Optimizing dewatering and soft tailings consolidation by enhancing tailings' composition

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Abstract: In order to reclaim ultra-soft tailings (e.g. oil sands) ponds great amount of research and technology work has been performed over the years to optimize the dewatering and consolidation of Fine Fluid Tailings (FFT), including the use of different chemical flocculants and mechanical deposition approaches. Yet, traditionally flocculation, hence settling, and consolidation are treated as two independent processes. Here integrate these two processes, proving how implementation of certain types of flocculants influences the consolidation rates and strength of the deposit.

Laboratory studies on small scale settling columns carried out at Deltares tested the settling and consolidation rates, and the strength development of FFT samples treated with different flocculants dosage under different water chemistry and pH conditions. These systematic tests revealed distinct correlations between flocculation and consolidation and strength properties. These studies also enabled us to find specific laboratory and analytical tools to assess the relevant properties of the tailings. We will show that using what is generally called "zeta potential" (in fact "electrophoretic") measurements allow obtaining fast and reliable information about the tailings' composition, such to estimate the required flocculant dose to optimize geotechnical properties. This, combined with the analytical methods to estimate consolidation rates from settling column, allowed us to distinctly correlate flocculation.

Keywords: correlating flocculation with consolidation, dewatering, zeta potential, flocculant treatment

1. INTRODUCTION

Different technologies are used to accelerate settling of Fine Fluid Tailings (FFT) across mining industries, e.g. the use of centrifugal force and polymers to speed removal of process water from the fluid fine tailings; a filtering technology to dewater tailings before they are deposited in the ponds increasing the proportion of solid content; and, addition of CO_2 to the tailings line to increase dewatering (Canadian Association of Petroleum Producers (www.capp.ca); Canada's Oil Sands Innovation Alliance (www.cosia.ca)).

The importance of the material composition (i.e. amount and type of fines / clay) and its evolution over time has been recognized, which led to a large increase in research in this area over the past years. Numerous studies headed in the direction of understanding the optimal use of chemical additives (such as polyelectrolytes, often called "flocculants") to enhance process water clarity, tailings dewatering and strength development (Novak and Langford,1977; Mpofu et al., 2003)).

In the present study, we extend the knowledge on flocculation to its correlation with consolidation. Specifically, we study the impact of two different types of flocculant on the settling and consolidation properties of flocculated natural clay. Ongoing experiments at the Deltares Physical Laboratory using the same methods to oil sands FFT will allow comparing the finding of this paper to oil sands tailings (completion date around end of 2015).

In particular, the "bridging" of polymers to fine particles (clay) is linked to the study of the interfacial properties of the clay-polymer system in terms of electrophoretic mobility (zeta potential) measurements. The zeta potential has proven to be a good indicator for predicting the changes (changes in particle size, density and floc strength) of clayey materials as a function of the fluid properties (changes in salinity, pH, shear stresses) (Chassagne et al., 2009; Ibanez et al., 2015; Mietta et al., 2009; Liu et al., 2002; Hu et al., 2003). We will show that these changes can in turn be related to changes in settling and consolidation behavior (Merckelbach and Kranenburg, 2004; Merckelbach et al., 2002; Winterwerp, 2002).

2. MATERIALS AND METHODS

2.1 Materials

Two different commercially available flocculants from the company BASF were used in the experiments. These flocculants are from the product line Zetag, which are dry powder flocculants. The cationic flocculant is a high charged polymer with medium molecular weight. The anionic flocculant is a medium charged polymer with high molecular weight.

The tests were done with very fine sediments which composition is quartz, calcite, anorthite and muscovite. The average size of the sediment particles is 6 microns and was determined by Static Light Scattering. All experiments were done in tap water with a conductivity of 0.5 ms/cm.

2.2 Electrophoretic mobility measurements (Zeta Potential)

The electrophoretic mobility of the suspensions was measured using a ZetaNano ZS device, at the Physical Laboratory of Deltares, The Netherlands. This mobility is measured using a patented laser interferometric technique (Zeta Sizer Nano Serie System 3.0 Operating Instructions) known as M3-PALS (Phase Analysis Light Scattering). The electrophoretic mobility values (typically in m2/V s units) are given as zeta potential values (V) using the Smoluchowski formula: , where is the called the electrophoretic mobility (velocity of the particle (m/s) divided by the applied electric field strength (V/m)) of the particle, is the viscosity of the suspending liquid, is the dielectric constant of the suspending medium, and is the zeta potential (Hunter 1981). The zeta potential can be used as a proxy for the coagulation/flocculation ability of clay and non-clay minerals. When the charge is low (nearly zero) coagulation/flocculation is promoted, when it is large (positive or negative) coagulation/flocculation is inhibited (Chassagne et al., 2009; Ibanez et al., 2015; Mietta et al., 2009).

The zeta potential measurements were carried out as a function of concentration of polyelectrolyte in solution.

