

THE ROLE OF MONO- AND DIVALENT IONS IN THE STABILITY OF KAOLINITE SUSPENSIONS AND FINE TAILINGS

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Abstract—A major issue for the oil sand industry is the settling of thin fine tailings (TFT) which are a byproduct of the oil sand extraction process. These tailings are deposited in large ponds and settling takes decades. The aim of the present study was to increase understanding of the role of specific ion types (monovalent/divalent) present in the water in flocculation behavior, and hence the settling of flotation fine tailings of the Athabasca oil sands (which consist predominantly of kaolinite). In this study, two series of measurements were conducted and compared: one with TFT and with varying pH and salinity, and another with kaolinite suspensions with varying pH, salinity, and volume fraction. The volume fraction of kaolinite and TFT used was in the range 0.01–1% volume fraction for any ionic strength or ion. In this range the electrophoretic mobility was constant indicating that there were no particle–particle interactions, a required condition for electrophoretic mobility measurements. Electrokinetic measurements were made as a function of concentration of salt added and pH. The flocculation behavior of both TFT and kaolinite can be linked to the electrokinetic mobility at high ionic strength. The electrophoretic mobility values and therefore the electrokinetic charge of the particles were smaller for divalent salt than for monovalent salt. As a consequence, both kaolinite and fine tailings should and do flocculate more quickly in the presence of a divalent electrolyte during settling-column experiments. The electrophoretic mobility of kaolinite and tailings in electrolytes containing a majority of monovalent ions (NaCl) decreased in absolute values with decreasing pH while their electrophoretic mobility in electrolytes containing a majority of divalent ions (MgCl₂) did not depend on pH. The flocculation of the fine tailings in an electrolyte where divalent ions are predominant is therefore not expected to be influenced by pH.

Key Words— Electrolyte Concentration, Electrophoretic Mobility, Fine Tailings, Flocculation, Kaolinite, Surface Charge.

INTRODUCTION

Canada has the third largest oil reserves in the world and 97% of these are in oil sands. The Athabasca oil sands, located in northeast Alberta, are the largest known crude bitumen deposit in the world. The Canadian government requires that all lands disturbed by oil sands operations should be reclaimed (Canadian Association of Petroleum Producers (www.capp.ca; www.oilsands.alberta.ca/FactSheets/FS-CES-Tailings.pdf)). Currently the tailings Environmental Priority Area of COSIA (Canada's Oil Sands Innovation Alliance) works together with universities, companies, the government, and research institutes to improve the management of the oil sand tailings.

The present study focuses on the fine tailings from Athabasca oil sands. The fine tailings are a by-product of the oil sand extraction process, containing suspended silts, clays, and hydrocarbon residues. In the Clark hot-water extraction process, bitumen is separated from the slurry, and tailings are pumped into tailing ponds (Clark and Pasternack, 1932; Clark, 1939). Upon deposition,

the tailings segregate with the sand plus about half of the fines, settling out to form dikes and beaches. The extremely large remaining waste volumes are composed of water, traces of bitumen, and fines which are discharged into tailings ponds as thin fine tailings (TFT). The existing tailings ponds cover 176 km² and are expected to be part of the active mining process for a period of up to 30–40 years. The Canadian government requires these ponds to be reclaimed as solid surfaces. A major issue for the oil sand industry is the settling of these fines, which can take several years. After a few years the fines settle and are referred to as mature fine tailings (MFT). The MFT will remain in a fluid-like state for decades because of their very slow consolidation rate (MacKinnon, 1989; Kasperski, 1992).

Different technologies are used to accelerate settling of TFT/MFT, *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 CO₂ to the tailings line to increase dewatering (www.cosia.ca).

Several studies (*e.g.* Liu *et al.*, 2002; Zhu *et al.*, 2011) have investigated the interfacial properties and the electrokinetic charge of TFT in relation to variations in their flocculation behavior induced by the addition of polymers, the presence of salts, and the reduction of pH

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by CO₂ bubbling. From the electrokinetic charge, the DLVO theory (Hunter, 2001) can be used to predict and quantify the aggregation between particles. It is therefore important to correctly assess the surface charge of the particles in order to obtain a realistic value for the DLVO forces (Gupta *et al.*, 2011; Liu *et al.*, 2002).

These previous studies are extended here as follows:

(1) A link is established between the electrophoretic mobility of TFT and that of kaolinite, a major constituent of the TFT. Electrophoretic mobility experiments give access to the electrokinetic charge of suspended particles when studied as a function of ionic strength, for monovalent and bivalent salt, and pH. These results are considered alongside the flocculation and settling properties of TFT.

(2) The effect of lowering the pH by bubbling with CO₂, a technique used often in the oil sands industry, is analyzed in the context of lowering the pH by adding HCl.

MATERIALS

Thin fine tailings

The TFT were sampled from Athabasca oil sands ponds, north of Edmonton (Alberta, Canada) and are referred hereafter to as 'SP02' samples. The samples are considered to be representative of tailings deposited in the ponds. The suspensions were prepared at the desired concentration by adding ultrapure water with a resistivity of 18 MOhm-cm. By doing so, the original ionic concentration was reduced to 0.03 mS/cm so that the ionic strength-dependence measurements could be performed. The sample contained kaolinite/muscovite, dickite, quartz, and NaCl. This composition was obtained from X-ray diffraction (XRD) measurements.

X-ray powder diffraction patterns were recorded in Bragg-Brentano geometry using a Bruker D5005 diffractometer equipped with a Huber incident-beam monochromator and a Braun PSD detector. The samples of ~20 mg were deposited on a Si <510> wafer and were rotated during measurement. The d_{50} of the SP02 sample (~17 μm) obtained from static light scattering was greater than that of the kaolinite sample (Figure 1).

Kaolinite

The kaolinite sample was polywhite-E from deposits in southwest England. The material has a surface area of 8 m²/g and a density of 2.6 g/cm³ (manufacturer values). The kaolinite sample composition was analyzed by XRD measurements and found to contain kaolinite, muscovite, and dickite. The d_{50} of the kaolinite sample was 5.7 μm , obtained from static light scattering (Figure 1).

Two samples of kaolinite were prepared in order to study their zeta potential. One was dialyzed; it consisted of a 20 wt.% suspension of kaolinite in water. The water remaining at the top was replaced by ultrapure water (18 MOhm-cm) every day until the conductivity reached a value of 3 $\mu\text{S/cm}$.

The non-dialyzed sample was a 20 wt.% solution of kaolinite, dispersed as received, in ultrapure water. The sample had a conductivity of 0.63 mS/cm.

