

# **University of Alberta**

Role of Carbon Dioxide in Densification of Oil Sands Tailings

by

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## **Abstract**

Carbon dioxide ( $\text{CO}_2$ ) was shown as a promising alternative for oil sands tailings treatment with economical and environmental benefits. This thesis aims to understand the role of  $\text{CO}_2$  addition in settling and densification of oil sands tailings. In this study,  $\text{CO}_2$  was pressurized into two industrial whole tailings provided by Syncrude Canada Ltd. and Canadian Natural Resource Ltd., respectively. The optimal initial settling rate, supernatant clarity and solids content of sediment were achieved at  $\text{CO}_2$  partial pressure of about 100 kPa. Increasing the processing temperature improved the effects of  $\text{CO}_2$  on the settling of tailings. The improvement on settling and densification of tailings by  $\text{CO}_2$  was mainly attributed to pH reduction, which led to a decrease in the value of zeta potential of the fines. On the other hand,  $\text{CO}_2$  bubbles formed by dissolved gas under super-saturation pressure caused a less clear supernatant by disturbing the formed sediments. In addition, pressurizing the tailings with  $\text{CO}_2$  under optional pressure increased the supernatant clarity and solids content of sediment of the tailings treated by cationic coagulants. The limit of  $\text{CO}_2$  sequestration by oil sands tailings was experimentally evaluated.

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## **List of Symbols, Abbreviations and Nomenclature**

### **Abbreviation**

AAS	Atomic absorption spectroscopy
Al-PAM	Aluminum-modified polyacrylamide
C Tailings	Tailings from Canadian Natural Resource Ltd.
Ca-tails	Tailings treated with Ca(OH) <sub>2</sub>
Ca-Mg-tails	Tailings treated with Ca(OH) <sub>2</sub> and Mg(OH) <sub>2</sub> simultaneously
CT	Composite/consolidated tailings
DDA	Dedicated disposal area
DIC	Dissolved inorganic carbon titration method
DLVO theory	Coagulation theory by Derjaguin, Landau, Verwey and Overbeek
ERCB	Energy and Resource Conservation Board
FBRM	Focused beam reflectance measurement
GHG	Green house gas
HWP	Hot water process for bitumen extraction
IC	Ion chromatography
ISR	Initial settling rate
iep	Iso-electric point
TT	Thickened tailings
MFT	Mature fine tailings
Mg-tails	Tailings treated with Mg(OH) <sub>2</sub>
NST	Non-segregating tailings

PSV	Primary separation vessel
SEM	Scanning electronic microscopy
SFR	Sands to fines ratio by weight
SSV	Secondary separation vessel
S Tailings	Tailings from Syncrude Canada Ltd.
WFR	Water to fines ratio by weight
XRD	X-ray diffraction

### **Letters and Notations**

$v$	Hindered-settling velocity of the suspension
$v_i$	Terminal settling velocity of a single particle
$\varepsilon$	Void ratio of the suspension
$n$	A parameter as a function of the flow regime
$n(\text{CO}_2)$	Molar amount of the $\text{CO}_2$ captured by fluid samples
$P_0$	Initial $\text{CO}_2$ pressure of the headspace of autoclave
$P_{\text{eq}}$	Equilibrium $\text{CO}_2$ pressure of the headspace of autoclave
$V_g$	Volume of the headspace
$R$	Ideal gas constant
$T$	Temperature
$\text{CO}_2 \text{ (aq)}$	$\text{CO}_2$ in aqueous form
$\Sigma E^+$	Total charge of cations other than $\text{H}^+$
$\Sigma E^-$	Total charge of anions other than $\text{OH}^-$ , $\text{HCO}_3^-$ , and $\text{CO}_3^{2-}$
Na-clay	Clays with sodium ions adsorbed on the surface

Ca-clay	Clays with calcium ions adsorbed on the surface
in	Inside the closed pressure vessel
atm	Under atmosphere
$K_{sp}$	Solubility constant in water
$CO_2$ (g)	Molar amount of the $CO_2$ gas released from the supersaturated solution
$V_1$	Volume of the tailings solution
$P_b$	Pressure of $CO_2$ gas in the bubbles
$V_b$	Total volume of the $CO_2$ gas bubbles formed in the solution
$C_{t0}$	Total dissolved inorganic carbon concentration of the initial tailings solution

## **Chapter 1     Introduction\***

Athabasca oil sands deposit in Alberta, northern Canada, is the largest and one of the most important resources to the global synthetic crude oil in the world. Based on the report of Alberta government, it has been proven that Alberta oil sands reserve 171.3 billion barrels which can meet the current oil demand of Canada for the next 400 years. The current methods for oil sands extraction could be generally divided into two types: surface mining and in-situ mining. Although about 80% recoverable bitumen can only be obtained through in-situ technology, open-pit mining followed by water-based extraction process is currently the major method of bitumen recovery for most of the large producers.

Oil sands typically contain 7 – 14 wt% bitumen, 83 – 88 wt% mineral solids, and 3 – 5 wt% water (Masliyah 2009). Similar to many other mine operations, water-based extraction of oil sands in open-pit mining produces slurry of tailings waste which is composed of residual bitumen, quartz sands, clays, silts, and water after the removal of most of the bitumen from the ore minerals (Long et al. 2006). This slurry goes into a tailings pond where the coarse sands settle down rapidly leaving solid-free supernatant water on the top and a stable suspension of fine solids in the middle. The top layer of water is recycled for the extraction process

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\* A version of this chapter has been published. Zhu, R.; Liu, Q.; Xu, Z.; Masliyah, J. H. and Khan, A. Energy Fuels, 2011, 25 (5), pp: 2049 - 2057. Copy right 2011 American Chemical Society. Reproduced with permission from the authors.

providing 90% of the company's water demand. However, the intermediate suspensions with a poor water releasing property stay as a stable state for 3 – 5 years, and then become mature fine tailings (MFT). The MFT will take centuries to consolidate without any treatment. The growing storage of the fluid-like MFT imposes huge pressures on landscape, environment, natural resources and operating cost such that it becomes one of the most critical challenges to the oil sands industry. It has been announced by Energy Resource and Conservation Board (ERCB) of Alberta that companies have the obligations to implement plans to substantially eliminate the fluid tailings between 2010 and 2016. After 2016, companies will have to treat the tailings at the same rate as they produce them. According to the long-term objectives of tailings managements raised by the ERCB Directive 074 (ERCB 2009), the criteria for judging the performance of industrial tailings processing basically lies on three aspects such as the efficiency of intermediate process water recycling, the controls of the inventory and contamination of fluid fine tailings disposal, and the liability of tailings for long-term landscape reclamation with the considerations of geotechnical and biological issues.

In order to achieve the objectives those ERCB Directive 074 indicated, a variety of techniques and processes regarding the tailings reduction and management have been studied and developed. One of the effective technologies,

namely composite/consolidated tailings (CT), has been investigated and implemented by Canada Syncrude Ltd. for decades (Matthews et al. 2002). CT process combines the hydro-cyclone underflow with a high percentage of coarse sands and MFT with a high fines content of above 93 wt% to produce non-segregating tailings (NST) having sands to fines ratio by weight (SFR) of 4. With the addition of proper coagulants, for example, gypsum, the fines and coarse sands start to form the networking, and settle simultaneously by self-weight in the ponds. The supernatant layer on the top of solid sediment can be recycled for subsequent extraction process or to water treatment plant. This technology does not only speed up the dewatering efficiency of tailings, but also consume the inventory of MFT. Meanwhile many conventional methods for waste water treatment, such as coagulation/flocculation, dry tailings filtration, centrifuge, membrane separation, reverse osmosis, and freeze thaw dewatering, have been experimented in laboratory or implemented in pilot-scale in order to tackle the tailings issue.

No matter the conventional or the advanced technologies, the essence of oil sands tailings treatment eventually comes down to transforming segregating fluid tailings into NST to accelerate the dewatering efficiency and generate the trafficable and reclaimable deposits. To achieve this purpose, chemical binding agents, such as coagulants and flocculants, are usually used in the process to

destabilize and flocculate the suspension of fines. The selection of chemical agents, which is important to a large scale and long term operation of tailings treatment, is based on a comprehensive assessment regarding performance, economics, and impacts on the environment. In the traditional CT process, the excess dosage of gypsum in MFT, in order to achieve sufficient coagulation of fine suspension, results in a significant amount of  $\text{Ca}^{2+}$  in the recycled water hampering the bitumen recovery in the following extraction.

Another popular technology is called thickened tailings (TT) which commonly employs synthetic polymers as flocculants. However, the high operating cost due to the flocculant normally builds an economical barrier to the wide application of TT. Besides, the organic contamination due to the residual polymers in the recovered water is also a concern.

Comparing to those traditional chemical agents used in CT and TT processes, carbon dioxide ( $\text{CO}_2$ ) is an ideal alternative because of the cheap price, the large and accessible resource, and the low impacts on the chemistry of recovered water. It has been reported by Mikula et al. (2004) that  $\text{CO}_2$  has the potential to be a chemical additive for the CT process. It was surprisingly found that the  $\text{CO}_2$ -treated CT settled as rapidly as, or even more rapidly than, the gypsum-CT for the CT samples with certain particular compositions. Moreover, the low  $\text{Ca}^{2+}$  concentration and high alkalinity of the released water of the  $\text{CO}_2$ -tailings is

beneficial for bitumen recovery in recycle use. In addition, the accessible resource of CO<sub>2</sub> is enormous since CO<sub>2</sub> is usually a by-product generated by many chemical manufactories. With a satisfactory performance on creating NST, CO<sub>2</sub> is superior to gypsum and polymeric flocculants in terms of the lower operating cost and the resulted water chemistry that is beneficial for the subsequent bitumen extraction. The Horizon Project of Canadian Natural Resources Ltd. (CNRL) has been injecting CO<sub>2</sub> into tailings pipelines in a pilot plant to improve the settling and densification of tailings.

The introduction of CO<sub>2</sub> to oil sands tailings also has the potential of physically trapping or chemically sequestering CO<sub>2</sub> which is a green house gas (GHG) (Mikula et al. 2004; 2010). As the international attention on global warming and climate change grows, the topics about the reduction and regulation of GHG emissions are being discussed at many occasions. Aggressive regulatory policies on the industrial GHG emission have been recently announced by the Canadian government. The Government of Alberta announced that now it is jurisdiction of Alberta to require large emitters over 100,000 tons of GHG per year to meet the mandatory reduction target. Potential CO<sub>2</sub> sequestration by oil sands tailings in the existing and upcoming tailings ponds would make a huge contribution to the GHG capture and storage, and support the sustainable development of oil sands industry.

Although the technology of using CO<sub>2</sub> for oil sands tailings treatment is implemented in pilot-scale, the mechanism of how CO<sub>2</sub> affects the coagulation and densification of oil sands tailings has not been systematically studied. One study on bubbling of CO<sub>2</sub> into oil sands tailings under ambient conditions only showed a qualitative direction (Mikula et al. 2004). In order to develop a robust, CO<sub>2</sub>-based oil sands tailings treatment technology, it is of critical importance to understand the working mechanism of CO<sub>2</sub> in oil sands densification. The effective dosage of CO<sub>2</sub> to be applied to oil sands extraction tailings and its effect on tailings densification must be investigated scientifically. In fact, the CO<sub>2</sub> partial pressure and temperature in pipelines where CO<sub>2</sub> is mixed with tailings need to be optimized for commercial operations. One approach is to change the CO<sub>2</sub> partial pressure above the tailings sample surface, which allows the concentration of CO<sub>2</sub> dissolved in tailings to be determined by Henry's law. Thus, a lab-scale experiment can be used effectively to study the effect of CO<sub>2</sub> partial pressure and processing temperature on tailings densification prior to plant implementation. In addition, the synergy of CO<sub>2</sub> with other chemicals is another aspect of the potential of CO<sub>2</sub> to be exploited for the tailings treatment. The preliminary study on the integrated use of CO<sub>2</sub> and other coagulants is also covered in this thesis.