2.3 Settling and consolidation test

With the settling column test the settling behavior of sediments can be recorded with a digital camera. The lay-out consists of 3 Perspex tubes with an inner diameter of 0.12 m and a height of 1 m, preferably placed in a temperature-controlled room.

At the start of an experiment the column(s) are filled with sediment suspensions. The starting time of all columns is synchronized by re-stirring (gently) all columns for a short while after the last column has been filled. After the water has come at a stand-still the camera recording is started. Pictures were

taking automatically at fixed time interval for the entire duration of the experiment (i.e. 4 to 6 weeks). From the image the interface between clean water and sediment bed as function of time is obtained.

RESULTS AND DISCUSSION

Figure 3.1 and Figure 3.2 illustrate the results obtained when studying the settling velocity of flocculated clay (10 g/L sediments) and the zeta potential of clay particles (0.1 g/L sediments) as function of the amount (mg) of added polelectrolyte. The first experiments are done with a cationic flocculant while the second an anionic flocculant. For both experiments the ratio flocculant/sediment (mg/g) was the same. The sediment concentration used in the zeta potential measurements is very low (even though the ratio of flocculant to clay is the same in the flocculation and zeta potential experiments). This is done in order to insure that at the time-scale of the experiment no flocculation occurs in the zeta potential measurements. Zeta potential experiments are performed in order to estimate the coverage of individual sediment particles by flocculant. Given this coverage, we will show that information can be gained about the flocculation behaviour of these particles for the higher clay concentrations.

3.1 Cationic flocculant

Three regions can be defined:

1) Underdosage of flocculant: For lower dose, the repulsive forces between particles (negatively charged in the absence or low amount of cationic polymers, implying negative zeta potentials) do not allow flocculation, and hence settling is minimal.

2) Optimal dosage: Cationic polyelectrolytes attach to the negatively charged particles, neutralizing their electrokinetic charge and making aggregation possible. At neutral zeta potential, flocculation is optimal and the supernatant is clear, indicating that the optimal polymer coverage is reached and the settling velocity is the highest.

3) Overdosage of flocculant: When the optimum dose is exceeded, flocculation still occurs, but at a lower rate. This is caused by the "excess" of positive charges at the clay surface, which increase the time for positive particles to encounter a negatively charged zone. The resulting flocs are large because of their high polymers content (particles bind with many polyelectrolytes in between them). When the flocculant dose is further increased, the particles become highly positively charged (positive and large zeta potentials), resulting in mutual steric repulsion, and a decrease in the settling velocity.



Figure 3.1 Settling rate and zeta potential measurements as function cationic polymer concentration.

3.2 Anionic flocculant

For anionic polymer (Figure 3.2) the zeta potential is always negative and increases in absolute value with concentration of flocculant, as more and more polyelectrolyte "glue" to the sediment particles.

Contrary to cationic flocculant, no optimal flocculant dose (zero zeta potential) can therefore be determined from zeta potential measurements. The reason is that anionic polyelectrolytes bind differently to sediment than cationic polyelectrolytes. In the case of cationic polyelectrolytes, the binding of the polyelectrolyte to the sediment is due to Coulombic attraction (positive charge of the flocculant and negative charge of the sediment are mutually attracted). At optimal flocculant dose, the flocculation is enhanced by the charge neutralization of the sediment particles coated by polyelectrolyte (Ibanez et al., 2015).

In the case of anionic polyelectrolyte, it was shown that the binding of the negatively charged polyelectrolyte to the negatively charged sediment could only occur in the presence of free cations contained in the water (Ibanez et al., 2015). These cations do not induce coagulation in the case studied here as their concentration is too low (tap water was used), but serve as "bridges" between the flocculant and the clay. Flocculation then occurs by another bridging mechanism, namely the attachment of two (or more) sediment particles to the same polyelectrolyte:

sediment - cation - polyelectrolyte - cation -sediment

This type of flocculation is promoted in the case of long polyelectrolyte (i.e. polyelectrolyte with a high molecular weight, as in the present study).

Three regions can also be defined:

1) Underdosage of flocculant: For lower dose, the repulsive forces between particles (negatively charged) do not allow for substantial flocculation, and hence settling is minimal. When the amount of anionic polymers increases, flocculation is made possible through the bridging mechanisms described above.

2) Optimal dosage: The zeta potential in this region does not vary; it is around -28 mV. Flocculation is optimal and the supernatant is less turbid. Contrary to cationic flocculation, the supernatant is not clear, indicating that many clay particles remain unflocculated. This is due to a deficit of cations in the water: we tested that in more saline water the supernatant clarity increased dramatically with salinity, as more and more clay particles could bridge to polyelectrolytes via cation links.

3) Overdosage of flocculant: More and more polyelectrolyte is present in the water, unbound to clay, due to cation shortage. The zeta potential decreases strongly. This decrease does not correspond to the adsorption of polymer to individual clay particles. As the polymer dose increases a gel starts to form and the electrophoretic mobility of the clay particles are altered as they have to move in a gel and not in water. The mutual steric repulsion between clay and polyelectrolyte and the increased viscosity of the suspending medium leads to a decrease in settling velocity.



