Investigating the settling behaviour of saline tailing suspensions using kaolinite, bentonite, and illite clay minerals

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ABSTRACT

This study aimed to understand the dewatering behaviour of three types of clay minerals (i.e. kaolinite, bentonite, and illite) in saline water, and in particular the effect of factors including clay mineralogy, clay suspended solid concentration, water salinity, and polymer flocculant dosage on dewatering behaviour. It was demonstrated that the addition of polymer flocculants helped all three clay types to settle due to the polymer bridging effect. In saline water, this bridging effect worked best above a certain threshold level for illite but tailed off for the other two clay types. As well, high-salinity water was observed to assist bentonite and illite to settle faster but to hinder the settling rate of kaolinite. In addition to inter-particle forces, the clay aggregate structures formed through the addition of the flocculants were identified to play an important role in determining the dewatering behaviour of clay minerals in saline water. Cryo-scanning electron microscopy (SEM) identified that, depending on the clay type, the floc structures in saline water were either dense (water-excluding) or loose (water-trapping). Dense flocs were observed to settle more quickly than loose flocs. This study has practical applications in providing guidance for the processing of complex tailings containing clay minerals in saline water.

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1. Introduction

Clay minerals are ubiquitously present in most mine tailings. They create widespread problems in transport of tailings slurries and affect the long-term stability of tailings storage facilities [1]. Fine particle size, surface chemistry, and the internal structure of clay minerals affect water-holding capacity, and the ease of transport or rheology and viscosity of tailings slurry. They also affect the capacity of tailings to release or capture contaminants. Clay minerals are anisotropic phyllosilicates which comprise one alumina octahedral (O) sheet and one or two silica tetrahedral (T) sheets that fit together to form a basic repeating unit of either 1:1 (TO) or 2:1 (TOT) layers [2]. They usually have a complex surface chemistry arising from the heterogeneity of the charged edges and faces of these layers. The basal faces carry a permanent pH-independent negative charge, while the edges possess a pH-dependent charge [3]. Owing to the different basal/edge surface characteristics, clay particles can aggregate to form edge-edge (EE), edge-face (EF), and face-face (FF) aggregate structures [4].

The flocculation and thickening of fine clay particles have been extensively studied both at the laboratory and industrial scale to enhance the efficiency of solid-liquid separation [5–10]. However, to date, there have been limited economical and practical methods for recovering process water from these tailings for further use [11,12].

Poor solid-liquid separation arising from the presence of clay minerals continues to impose high operational and capital costs [13].

The increasing use of saline water has made the tailing management situation even more complicated. In some mines, for example coal mines, salts are present in the sedimentary geology or are generated by weathering processes which cause the process water to be saline. Also, many mine sites, particularly those in water-sensitive environments, are introducing new sources of water for processing purposes including saline groundwater and seawater. The use of saline water may negatively (or positively) affect the settling behaviour of clay particles in the tailings and therefore the turbidity of the recycled water. However, to date, research has focused mainly on the dewatering behaviour of tailings in fresh water. This means that the settling rate of saline tailings remains poorly understood.

In the absence of polymer flocculants, Nasser and James [14] found that, in acidic pH conditions (e.g. pH 2), kaolinite particles settle in flocculated form regardless of electrolyte concentration. This is due to the strong oppositely-charged electrostatic interactions of basal and edge planes. However, in basic pH ranges, the particles settle in both dispersed form (in 0.001 M NaCl electrolyte concentration) and flocculated form (in 0.1 and 1 M NaCl electrolyte concentration). Gorakhki and Bareither [15] evaluated the effect of salinity and cation valence on the sedimentation behaviour of kaolinite, bentonite, and soda ash mine tailings without addition of polymers and suggested that an increase in salinity led to higher sedimentation rates and final solids contents for bentonite. In contrast, a salt concentration of 100 mM

was identified as a critical concentration whereupon the settling rate of kaolinite decreases regardless of salt type. This decrease was attributed to an increase in sedimentation fluid density and viscosity.

On the other hand, other studies reported that when polymer was present, it may interact with saline water so as to affect the dewatering of clay minerals. Siffert and Bocquenet [16] investigated the adsorption of partially hydrolyzed polyacrylamides onto kaolinite, and found that adsorption was higher in a strongly saline medium than in pure water due to a change in polymer conformation. They found that in a $CaCl_2$ medium, the adsorption was more significant than in a NaCl medium. In addition, Mpofu et al. [8] studied the effect of hydrolysable ions Mn^{2+} and Ca^{2+} in combination with anionic polyacrylamide flocculant on the surface chemistry, particle interactions, and dewatering behaviour of kaolinite. They found that the specific adsorption of hydrolyzed metal ions led to an increased settling rate at pH 7.5 and 10.5. Ji et al. [17] studied the settling behaviour of coal tailings in the presence of three polymer flocculants, non-ionic polyacrylamide (PAM), anionic Magnafloc 1011 (MF) and cationic $Al(OH)_3$-polyacrylamide (Al-PAM) in both fresh water and saline solution. They identified that the settling of tailings depended significantly on solution salinity, as well as flocculant type and dosage. MF showed the best settling performance among the three polymers in both fresh water and saline solutions.

Based on previous studies, it is expected that saline water may interact with clay minerals, making commonly-used flocculants less effective and leading to a different dewatering performance in dewatering of clay-rich tailings. As clay tailings are increasingly treated in saline water [17–20], there is an increased need to understand the dewatering behaviour of saline clay-rich tailings. The dewatering behaviour of clay minerals in saline water is of importance to both fundamental understanding and industry practice.

The structure of clay aggregates plays an important role in dewatering of tailings. Although extensive studies have examined how to improve the recovery of water from mineral tailings, low settling rates and consolidated waste slurries with a low solid density are commonly observed in thickeners [21]. While an increased floc size can increase the settling rate, compact consolidation of the resulting sediment can be diminished if the flocs are not also dense in structure [5]. Mpofu et al. [7] studied the effect of polymer structure type on flocculation, interfacial chemistry, particle interactions and dewatering behaviour of smectite dispersions in fresh water. According to Mpofu et al. [7], compared to PAM, polyethylene oxide (PEO) produces better inter-particle bridging, a higher settling rate and higher floc compaction behaviour upon shear. For PAM, the hydrogen bonding interactions appear to be weakened as a consequence of electrostatic repulsion between the polymer's COO^- pendant groups and the negatively charged clay particle surfaces. This, in conjunction with possible steric hindrance due to PAM polymer chain branching, leads to the formation of loose, open and fragile flocs and therefore a slower settling rate.

It is interesting to note that flocs structures may be affected by external parameters, such as water salinity. It was found that high-salinity water can influence the efficiency of polymeric flocculation of clay minerals, leading to a different solid-liquid separation performance compared to fresh water [8,17,20,22]. This is probably because the presence of salts alters the interaction between flocculants and clay particles leading to different clay aggregate structures. It is therefore posited that saline water may cause clay minerals to aggregate differently, in ways which release or entrap water, affecting their dewatering performance.