The salts used during the experiments were provided by the manufacturer, Merck, (Darmstadt, Germany). The element compositions of the SP02, kaolinite, and dialyzed kaolinite samples were also analyzed using environmental scanning electron microscopy (ESEM). The compositions showed a difference in Si contents between the SP02 supernatant and bulk, denoting a predominance of silica-based particles (SiO₂) in the bulk (Table 1).

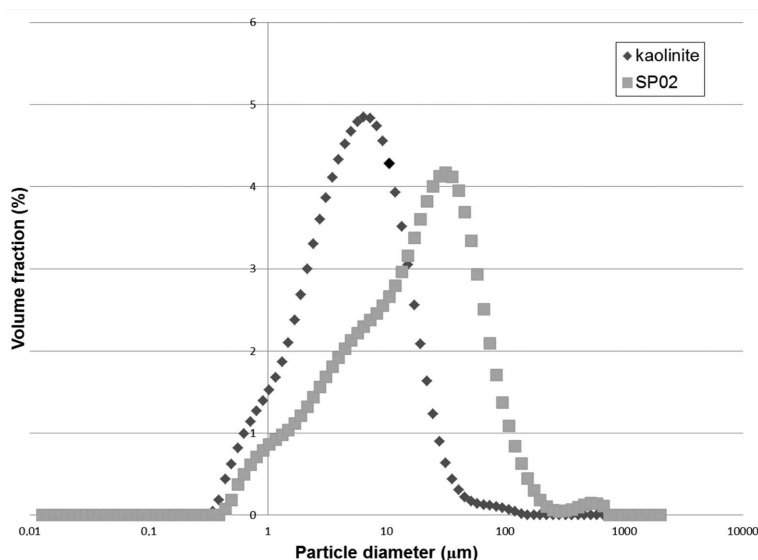


Figure 1. Particle-size distribution of kaolinite (black) and SP02 (gray) samples.

Table 1. Compositions (wt.%) of the kaolinite and SP02 samples.

	SP02 bulk	SP02 supernatant	Dialyzed kaolinite	Non-dialyzed kaolinite
C	20.02	23.72		
O	41.63	39.78	50	46.58
Na	1.17		4.66	
Mg	0.63	0.99		
Al	4.61	9.64	21.21	21.48
Si	29.13	14.53	24.98	25.9
S			1.07	
Cl		2.33		
K	1.33	1.58	2.82	4.33
Fe	1.49	1.72	0.99	1.71

METHODS

XRD measurements

X-ray diffraction measurements were performed at the Faculty of Mechanical, Maritime and Materials Engineering (3mE), TUDelft, The Netherlands. Data collection was carried out at room temperature using monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda = 0.154056$ nm) in the 2θ region between 5 and 90° , step size = $0.038^\circ/2\theta$. All samples were measured under identical conditions. The data evaluation was done using the Bruker program *EVA*.

ESEM measurements

The untreated samples (no conductive coating was applied) were deposited on aluminum stubs using double-sided carbon tape, 2.5 mm in diameter (PELCO Tabs, TED PELLA Inc, Redding, Canada). The samples were analyzed using a Philips XL30 Environmental Scanning Electron Microscope (ESEM), from Microlab in the Faculty of Civil Engineering and Geosciences, TU Delft, The Netherlands. During the ESEM measurements the samples were kept under vacuum, with a beam acceleration voltage of 20 kV, with backscattered electron imaging mode and a spot size of 4 μm for Figures 2a–c and 5 μm for Figures 2d–f.

Particle size from static light scattering

The particle-size distributions (Figure 1) of kaolinite and the fine tailings samples (SP02) were measured at $\text{pH} = 7$ with a Malvern MasterSizer using Static Light Scattering, at the Physical Laboratory of Deltares, The Netherlands. The conductivity of the samples was <1 mS/cm (no salt added) to prevent flocculation.

Electrophoretic mobility measurements

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 $\text{m}^2/\text{V s}$ units) are given here (following the example of other authors) as ‘apparent’ zeta potential values (mV) using the Smoluchowski formula: $\zeta = \eta u/\epsilon$, where u is electrophoretic mobility of the particle, η is the viscosity of the suspending liquid, ϵ is the dielectric constant of the suspending medium, and ζ is the zeta potential (Hunter 1981). In water we obtain the linear relationship: ζ (mV) = $0.14 u$ ($10^{-8} \text{ m}^2/\text{V s}$)

The ‘apparent’ zeta potential measurements were carried out as a function of pH, type, and concentration of electrolyte, and concentration of solid in solution. An average of ten measurements was taken to represent the measured potential. The voltage applied during the measurements was 50 V, an optimal value for these types of measurements as established by Chassagne and Ibanez (2013).

The series of measurements in which the salt concentration was varied was performed following the protocol of Chassagne and Ibanez (2013).

CO₂ bubbling

For the preliminary experiments, only water was used in order to check the dependence of pH on the time spent bubbling. A closed cylinder (a triaxial cell) was used with a gas inlet and an open gas outlet. One liter of water was bubbled with a gas mixture of 90% N_2 and 10% CO_2 , with a flow rate of 200 mL/min. The gas was pre-wetted by using a water-filled container to prevent evaporation in the triaxial cell. A pH meter was mounted within the triaxial cell. Bubbling was stopped when the desired pH (6.3) was reached. A pH check after finishing the measurements showed a maximum pH increase of 0.1 units during the time of measurement.

The pH of the studied suspension kaolinite was reduced by bubbling with 100% pure CO_2 gas until the pH achieved the value of 5. The suspension was then used directly in the zeta nano measurement cell. The measurements were performed immediately.

Fine tailings (SP02)

The SP02 sample was diluted with ultrapure water until a concentration (0.1 g/L) giving a good signal-to-noise ratio in the electrophoresis measurements was obtained. The zeta potential experiments were carried out at different pH values; the pH was adjusted by addition of NaOH or HCl. The pH values were 4, 6, and 8 with divalent salt (MgCl_2) or monovalent salt (NaCl).

Kaolinite

The kaolinite samples (dialyzed or not) were diluted with ultrapure water until a concentration (0.26 g/L) giving a good signal-to-noise ratio in the electrophoresis measurements was obtained. For the non-dialyzed samples, the influence of the particle volume fraction

was investigated. The zeta potential experiments were carried out at different pH values; the pH was adjusted by addition of NaOH or HCl. The pH values were 4, 6, and 8 with divalent salt (MgCl_2) or monovalent salt (NaCl).