Although many researchers have interests in quantification and optimization of CO<sub>2</sub> sequestration by oil sands tailings, the limit of sequestration has never been precisely probed experimentally. Another objective of our study is to experimentally evaluate the potential of oil sands tailings for the sequestration of CO<sub>2</sub>.

This thesis is divided into 9 chapters: *Chapter 1, Introduction; Chapter 2, Literature review; Chapter 3, Experimental section; Chapter 4, Effect of CO<sub>2</sub> on densification of tailings; Chapter 5, Mechanism of CO<sub>2</sub> enhanced densification of tailings; Chapter 6, Synergy of CO<sub>2</sub> with cationic coagulants on densification of tailings; Chapter 7, Potential of CO<sub>2</sub> sequestration by tailings; Chapter 8, Conclusions; and Chapter 9, Recommendations.*

## **Chapter 2    Literature Review**

### **2.1. Generation of oil sands tailings from water-based process**

Oil sands are proven the second-largest crude oil reserve in the world. The oil sands area in north-eastern Athabasca has the rough size as large as Florida in the US and 0.42% of the area has been disturbed by mining activities to date. Although 80% of the oil sands reserve has to be exploited by in-situ recovery, surface mining operation is currently the major method. Oil sands are composed of quartz sands, highly viscous bitumen and connate water (Long et al. 2006). They are dug up from the mining pit and transported by giant shovelling trucks to extracting facilities where bitumen is obtained. The commercial hot water process (HWP) for extraction, also known as the Clark Process (Clark et al. 1932), can achieve over 90 wt% bitumen recovery efficiency at 80 – 85 °C and pH 8 – 9 using caustic soda (NaOH). Bitumen is liberated from oil sands resulted from the decrease of interfacial tension with increasing pH values. The quantity of caustic soda actually depends on the quality of the oil sands which ranges within 0.04 – 0.1 kg/t of oil sands ore (Chalaturnyk et al. 2002). With the optimization of the process technologies and the development of the efficient additives, some companies, for example, Syncrude Canada Ltd., have lowered the temperature of extraction process down to 50 °C to save the energy than the old process.

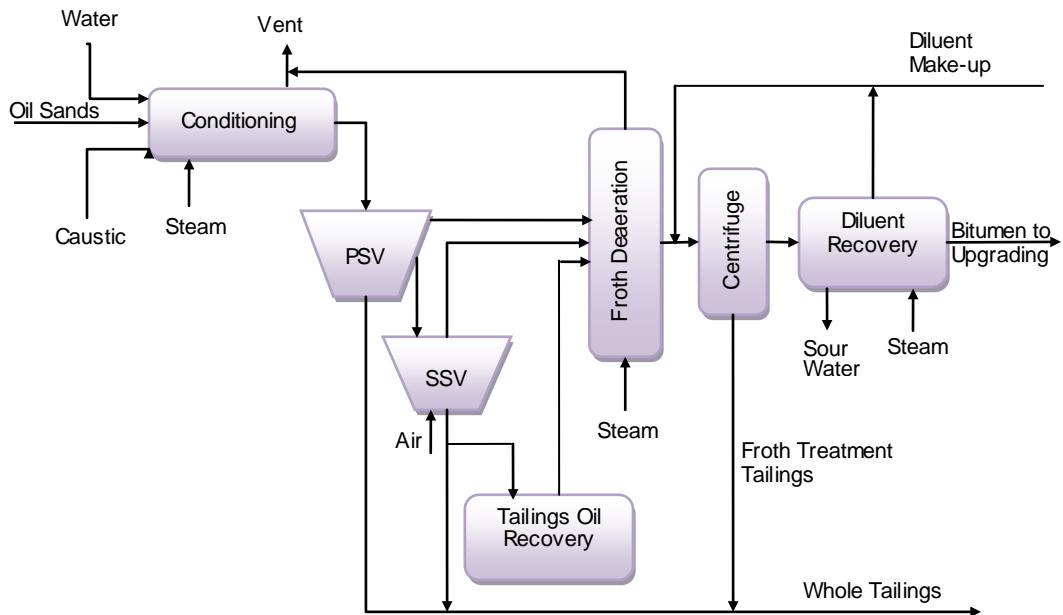


Figure 2-1 Schematics of HWP for bitumen extraction from oil sands (Chalaturnyk et al. 2002).

The commercial HWP flow sheet is described in Figure 2-1. First, the oil sands from mining site are transported into a conditioning vessel where hot caustic water is mixed and temperature is controlled. At the same time, steam is introduced to float the liberated bitumen. The flotation mainly takes place in the following primary separation vessel (PSV). The air-trapped bitumen froth floats to the top of the vessel, and is skimmed off and pumped into froth treatment plant where bitumen is recovered by solvent. The middling part of the vessel is drained out and fed into a secondary separation vessel (SSV) for second-flootation. The underflows of the separation vessels containing sands, fines, clays, water and residual hydrocarbon are called flotation tailings. Usually flotation tailings and

froth treatment tailings are mixed and discharged into a disposal area as whole extraction tailings. During the disposal process of the tailings, the coarse sands settle fast to form a stable and sloped sand beach, also known as the dyke of a tailings pond, while the fines and clay minerals remain suspended and form fluid tailings with water on the top of the sands. Over a few years the fine fluid tailings in the ponds become MFT with the fines content as high as 97 wt% which take decades to be consolidated without treatment! To date, the area of tailings ponds reaches 10 km<sup>2</sup> and still expands with an accelerated speed. The tailings ponds put a gigantic pressure on landscape reclamation, environment protection and operating costs. Therefore, the development of the modern oil sands industry is strongly bonded with the effective and economical technologies of tailings treatment.

## **2.2. Technologies for oil sands tailings treatment and challenges**

As early as 1950s, researchers started working on the treatment of clay-rich tailings from water-based bitumen extraction process. To date, many methods and concepts of consolidating and eventually reclaiming fluid tailings have been explored. Those methods employed different technologies such as chemical amendment, mechanical enhancement, physical transformation and bioremediation. In the past three decades, the chemical-assisted processes have

been drawing the major interest of researchers and industries because the solutions such as coagulation and flocculation give tailings a fast dewatering efficiency and produce deposits with high solids content (Caughill et al. 1993; Matthews et al. 2002). Currently, the representatives of commercialized chemical-assisted technologies are CT by Syncrude Canada Ltd. and TT by Shell Canada Ltd.

#### *2.2.1. Composite/consolidated tailings*

Syncrude Canada Ltd. started a pilot of CT process in 2000 utilizing the mine-out area for CT placement. The science of CT process is disclosed in a Matthews' review on the development of CT technology at Syncrude (Matthews et al. 2002). As shown in Figure 2-2, point A represents the original composition of the tailings slurry, and the areas above and under the segregation line are the non-segregating zone and the segregating zone, respectively. There are basically three approaches to transfer segregating tailings into NST: increasing the solids content without changing fines content to get A' in Figure 2-2, increasing fines content without changing solids content to get A'' in Figure 2-2, and adding coagulants to shift the boundary line of segregation towards down-left letting A fall in the non-segregating zone in Figure 2-2. Corresponding to these three approaches above in sequence, the three steps of CT process to achieve NST are as following: the flotation tailings from the PSV are densified by hydro-cyclone to increase the

total solids content of slurry; the densified cyclone underflow is combined with MFT with over 93 wt% fines to form a CT slurry having 60 wt% solids; and the addition of coagulants, such as gypsum. As a result, the non-segregating CT would perform a fast sedimentation in the disposal area and produce solid-free supernatant water which could be recycled for the subsequent bitumen extraction. About 90% of the company's water demand can be satisfied by the recycled water from the CT process. The CT process benefits the water-based oil sands extraction in terms of the reclamation of disturbed land, the consumption of MFT inventory, and the reduction of managing cost of tailings storage. CT has been known as an effective technology with a decade of research and piloting.

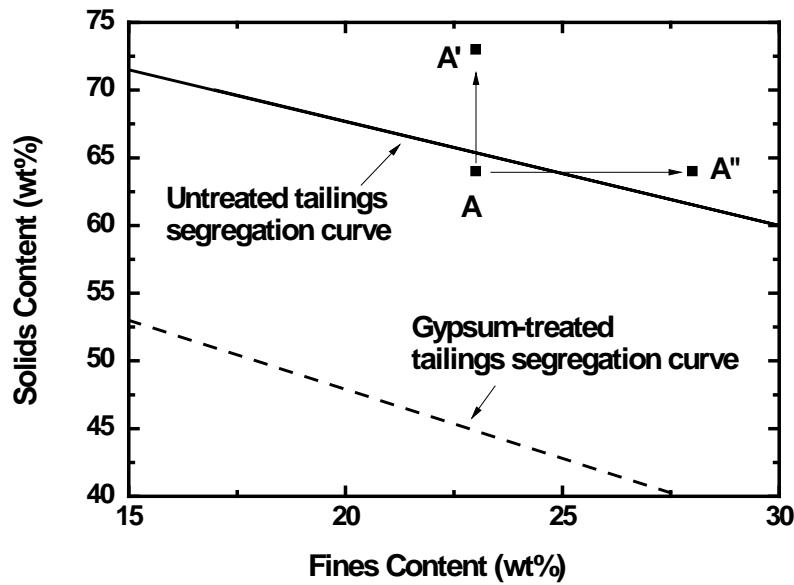


Figure 2-2 Different approaches to achieve non-segregating tailings slurry (Matthews et al. 2002).

The application of a coagulant is a critical step in CT process because the coagulation reduces the repulsion between fine particles and destabilizes the suspension. As a result, the sands being “trapped” in the networking of the coagulated fine particles could settle together with fines and clays by self-weight. In the early 1980s, extensive lab works suggested that calcium salt was an effective coagulant candidate for the consolidation of fluid tailings (Liu et al. 1980; Erno et al. 1981; Marsh et al. 1984). Lime was used as a process aid in the extraction tailings stream at Syncrude in 1990, but failed to create compact and reclaimable tailings deposits. With a further evaluation of a large pool of calcium salts, Syncrude found that gypsum was the most effective and economically-accessible coagulant for CT operation. However, the addition of gypsum to CT process brings adverse effects to the released water and consolidated deposits, which is considered as the bottle-neck to the present CT technology. Firstly, the high calcium concentration of gypsum-affected CT water is detrimental to the bitumen recovery in subsequent extraction step (Fong et al. 2004). Secondly, the large demand for sands (current minimum SFR of CT is 4) is hard to be met since sands are usually valuable for the construction of tailings ponds and other facilities in the operation site. Even if there is a sufficient sand supply, a general and optimal “recipe” of CT mixture is still unknown. The “recipe” normally refers to the combination of solids content, SFR, and water to fines ratio by weight

(WFR) (Matthews et al. 2002; Pollock et al. 2000). They are essential for creating a successful NST regardless of which process aid is used. The “recipe” highly depends on the specified water chemistry, mineralogy, and particle size distribution of tailings so that an appropriate formula of CT is usually empirical. In addition, the high salinity of the reclaimed tailings solids would contaminate the top soil, and consequently harm the boreal growing (Renault et al. 1998).

#### *2.2.2. Thickened tailings*

TT technology, also known as paste technology, is derived from the concept of eliminating the fine portion of fresh tailings by creating paste-like mine tails before it is discharged into tailings ponds. It applies the benefits of coagulation and flocculation to make the fluid tailings non-segregating and settle in a cone-shaped tank namely thickener. The highly consolidated underflow of the thickener with a solids content of 40 – 50 wt% will be pumped and transported through pipeline to the dedicated disposal area (DDA) for sedimentation and dewatering. In a sloped DDA, the moisture of the deposits will then decrease by gravity draining and evaporation. After the deposits are sufficiently dried, they are transported back to the mine-out area for reclamation by shovel trucks. With the collaborative frame work between industry and research facilities, Albian Sands Energy and Shell Canada Ltd. have been implementing TT in pilot-scale for 6 years, and many other companies have participated in the research and the

development of the thickener technology. Synthetic organic polymers are commonly employed as efficient flocculants. They flocculate dispersed or coagulated particles through various postulated mechanisms such as electrostatic adsorption, charge neutralization, inter-particle bridging, and enmeshment in a precipitation (Crittenden et al. 2005). Especially, when polyelectrolyte flocculants are added into dispersions of opposite charged particles, the electrostatic attraction acts as the major driving force for adsorption and the destabilization of colloids leading to a much stronger flocculation (Gregory 1987). University of Alberta has exploited the potential of cationic alumina-modified polyacrylamide (Al-PAM) polymer on the fine tailings thickening in the purpose of recycling a high quality supernatant and reclaiming a compact solid deposit (Li et al. 2008; Wang et al. 2010). It was also found that Al-PAM was a robust chemical agent to produce solid “cakes” with low moisture contents by pressure filtration following the flocculation settling, in which case Magnafloc 1011 (Percol 727) was ineffective (Wang et al. 2010). Apart from the selection of effective flocculants, determining factors influencing the flocculation process include pH, polymer dosage, presence of divalent cations, and hydrodynamic conditions (Sworska et al. 2000a; Sworska et al. 2000b).