In this study, kaolinite, a non-swelling clay mineral with a 1:1 (TO) structure, bentonite, a swelling clay mineral with a 2:1 (TOT) structure, and illite, a non-swelling clay mineral with a 2:1 (TOT) structure, were used to represent three typical types of clay minerals commonly found in mine tailings. The aim was to understand how clay minerals interact with saline water so as to affect dewatering behaviour of clay-rich tailings. The settling behaviour of pure kaolinite, bentonite and illite clay minerals were studied and the relationship between the

dewatering rate of clay minerals and the driving factors (clay type, clay suspended solid concentration, water salinity, and polymer flocculant dosage) were summarised. In addition, through the use of cryo-SEM, the effect of water salinity on clay aggregate structure was investigated in the presence of a range of water salinities. This study may provide strategies to improve the separation of clay-rich tailings in the presence of saline water.

2. Material and methods

2.1. Raw materials

The kaolinite Q38 mineral was purchased from Sibelco Australia Limited Company, South Australia. A quantitative XRD analysis showed that it contained 85 wt% kaolinite, 11 wt% muscovite, and 4 wt% quartz [23]. Murray and Lyons [24] and Du et al. [25] indicated that there are two types of kaolinite minerals, well-crystallized and poorly crystallized kaolinite. Kaolinite Q38 belongs to the latter category. Poorly crystallized kaolinite particles are poorly ordered and have more complex surface structures and higher specific surface areas than their well crystallized counterparts, as identified by SEM [25]. Bentonite was purchased from Sibelco Group, Australia. Quantitative XRD analysis showed that the sample contained 63 wt% montmorillonite, 25 wt% albite, and 12 wt% quartz. The illite sample was purchased from New Directions Laboratory, Australia and contained 75 wt% illite, 15 wt% kaolinite, and 10 wt% argilla. One type of anionic polyacrylamide/ polyacrylate (PAM) copolymer with a trade name of Magnafloc 1011 (MF1011) powder was supplied by BASF Australia Limited and was used as the polymer flocculant. Polymer stock solution (1 g/L) was prepared in deionised water daily. MF1011 was selected for this study as the flocculant because Ji et al. [17] investigated the settling behaviour of clay-rich coal tailings in saline solutions and identified that anionic PAM MF1011 exhibited good settling performance in saline water.

In addition, three types of saline water with low-, medium-, and high-salinity were used for the dewatering tests in this study to represent the common range of saline process water used in the coal preparation plants in Queensland. The range of salinities was based on a survey conducted by Ofori, Firth, McNally and Nguyen [26] of Australia coal preparation plants regarding the quality of process and make-up water. The minimum, medium and maximum values of the concentration of major ions in low-, medium-, and high-salinity water indicated the variation in composition of process water used in the coal processing plants. In the lab, synthetic saline water was prepared by mixing a known amount of analytical grade salts such as $CaCl_2 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, KCl, Na_2SO_4, NaCl, $NaHCO_3$, and $MgSO_4 \cdot 7H_2O$ in deionised water. The salts were purchased from Sigma-Aldrich and used directly without further purification. The saline water was well mixed using a mechanical stirrer and used for settling, zeta potential, and cryo-SEM tests. The composition of low-, medium-, and high-salinity water is summarised in Table 1. The water composition was also compared with some other process saline water used in metallic mines [19,27, 28] listed in Table 2. These showed even higher concentrations of sodium and chloride ions.

The size distribution of the clay particles was measured by a Laser Diffraction Malvern Mastersizer (Model No MSX14) and the results are shown in Fig. 1. Kaolinite had greater than 80% particles smaller than 19.2 μm. Bentonite had greater than 80% particles smaller than 28.6 μm and illite had greater than 80% particles smaller than 14.8 μm.

Nitrogen sorption experiments were carried out on a Micromeritics TriStar 3020 analyser after degassing under vacuum on a Micromeritics VacPrep061 at 200 °C for a minimum of 6 h. The specific surface areas were calculated from the adsorption isotherms via a multi-point Brunauer–Emmett–Teller (BET) model. The BET surface area of kaolinite, bentonite, and illite were 14.30 $m^2\ g^{-1}$, 37.15 $m^2\ g^{-1}$, and 56.89 $m^2\ g^{-1}$, respectively. It was interesting to find that the size of the kaolinite was finer than bentonite whilst its specific surface area

Table 1
The composition of synthetic saline water (mg/L).

Saline water	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO^{3-}	SO_4^{2-}	Cl^-	Conductivity (ms/cm)	pH
Low-salinity	6.6	6.4	19.2	2.1	56.5	10.6	11.6	0.3	7.2
Medium-salinity	93.0	126.8	1136.8	20.9	726.2	1177.8	1020.3	4.8	8.2
High-salinity	360.5	470.7	3060.3	58.1	2323.8	4536.9	2101.0	10	9.1

was smaller. Similar BET results were also reported by researchers [29–32]. This is probably due to a difference in the particle structures of the two clays. As is known, specific surface area is a fundamental and intrinsic property of solids which depends primarily on the size, shape, and surface roughness of the particles. Unlike kaolinite, swelling bentonite particles additionally exhibit internal surfaces in their inter-layer spaces [33]. Micro- and mesopores were generated on the partly N^2-accessible interlayer space at the bentonite particle edge surfaces and also contributed significantly to the total specific surface area of gas adsorption measurement [34].

2.2. Settling tests

Settling tests were conducted with 5 wt% and 10 wt% suspensions of single clay minerals (kaolinite, bentonite, and illite) using deionised water and low-, medium-, and high-salinity water. After transferring the well-dispersed clay slurry to a 500 mL graduated cylinder, a known volume of 0.1 wt% PAM solution was added in a single step at the top of the slurry. The cylinder was then stoppered and inverted 10 times to ensure the polymer was well mixed. The settling rate of the flocculated suspension was then determined by recording the time taken for the "mud line" (solid–liquid interface) to pass between the 500 and 300 mL marks (over a distance of 106 mm).

2.3. Zeta potential test

The zeta potential of clay mineral suspensions was determined using a Zeta Probe instrument (M/s Colloidal Dynamics Ltd., USA). This electroacoustic-based equipment can measure the zeta potential of very concentrated slurries. The measurement was carried out on agitated suspensions (5 wt% or 10 wt%) of kaolinite, bentonite, and illite particles dispersed in low-, medium-, and high-salinity water. Depending upon the state or flow behaviour of the dispersion, the fixed agitation rate of 250 rpm was used. Experiments were carried out at different flocculant dosages in the range of 0–200 g polymer/t solid to study the effect of flocculant dosages on the zeta potential of clay particles. Particle electrophoretic mobilities were measured in a

vertically mounted glass cell inside a Zeta Probe apparatus. At least 10 mobility measurements were performed at each of the two stationary planes at each polymer dosage, and the average mobility was converted to zeta potential using the Smoluchowski equation. This equation was chosen as the size of the particles was large compared to the double layer thickness of the clay particles.

2.4. Cryo-SEM test

The flocculated clay slurry was prepared according to the process set out in Section 2.2 and used for the cryo-SEM testing. A drop of flocculated sample was taken shortly after introduction of the flocculant using a wide bore pipette. The sample was then mounted onto the top of a 3 mm long copper rivet with an outer diameter of 2.4 mm and an inner diameter of 1.7 mm. The copper rivet was fixed on a sample holder and plunged into liquid nitrogen at −210 °C, at which temperature the sample was converted into a glassy-like amorphous solid without any ice crystals forming. The small volume of the sample (about 0.01 mL) and the high heat conduc-tivity of copper minimized shrinkage and distortion of the sample during freezing. The very fast freezing process avoided crystallization of water to ice and associated volume changes which could alter structures. The sample was then transferred under vacuum to the sample preparation chamber equipped with an Oxford Instruments cryo-transfer and fracture stage, where the frozen sample was fractured to expose a fresh surface. The sample temperature was then raised from −145 °C to −100 °C over 3 min and the samples left to stabilize at this temperature over 5 min to remove partial frozen water from the upper exposed surface of the sample to reveal surface structure. The temperature was reset to −145 °C afterwards which took over 4 min. The sublimation time was optimized empirically to expose the internal floc structures and preserve the aggregate's integrity and pore structures.