In one of the experiments the pH was also reduced by increasing the amount of dissolved CO_2 . The ‘apparent’ zeta potential value obtained was compared with that obtained by changing the pH through the addition of HCl. For this experiment a pH value of 5 was chosen and the salt concentration was varied using CaCl_2 .

RESULTS AND DISCUSSION

Particle size

Both kaolinite and SP02 samples are polydisperse, as confirmed by static light scattering (Figure 1). The ESEM images of the SP02 sample are shown in Figure 2d–f. Flocculated material is apparent in the ESEM image of the SP02 supernatant (Figure 2f). The carbon content given in Table 1 is unreliable because of the presence of carbon-based wafers onto which the sample had been deposited; the authors assume that hydrocarbons (bitumen) form the observed matrix in which the smallest colloidal particles are trapped. Environmental scanning electron microscopy images of kaolinite (Figure 2a) and of dialyzed kaolinite (Figure 2b,c) are shown.

The supernatant particle size of SP02 could not be measured because (Figure 2f) bitumen was present and the material was aggregated. Similarly, it was not possible to measure the particle-size distribution of the kaolinite supernatant using the Malvern MasterSizer, because the concentration of the sample was too low. The particle size was therefore measured using the

ZetaNano ZS device by means of dynamic light scattering. The mean radius of the supernatant particles (10 measurements) of the kaolinite sample was found to be 92 nm at pH 7.

Kaolinite consists of successive layers of octahedral alumina and tetrahedral silica which alternate to form plate-like hexagonal particles. The particles are flat disks or plate-like in shape, with the disk radius of the order 5–15 times larger than the thickness (Solomon and Hawthorne, 1983). The kaolinite surface properties are known to be sensitive to both pH and ionic strength and ion type (Vane and Zang, 1997; Ma and Pierre, 1999; Kaya *et al.*, 2006; Ma, 2011). The platelet particle has pH-dependent edge and surface charges (Mitchell and Soga, 2005). Recently Gupta and Miller (2010) demonstrated that the point of zero charge of the alumina face of kaolinite is $\sim 6\text{--}8$. This confirmed previous work by Zhou and Gunter (1992), and implies that only at $\text{pH} > 8$ are the kaolinite platelets fully negatively charged. This should have an effect on the flocculation behavior of kaolinite at $\text{pH} < 8$.

Electrophoretic mobility

Electrophoretic mobility data give information about the electrokinetic charge of particles. This electrokinetic charge is related to the surface charge of the particles and its zeta potential but the relationship between electrokinetic charge and surface charge is only available for simple systems, *e.g.* homogeneously charged spherical particles. The ‘apparent’ zeta potential defined above *via* the Smoluchowski formula is equal to the actual zeta potential when the Debye length, $1/\kappa$, is much smaller than the particle size, L ($\kappa L \gg 1$), for particles of any shape, provided that the contribution of surface conductivity is ignored (Morrison, 1970). For the

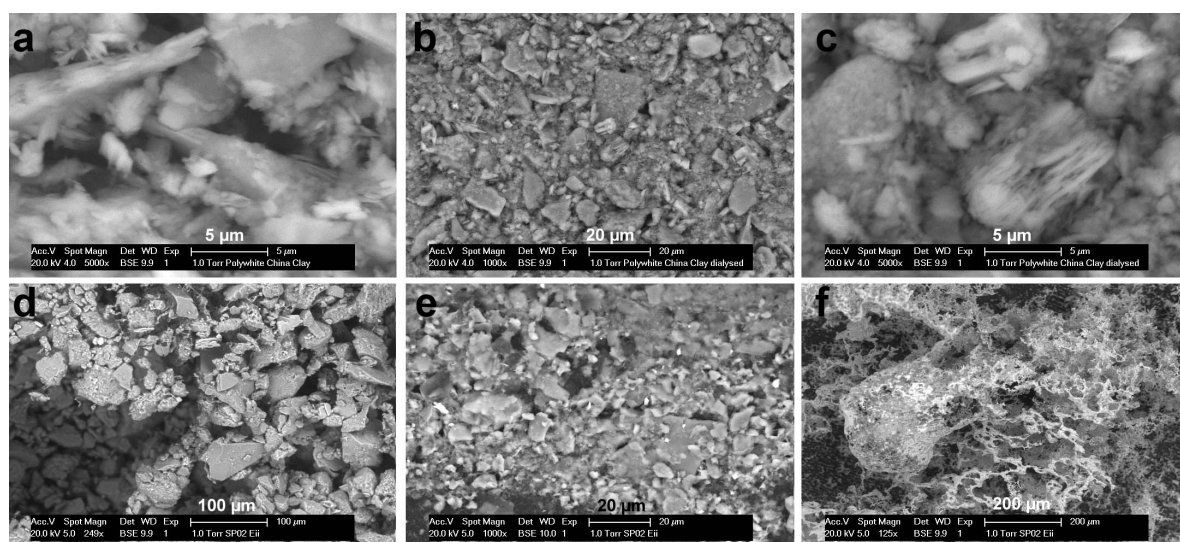


Figure 2. ESEM backscattered electron images: (a) kaolinite; (b,c) dialyzed kaolinite samples at different magnifications; (d,e,f) SP02 samples at different magnifications.

smallest particles in the present study, the kaolinite particles, the κL value was ~ 10 for the smallest ionic strength used (KCl, monovalent salt) and 16 for MgCl_2 (divalent salt). Morrison's (1970) condition is, in principle, respected for ionic strength >10 mM where $\kappa L >1000$ for both mono and divalent salts. However, the condition is only valid for particles with an 'ideal' surface, implying that the shear plane is located at the particle surface (no Stern layer) and that the electric surface potential is the same everywhere on the surface and equal to the zeta potential. These two last conditions are not true for kaolinite, as demonstrated by Chassagne *et al.* (2009) and probably not for SP02 either.

Ideally, the electrophoretic mobility of particles should be independent of the particles' concentration during the time of the electrophoresis measurements, meaning that there are no particle–particle interactions and that the 'apparent' zeta potential is representative of the electric potential at the shear plane of one particle. However, at (very) low ionic strength, the double layers around the particles could overlap, leading to inter-particle interactions. The mobility of the particles would then be affected by the presence of neighboring particles.