The biggest merit of TT lies on the fast dewatering efficiency and water-less underflow paste. The big flocs formed in the thickener have high permeability for

water release which is beneficial for the cross-linking and entanglement of fine particles by high molecular weight polymers. As a result, the strength of the deposits in DDA would increase as disposal time elapses until it meets the requirements for traffic and reclamation. The ERCB Directive 074 (ERCB 2009) indicates that the minimum undrained shear strength of the deposits produced in the previous years is 5 kPa. It appears that the thickener is so far the best approach to achieve this goal without requiring a long sedimentation time and a large disposal area. In addition, organic polymer additives would not cause any problem of high ionic loading to the affected-water as inorganic chemicals would. However, the huge economical burden of the large demand for flocculants holds back the further commercialization of TT technology. At this stage, searching an efficient and costly-accessible flocculating agent is one of the key items of the development of TT technology.

### **2.3. Research and application of CO<sub>2</sub> in current tailings treatment**

As described above, the major challenges for CT and TT technologies are either related to the adverse effects of the process additives or to the high cost. Over the past decades, millions of research funds have been spent on minimizing the adverse effects of conventional additives and exploring alternate or new chemical agents. The application of CO<sub>2</sub> was motivated by the superiority of CO<sub>2</sub>

in an overall assessment considering performance, operating cost and environmental hazards. Firstly, CO<sub>2</sub> does not cause the increase of Ca<sup>2+</sup> concentration as gypsum or lime does. Secondly, the increase of alkalinity (HCO<sub>3</sub><sup>-</sup>) due to the dissolution of CO<sub>2</sub> favours the subsequent bitumen extraction (Zhao et al. 2009). Last but not least, CO<sub>2</sub> as a by-product from many chemical manufactories is a more economical choice to treat a giant amount of oil sands tailings produced every day. There is also a potential of recycling the CO<sub>2</sub> generated by upgrading unit of oil sands industries.

It was reported that CO<sub>2</sub> was an effective coagulant for creating NST in CT process (Matthews et al. 2002). Syncrude found that the segregation boundary of CO<sub>2</sub> was similar to that of the aluminium compound (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) at a given molar dosage in the sand-fines composition diagram as shown in Figure 2-2. The CANMET Energy Technology Centre evaluated the effect of CO<sub>2</sub> on the consolidation of CT and estimated the potential of CO<sub>2</sub> sequestration by tailings stream in lab scale (Mikula et al. 2004). In their study, CO<sub>2</sub> was bubbled into MFT before making CT mixture. They found that CO<sub>2</sub>-CT achieved the similar rheological and settling characteristics as gypsum-CT did. On the other hand, the Ca<sup>2+</sup> concentration of released water from CO<sub>2</sub>-CT was lower than that from gypsum-CT. It was also surprisingly found that CO<sub>2</sub>-CT dewatered significantly faster than gypsum-CT at a given CT composition (SFR = 4.7, clays/water by

weight = 0.11, and solids content = 55 wt%). Based on the water chemistry analysis, they conservatively estimated that the sequestration limit of CO<sub>2</sub> was 75 – 200 t/Mt of CT. This number indicates a tremendous potential of CO<sub>2</sub> capture by tailings in terms of the scale of the entire oil sands tailings ponds. This estimation was made based on the calculation of the change of the amounts of bicarbonate and carbonate ions in the tailings solution.

Besides the potential of being the alternative process aid for CT, CO<sub>2</sub> was also applied together with other chemical binding agents in thickener. Apex Engineering Inc. once developed a process of thickened tailings with CO<sub>2</sub> (Chalaturnyk et al. 2002). In this process, Ca(OH)<sub>2</sub> lime was added into fresh tailings as a binding agent followed by injecting CO<sub>2</sub> to form CaCO<sub>3</sub> precipitation with slight pH reduction from 12.0 to 11.6. It was found in this research that water release rates for the tailings treated with Ca(OH)<sub>2</sub> and CO<sub>2</sub>, to some extent, were improved comparing to the tailings treated only with Ca(OH)<sub>2</sub>. The mechanism of this finding was still unclear due to the lack of study on other aspects of the effects of CO<sub>2</sub>, such as densification behaviour and water chemistry. Based on the Scanning Electronic Microscopy (SEM) images, they asserted the large openings in the floc structures generated by the treatment of Ca(OH)<sub>2</sub> and CO<sub>2</sub> were responsible for the improvement of settling and consolidation performance. This process worked more effectively at a higher temperature such as 70 °C, at which

more  $\text{CaCO}_3$  crystals could be formed. To further investigate this interesting phenomenon, the synergy of  $\text{CO}_2$  with lime and brucite on the tailings treatment will be studied in this thesis (see Chapter 6).

## 2.4. Influence of $\text{CO}_2$ on oil sands tailings

### 2.4.1. Water chemistry and interfacial properties of solids

One of the most important influences that  $\text{CO}_2$  has on tailings is to change the water chemistry.

Firstly,  $\text{CO}_2$  as an acidic gas can reduce the pH of water when being dissolved so that natural water has a pH 5.65 at atmospheric pressure (0.0355 vol% of air is  $\text{CO}_2$ ). As is known, the solution pH is critical for destabilization of the tailings suspension. As a matter of fact, acid was used as a coagulant to reduce the pH of tailings. Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) was once found effective on consolidating the whole oil sands tailings with 54 wt% solids and 17 wt% fines ( $< 44 \mu\text{m}$ ) in a quiescent environment (Caughill et al. 1993). Caughill et al. reported that the final void ratio of the  $\text{H}_2\text{SO}_4$ -treated tailings was about 0.168 at an optimal concentration of  $\text{H}_2\text{SO}_4$  higher than that of lime-treated tailings. The electrostatic properties of the solid surface, especially the clays and fines, in oil sands tailings are strongly dependent on pH. The zeta potentials of kaolinite clays and quartz which are the major solids of oil sands mineral changed as a function of pH with

iso-electric points (iep) of pH 3 – 5.5 and pH 2<sub>2</sub>, respectively (Johnson et al. 1998; Johnson 1999; Mpofu et al. 2004). With the dependence of zeta potential on pH, it was found that the yield stress, sedimentation rate, and consolidation characteristics of kaolinite dispersion all reached maximum values at the iep, which could be in-depth explained with the typical theory by Derjaguin, Landau, Verwey and Overbeek on coagulation (DLVO theory) (Addai-Mensah and Ralston 2005).

Secondly, the concentration of bicarbonate ions ( $\text{HCO}_3^-$ ) resulted from the dissociation of carbonic acids ( $\text{H}_2\text{CO}_3$ ) also affects the stability of colloidal suspension. As a dispersant,  $\text{HCO}_3^-$  creates the dispersion of fines-fines and fines-bitumen in the bitumen extraction process, especially with the presence of calcium ions, and improves the bitumen recovery efficiency and froth quality-<sub>2</sub> (Zhao et al. 2009). However,  $\text{HCO}_3^-$  increases the difficulty for tailings treatment which preferably requires the attraction between fine solids. The effect of  $\text{HCO}_3^-$  on the interaction of the clays is dependent on the concentration of electrolyte in the solution and the total amount of clays. Kotlyar et al. (1995) studied the role of bicarbonate on the stability of ultra-fine particles suspension using oil sands fine tailings samples. They found that the aggregation of  $\text{NaHCO}_3$ -flocculated suspension increased dramatically beyond a “critical concentration” of  $\text{NaHCO}_3$  which was 100 mM in that case. On the other hand, in their study, the final

sediment volume and their solid content were virtually independent on the type and concentration of the electrolyte, or the initial solids amount once the clay concentration exceeded the gelation point.

#### 2.4.2. *CO<sub>2</sub> gas bubble*

The formation of massive CO<sub>2</sub> gas bubbles in a supersaturated solution would also affect the flocculation and sedimentation of tailings. It was found that bubbles formed from supersaturated dissolved gas floated the flocs during coagulation/flocculation process and hence hindered the following sedimentation and filtration in the conventional water treatment process (Scardina and Edwards 2002). The formation and stability of floated flocs are correlated with the local solution pressure, the amount and type of dissolved gas, the temperature, and the hydrodynamic conditions (Scardina and Edwards 2006). Since CO<sub>2</sub> has a higher solubility in water than in air, the CO<sub>2</sub> bubble formation easily occurs in a real practice whenever total dissolved gas pressure exceeds the local CO<sub>2</sub> pressure (Scardina and Edwards 2001). For instance, the partial CO<sub>2</sub> pressure in the tailings pipelines of CNRL's plant (about 400 kPa – 10 kPa) is usually much higher than that under atmosphere (0.035 kPa). As a result, massive CO<sub>2</sub> bubbles would be generated when the tailings solution is discharged into the ponds which are open to atmosphere.

In a bubbly-liquid, the settling velocity of solid particle would no longer be the same as the settling velocity in a liquid. It was found that the settling velocity of a solid particle in bubbly-liquid decreased slightly with the increasing gas flow rate in the system (Yianatos et al. 1986). However, a contradictory theory claimed that the addition of buoyant phase would cause convection and streamlines between phase and phase leading to a stable or even accelerated settling velocity of the heavy phase (Fessas et al. 1981). The buoyant phase could be gas bubbles in the CO<sub>2</sub>-tailings. Nevertheless, the two theories above were based on the modeling calculation and the experiments of single particles. In a three-phase system, such as the CO<sub>2</sub>-tailings system where multiple solid and gas particles aggregate in a liquid solution, the scenario becomes much more complex. In addition, the mechanism of the floc-bubble attachment is not fully understood. Four plausible mechanisms of floc-bubble attachment were proposed as following (Crittenden et al. 2005): (1) preformed bubbles adhere to preformed flocs (Figure 2-3a); (2) preformed bubbles are physically entrapped within preformed flocs while rising up (Figure 2-3b); (3) aggregation of particles entraps preformed bubbles inside of floc (Figure 2-3c); and (4) floc nucleates bubble formation (Figure 2-3d). With postulated mechanisms like those, the CO<sub>2</sub> bubbles generated by the excessive dissolved CO<sub>2</sub> are highly suspicious to exert an adverse impact on the flocculation and settling of the tailings.

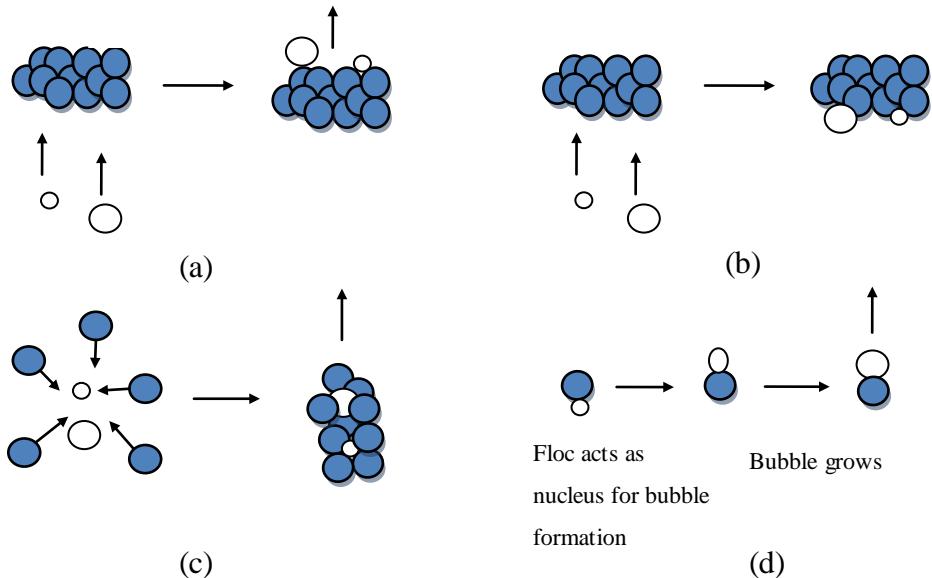


Figure 2-3 Illustration of four types of floc-bubble attachments (Crittenden et al. 2005).