The sample was eventually coated with iridium plasma for 6 min to avoid charging during the imaging process by a JSM 7100F scan-ning electron microscope (SEM) normally operated at 7 kV voltages for Energy Dispersive Spectroscopy (EDS) analysis with a stage

Table 2
The composition of synthetic saline water used in the coal industry and some other saline process water used in metallic mines (mg/L).

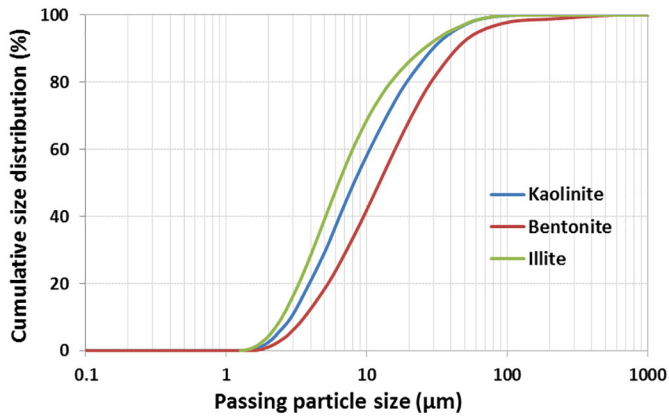|	Country company	Saline water	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO^{3-}	SO_4^{2-}	Cl^-
Coal flotation plant	QLD Australia	Low salinity	6.6	6.4	19.2	2.1	56.5	10.6	11.6
		Medium salinity	93.0	126.8	1136.8	20.9	726.2	1177.8	1020.3
		High salinity	360.5	470.7	3060.3	58.1	2323.8	4536.9	2101.0
Nickel flotation plant [25]	Mt Keith operation, BHP Billiton, Australia	Saline water	400	5100	20,000	940		23,000	32,000
Sulphide flotation plant [26]	Batu Hijau, Newmont, Indonesia	Sea water	7.6	0.48	13,940	9.36		22.08	21,250
	Las Luces, Minera Las Cenizas, Chile	Sea water	7.6	0.48	13,940	9.36		22.08	21,250
	Texada, Closed, Canada	Sea water	7.6	0.48	13,940	9.36		22.08	21,250
	Tocopilla, Closed, Canada	Sea water	7.6	0.48	13,940	9.36		22.08	21,250
	Esperanza-under development, Antofagasta, Chile	Sea water	7.6	0.48	13,940	9.36		22.08	21,250
Copper deposit	Mantos Blancos deposit, Northern Chile [27]	Saline ground water Sample 14877	290	20	1570	20		1250	2025
		Saline ground water Sample 14253	730	100	11,470	70		8220	11,850
		Saline ground water Sample 14894	950	2070	35,920	620		4560	55,710
		Saline ground water Sample 13965	870	3350	74,800	640		6650	125,500

Fig. 1. The size distribution of kaolinite, bentonite, and illite minerals.

temperature of − 145 °C. A series of images with magnifications from 1000× to 10,000× covering micro- and macro-flocs were taken for analysis by statistical image.

3. Results and discussions

3.1. Settling test

The settling performance of kaolinite, bentonite, and illite in the presence of MF1011 in deionised water and saline water is shown in Fig. 2a, b, and c respectively. For 5 wt% and 10 wt% of bentonite in deionised water and low-salinity water, and 10 wt% in medium-salinity water, negligible settling was triggered by polymer addition. With the exception of those samples, the addition of polymer flocculant accelerated the settling rate of a known concentration of all clay minerals to some extent, suggesting that the flocculation of clay particles was triggered and more and larger flocs were produced at a higher polymer amount.

As shown in Fig. 2a, at all the polymer dosages tested, 5 wt% kaolinite suspension showed a better settling performance in deionised water than in saline water. The settling rate decreased with an increase in water salinity especially when polymer dosage was high. Settling rates of the flocculated 10 wt% kaolinite suspensions were much slower compared to 5 wt% suspensions at all salinity levels and flocculant dosages.

Previously, several of experiments demonstrated that particle settling velocities are lower at higher solid concentrations due to the modification of the flow induced by falling particles [35,36]. Winterwerp [37] attributed this effect to three main hindering factors: a) return flow and wake formation; b) viscosity; and c) buoyancy or reduced gravity.

Low-salinity water showed the highest settling rate for 10 wt% kaolinite while deionised and high-salinity water showed slower rates. With the change of concentration from 5 wt% to 10 wt%, the decrease in the settling rate was much greater in deionised water. This was possibly because the increased hindering effect of the high kaolinite concentration was the dominant factor in deionised water. In saline water, however, electrostatic repulsion between the particles was reduced because of the electrical double layer compression or ion shielding of the surface charges, and may have induced the particles to form more and denser aggregates. The formation of aggregates may have caused the kaolinite to settle faster at higher clay concentrations in saline water. From this, it seemed clear that the suspended solid percentage and water salinity were two important driving factors affecting the settling rate of kaolinite minerals. According to Liu and Peng [22], kaolinite may generate more of less dense EF aggregates in high-salinity water due to the presence of calcium ions and the complex structure of kaolinite Q38, leading to a reduced settling rate with increased water salinity. The aggregate structure of kaolinite was further investigated in this study.
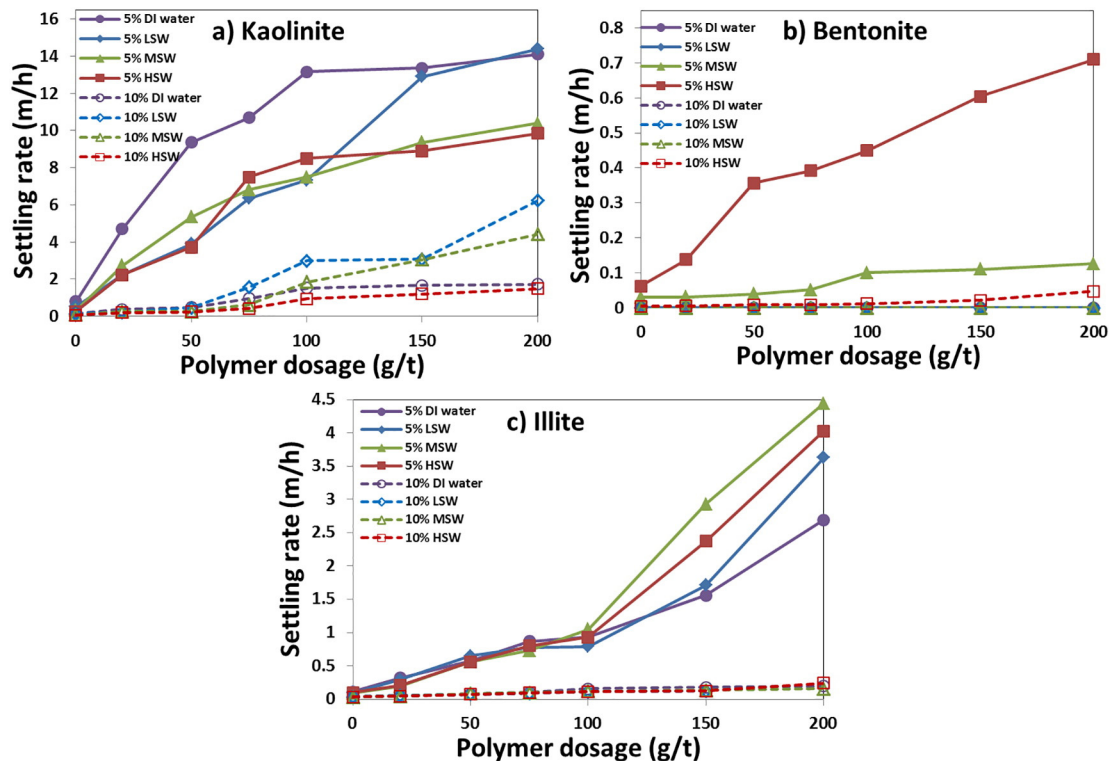