The 'apparent' zeta potential of the dialyzed kaolinite sample did not vary much as a function of the solid concentration (Figure 3), even when no salt had been added, when the double layers are large. The interaction between particles can therefore be ignored. Also, the experimental time is fast enough (<2 min) to ensure that even at low pH, attraction between particles will not lead to flocculation which is known to occur at pH values near the point of zero charge. The points of zero charge for kaolinite clays were previously found to be between 2.8 and 4.8 (Tschapek *et al.*, 1974). The silica face is negatively charged for $\text{pH} >4$ and the aluminum face is positively charged for $\text{pH} <6$ (Gupta *et al.*, 2011). These

differences in charge lead to aggregation between the positive edges and the negative faces of the clay. The electrophoretic mobility measurements performed in the rest of the study were done at a volume fraction of $\sim 0.1\%$ (0.26 g/L), small enough to ensure that the particles were dispersed and that there was no particle–particle interaction.

A systematic investigation of the particle-concentration dependence of the electrophoretic mobility of fine tailings (SP02) was not done, but within the range of volume fraction used (0.1–0.3%), the electrophoretic mobility did not vary.

The apparent zeta potential of kaolinite as a function of mono- and divalent salts was studied.

Compression of the double layer is affected in different ways by monovalent and divalent salts: for the same salt concentration, the double layer formed by monovalent salt is $\sqrt{3}$ times larger than the double layer formed by divalent salt. Information about the surface charge of particles can therefore be gained by studying the electrophoretic mobility behavior as a function of different monovalent and divalent salts. Some types of salt are indifferent meaning that they only contribute to the double layer; others may react with the particle surface, thereby changing its surface charge. The samples were dispersed in two types of electrolyte solutions, containing divalent salt (MgCl_2) and monovalent salts (KCl and NaCl) at $\text{pH} = 6$ (Figures 4, 5). The potential-determining counterions are Mg^{2+} , K^+ , and Na^+ . The electrophoretic mobility experiments revealed that, in the ionic strength range investigated, the apparent zeta potential was always negative.

From the particle-size distribution of the sample the supernatant particle size was found to be ~ 10 times smaller than the bulk size. The zeta potential of the non-dialyzed kaolinite supernatant was always less, in absolute terms, than the zeta potential of the bulk (Figure 4a).

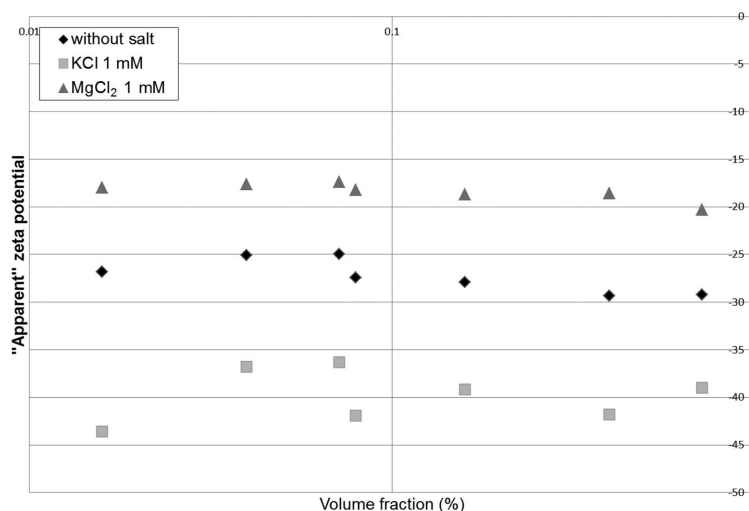


Figure 3. Zeta potential of the kaolinite sample as a function of volume-fraction percentage.

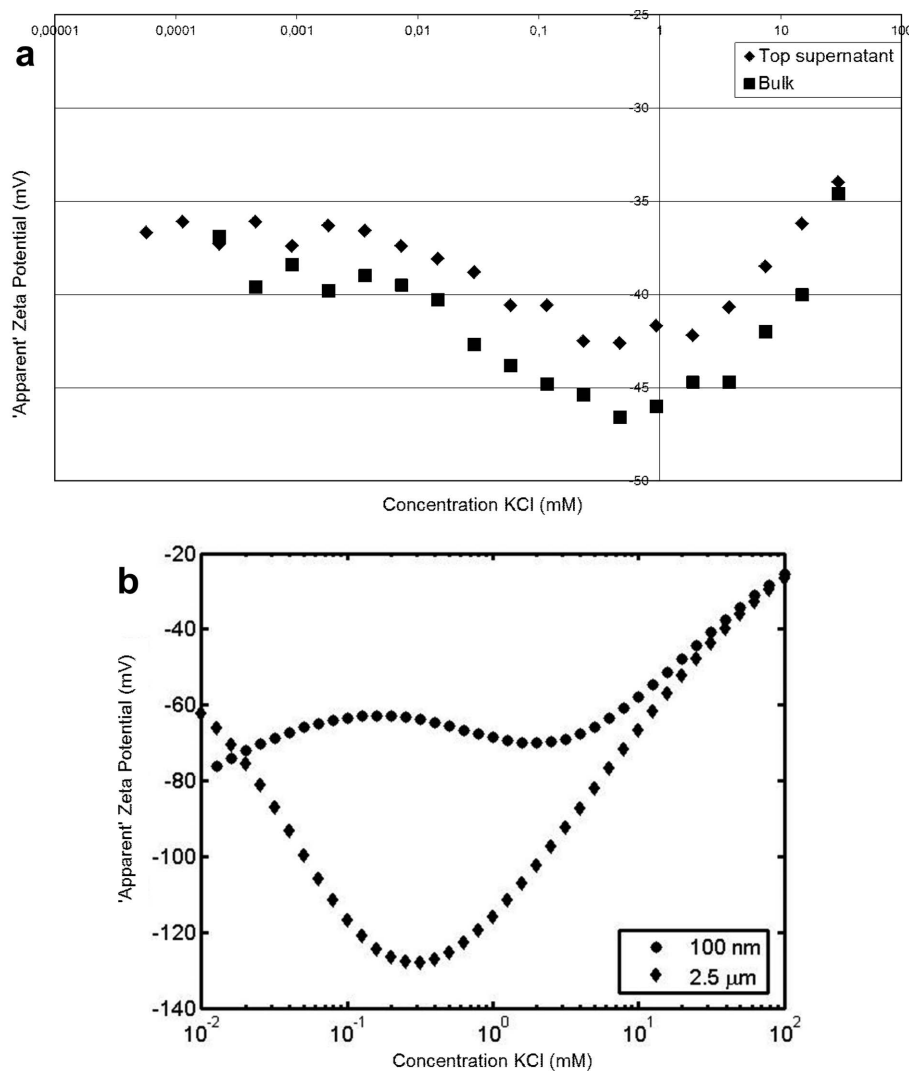


Figure 4. (a) Zeta potential of bulk and supernatant kaolinite samples as a function of the concentration of KCl salt. (b) Theoretical values of zeta potential of the bulk and supernatant kaolinite samples as a function of the concentration of KCl salt.