## 2.5. Sedimentation mechanisms of oil sands tailings

According to the work of Pierre et al. (1995; 1999), three types of sedimentation behaviours of clay suspensions were observed, namely accumulation, flocculation, and mixed-accumulation. Accumulation sedimentation usually occurs when no flocculant is added and discrete particles or aggregates settle freely accumulating at the bottom due to gravity, e.g., the sedimentation of coarse sands in the tailings. However, this accumulation sedimentation model usually could not be applied for the sedimentation of oil sands tailings. With a significant high solid concentration, normally above 30

wt%, the dispersed particles of oil sands tailings no longer settled individually but would perform hindered-settling (Type-III settling) affected by the interaction with other particles around. In the hindered settling, also known as zone settling, the individual particle is affected by the interaction with other particles around, and the interacted particles formed a settling blanket to sweep the discrete particles (Crittenden et al. 2005). Even without any flocculant, the suspension of tailings separated into a fluid-like sediment and a supernatant layer on the top of sediment when a sufficient sedimentation time is given. With addition of coagulants or flocculants, the sedimentation mode was changed to the flocculation settling (Type-II settling) (Crittenden et al. 2005) which was beneficial for the principles such as growth of flocs and sweeping effect to remove the smaller discrete particles.

The structures of the sediments formed by the different sedimentation modes are also different. It has been found that the accumulated sediment of clays with low volume is usually uniformly packed by the face-face (FF) associations of clays while the flocculated sediments with high volume are loosely structured by open flocs with edge-face (EF) and edge-edge (EE) associations of clays (Pierre et al. 1995; Ma et al. 1998; Pierre et al. 1999).

The sedimentation velocity of the solid-liquid suspension is critical for tailings treatment because it determines the dewatering efficiency and the throughput of

the materials. In principal, the hindered-settling velocity of a concentrated solid suspension of rigid and uniform sphere particles could be empirically predicted with the most well-known empirical relationship Richardson and Zaki equation (Coulson and Richardson 1978):

$$v = v_i \epsilon^n \quad (2-1)$$

where  $v$  = hindered-settling velocity of the suspension;  $v_i$  = terminal settling velocity of a single particle;  $\epsilon$  = void ratio of the suspension;  $n$  = a parameter as a function of the flow regime.

Unfortunately, this quantitative relationship cannot be used in the settling of the coagulated or flocculated tailings, even if the correction factors were taken into account (Bache and Gregory 2010). The reasons are as following: (1) the Richardson and Zaki equation was developed for coarse particles larger than 0.1 mm in diameters, whereas the fines and clays of the tailings are smaller than 44  $\mu\text{m}$ ; (2) the particles, aggregates and flocs in tailings have a wide size distribution and irregular shapes; and (3) the flocs formed in the tailings are not rigid, and they have compressible structures. Therefore, the settling rate of sediment in the tailings can only be determined by the settling experiment in the graduated cylinder.

## **Chapter 3      Experimental Section<sup>†</sup>**

### **3.1. Materials**

In this thesis, two plant whole tailings, provided by Syncrude Canada Ltd. (S) and Canadian Natural Resources Ltd. (C), were studied. Dean Stark method was used to determine the compositions of the tailings (Bulmer et al. 1979). The weight percentages of water, solids and bitumen in the tailings slurries are listed in Table 3-1.

Table 3-1 Composition of oil sands tailings samples

Sample Source	Components, wt%			
	Water	Bitumen	Solids	Fines Content*
Syncrude	62.5	< 0.1	37.5	27.5
CNRL	68.2	0.7	31.1	42.9

The particle size distributions of the solids in sample slurry were measured on an iC S400A portable particle characterization analyzer known as focused beam

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<sup>†</sup> A version of this chapter has been published. Zhu, R.; Liu, Q.; Xu, Z.; Masliyah, J. H. and Khan, A. Energy Fuels, 2011, 25 (5), pp: 2049 - 2057. Copyright 2011 American Chemical Society. Reproduced with permission from the authors.

\* Fines Content is calculated as a percentage ratio of fines (< 44  $\mu\text{m}$ ) to total mineral solids by weight.

reflectance method (FBRM; METTLER TOLEDO, US). Figure 3-1 shows the cumulative curves of weighted square percentage as a function of the chord length of the particles. The concentrations of fines, which are defined as the particles with size less than 44  $\mu\text{m}$ , were 27.5 wt% and 42.9 wt% for S and C tailings, respectively. The fines content were considered high, especially for C sample.

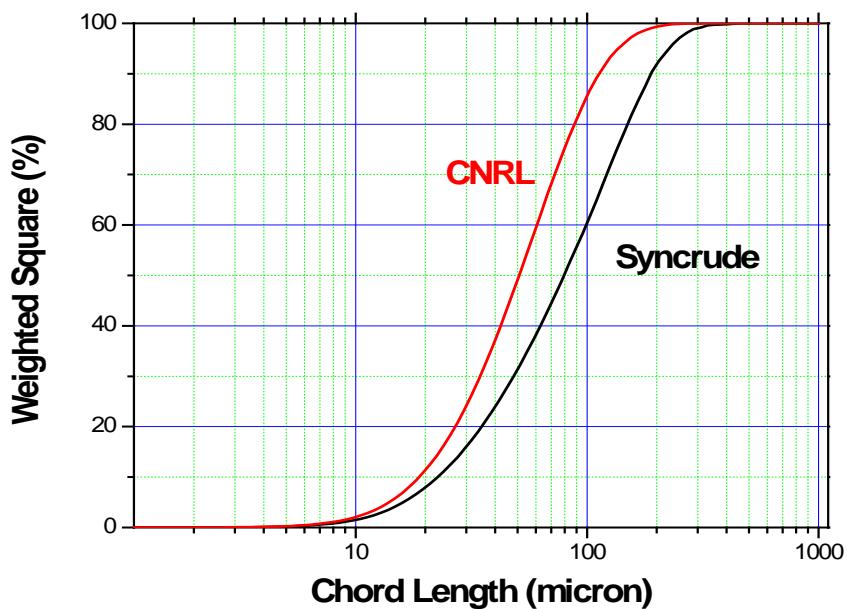


Figure 3-1 Particle size distribution of tailings samples.

The mineral compositions of solids were analyzed by powder X-ray diffraction (XRD). As shown in Figure 3-2, both solids in the two tailings have similar mineralogical compositions, composed mainly of silica (quartz), a small portion of kaolinite clays, and minor illite and montmorillonite clays.

The reactive CO<sub>2</sub> and N<sub>2</sub> gas had 99.9% and 99.998% purity, respectively, purchased from Praxair Canada Inc. HCl acid and NaOH base were used for adjusting pH values. Ca(OH)<sub>2</sub> lime and Mg(OH)<sub>2</sub> brucite were used as the sources of divalent cations. All the chemicals used were reagent grade provided by Fisher Scientific Inc., US.

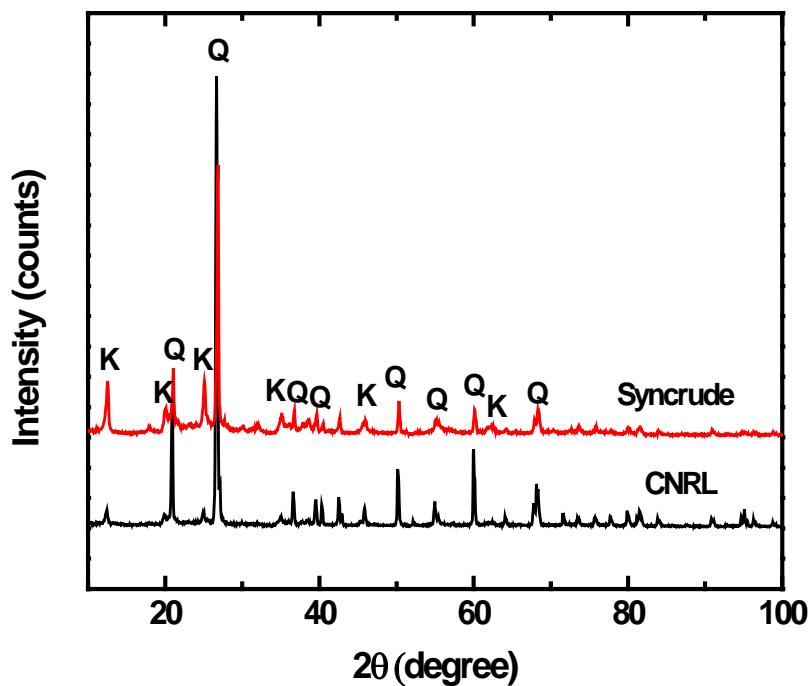


Figure 3-2 X-ray diffraction patterns of tailings solids: Q-Quartz ( $\text{SiO}_2$ ); K-Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). Trace amounts of illite ( $(\text{K},\text{H}_3\text{O})\text{Al}_2\text{SiAl}_3\text{O}_{10}(\text{OH})_2$ ) and montmorillonite ( $(\text{Na}_{0.3}\text{Al,Mg})_2\text{SiO}_{10}(\text{OH})_2\cdot\text{nH}_2\text{O}$ ) are not marked in this pattern for clarity.

### 3.2. Autoclave

In this study, a 400-mL bench-top autoclave 4560 (Parr Instrument, US) was used to introduce CO<sub>2</sub> into tailings (Figure 3-3). The pressure sensor and temperature probe were installed on the head fitting to measure the pressure of the headspace and the temperature of the aqueous sample in the autoclave. A steel agitator driven by a motor on the top of the head fitting provided a sufficient mechanical mixing to homogenize tailings slurry with the aid of an affiliated baffle.



Figure 3-3 Bench-top autoclave used for pressurizing the tailings with CO<sub>2</sub>.

As shown in Figure 3-4, a hollow impeller was fixed at the end of a hollow shaft as the agitator. There were gas inlet/outlet fittings on the upper shaft and on the impeller. This structure was designed for gas entrainment, by which mass transfer of gas into slurry phase was significantly improved once the agitator started stirring at speeds above 800 rpm. The autoclave was connected to a Parr 4848 central processor, which could display the digital readings of pressure and temperature in the autoclave, and allow control of rotating speed of the agitator. A heating jacket was equipped to achieve desirable temperatures for the reactions with the assistance of an electronic auto-tuning module installed on the processor.

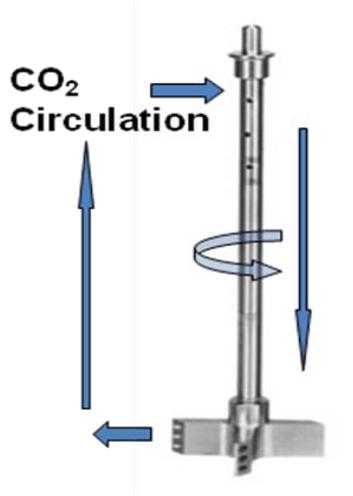


Figure 3-4 Gas entrainment agitator installed on the head fitting of the autoclave.

