<table>
<thead>
<tr>
<th></th>
<th>T6 PD0053J/39 -75 µm</th>
<th>T2 PD71J/42 -75 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haematite</td>
<td>0.41</td>
<td>1.63</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.13</td>
<td>2.98</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>21.4</td>
<td>75.63</td>
</tr>
<tr>
<td>Muscovite</td>
<td>4.9</td>
<td>5.34</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>18.45</td>
<td>0</td>
</tr>
<tr>
<td>Pseudobrookite</td>
<td>0.37</td>
<td>0</td>
</tr>
<tr>
<td>Quartz</td>
<td>19.96</td>
<td>12.49</td>
</tr>
<tr>
<td>Rutile</td>
<td>1.16</td>
<td>1.41</td>
</tr>
<tr>
<td>Smectite</td>
<td>32.9</td>
<td>0</td>
</tr>
<tr>
<td>Zircon</td>
<td>0.31</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Figure 7 shows the settling results for type 5 with the addition of Na⁺, Ca²⁺ and K⁺.
All the cations improved the settling rate with a similar settling rate for all the cations. Ca²⁺ proved, however, to be superior in supernatant clarity.

**Flocculant settling**

Figure 8 shows the flocculant screening results for T2 and Figure 9 shows similar results for T6.
As indicated in Figures 8 and 9, Magnafloc 5250 proved to have the best results for settling rate in both the T2 and the T6 samples. As expected from literature, the anionic flocculants had the best results in settling the clay minerals. The results for flocculant dosage test work are shown in Figure 10. From this test work 73 g/t slimes showed the best settling rate.

**Flocculant and coagulant settling**

Figure 11 compares the settling results for natural settling, Magnafloc 6260 settling, Ca²⁺ coagulant settling and Magnafloc 6260 with Ca²⁺ coagulant settling.
Figure 11 shows that the addition of only flocculant has the best settling rate results. It is interesting to see that the addition of both flocculant and Ca²⁺ reduced the settling rate to a rate lower than the natural settling rate for kaolinite rich T2 material, as indicated in Figure 11A. However, Figure 13 shows that the flocculant and cation combination greatly improved the settling rate of smectite rich T6 and
The change in surface charge due to the addition of cations could be the result of the improved or detrimental effect of the flocculant. When one considers the compaction behaviour of the flocculant and cation combination (Figure 12), the volume of the solids bed almost halved from that obtained by using flocculant only. The use of only cations also improved solid bed compaction. This could have a dramatic impact on the footprint of the tailings deposit site.

Organics
Organics screening
The results for organic agents as a coagulant are shown in Figure 14.

As indicated in Figure 14, pentonic acid had the best results for improving the settling rate of all three zone types (T2, T5 and T6). In Figure 14 it is shown that for sample T2 pentanoic acid and formic acid improved the settling rate to a similar extent. The concentration of the organic coagulant (pentanoic acid in this case) was tested at 0.5, 1 and 2 M and showed that a concentration of 0.1 M proved to be best.

Conclusions
• Cations can be used to improve the settling rate of clay rich slimes. Ca²⁺ proved to be the most effective coagulant in this test work
• Flocculant settling test work produces the highest settling rate
• A combination of flocculant and cations is detrimental to the settling rate of kaolinite rich slimes but beneficial to the settling rate of smectite rich slimes
• Cations are superior to flocculants in solid bed compaction
• Organics can be used to improve the settling of clay rich slimes. Pentonic acid proved to be the most effective organic coagulant.

Recommendations
Further test work on the effect of the higher degree of bed consolidation on the rheology of the slimes need to be carried out as this will influence the manner in which it can be transported to the tailings disposal site.
A complete flocculant screening using anionic, cationic as well as non-ionic flocculant needs to be performed after the addition of cations. This might result in a different type of flocculant proving to be best due to the surface charge change resulting from cation addition.

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