Even if the surface-charge properties of the supernatant and bulk particles are the same, their apparent zeta potential should indeed be smaller for the smallest particle size in the salt concentration investigated. The curve minimum was shifted to greater ionic strength. This qualitative behavior was also found in the theoretical prediction shown in Figure 4b where spherical particles of radius 1 μm and 100 nm with constant charge (0.02 C/m²) and no Stern layer were used.

The differences between the apparent zeta potential of dialyzed and non-dialyzed kaolinites for different types of cations (NaCl and MgCl₂) are presented in Figure 5. The behavior of the apparent zeta potential of non-dialyzed kaolinite, as a function of NaCl was different from its behavior upon addition of KCl. The magnitude of the apparent zeta potential values is lower in the case of NaCl than for KCl, and the apparent zeta

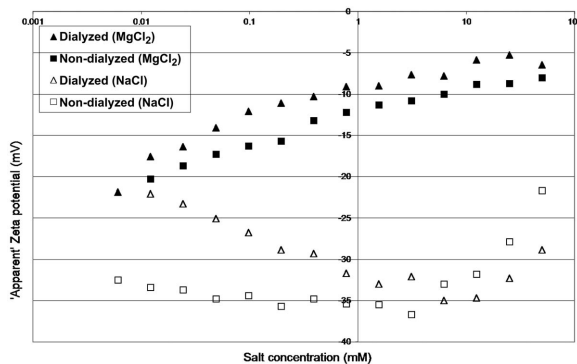


Figure 5. Zeta potential of a dialyzed kaolinite sample as a function of MgCl₂ salt (filled triangles); zeta potential of a dialyzed kaolinite sample as a function of NaCl salt (open triangles); zeta potential of a non-dialyzed kaolinite sample as a function of MgCl₂ salt (filled squares); zeta potential of non-dialyzed kaolinite sample as a function of NaCl salt (open squares).

potential is less sensitive upon addition of NaCl than KCl in the range of [0–0.1] mM of added salt. Moreover, the variation in conductivity with concentration of salt added for both NaCl and KCl (not shown here) revealed that, due to impurities in the non-dialyzed sample, ions were present in the suspension in an amount equivalent to 0.1 mM of monovalent salt added.

An explanation for such behavior could be that the non-dialyzed sample contains K^+ ions in solution and K^+ ions adsorbed on the kaolinite surface. In that case the surface charge of kaolinite would be insensitive to the addition of extra K^+ ions in suspension. The addition of extra K^+ ions would contribute only to an increase in the conductivity and reduce the size of the double layer around the particles. The apparent zeta potential shown in Figure 4a corresponds to the expected behavior of the apparent zeta potential for a constant-charge particle in the presence of indifferent ions (Figure 4b).

In the case of added Na^+ ions, the variation in the apparent zeta potential with the addition of salt does not correspond to a constant surface-charge behavior. This indicates that the Na^+ ions probably adsorb on the kaolinite within the time of the experiments (~2 min), making the surface charge less negative. This explains why the values obtained for the apparent zeta potential are smaller in absolute values than those obtained for KCl. At very low concentrations of added salt, the conductivity should vary less than the theoretical conductivity; this could not be measured as the change would be very small for the small particle volume used. In the [0.01–0.1] mM range of salt added the apparent zeta potential of the dialyzed sample changes significantly compared to the apparent zeta potential of the non-dialyzed sample. For the dialyzed sample, the double-layer thickness varies much more upon addition of salt because there is no background electrolyte present, giving a larger variation in the apparent zeta potential.

A washed Georgia kaolinite was used by Kaya *et al.* (2006) who found values intermediate between the dialyzed and non-dialyzed values for the zeta potential as a function of NaCl concentration at the same pH. Their kaolinite was first saturated with ammonium acetate (CH_3COONH_4) and then washed thoroughly with demi-water until the electrical conductivity of the supernatant was <100 mS.

From the flocculation studies combined with zeta-potential studies of Kaya *et al.* (2006), samples at low ionic strength (0.1 mM) are not expected to flocculate and samples at high ionic strength (10 mM) are expected to flocculate. As the apparent zeta potential for monovalent salt is roughly the same at 0.1 and 10 mM as expected for constant charged particles, this parameter alone is clearly unsuitable for predicting flocculation.

In the case of divalent salt ($MgCl_2$ and $CaCl_2$, Figures 5, 8, respectively), both dialyzed and non-dialyzed kaolinite displayed the same behavior upon addition of salt. This behavior was different from what

would be expected for particles with fixed charge (see figure 10 of Chassagne and Ibanez, 2014). Similar trends and values were found by Yukselen and Kaya (2002) and Kaya *et al.* (2006) with their samples containing 96% kaolinite (Evans Clay $\text{\textcircled{R}}$, Georgia, USA). For any divalent salt, at concentrations >1 mM of added salt, the zeta potential became so small that flocculation was expected. This probably did not occur at the time-scale of the electrophoretic measurements, as the measurements were quick (minutes) and the suspensions were very dilute.

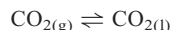
Samples at low ionic strength (0.1 mM) in the presence of divalent salt are not expected to flocculate and samples at high ionic strength (10 mM) are expected to flocculate for all pH values (Kaya *et al.*, 2006). This is in line with the rule of thumb in which a zeta potential below 25 mV ($\sim kT/e$, where k is the Boltzmann constant, T is the temperature, and e the electron charge) in principle, indicates flocculation (Hunter, 2001). In the experiments of Kaya *et al.* (2006) this was true. In the present experiments, even if the apparent zeta potential for divalent salt was much smaller (in absolute terms) at 10 mM than at 0.1 mM, the apparent zeta potential was still not a good measure of the flocculation ability of the suspension because, over the range of ionic strengths investigated, the zeta potential was <25 mV in absolute terms.

The validity of the rule of thumb using the apparent zeta potential values has already been studied (Chassagne *et al.*, 2009): taking into account the anisotropy of the particles and the surface conductivity (Stern layer conduction), the zeta potential estimated at pH 8 at 1.5 mM of added KCl from electrophoretic mobility and dielectric spectroscopy measurements was three times larger (in absolute value) than the apparent zeta potential. The model linking zeta potential and mobility/dielectric response from Chassagne *et al.* (2009) did not, however, take into account the inhomogeneous distribution of surface charge. As the isoelectric point of the alumina octahedral face lies between pH 6 and 8 (Gupta and Miller, 2010), the surface charges of the kaolinite faces could have opposite signs at pH 6. This could lead to face–face attraction in this pH range and therefore settling.