### **3.3. Sample treatment**

#### *3.2.1. Treatment with CO<sub>2</sub>*

Tailings samples were transferred from pails shipped from plants to 4-L jars by using a high pressure drill mixer and pump. Then the 4-L sample was divided into 200 mL each by pumping the slurry under high speed agitation provided by RW 20 stand agitator (IKA Works Inc., US). The samples prepared as such were of same composition for better comparison. In each test, a 200-mL tailings sample was loaded into the autoclave. The venting valve was closed and the headspace was charged with CO<sub>2</sub> at a desirable partial pressure ranging from 0.035 to 1000 kPa at 25°C (100 kPa partial pressure of CO<sub>2</sub> ≈ 1 atm of pure CO<sub>2</sub>) and temperature ranging from 22 to 80 °C. The hydrodynamic conditions, such as mixing speed, mixing time, sample volume and baffling, were controlled to be the same for each run. After the pressure reading became stable, the slurry was agitated at 800 rpm to allow fully contact of CO<sub>2</sub> gas with slurry. The reaction would last 20 minutes to ensure the solution was saturated with CO<sub>2</sub>. During this period, pressure was maintained manually otherwise it would drop due to the CO<sub>2</sub> dissolution. Upon completion of the pressurizing treatment, the pressure was vented out and the sample was measured for pH immediately.

### 3.3.2. Treatment with $\text{CO}_2$ and cationic coagulants

The tailings were pre-treated with  $\text{Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$  before pressurization with  $\text{CO}_2$  to study the synergy of  $\text{CO}_2$  and cationic coagulants. The dosages of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were six times of the molar concentration of  $\text{Ca}^{2+}$  applied in the commercial operation of gypsum-CT which is 0.01 mol/L of tailings slurry. The sufficient dosage of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  was for enhancing the precipitation of carbonate. The stoichiometric amount of aqueous  $\text{CO}_2$  required for this amount of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  to form carbonate was 0.078 mol/L. According to Henry's law, 400 kPa absolute  $\text{CO}_2$  pressure at room temperature was needed to provide the carbon resource for the reactions. The dosages of chemicals for  $\text{Ca}(\text{OH})_2$ -treated tailings (Ca-tails),  $\text{Mg}(\text{OH})_2$ -treated tailings (Mg-tails), and  $\text{Ca}(\text{OH})_2\text{-Mg}(\text{OH})_2$ -treated tailings (Ca-Mg-tails) are listed in Table 3-2.

Table 3-2 Chemical dosages used in various treatments of tailings

Treatment	$\text{Ca}(\text{OH})_2$ (g/L)	$\text{Mg}(\text{OH})_2$ (g/L)	$\text{CO}_2$ (kPa)
Untreated	-	-	-
Ca-tails	4.3	-	-
Mg-tails	-	3.4	-
Ca-Mg-tails	2.15	1.7	-
Ca-tails + $\text{CO}_2$	4.3	-	400
Mg-tails + $\text{CO}_2$	-	3.4	400
Ca-Mg-tails + $\text{CO}_2$	2.15	1.7	400

### **3.4. Bench settling test**

The sedimentation of tailings was monitored through bench settling test. After proper treatment under a given condition, slurry samples were transferred into 200-mL graduated cylinders and allowed to settle under the atmosphere and the quiescent condition. In order to obtain the settling rate of solids in suspension, the position (height) of the sharp interface between the supernatant layer and fluid sediment was recorded every hour during the first 6 hours and every day afterwards. As illustrated in Figure 3-5, the normalized height was plotted as a function of time. In Figure 3-5,  $h$  and  $H$  stand for the instant height of the interface at a given settling time and the initial height of the suspension, respectively. The slope of the linear part of the settling curve was defined as the initial settling rate (ISR) (Gregory et al. 1999).

After 6 hours of settling, the separated supernatant was taken out by pipette and its turbidity was measured by Micr-100 Turbidimeter (Fisher, US). The settling was allowed for several weeks or until no further sign of settling was shown. At the end of the each test, the final height of the bottom layer, here defined as the final sediment, was recorded. The solids content of the final sediment was measured by weighing the wet sediments and dried solids.

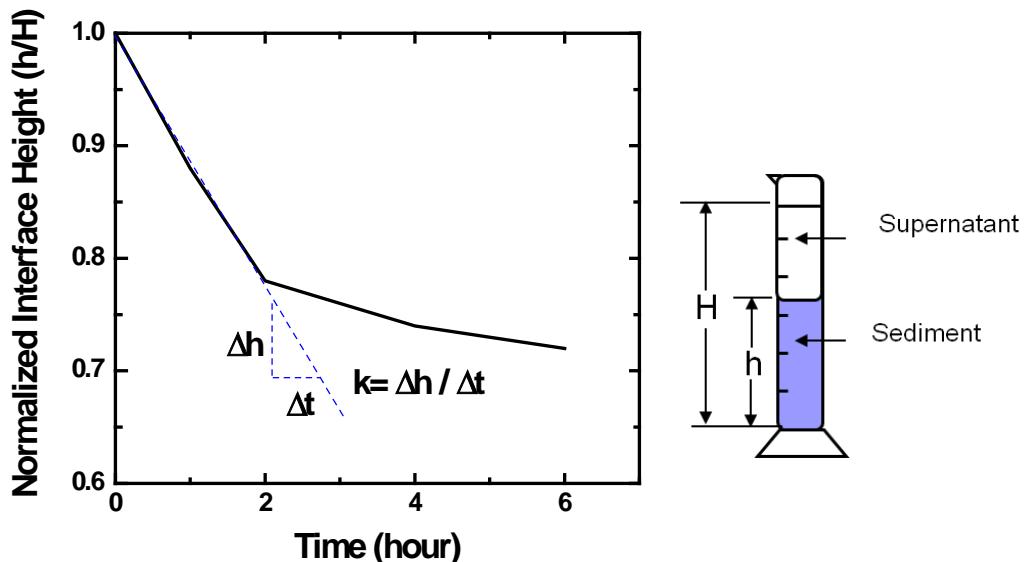


Figure 3-5 Typical batch-settling schematic and settling curve.

### 3.5. Water chemistry analysis

The pressure filtration with nitrogen was used to get the tailings water out of slurry for water chemistry analysis. The filter paper had a pore diameter of  $0.2 \mu\text{m}$ . The concentration of bicarbonate ions in the tailings water was measured by acid-base titration while other ions were analyzed by ICS-3000 ion chromatography (Dionex, US). Atomic adsorption spectroscopy (AAS) technique was also used to assist measuring the concentrations of divalent cations when sample was pre-treated with  $\text{Ca(OH)}_2$  or  $\text{Mg(OH)}_2$ . AAS technique can accurately measure the metal elements in soluble forms in the solution.

### **3.6. Zeta potential measurement**

Average zeta potential of fines was measured to understand the electrokinetics that heavily determines the coagulation/flocculation efficiency of suspension. Two commercial instruments, Zetaphoremeter Z3110 (CAD Instrumentation, France) and ZetaPALS (Brook Haven Instruments, US), were applied to the zeta potential measurements as will be discussed in Chapter 5 and Chapter 6, respectively, because of the different purposes and precision requirements. In a zeta potential measurement, the sample was prepared by diluting one drop of the tailings slurry with its own water isolated by filtration of the tailings. This drop of tailings was collected from the upper layer of the suspension after the settling of coarse sands. The dilution of fine tailings was necessary to prepare samples of desired solid concentration suitable for zeta potential measurement by electrophoresis technique. The detailed procedures of zeta potential measurement have been given elsewhere (Liu et al. 2002; Xu et al. 2003).

### **3.7. Carbon dioxide uptake test**

In Chapter 7, the capacity of oil sands tailings to sequester CO<sub>2</sub> was investigated by conducting carbon uptake experiments with autoclave. The principles and procedure of the experiment were referred to the carbonation experiment of bauxite residue/brine mixture (Dilmore et al. 2009). In our

experiment, the 422-mL vessel was loaded by 200 mL tailings slurry leaving a headspace of 222 mL. After purging with 100 kPa CO<sub>2</sub> three times to remove all the air entrained in the reactor, the headspace was charged with an initial pressure of CO<sub>2</sub>, “P<sub>0</sub>”. Then the valve was closed and the agitator started at 800 rpm to make the slurry homogeneous with the gas in headspace. The reaction was allowed to continue for several hours until the display on the digital pressure gauge reached stable. The headspace pressure at equilibrium was recorded as “P<sub>eq</sub>”. With the change of pressure at the start and the end of carbon uptake, the total CO<sub>2</sub> amount captured can be calculated by equation (3-1):

$$n(CO_2) = \frac{(P_0 - P_{eq})V_g}{RT} \quad (3-1)$$

where n(CO<sub>2</sub>) = molar amount of the CO<sub>2</sub> captured by fluid samples (mol); P<sub>eq</sub> = equilibrium pressure of the headspace of autoclave (Pa); P<sub>0</sub> = prescribed initial pressure of the headspace of autoclave (Pa); V<sub>g</sub> = volume of the headspace (m<sup>3</sup>); R = gas law constant ( $\approx 8.314 \text{ J/(K}\cdot\text{mol)}$ ); T = temperature (K).

A series of tests were performed with various initial CO<sub>2</sub> pressures ranging from 300 kPa to 700 kPa under room temperature (22 °C). In order to differentiate the capacity for the solids and the liquids in tailings to capture CO<sub>2</sub>, tailings slurry and solid-free tailings filtrate were evaluated under the same experiment conditions.

## **Chapter 4     Effect of CO<sub>2</sub> on Densification of Tailings<sup>‡</sup>**

The S and C tailings were treated with CO<sub>2</sub> in autoclave at various pressures and temperatures. The following graduated cylinder settling test was carried out at atmosphere and room temperature. Such experimental procedure was designed to simulate the process of the real operation.

### **4.1. Sedimentation behaviour**

The sedimentation characteristics of tailings with and without the addition of CO<sub>2</sub> were illustrated in Figure 4-1. With no treatment, the original tailings exhibited segregating deposition. As shown in Figure 4-1(a), the coarse sands fell rapidly under gravity and accumulated on the bottom of cylinder within a few seconds at the beginning. The diffuse layer which contained dispersed solids remained stable for a while. After an induction period, a sharp interface between the suspension layer on the top of the settled coarse sand sediments, here defined as fluid-sediment, and supernatant layer could be observed. With significant high solid concentrations, such as 37.5 wt% for S tailings and 31.1 wt% for C tailings, the fluid-sediment performed hindered-settling (Type-III settling) (Crittenden et al. 2005). The particles or aggregates formed a blanket of particles to sweep the

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<sup>‡</sup>A version of this chapter has been published. Zhu, R.; Liu, Q.; Xu, Z.; Masliyah, J. H. and Khan, A. Energy Fuels, 2011, 25 (5), pp: 2049 - 2057. Copy right 2011 American Chemical Society. Reproduced with permission from the authors.

discrete particles and the interface between supernatant and sediment moved downwards slowly. The supernatant layer contained a significant amount of dispersed fine particles because of the lack of destabilization to the suspension.

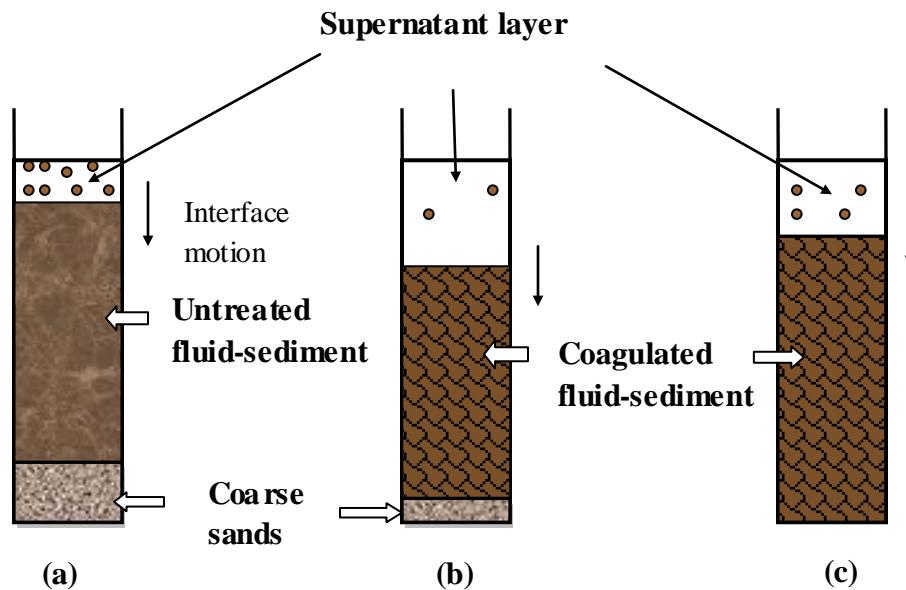


Figure 4-1 Sedimentation behaviour modes of oil sands tailings slurry: (a) Blank tailings of S or C; (b) S tailings treated with CO<sub>2</sub>; and (c) C tailings treated with CO<sub>2</sub>.