Fig. 2. Settling rates of 5 wt% and 10 wt% of a) kaolinite, b) bentonite, and c) illite dispersions as a function of polymer dosage in deionised (DI) water, low-salinity water (LSW), medium-salinity water (MSW), and high-salinity water (HSW).

Bentonite has a high weight percentage of sodium montmorillonite, which can swell in contact with water and produce a viscous gel-like structure, hindering its settling rate [38]. As shown in Fig. 2b, in deionised and low-salinity water, bentonite hardly settled. However, the gelation structure was interrupted and the settling rate increased with an increase in polymer dosage and water salinity. 5 wt% of bentonite showed a relatively high settling rate of 0.047 m/h in high-salinity water at 200 g/t polymer dosage. Compared to kaolinite, the settling rate of bentonite was negligible even in the presence of a high dosage of polymers. The improved settling rate of bentonite may have resulted from the presence of Ca^{2+} ions in saline water [39]. The role of divalent and trivalent metal ions such as Ca^{2+} and Al^{3+} was to first exchange with the sodium ions on the clay and secondly, to act as coagulants for the clay particles to form denser FF aggregates of the clay platelets, leading to a reduced effective volume of the clay network and therefore improved settling behaviour [40]. According to Mpofu et al. [6], in the presence of polymer flocculant, flocculant adsorption is also significantly enhanced by the presence of Ca^{2+} ions due to the adsorption of the first hydrolysis products of metal ions, contributing to more effective polymer bridging and an increase in settling rate.

The settling rate of illite was lower than kaolinite but higher than bentonite under the same test conditions (Fig. 2c). An increase in water salinity was observed to assist illite to settle faster. Also, illite settled much faster at a solid percentage of 5 wt% than 10 wt%. At 5 wt%, the polymer worked best above a certain threshold level. When polymer dosages were lower than 100 g/t, illite settling rates were quite similar and low. With an increase in polymer dosage to more than 100 g/t and in medium- and high-salinity water, the settling rate increased significantly. It seems that 100 g/t was the turning point dosage for illite, and the formation of more and denser aggregates due to stronger polymer bridging effect may contribute to the faster settling rate at higher polymer dosages. The aggregate structures were further investigated.

The studies on dewatering of tailings using flocculants are well documented [41–45]. However, not many studies are available for dewatering of tailings and quantifying the solid–liquid separation process in saline water. The current study of settling behaviours of kaolinite, bentonite, and illite in the presence of different salinity water showed that the settling rate of a single clay mineral can be affected by many factors including clay solid percentage, clay minerology, polymer dosage, and water salinity. The overall relationship between clay settling behaviour and various affecting parameters investigated in this study is summarised in Table 3.

As shown, an increase in polymer dosage increased the settling rate of kaolinite while an increase in water salinity and solid percentage played an opposite role. For bentonite, an increase in polymer dosage and water salinity only slightly accelerated the settling rate, and the increase in solid percentage decreased the settling rate significantly. Illite showed a similar trend to bentonite, but the effect of polymer dosage and water salinity was stronger.

In addition, the resulting turbidity of the supernatant for both 5 wt% and 10 wt% of all three flocculated clays was also measured and found to be well below 50 NTU. For example, the measured turbidities in the first 30 min of the turbidity experiments with 5 wt% kaolinite, bentonite, and illite (for 200 g/t of polymer added) were 12 NTU, 10 NTU, and 23 NTU, compared to turbidities of unflocculated clay suspensions in high salinity water of 416, 34, 455 NTU respectively. This indicated that the supernatant had very good water clarity which would be suitable for recycling.

3.2. Zeta potential

Zeta potential represents the surface charge of clay particles in suspension and can be correlated with clay inter-particle forces. The zeta potential of kaolinite, bentonite, and illite was determined as a function of polymer dosage as shown in Fig. 3a, b, and c respectively. The pH of the three saline waters ranged from 8 to 9. At this pH range, pre-flocculated kaolinite aggregates that form through inter-particle interactions possessed a negative zeta-potential of −14.2 mV and −17.9 mV for 5 wt% and 10 wt% respectively in low-salinity water, −29.8 mV and −28.8 mV in medium-salinity water, and −23.5 mV and −24.4 mV in high-salinity water. It was noted that the zeta potential of kaolinite was not affected by solids concentrations as 5 wt% and 10 wt% kaolinite slurry showed similar zeta potentials at the same water salinity, consistent with results report by Teh et al. [46].

Water salinity was observed to affect the zeta potential of kaolinite. With the increase in water salinity, due to the electrical double layer compression or ion shielding effect, surfaces charges were expected to be less negative. However, medium- and high-salinity water showed greater zeta potential than low-salinity water. This was probably caused by the precipitations formed in medium- and high-salinity water during the preparation process. Since the two waters were used directly to keep the natural chemistry without filtration for zeta potential tests, the presence of the precipitation may have affected the zeta potential results by increasing the zeta potential values.

When polymeric flocculant PAM was added, the magnitude of the zeta potential of 5 wt% kaolinite decreased greatly with increasing PAM dosage in low-salinity water and high-salinity water. Addition of 200 g/t polymer in 5 wt% of kaolinite in low-salinity water decreased the zeta potential to almost zero. This decrease in the magnitude of the zeta potential implied the presence of strong bridging interactions, leading to increased flocculation and showing that the highest settling rate occurred at zero zeta potential. This was consistent with the highest settling rate being observed in low-salinity water as shown in Fig. 2a. However, flocculated kaolinite showed a slow settling rate in high-salinity water, and this may be because of the formation of less dense EF network structures [46].

On the other hand, the addition of PAM to 10 wt% kaolinite slurry in low-, medium- and high-salinity water only slightly decreased the magnitude of the zeta potential. Even in the presence of 200 g/t PAM, zeta potential values stayed at around −20 to −30 mV. This implied that polymer adsorption on kaolinite surfaces may be weaker, and correspondingly, that the bridging interactions brought about by the polymers were also weaker. Greater viscosity and buoyancy were expected for 10 wt% kaolinite, hindering the settling of flocculated kaolinite at high solid percentages.