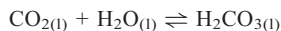
Difference between changing pH with HCl and CO₂

In the Canadian oil sands mining industry, the pH of the fine tailings is controlled *in situ* by adding CO₂. A systematic study of the pH dependence (adjusted by CO₂ bubbling) on the densification of oil sands tailings was performed by Zhu *et al.* (2011). In that study, the authors described how bubbling of CO₂ into fine tailings improved the supernatant clarity and the initial settling rate of the sediment. They correlated these findings with the fact that the zeta potential decreases in absolute terms upon decrease of pH when either CO₂ is bubbled through or HCl is added.

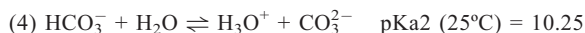
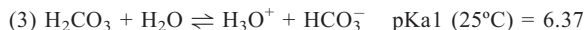
The injection of CO₂ bubbles leads to the dissolution of carbon dioxide in water:



Equilibrium is established between the dissolved CO₂ and H₂CO₃, carbonic acid.



Carbonic acid is a weak acid that dissociates in two steps:



The injection of CO₂ therefore led to the production of H⁺(H₃O⁺) which led to a reduction in pH (Figure 6) for an un-buffered water system with an increasing CO₂ percentage inside the gas bubble, from atmospheric (0.4%) to 100% CO₂. The model assumes equilibrium between the gas phase and the water phase.

The kaolinite suspension was injected quickly (<5 min) in the measurement cell and put into the Zeta Nano device to measure the zeta potential. The degassing of CO₂ could not be measured directly due to the small size of Zeta Nano measurement cell. For validation, a glass beaker was used to test the atmosphere/water transfer rate for over-/under-saturation. An oxygen sensor was used to determine the transfer rate (Figure 7). The timescale for completely (de)gassing is hours. If the CO₂ loss during the zeta potential measurement is comparable to the degassing rate found in Figure 7 then the pH loss would be <0.2.

Like Zhu *et al.* (2011), the present study found for the fine tailings, that for divalent salt there was no difference

between changing the pH to 5 either by adding CO₂ gas or HCl (Figure 8) in the same range of concentration. Samples dispersed in process water which contains <25 mg/L of CaCl₂ (equivalent to <1 mM of added salt) were investigated (Zhu *et al.*, 2011). At >10 mM of CaCl₂ added, a difference was found between bubbling with CO₂ or adding HCl (Figure 8). The fact that the zeta potential became positive at high ionic strengths was also found by Chassagne *et al.* (2009) who examined a china clay diluted in tap water and found a similar behavior and similar values for the zeta potential as a function of pH and added CaCl₂. The values were not exactly the same due to the fact that in the present study ultrapure water was used and tap water in that by Chassagne *et al.* (2009). Almost the same values were found by Kaya *et al.* (2006) as in the present study for the zeta potential as a function of pH and CaCl₂ concentration.

The measurements at such high ionic strength were very difficult, however: the apparent zeta potential values increased in time during the measurements as did the conductivity. The apparent zeta potential values given here are the average of the three first measurements. Bubbles were created during the measurements, and the electrodes turned black, so only a few measurements were performed in this concentration range.

Effect of pH on SP02 and kaolinite in the presence of monovalent and divalent electrolyte

Different behavior between the zeta potential of SP02 and kaolinite was observed upon addition of monovalent and divalent electrolyte at different pH values.

In the case of a monovalent electrolyte like NaCl, the zeta potential varied significantly with pH. The zeta

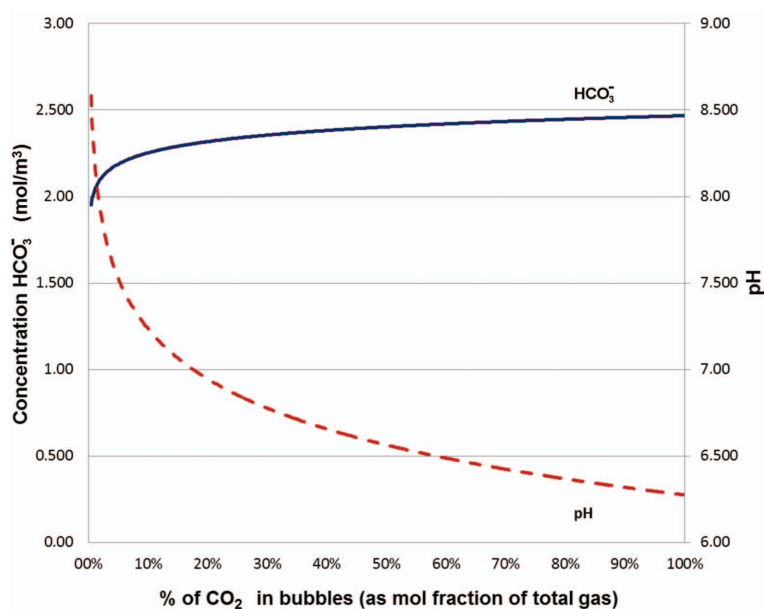


Figure 6. Impact of increased CO₂ fraction in the gas phase on pH.

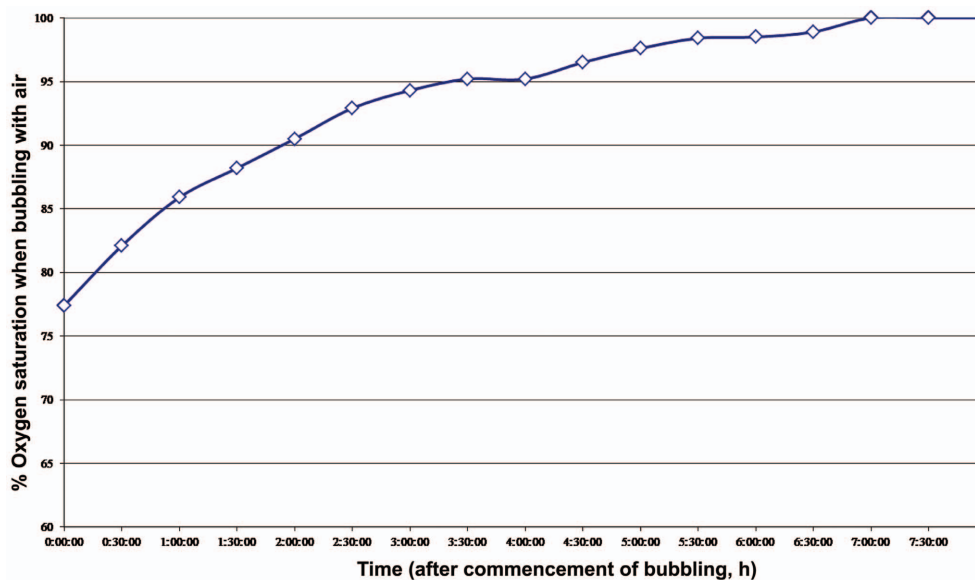


Figure 7. Evolution of oxygen concentration in water when bubbling with air.