With addition of CO<sub>2</sub>, the suspension was destabilized and the fluid-sediment of CO<sub>2</sub>-treated tailings acted flocculation settling (Type-II settling) (Crittenden et al. 2005). As depicted in Figure 4-1(b) and Figure 4-1(c), the fine particles and sands were coagulated and the suspension became non-segregating. The non-segregating sediments showed uniform visual characteristics with wrinkles and cracks on the surface, which was not observed for the sediments of the untreated

tailings. For S tailings treated with CO<sub>2</sub> as shown in Figure 4-1(b), a few amount of coarse sands with very large size precipitated at the bottom of the cylinder.

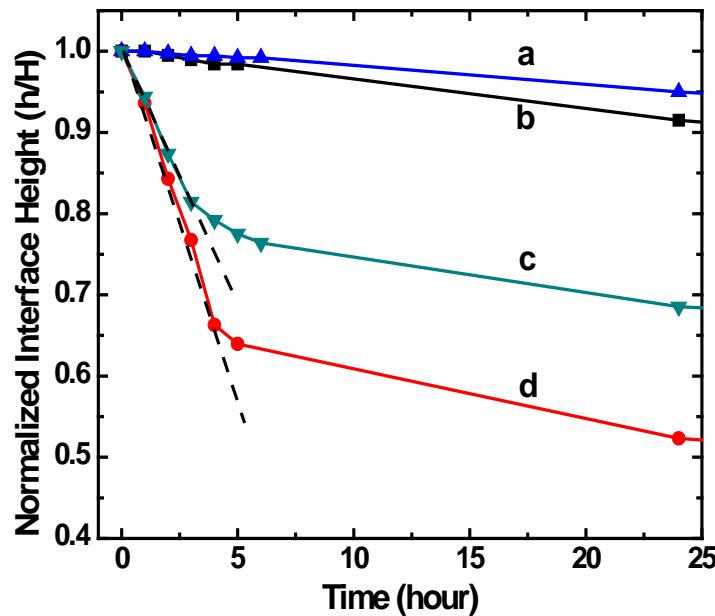


Figure 4-2 Settling of (a) the untreated C tailings, (b) the untreated S tailings, (c) the CO<sub>2</sub>-treated C tailings, and (d) the CO<sub>2</sub>-treated S tailings. The pH of (a) – (d) is 8.2, 8.4, 6.2 and 5.8, respectively.

The descending of the interface between the supernatant and sediment for the first 24 hours is reported in Figure 4-2. As shown by curves “a” and “b” in Figure 4-2, the fluid fines in the untreated tailings settled down slowly. As shown by curves “c” and “d” in Figure 4-2, the pressurization of tailings with 100 kPa CO<sub>2</sub> improved the settling of fluid fines drastically. The nature of CO<sub>2</sub>-treated tailings made the interface between the supernatant and the fluid-sediment appear much sooner and descended faster. The settling results of these four samples after 24 hours are shown in Figure 4-3 in which the difference in the supernatant clarity

can be observed visually. The supernatant of the CO<sub>2</sub>-treated samples had a significantly lower turbidity than that of the untreated ones after overnight settling. The long term sedimentation kinetics is reported in Figure 4-4. As shown in Figure 4-4, all the settling curves levelled off after 30 days. Comparing the curve “a” with “c” and the curve “b” with “d” in Figure 4-4, the thickness of final sediment was significantly compressed by the treatment with CO<sub>2</sub>. Also the solids content of the final sediment increased from 52 wt% to 72 wt% for S tailings and from 37 wt% to 49 wt% for C tailings. The decrease of the thickness and the increase of the solids content of the final sediment show that the oil sands tailings were remarkably densified by CO<sub>2</sub>-treatment.

Although the settling of fine solids in both tailings samples was improved by CO<sub>2</sub>, the CO<sub>2</sub>-treated S tailings settled much faster than the CO<sub>2</sub>-treated C tailings as shown in Figure 4-2, accompanied by a much clearer supernatant as shown in Figure 4-3 and a denser sediment as shown in Figure 4-4. The different responses of these two samples to CO<sub>2</sub> treatment were attributed to the difference in fines concentration in the original tailings. The initial fines content of S tailings was 27.5 wt% while that of C tailings was 42.9 wt%. It appears that high concentration of fines makes CO<sub>2</sub> treatment less effective.

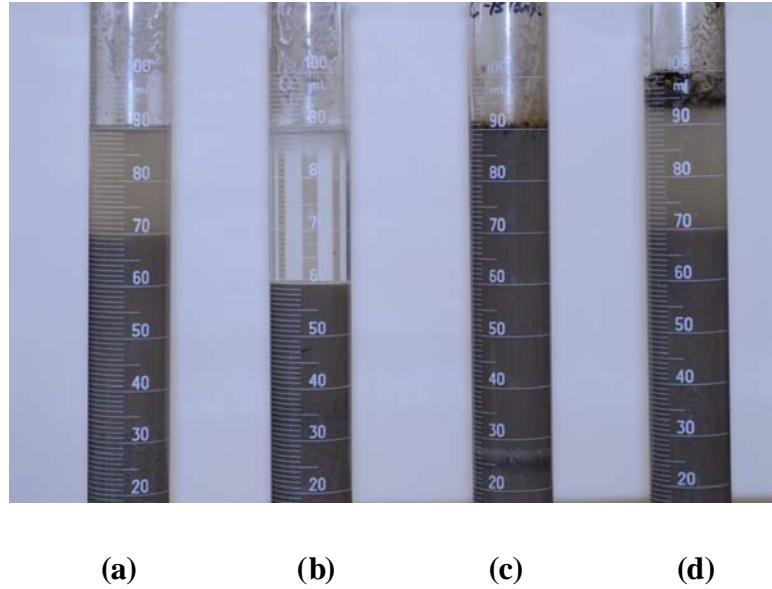


Figure 4-3 Overnight settling of (a) the untreated S tailings, (b) the  $\text{CO}_2$ -treated S tailings, (c) the untreated C tailings, and (d) the  $\text{CO}_2$ -treated C tailings. The tailings were pressurized with 100 kPa  $\text{CO}_2$ . The pH values of (a) – (d) are 8.4, 5.8, 8.2, and 6.2, respectively.

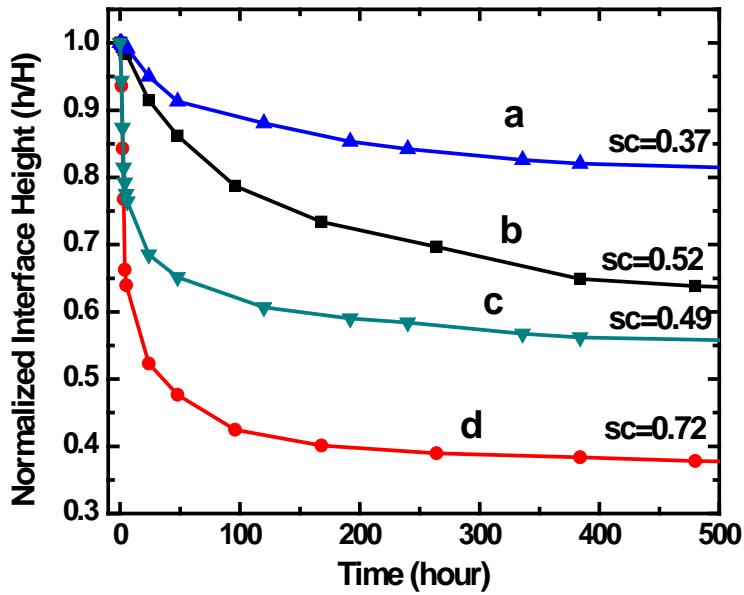
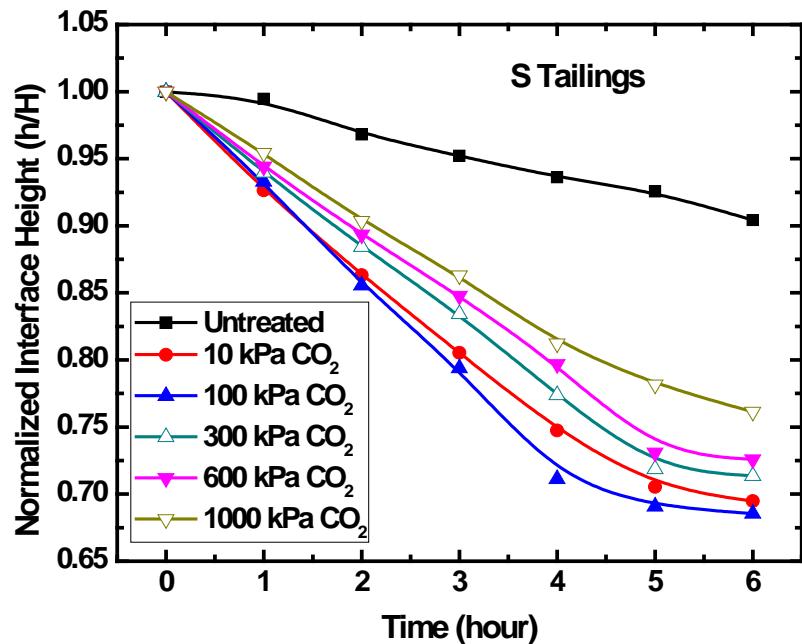


Figure 4-4 Long term settling of fluid fines of (a) the untreated C tailings, (b) the untreated S tailings, (c) the  $\text{CO}_2$ -treated C tailings and (d) the  $\text{CO}_2$ -treated S tailings. “Sc” represents solids content of final sediment.

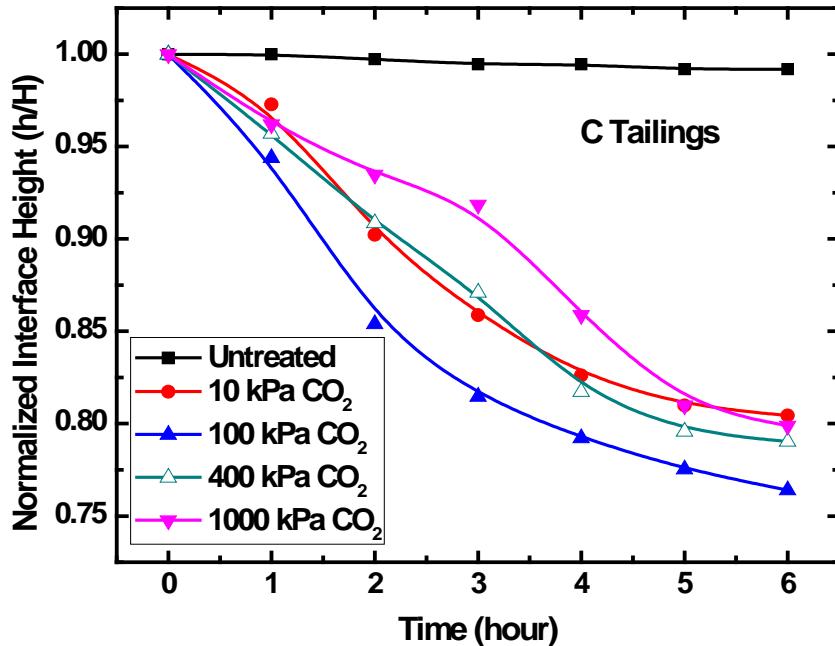
#### **4.2. Effects of CO<sub>2</sub> partial pressure**

As it was discussed above, CO<sub>2</sub> was able to improve the sedimentation and densification of oil sands tailings. In the current and next section, the physical conditions of CO<sub>2</sub>-treatment, such as pressure and temperature, will be investigated to optimize the effect of CO<sub>2</sub> on densification of tailings.