The overall magnitude of negative zeta potential for bentonite was greater than kaolinite at the same chemical conditions tested, as shown in Fig. 3b. This suggested greater viscosity and buoyancy existed in bentonite slurries, hindering bentonite settling. Unlike kaolinite, 5 wt% and 10 wt% bentonite showed the lowest zeta potential in high-salinity water among the three saline waters tested. Also, the addition of PAM to high-salinity water reduced the zeta potential of bentonite. This allowed more PAM to adsorb to clay surface as dosage levels increased, increasing the strength of bridging interaction and creating more flocs. This meant that the maximum flocculation and highest settling rate for bentonite occurred with higher PAM dosages as indicated in Fig. 2b.

By comparison, medium- and low-salinity water showed only a slight decrease in zeta potential as PAM dosages increased. This may

Table 3
The effect of polymer dosage, water salinity, and clay solid percentage on the settling rate of clay minerals. The blue arrows represent increases and the green arrows represent decreases in settling rates.

Settling rate of clay	Kaolinite	Bentonite	Illite
Polymer dosage	↕	↑	↑
Water salinity	↓	↑	↑
Solid percentage	↓	↓	↓
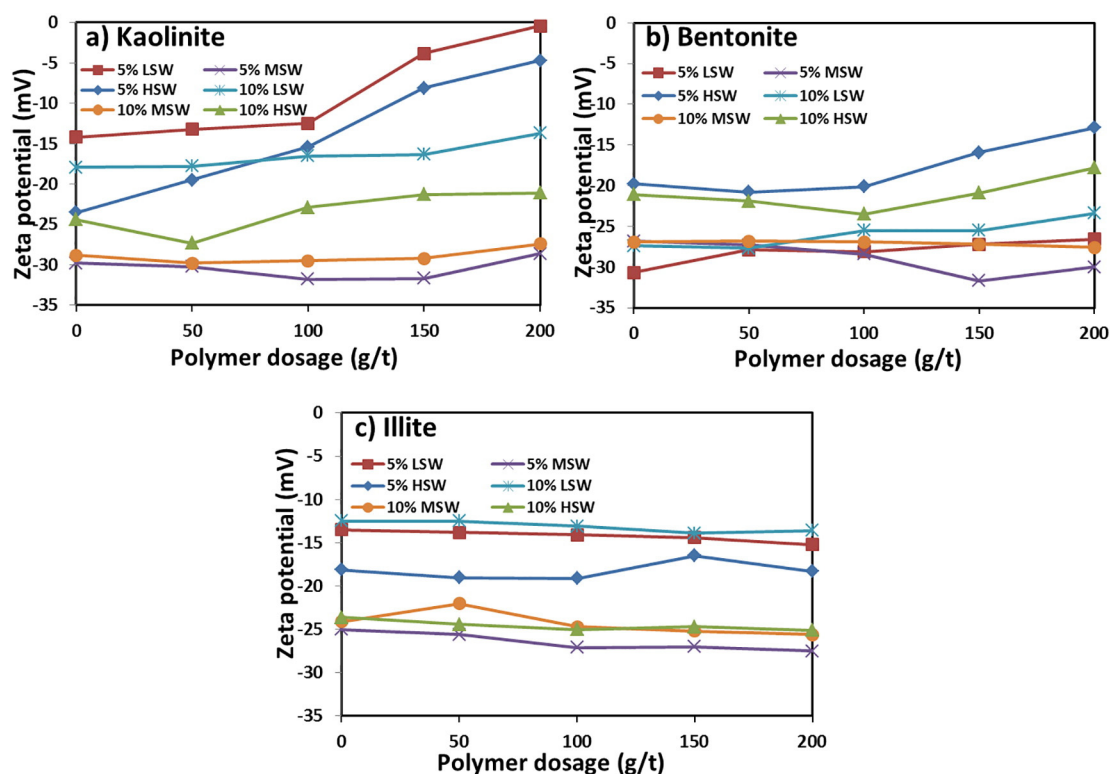
Fig. 3. Zeta potential of 5 wt% and 10 wt% of a) kaolinite, b) bentonite, and c) illite dispersions as a function of polymer dosage in low-salinity water (LSW), medium-salinity water (MSW), and high-salinity water (HSW).

be because the polymer adsorption on bentonite surface was weaker in low- and medium-salinity water due to less effective ion shielding. The adsorption of the polymer PAM on bentonite due to hydrogen bonding interactions appeared to be weakened by the stronger electrostatic repulsion between the polymer's COO^- pendent groups and the negatively charged particle surfaces, leading to weaker polymer adsorption in low- and medium-salinity water. On the other hand, the formation of more EF network structures in low- and medium-salinity water might also affect zeta potential values, reducing the effect of polymer dosages. Teh et al. [46] reported higher yield stress at higher zeta potentials due to the formation of EF network structures. The weaker bridging effect of PAM and the formation of EF network structures may explain why a very slow settling rate was observed even in the presence of high dosages of polymer in low- and medium-salinity water.

Fig. 3c shows that the increase in PAM concentration had negligible impact on the magnitude of zeta potential of illite in all three types of saline water tested. However, Fig. 2c shows that settling rate of illite was between those of kaolinite and bentonite, and increased rapidly when PAM dosage was higher than 100 g/t. This suggested that polymer adsorption on illite occurred but the degree of adsorption may be weak and also EF network structures might be generated [46].

Apart from inter-particle forces, clay flocculation structures can be affected by polymer dosage, clay type, clay minerology, and water salinity and these may also play a vital role in determining the settling rate of illite. The floc structures of clay minerals were further investigated by cryo-SEM.

3.3. Cryo-SEM

To investigate the impact of PAM in the presence of saline water on the floc structures of kaolinite, bentonite, and illite, the flocculation points where the highest settling rates were obtained were selected for cryo-SEM tests. For kaolinite, the cryo-SEM images of 5 wt% kaolinite flocculated by 200 g/t MF1011 in low-salinity water and high-salinity

water are shown in Fig. 4 and Fig. 5, respectively. Fig. 4 shows the presence of large aggregates, suggesting that the addition of PAM triggered strong flocculation of kaolinite particles in low-salinity water. A close inspection shows more particles appear to be linked in a linear lamellar pattern predominantly of FF aggregates. The denser FF aggregates increased kaolinite floc density and therefore likely improved dewatering in low-salinity water.

On the other hand, Fig. 5 shows that an increase in water salinity affected kaolinite aggregate structures and led to the formation of network structures for 5 wt% of kaolinite flocculated by 200 g/t MF1011 in high-salinity water. Although compact FF structures and loose EF structures coexisted, the presence of more EF structures in high-salinity water was apparent and contributed to a more network structure. This type of structure is more likely to trap water resulting in added buoyancy and therefore a slower settling rate. According to Lagaly [47], divalent ions including Ca^{2+} can more strongly attract clay particles than monovalent cations, such as Na^+, and therefore have a more important effect on the coagulation of clay particles. Poorly crystallized Kaolinite used in this study had a complex structure featuring coexisting multiple edge surfaces on the basal surface [25]. In the presence of a high concentration of divalent ions in high-salinity water, the negative charges of edge and basal surfaces on kaolinite were minimized at pH 8–9. Under these circumstances, van der Waals forces prevailed in drawing particles towards each other. This, together with hydrogen bonding, allowed more contact opportunities for kaolinite edge and basal surfaces to form loose EF aggregates in high-salinity water. This phenomenon may be more obvious when polymer was present and bridging effects applied. Consequently, even in the presence of polymers, kaolinite exhibited a slower settling rate as water salinity increased. This was consistent with the settling behaviour shown in Fig. 2a.