potential of the samples decreased in absolute value when pH decreased. This was true for both kaolinite and SP02 samples (Figure 9). Both Kaya *et al.* (2006) and Yukselen and Kaya (2002) found similar values as a function of pH and NaCl concentration for their kaolinite samples. The zeta potential was always smaller in absolute terms for the SP02 sample than the zeta potential of kaolinite below 1 mM of added NaCl. For greater ionic strengths, the zeta potentials of the SP02 samples were systematically larger in absolute terms than the kaolinite samples and the differences between the zeta potentials of kaolinite and SP02 are greater than at low ionic strength. The kaolinite zeta potential was decreased with increasing ionic

strength, in line with expectations from the shielding of the surface charge by double layer ions (Hunter, 2001) as can be seen in Figure 4b. The behavior of the SP02 surface charge at large ionic strength appeared to be more complex. An earlier study by Liu *et al.* (2002) demonstrated the impact of bitumen on the zeta potential of tailings. Those authors showed that kaolinite samples with bitumen at 1 mM KCl at pH = 8 had an average zeta potential larger in absolute values than kaolinite samples without bitumen at 1 mM KCl at pH = 8. The zeta potential of the bitumen emulsion alone was ~ -70 mV at pH = 8. As traces of bitumen are present in the SP02 samples, this could be the reason for the large (in absolute

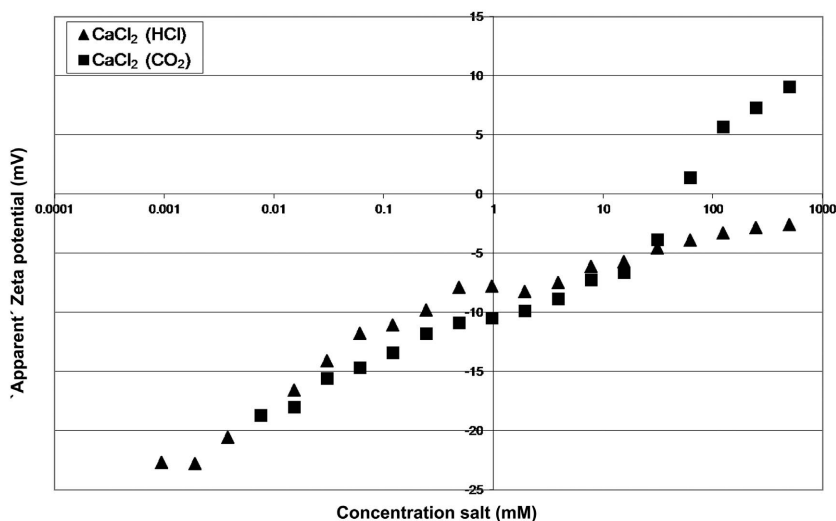


Figure 8. Zeta potential at pH = 5 of a kaolinite sample as a function of CaCl₂ salt when the pH is adjusted with HCl (triangles) and with CO₂ (squares).

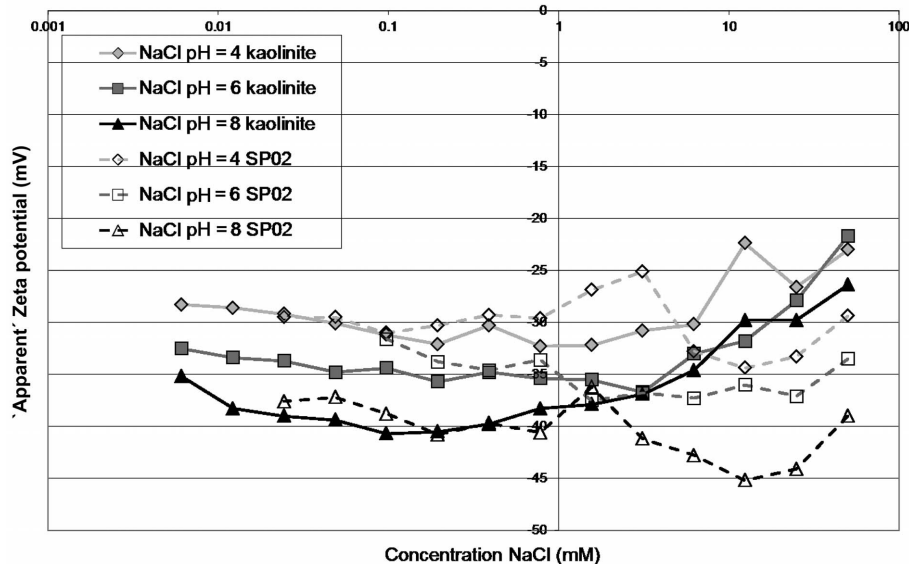


Figure 9. Zeta potential as a function of the NaCl salt kaolinite sample at pH = 8 (filled triangles); SP02 samples at pH = 8 (open triangles); kaolinite sample at pH = 6 (filled squares); SP02 samples at pH = 6 (open squares); kaolinite sample at pH = 4 (filled diamonds); SP02 samples at pH = 4 (open diamonds).

terms) zeta potentials at ionic strengths above 1 mM of NaCl. This should be confirmed by studying samples in the presence and in the absence of bitumen.

The zeta potential of kaolinite and fine tailings suspended in $MgCl_2$ solution with different values of pH was studied. The zeta potential of the kaolinite immersed in the $MgCl_2$ electrolyte behaved similarly to the zeta potential of the fine tailings. Where divalent ions were present in the electrolyte, the presence or absence of bitumen was found not to change the zeta potential of

kaolinite (Liu *et al.*, 2002). The differences between both samples were that the SP02 had slightly larger zeta potentials in absolute values than the kaolinite (Figure 10). The zeta potential behavior was independent of the value of the pH, so a trend could not be found as for monovalent salts (Figure 9).