With the change of headspace pressure of autoclave, the effect of CO<sub>2</sub> partial pressure on sedimentation of tailings at ambient environment was studied. It is shown in Figure 4-5 that different CO<sub>2</sub> partial pressures give different effects on the settling kinetics of S and C tailings. The ISR can be calculated from the linear part of the settling curves. The results in Figure 4-6 showed a significant increase in ISR of oil sands tailings with increasing CO<sub>2</sub> partial pressure initially, reaching a maximum ISR of 14.3 and 9.3 mm/h for S and C tailings at 100 kPa, respectively. However, the ISR for both tailings samples decreased gradually as the CO<sub>2</sub> partial pressure increased from 100 to 1000 kPa. The pH values of the tailings were labeled for important points on Figure 4-6. Clearly, the pH of the tailings decreased with increasing CO<sub>2</sub> partial pressure. The details for the pH effect on the treatment will be discussed in section 5.2.



(a)



(b)

Figure 4-5 Settling curves of S and C tailings at different CO<sub>2</sub> partial pressure.

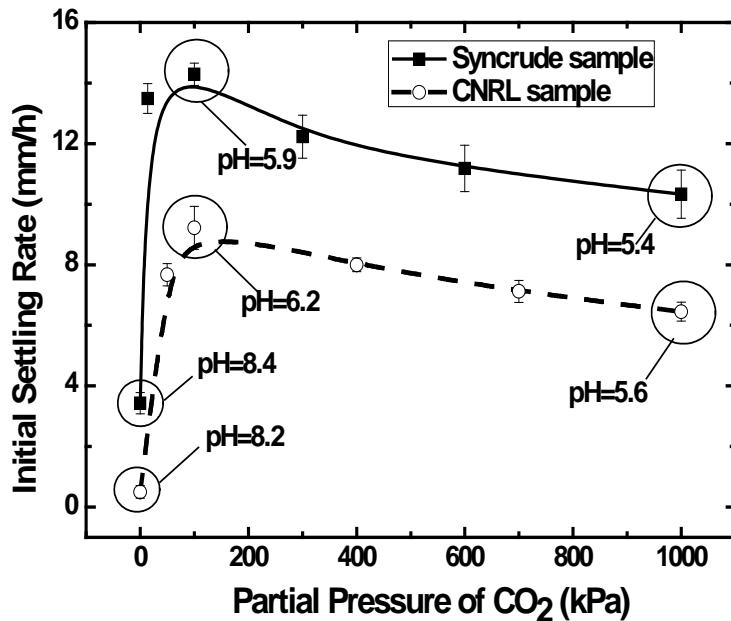


Figure 4-6 Initial settling rate of tailings as a function of CO<sub>2</sub> pressure.

It is interesting to note that the ISR curve for sample C is always below the curve for sample S, indicating the amount of CO<sub>2</sub> is not the limiting factor for inferior settling of C samples. Since blank sample S also exhibited a higher ISR than blank sample C and two settling profiles were almost parallel, higher fines content in sample C was definitely a concern. However, investigation needs to be done to clarify whether it was due to increase in viscosity or in hindered settling.

To further assess the effect of CO<sub>2</sub> on fluid fines settling and hence tailings treatment, the turbidity of the supernatant layer was measured at the end of initial settling stage of 6 hours. The turbidity of the supernatant as a function of CO<sub>2</sub> pressure is shown in Figure 4-7. For S tailings, the turbidity of supernatant for the

blank sample was as high as 864 NTU (Nephelometric Turbidity Units). As CO<sub>2</sub> pressure increased, the turbidity of S tailings decreased drastically and leveled off at 200 NTU at 100 kPa.

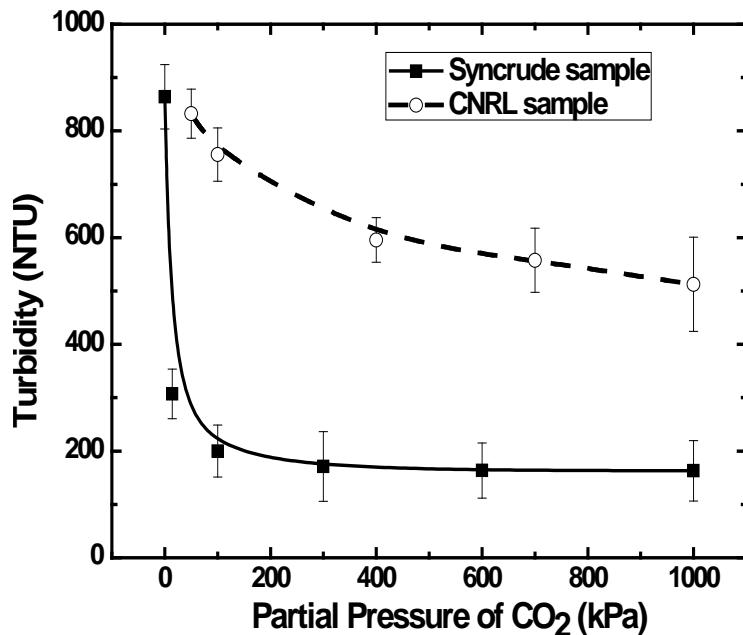


Figure 4-7 Turbidity of the supernatant of tailings after 6 hours of settling as a function of CO<sub>2</sub> pressure.

For C tailings, the turbidity of the supernatant remained higher than that of S tailings at a given CO<sub>2</sub> treatment, confirming that aggregation of fines in C tailings was less effective than in S tailings. The turbidity data for C tailings without treatment and at 0.035 kPa CO<sub>2</sub> were not collected because they were too high, exceeding the measurement limit of the instrument. As CO<sub>2</sub> pressure was increased from 100 to 1000 kPa, the turbidity for C tailings decreased gradually

from 756 to 513 NTU. For each result of Figure 4-5 to Figure 4-7, the experiment was replicated for three times so that the standard deviations of the data at the same condition could be obtained. It should be noted that the standard deviations of the data points in Figure 4-7 were quite large. This was attributed to the disturbance to measurement caused by the presence of CO<sub>2</sub> gas bubbles. In fact, large bubbles were observed being trapped in the fluid sediment and occasionally trespassing through the interface between the sediment and supernatant, suspending settled aggregates. The effect of gas bubbles on fine tailings densification will be elaborated in section 5.3.

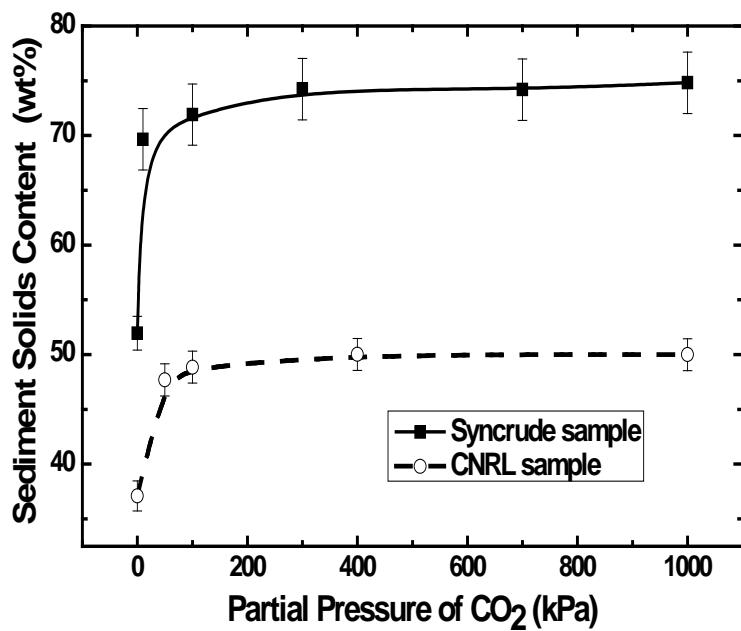


Figure 4-8 Solids content of final sediment of tailings as a function of CO<sub>2</sub> pressure.

To assess the effect of CO<sub>2</sub> treatment on densification of fluid sediments, the sediment solids content was recorded when there was no settling visible. As shown in Figure 4-8, the sediment solids content also varied as a function of CO<sub>2</sub> pressure. For S tailings, the solids content of the sediment increased drastically from 52 wt% at 0.035 kPa and leveled off at 74 wt% after 100 kPa. For the C tailings, the changing trend of solids content was similar to that of S tailings with an increase from 37 to 50 wt%. From these results, it can be concluded that effective densification of the final sediment of tailings by CO<sub>2</sub> occurs when CO<sub>2</sub> partial pressure increases from 0.035 to 100 kPa. The optimal CO<sub>2</sub> pressure for the compaction of final sediment was at about 100 kPa.

The results in Figure 4-6 to Figure 4-8 all showed dramatic changes in slope at CO<sub>2</sub> partial pressure of about 100 kPa. The ISR curves exhibited a maximum at CO<sub>2</sub> pressure of 100 kPa. Considering the economics and process feasibility, 100 kPa should be chosen as the optimal CO<sub>2</sub> partial pressure for treating oil sands tailings regardless of the source of the tailings.

#### **4.3. Influence of processing temperature**

The S tailings were used as sample for the study on the effect of processing temperature on the CO<sub>2</sub>-treated tailings because CO<sub>2</sub> had more obvious effects on S tailings. The temperature of the tailings was adjusted to the desired value before

introducing CO<sub>2</sub>, and maintained as a constant during the pressurization. The following quiescent settling in the cylinder was done at room temperature and atmosphere. The purpose of letting the tailings settle at room environment where the tailings would naturally cool down and the dissolved CO<sub>2</sub> in tailings would escape was to simulate the sedimentation of CO<sub>2</sub>-treated tailings in the ponds of oil sands field.

As shown in Figure 4-9 , the ISR of tailings treated with CO<sub>2</sub> was enhanced with increasing temperature. With the temperature increased from 25 to 80 °C, the ISR of the tailings treated with 200 kPa CO<sub>2</sub> increased from 13.6 to 20.3 mm/h and the ISR of the tailings treated with 600 kPa CO<sub>2</sub> increased from 12.7 to 16.1 mm/h. Meanwhile, as shown in Figure 4-10, the turbidity of supernatant of the tailings treated with 200 and 600 kPa CO<sub>2</sub>, respectively, decreased significantly as temperature increased. At 25 °C, the supernatant of CO<sub>2</sub>-tailings after 24-h settling was still muddy. At 50 or 80 °C, the supernatant of CO<sub>2</sub>-tailings barely contained visible dispersed particles after 24-h settling.

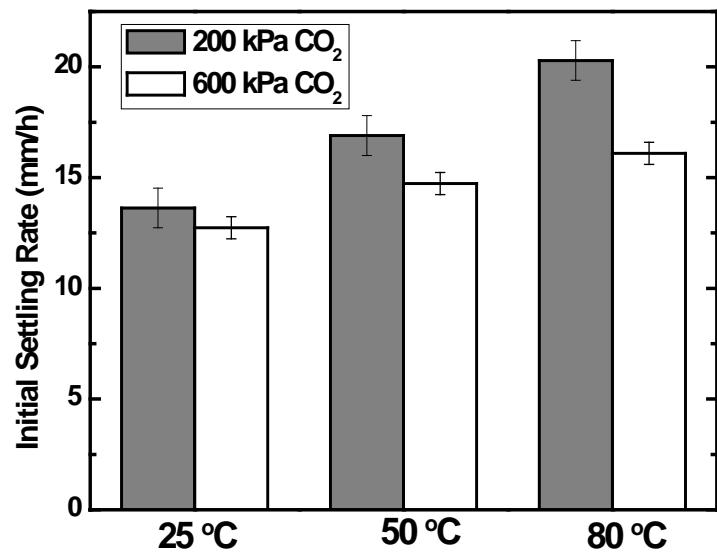


Figure 4-9 Effect of temperature on the ISR of tailings.