In contrast, polymer-flocculated bentonite showed different aggregate structures. Fig. 6 shows the cryo-SEM image of 5 wt% bentonite in the presence of 200 g/t MF1011 in high-salinity water where the
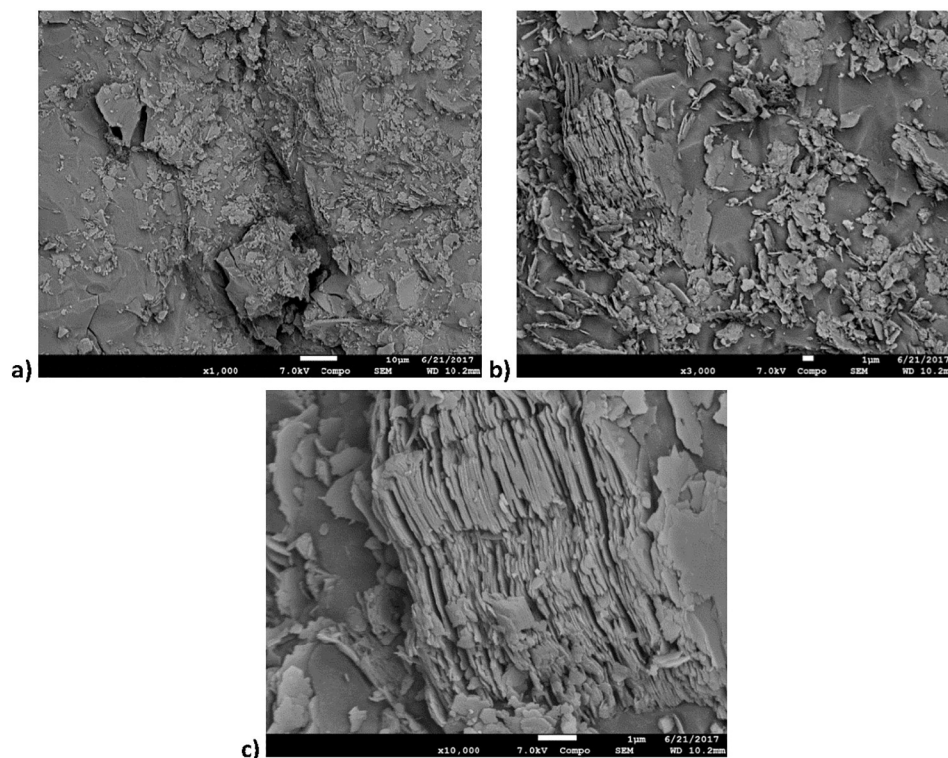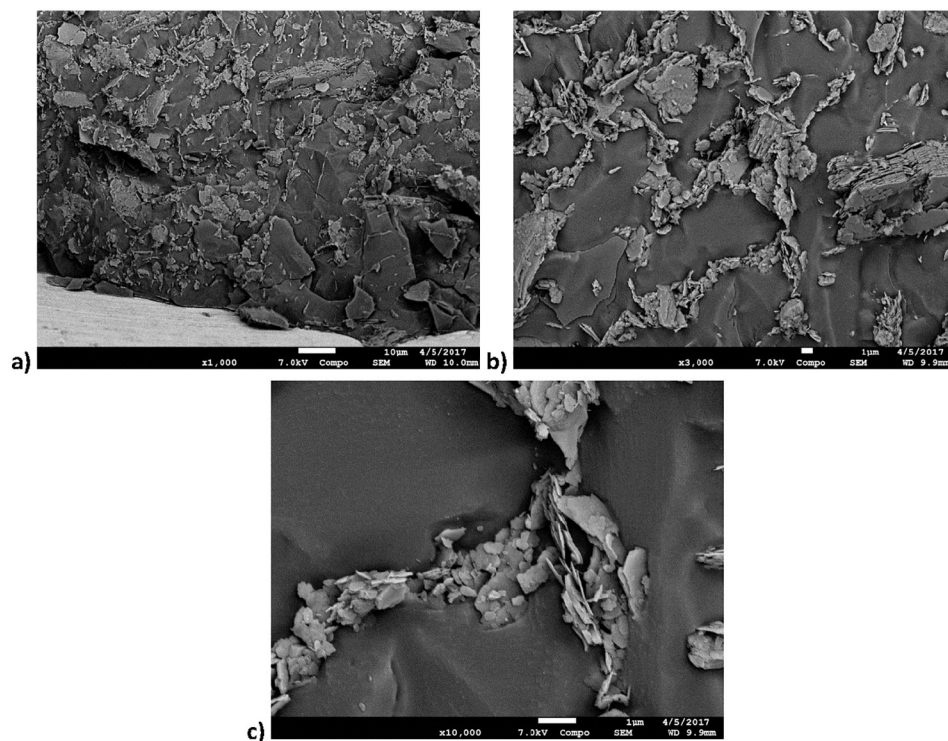
Fig. 4. Cryo-Scanning electron micrographs of 200 g/t PAM flocculated 5 wt% kaolinite dispersions in-low salinity water ranking at (a) 1000× and (b) 3000× and (c) 10,000× (with sublimation at −100° for 5 min).

highest settling rate was observed. As shown, bentonite flocs were in a much more dispersed state and present in a linear, network pattern. The three dimensional network structures were dominated by EF associations with a lower density and a poorly compressible structure which readily traps water [38], and presents difficulties in dewatering

that lead to a much slower settling rate of bentonite compared to kaolinite (confirmed by the settling results in Fig. 2).

The flocculated illite structure was also studied by cryo-SEM. 5 wt% of Illite flocculated by 200 g/t PAM in medium-salinity water showed the highest settling rate. The floc structure was investigated by