From the apparent zeta potential results, quick flocculation above 5 mM of added salt for any pH in the presence of divalent salt was expected (as the apparent zeta potential becomes very small for these

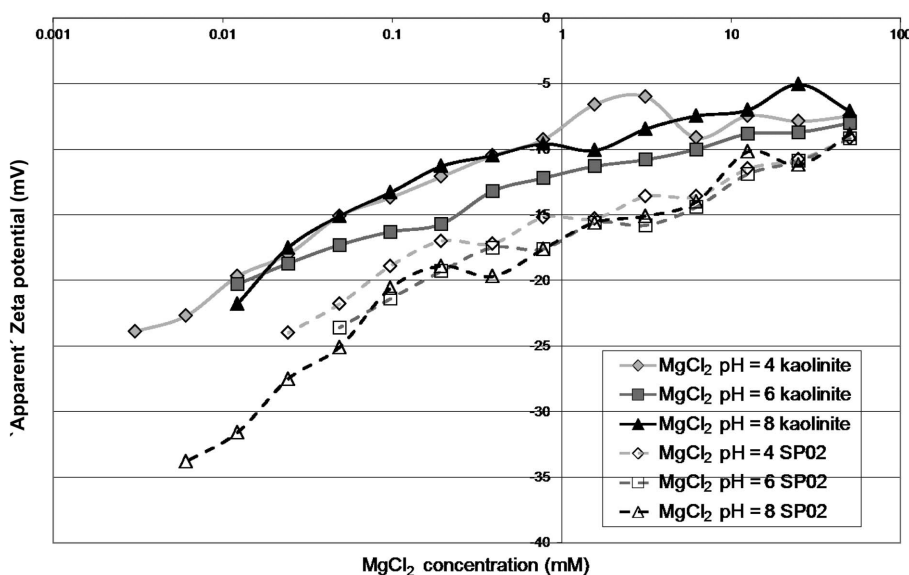


Figure 10. Zeta potential as a function of $MgCl_2$ salt kaolinite sample at pH = 8 (filled triangles); SP02 samples at pH = 8 (open triangles), kaolinite sample at pH = 6 (filled squares); SP02 samples at pH = 6 (open squares); kaolinite sample at pH = 4 (filled diamonds); SP02 samples at pH = 4 (open diamonds).

ionic strengths). This conclusion was confirmed by settling-column experiments for which a greater clarity in the supernatant and quicker settling were observed with the divalent salt (for both kaolinite and SP02) compared to monovalent salt. Similar results were found by Kaya *et al.* (2006) when studying the settling of kaolinite in different aqueous environments.

In an electrolyte where monovalent ions are dominant, the flocculation ability would be more sensitive to pH as the apparent zeta potential is reduced with decreasing pH (more acidic solution). The values of the apparent zeta potential for added monovalent ions even at the smallest pH were always larger (in absolute values), however, than the apparent zeta potential for divalent ions for ionic concentration >0.1 mM of added salt. This is due to the fact that in the presence of divalent salt more counter-charge is present between the surface of the particle and the surface of shear. The Coulombic repulsion will be reduced and aggregation promoted. The *in situ* flocculation of the fine tailings will be greatly influenced by the presence of even a small amount of divalent salt, independent of pH.

A clear supernatant and quicker settling of samples treated with CO₂ was found by Zhu *et al.* (2011). When the samples were treated with CO₂, the amount of divalent ions increased in the process water (table 2 of Zhu *et al.*, 2011). In the Syncrude process water used in the Zhu *et al.* (2011) study, the concentration of Ca²⁺ was 0.18 mM (7.3 mg/L) whereas it was three times greater (0.57 mM) when the pH was adjusted. It is not clear if the increase in settling velocity is primarily due to the change in pH or in divalent ion concentration.

CONCLUSIONS

The electrophoretic mobility properties of kaolinite and fine tailings were studied.

(1) The electrophoretic mobility (apparent zeta potential) of kaolinite and tailings did not vary significantly over the experimental concentration range of solid in the solution for any ionic strength or ion type (pH = 6), suggesting that there were no particle–particle interactions in these particle concentration ranges at the timescale of the experiment.

(2) The finding of Zhu *et al.* (2011), *i.e.* that the zeta potential was the same when pH was controlled by adding HCl and CO₂ at reasonable ionic strengths (<50 mM of added divalent salt), was confirmed.

(3) Both kaolinite and fine tailings (TFT) exhibited the same electrokinetic behavior as a function of pH and ionic strength for divalent salt added and for ionic strengths below 5 mM of added monovalent salt. This was expected because kaolinite is the predominant clay in the tailings. The observations also suggested that traces of bitumen that might still be present in the tailings did not influence significantly the surface charge of these tailings for these concentrations.

(4) For both kaolinite and fine tailings the apparent zeta potential in an electrolyte containing predominantly monovalent ions was found to decrease in absolute terms with decreasing pH (more acidic solution).

(5) The apparent zeta potential of kaolinite and tailings in electrolytes containing predominantly divalent ions did not depend on the pH.

(6) Both kaolinite and fine tailings flocculated faster in the presence of a divalent electrolyte than a monovalent electrolyte, consistent with the fact that the apparent zeta potential was smaller for divalent salt than for monovalent salt (in absolute values) for any pH at high ionic strength.

(7) Even though the apparent zeta potential appears to be a good indicator for predicting the flocculation of fine tailings at a reasonable amount of salt (>1 mM), one should keep in mind that neither the behavior nor the values of this apparent zeta potential (in fact the electrophoretic mobility) as a function of ion strength or pH give information about the surface charge of the particles. This could lead to interpretation errors especially for low ionic strength where the apparent zeta potential indicates flocculation where there is none. More theoretical work is needed to link the electrophoretic mobility of clays to their surface charge which will allow us to estimate the DLVO (Hunter, 2001) interactions between particles and hence their flocculation ability.

It is not clear at this time, in the case where both monovalent and divalent ions are present and the pH is adjusted, how the surface charge of the tailings is affected. As table 2 of Zhu *et al.* (2011) shows, the chemistry of the process water is changed when the pH is adjusted. The amount of divalent salt is increased when the pH is reduced which would suggest that these divalent ions are leached from the clay, thereby changing the tailing chemistry. Moreover, as discussed in the present article, the fact that the zeta potential of kaolinite and SP02 differ at ionic strength >5 mM of added salt might be due to the presence of bitumen in the SP02 samples.

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