3.3 Settling columns

Figure 3.3 shows the interface between clean water and sediments as function of time during the settling columns experiments carried out with optimum flocculant dosage as highlighted by the zeta-potential study: 70 mg/L for the cationic flocculant and ; the optimum 5 mg/l for anionic flucculant, The settling is faster and the water (supernatant) is clearer when cationic polymer is added than when anionic is used. The height of sediment beds at the end of the consolidation test is shown in Figure 3.4. The bed height at the end of the consolidation experiment is the highest when cationic polymer is used. However, the cationic polymer makes a fluffier layer and consequently its strength is lower. The reason is linked to the study presented above, namely that flocculation by cationic polyelectrolyte is due to Coulombic attraction. This results in DLA (Diffusion Limited Aggregation) which is known to produce large open flocs (Witten, 1981). With data from the consolidation test the permeability and strength parameter can be obtained (Merckelbach and Kranenburg, 2004; Merckelbach et al., 2002; Winterwerp, 2002).



Figure 3.3 Height interface between clean water and sediments as function of time.



Figure 3.4 Pictures of the consolidation tests at the end of the experiment. Picture on the left contains 30 g/l sediment, middle picture is 30 g/l sediment with 70 mg/l cationic flocculant and picture on the right panel is composed of 30 g/l sediment and 5 mg/l anionic flocculant.

Relative permeability and effective stress parameters are given in Table 3.1. The formulas used to obtain effective stress and permeability are shown below (Winterwerp, 2002):

Permeability: (eq.1)

Effective stress: (eq.2)

When cationic polyelectrolyte is used the permeability parameter is the lowest. In addition, the bed sediment height is higher and less compact, resulting in a lower effective stress.

When the consolidation test is performed with anionic polymer the permeability obtained is smaller, although it is still higher than the one obtained from the sediments alone. The sediment bed formed has almost the same height than the one obtained from the clay alone. The sediment bed is more compact than the bed formed by cationic polymer. The effective stress of this bed is larger than the bed formed with cationic but it is still lower than clay.

Table 3.1 Permeability and effective stress parameters after Merckelbach and Kranenburg (2004).

Sample	Permeability parameter Kk [m/s]	Effective stress parameter Kp [Pa]	Permeability [m/s]	Effective Stress [Pa]	Fractal dimension nf
30 g/l sediment	2.4 e-13	9.92 e+06	2.36 e-24	0.00102	2.63
30 g/l sediment + 70 mg/l cationic	4.6 e-18	2.2 e+13	2.22 e-37	0.00012	2.79

30 g/l sediment + 5	5.6 e-15	8.9 e+13	1.82 e-29	0.00025	2.74
mg/l anionic					

CONCLUSIONS

This study correlates flocculation to consolidation and strength development properties (indicated here as effective stress). It was shown that the flocs properties (linked to the flocculant properties used to create them) determine the settled bed consolidation and strength properties.

In particular, the combination of all the tests performed enables to link the physics properties (settling / consolidation) of the flocculated material with the geo-chemical properties (polyelectrolyte dosage, water chemistry) of the suspending medium. It was confirmed that zeta potential measurements provide useful information on the flocculation and settling behavior of the material. In particular, it provides a good method to identify the optimum flocculant dosage in the case of cationic flocculant. As zeta potential measurements are fast, easy and relatively cheap to perform, their systematic use will provide to be an asset for further investigation. Even though this preliminary flocculation study was done on a model system, it was already demonstrated (Ibanez, 2014) that zeta potential measurements could be useful in the case of coagulation of TFT.

The general results for anionic and cationic polyelectrolyte aided flocculation are:

Cationic polyelectrolyte: the zeta potential measurement has a clear relation with the settling rate. When the zeta potential is close to zero the settling is fastest, this point gives the optimal dose of polymer. Settling is improved by cationic polymers, resulting in a clean supernatant. Since the flocculation is induced by Coulombic attraction, the aggregation is diffusion-limited (DLA), resulting in open flocs with relatively thick settled bed. The permeability parameter is low as it is the effective stress.

Anionic polyelectrolyte: the zeta potential measurements give an indication of the polyelectrolyte coverage of individual clay particles. When this coverage is low, the settling rate is low. However, aggregation by anionic polyelectrolyte requires the presence of free cations in the water. From very systematic experiments (varying both clay and polyelectrolyte doses), it was shown from zeta potential measurements that flocculation is limited by the availability of cations (Ibanez, 2015). It is important to note that the concentration of cations required to achieve flocculation is below the concentration required for coagulation. The structure of the obtained flocs is different than cationic flocs, as they are more compact, resulting in a stronger bed with higher stress and a higher permeability than for the cationic bed.

These results are based on natural (river) clay material. Similar experiments are ongoing in our laboratory for Oil Sands FFT .

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