Fig. 5. Cryo-Scanning electron micrographs of 200 g/t PAM flocculated 5 wt% kaolinite dispersions in high-salinity water ranking at (a) 1000× and (b) 3000× and (c) 10,000× (with sublimation at −100° for 5 min).
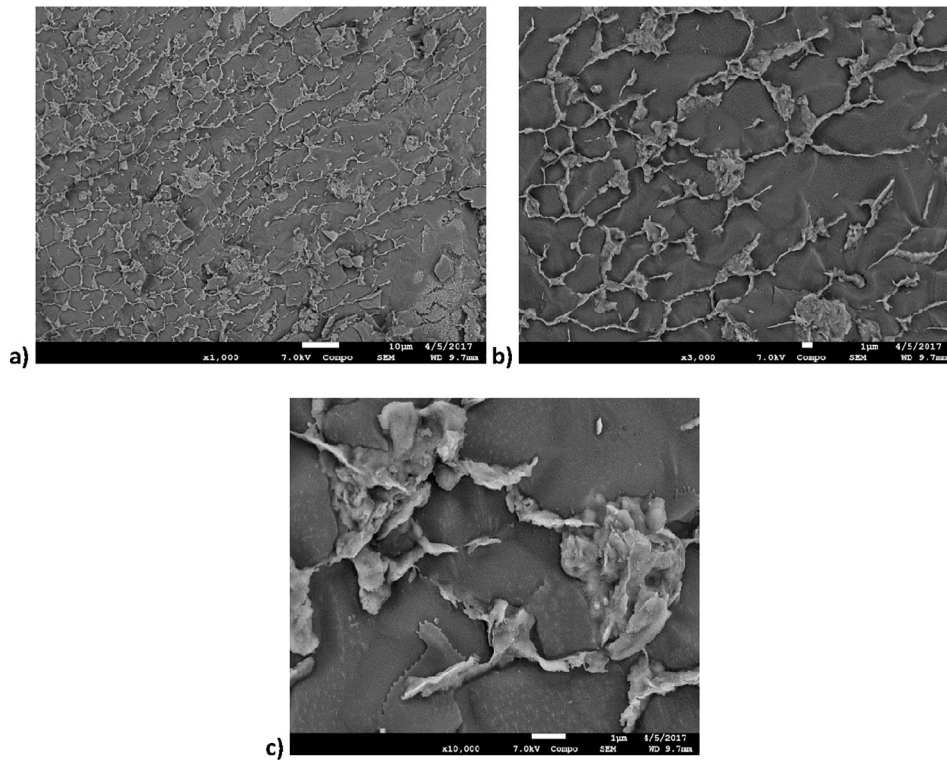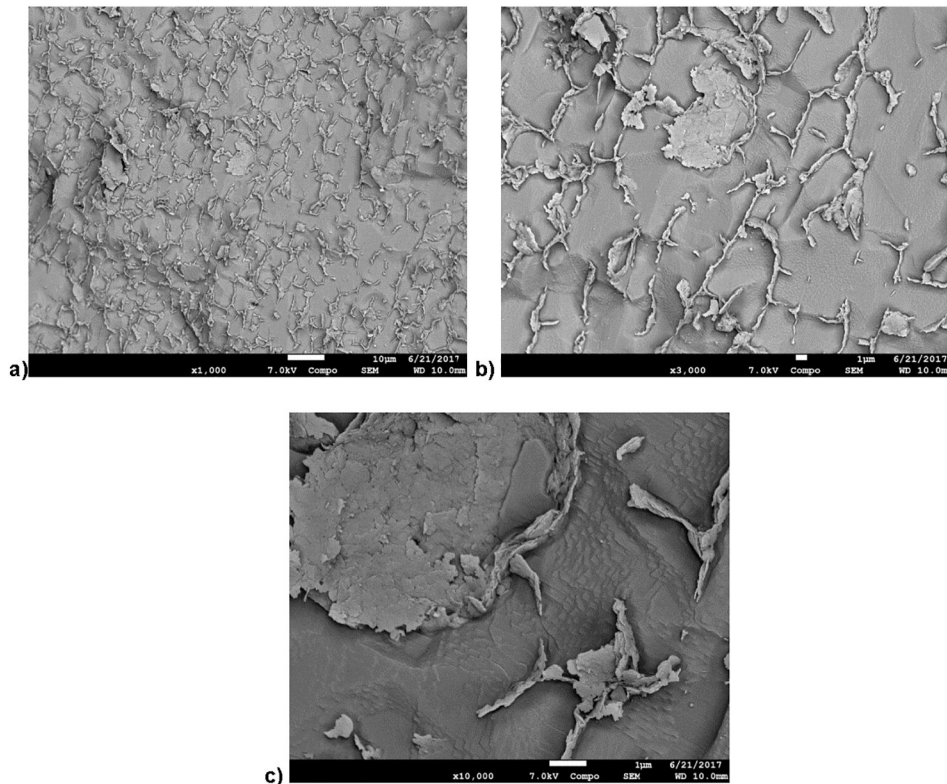
Fig. 6. Cryo-Scanning electron micrographs of 200 g/t PAM flocculated 5 wt% bentonite dispersions in high-salinity water ranking at (a) 1000× and (b) 3000× and (c) 10,000× (with sublimation at −100° for 5 min).

cryo-SEM as shown in Fig. 7. Illite flocs showed a similar network structure to bentonite. The three-dimensional illite network structures do not assist in dewatering as they easily retain water. This was consistent with the overall low settling rate of illite as shown in Fig. 2c. Despite their network structures, larger illite aggregates were detected in Fig. 7. These aggregates were different from bentonite flocs where

Fig. 7. Cryo-Scanning electron micrographs of 200 g/t PAM flocculated 5 wt% illite dispersions in medium-salinity water ranking at (a) 1000× and (b) 3000× and (c) 10,000× (with sublimation at −100° for 5 min).

only small aggregates were detected. This may explain the better settling rate of illite than bentonite.

4. Conclusions

The dewatering behaviour of clay minerals in saline water was found to be governed by clay mineralogy, clay suspended solid concentration, water salinity, and flocculant dosage. The driving parameters not only affected clay settling by modifying inter-particle interactions but also by creating different clay flocculation structures. An increase in polymer dosage increased the settling rate of kaolinite while an increase in water salinity and solid percentage had an opposite effect. More EF network structures were generated in high-salinity water for kaolinite, leading to a slower settling rate. For bentonite and illite, the increase in polymer dosage and water salinity only slightly accelerated the settling rate with the effect being greater for illite. Bentonite and illite generated similar EF networks with larger aggregates observed for illite, explaining the higher settling rate of illite. Cryo-SEM was found to be a useful tool for understanding clay aggregate structures under different chemical conditions. Future studies could focus on developing models to predict the separation of clay tailings from saline water by integrating all major variables. The current study provides guidance on processing complex tailings containing clay minerals in saline water and may assist in mine planning and operation as well as closure and rehabilitation of tailings storage facilities.

Acknowledgements

References

[1] R. de Kretser, P.J. Scales, D.V. Boger, Improving clay-based tailings disposal: case study on coal tailings, AICHE J. 43 (1997) 1894–1903.

[2] F. Bergaya, B.K.G. Theng, G. Lagaly, Handbook of Clay Science, Elsevier Science, Burlington, 2006.

[3] S.L. Swartzen-Allen, E. Matijevic, Surface and colloid chemistry of clays, Chem. Rev. 74 (1974) 385–400.

[4] A.J. McFarlane, J. Addai-Mensah, K. Bremmell, Rheology of flocculated kaolinite dispersions, Korea Australia Rheology, Journal 17 (2005) 181–190.

[5] A. Mierczynska-Vasilev, M. Kor, J. Addai-Mensah, D.A. Beattie, The influence of polymer chemistry on adsorption and flocculation of talc suspensions, Chem. Eng. J. 220 (2013) 375–382.

[6] P. Mpofu, J. Addai-Mensah, J. Ralston, Interfacial chemistry, particle interactions and improved dewatering behaviour of smectite clay dispersions, Int. J. Miner. Process. 75 (2005) 155–171.

[7] P. Mpofu, J. Addai-Mensah, J. Ralston, Flocculation and dewatering behaviour of smectite dispersions: effect of polymer structure type, Miner. Eng. 17 (2004) 411–423.

[8] P. Mpofu, J. Addai-Mensah, J. Ralston, Influence of hydrolyzable metal ions on the interfacial chemistry, particle interactions, and dewatering behavior of kaolinite dispersions, J. Colloid Interface Sci. 261 (2003) 349–359.

[9] P. Mpofu, J. Addai-Mensah, J. Ralston, Investigation of the effect of polymer structure type on flocculation, rheology and dewatering behaviour of kaolinite dispersions, Int. J. Miner. Process. 71 (2003) 247–268.

[10] I. Cengiz, E. Sabah, S. Ozgen, H. Akyildiz, Flocculation of fine particles in ceramic wastewater using new types of polymeric flocculants, J. Appl. Polym. Sci. 112 (2009) 1258–1264.

[11] A. McFarlane, K. Bremmell, J. Addai-Mensah, Improved dewatering behavior of clay minerals dispersions via interfacial chemistry and particle interactions optimization, J. Colloid Interface Sci. 293 (2006) 116–127.

[12] M. Rahman, Dewatering of phosphatic clay waste by flocculation, Chem. Eng. Technol. 23 (2000) 457–461.

[13] H.J.L. Wright, J.A. Kitchener, The problem of dewatering clay slurries: factors controlling filtrability, J. Colloid Interface Sci. 56 (1976) 57–63.

[14] M.S. Nasser, A.E. James, Settling and sediment bed behaviour of kaolinite in aqueous media, Sep. Purif. Technol. 51 (2006) 10–17.

[15] M.H. Gorakhki, C.A. Bareither, Salinity effects on sedimentation behavior of kaolin, bentonite, and soda ash mine tailings, Appl. Clay Sci. 114 (2015) 593–602.

[16] B. Siffert, Y. Bocquenet, Polyacrylamide adsorption onto kaolinite in the presence of sodium dodecylbenzenesulfonate in saline medium, Colloids Surf. 11 (1984) 137–143.

[17] Y. Ji, Q. Lu, Q. Liu, H. Zeng, Effect of solution salinity on settling of mineral tailings by polymer flocculants, Colloids Surf. A Physicochem. Eng. Asp. 430 (2013) 29–38.

[18] M. Zhang, Y. Peng, N. Xu, The effect of sea water on copper and gold flotation in the presence of bentonite, Miner. Eng. 77 (2015) 93–98.

[19] B. Wang, Y. Peng, The effect of saline water on mineral flotation – a critical review, Miner. Eng. 66 (2014) 13–24.

[20] S. Wang, L. Zhang, B. Yan, H. Xu, Q. Liu, H. Zeng, Molecular and Surface Interactions between Polymer Flocculant Chitosan-g-polyacrylamide and Kaolinite Particles: Impact of Salinity, The Journal of Physical Chemistry C, 2015.

[21] J.B. Farrow, R.R.M. Johnston, K. Simic, J.D. Swift, Consolidation and aggregate densification during gravity thickening, Chem. Eng. J. 80 (2000) 141–148.

[22] D. Liu, Y. Peng, Reducing the entrainment of clay minerals in flotation using tap and saline water, Powder Technol. 253 (2014) 216–222.

[23] N. Cruz, Y. Peng, S. Farrokhpay, D. Bradshaw, Interactions of clay minerals in copper–gold flotation: part 1 – rheological properties of clay mineral suspensions in the presence of flotation reagents, Miner. Eng., 50–51 (2013) 30–37.

[24] H.H. Murray, S.C. Lyons, Further correlations of kaolinite crystallinity with chemical and physical properties, Clay Clay Miner. 8 (1960) 11–18.

[25] J. Du, G. Morris, R.A. Pushkarova, R. St, C. Smart, Effect of surface structure of kaolinite on aggregation, settling rate, and bed density, Langmuir 26 (2010) 13227–13235.

[26] P. Ofori, B. Firth, C. McNally, A. Nguyen, Working Effectively With Saline Water in Coal Preparation, CSIRO Energy Technology, the University of Queensland, 2009.

[27] Y. Peng, D. Seaman, The flotation of slime–fine fractions of Mt. Keith pentlandite ore in de-ionised and saline water, Miner. Eng. 24 (2011) 479–481.

[28] M. Reich, C. Palacios, M.A. Parada, U. Fehn, E.M. Cameron, M.I. Leybourne, A. Zúñiga, Atacamite formation by deep saline waters in copper deposits from the Atacama Desert, Chile: evidence from fluid inclusions, groundwater geochemistry, TEM, and 36Cl data, Mineral. Deposita 43 (2008) 663.

[29] T. Kasama, Y. Watanabe, H. Yamada, T. Murakami, Sorption of phosphates on Al-pillared smectites and mica at acidic to neutral pH, Appl. Clay Sci. 25 (2004) 167–177.

[30] J. Ravichandran, B. Sivasankar, Properties and catalytic activity of acid-modified montmorillonite and vermiculite, Clay Clay Miner. 45 (1997) 854–858.

[31] T. Grzybek, The influence of montmorillonite treatment on structure, sorption properties and catalytic behaviour: part I. Zirconia pillared clays modified with manganese as denox catalyts, Pol. J. Chem. 75 (2001) 857–868.

[32] K.G. Bhattacharyya, S.S. Gupta, Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution, Sep. Purif. Technol. 50 (2006) 388–397.

[33] F. Macht, K. Eusterhues, G.J. Pronk, K.U. Totsche, Specific surface area of clay minerals: comparison between atomic force microscopy measurements and bulk-gas (N2) and -liquid (EGME) adsorption methods, Appl. Clay Sci. 53 (2011) 20–26.

[34] S. Kaufhold, R. Dohrmann, M. Klinkenberg, S. Siegesmund, K. Ufer, N2-BET specific surface area of bentonites, J. Colloid Interface Sci. 349 (2010) 275–282.

[35] T.E. Baldock, M.R. Tomkins, P. Nielsen, M.G. Hughes, Settling velocity of sediments at high concentrations, Coast. Eng. 51 (2004) 91–100.

[36] B. Camenen, Chapter 15 Settling velocity of sediments at high concentrations, in: T. Kusuda, H. Yamanishi, J. Spearman, J.Z. Gailani (Eds.), Proceedings in Marine Science, Elsevier 2008, pp. 211–226.

[37] J. Winterwerp, On the flocculation and settling velocity of estuarine mud, Cont. Shelf Res. 22 (2002) 1339–1360.

[38] P.F. Luckham, S. Rossi, The colloidal and rheological properties of bentonite suspensions, Adv. Colloid Interf. Sci. 82 (1999) 43–92.

[39] H.V. Olphen, An Introduction to Clay Colloid Chemistry, Second edition National Academy of Sciences, Washington, DC, 1977.

[40] R. Kjellander, S. Marcelja, R.M. Pashley, J.P. Quirk, Double layer correlation forces restrict calcium clay swelling, J. Phys. Chem. 92 (1988) 6489–6492.

[41] R. Hogg, Flocculation and dewatering, Int. J. Miner. Process. 58 (2000) 223–236.

[42] A.-M. Jonas, Enhanced flocculation and dewatering of clay mineral dispersions, Powder Technol. 179 (2007) 73–78.

[43] N. Alam, O. Ozdemir, M.A. Hampton, A.V. Nguyen, Dewatering of coal plant tailings: flocculation followed by filtration, Fuel 90 (2011) 26–35.

[44] M. Dash, R.K. Dwari, S.K. Biswal, P.S.R. Reddy, P. Chattopadhyay, B.K. Mishra, Studies on the effect of flocculant adsorption on the dewatering of iron ore tailings, Chem. Eng. J. 173 (2011) 318–325.

[45] C. Wang, D. Harbottle, Q. Liu, Z. Xu, Current state of fine mineral tailings treatment: a critical review on theory and practice, Miner. Eng. 58 (2014) 113–131.

[46] E.J. Teh, Y.K. Leong, Y. Liu, A.B. Fourie, M. Fahey, Differences in the rheology and surface chemistry of kaolin clay slurries: the source of the variations, Chem. Eng. Sci. 64 (2009) 3817–3825.

[47] G. Lagaly, Chapter 5 Colloid clay science, in: B.K.G.T. Faïza Bergaya, L. Gerhard (Eds.), Developments in Clay Science, Elsevier 2006, pp. 141–245.