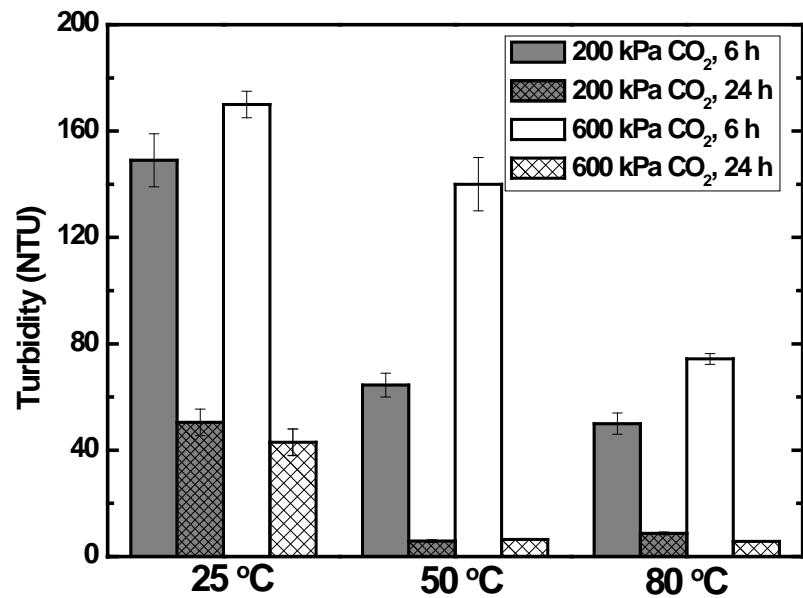


Figure 4-10 Effect of temperature on the turbidity of supernatant of tailings after 6 hours and 24 hours of settling.

In addition, as shown in Figure 4-9 and Figure 4-10, the effects of increasing temperature on the ISR and the supernatant clarity of the tailings treated with 200 kPa CO<sub>2</sub> was greater than those on the tailings treated with 600 kPa CO<sub>2</sub>.

One of the major mechanisms for enhanced sedimentation of tailings could be the lowered viscosity of tailings water with increasing temperature according to Stokes' Law for the particle settling system (Nguyenvan et al. 1994). Moreover, at the conditions of a high ionic strength and an intermediate pH, the stability of colloidal particles, such as montmorillonite and kaolinite clays, would decrease with increasing temperature and hence the aggregation rate and collision efficiency of colloidal particles would increase (Garcia-Garcia et al. 2006; Garcia-Garcia et al. 2009).

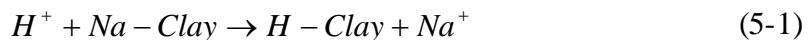
It is disappointing that no influence of the processing temperature on the solids content of final sediment was observed after a long term settling at room temperature. This implied that the increase in temperature did not change the internal structure of the sediment but only increased the initial settling speed of the sediment.

## **Chapter 5    Mechanism of CO<sub>2</sub> Enhanced Densification of Tailings <sup>§</sup>**

As discussed in Chapter 4, CO<sub>2</sub> improves the sedimentation and densification of oil sands tailings as functions of CO<sub>2</sub> partial pressure and processing temperature. In this chapter, a mechanistic study about the effects of CO<sub>2</sub> on the densification of tailings will be performed.

### **5.1. Review on water chemistry of tailings**

The typical mechanisms of coagulation of colloidal suspension are that counter ions in bulk solution compress the double layers of colloidal particles or change the surface potential of colloids by specific adsorption. As shown in Table 5-1, process-affected water of the oil sands tailings has a significantly high salinity with variety of ions. With addition of CO<sub>2</sub>, the ion concentrations and pH of tailings water was significantly changed. The increase in the concentrations of cations was attributed to the reactions of ion exchange between [H<sup>+</sup>] and clays in tailings water as described in equations (5-1) and (5-2) (McBride 1994; Zhao et al. 2009).



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<sup>§</sup> A version of this chapter has been published. Zhu, R.; Liu, Q.; Xu, Z.; Masliyah, J. H. and Khan, A. Energy Fuels, 2011, 25 (5), pp: 2049 - 2057. Copyright 2011 American Chemical Society. Reproduced with permission from the authors.

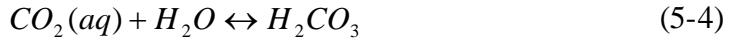
The decrease of pH would accelerate the reactions above towards the right side releasing sodium, calcium and magnesium ions. The similar results of the HCl-treated tailings given in Table 5-1 were also attributed to the same mechanism.

Table 5-1 Water chemistry of two tailings water samples

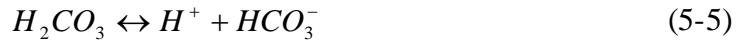
Sample Source	Treatment	Ion Concentration (mg/L)						
		Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
Syncrude		842	18	6	7	496	582	106
	CO <sub>2</sub>	937	23	12	19	569	675	166
	HCl	963	24	14	23	1122	617	18
CNRL		604	15	3	4	234	38	311
								8.0-8.2

It is well known that pH plays a critical role in oil sands tailings treatment by affecting the surface electrical properties of fines and hence solid-solid interactions. The water-based oil sands extraction tailings have pH values between 8 and 9. Over this pH range, the fine suspension remains stable. The addition of CO<sub>2</sub> would significantly reduce the pH of the tailings as shown in Table 5-1. To understand the effect of CO<sub>2</sub> saturation on slurry pH, the solution chemistry of CO<sub>2</sub>-tailings system is analyzed as following.

For an open system where CO<sub>2</sub> could be continuously supplied to the water, such as in a pressurized autoclave, the dissolved CO<sub>2</sub> reacts with water and forms carbonic acids as shown in reactions (5-3) and (5-4).



Through a two-step dissociation of carbonic acid, protons are released by reactions (5-5) and (5-6) decreasing solution pH.



All these reactions are bounded by the condition of charge neutrality, written in equation (5-7) below.

$$\sum E^+ + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] + \sum E^- \quad (5-7)$$

where  $\sum E^+$  and  $\sum E^-$  are total charge of other cations and anions in the bulk solution, respectively. Regardless of the possible ion exchange between clays and the bulk solution, which causes no net charge in the whole system,  $\sum E^+$  and  $\sum E^-$  in equation (5-7) are calculated from the average ionic concentrations determined by IC as shown in Table 5-1. The Henry's law constant at standard condition of 27.78 atm/(mol/L) is used to calculate soluble CO<sub>2</sub> concentration (Zheng et al. 1997). All the equilibrium constants of reactions at 25 °C are obtained from reference (Sawyer et al. 2003). The reactions of calcium or magnesium with carbonates are not considered here, because no calcium or magnesium carbonate

precipitation was observed in the XRD patterns of the tailings solids after CO<sub>2</sub> treatment.

From equations (5-3) through (5-7), the pH values as a function of CO<sub>2</sub> partial pressure are calculated as shown in Figure 5-1. The data points in Figure 5-1 are the measured pH values. Deviation between the data points and curves at high CO<sub>2</sub> pressure is noted. This deviation is attributed to the pH measurement under atmospheric pressure, under which a part of dissolved CO<sub>2</sub> may have already escaped from the solution, leading to a slightly higher value of measured pH than the actual pH value in the autoclave. The reactions of ion exchange between H<sup>+</sup> and clays in tailings water as described in equations (5-1) and (5-2) may also contribute to a higher value of measured pH. Nevertheless, the trends of calculated and measured pH with increasing CO<sub>2</sub> pressure are about the same: a sharp decrease in pH at lower CO<sub>2</sub> saturation pressure, followed by a moderate reduction with further increasing the pressure of CO<sub>2</sub> saturation. The transition point is around 100 kPa. This trend corresponds well with the aforementioned effect of CO<sub>2</sub> saturation on ISR, supernatant turbidity and solids content of final sediment, providing a scientific basis as to why the sedimentation, densification and water clarity were remarkably improved with the increasing CO<sub>2</sub> pressure from 0.035 to 100 kPa.

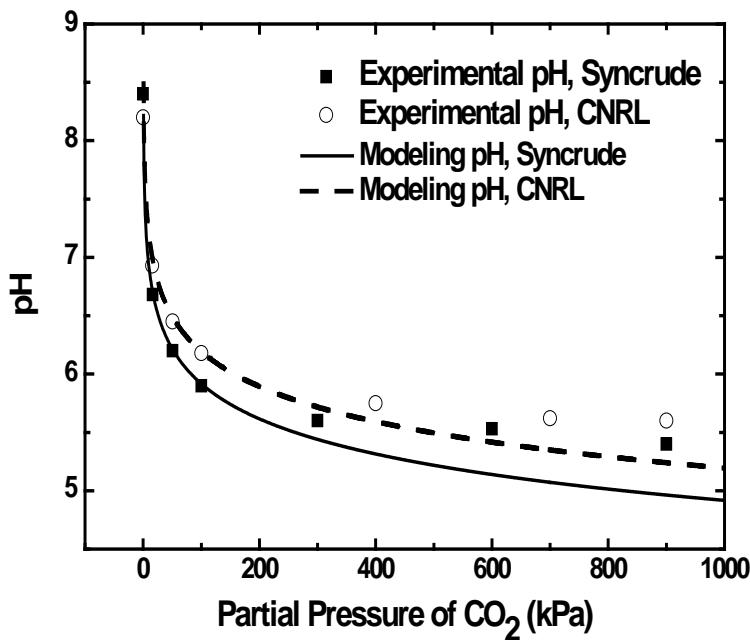


Figure 5-1 Measured and calculated pH of tailings as a function of CO<sub>2</sub> pressure.

Changing pH is anticipated to change the electrostatic properties of colloidal particles. As shown in Figure 5-2, the magnitude of average zeta potential of tailings fines treated either by HCl or CO<sub>2</sub> became less negative with decreasing pH. Decreasing the magnitude of the zeta potential reduces electrostatic repulsion between particles and eventually leads to destabilization of the suspension and improved densification. Plotted as a function of pH, the zeta potential curve of the HCl-treated fines follows that of the CO<sub>2</sub>-treated fines, indicating that the effect of CO<sub>2</sub> on zeta potential of fines is mainly attributed to the change of pH. Based on extensive studies on the surface electrical properties of clay minerals and quartz (Franks 2002; Liu et al. 2004; Kaya et al. 2005), there are two reasons for

the decrease of the magnitude of zeta potential. Firstly, the protons as potential determining ions change the surface potential of fines. The charges of the surfaces of quartz, kaolinite, and illite are pH-dependent, which become less negative with decreasing pH. On the other hand, the zeta potential of montmorillonite is not pH-dependent. Secondly, the increase in the amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as shown in Table 5-1 would also change the zeta potential by specific adsorbing and compression of the electrical double layers of particles with high valence.

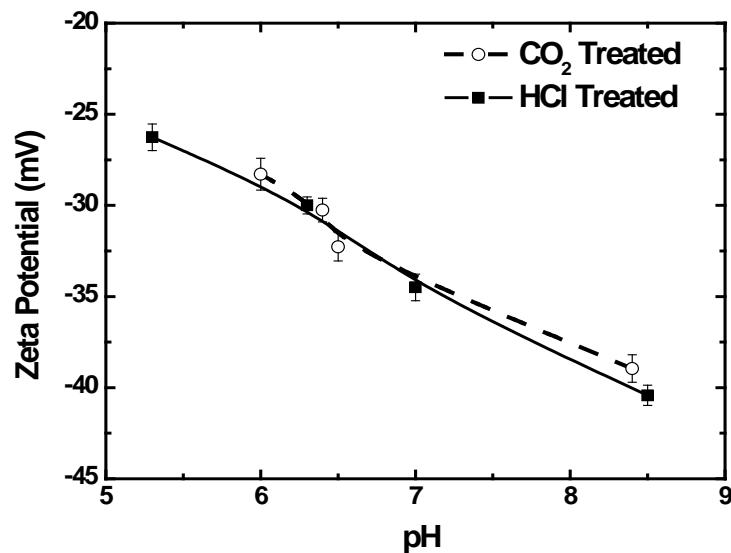


Figure 5-2 Zeta potential of the fines of S tailings as a function of pH.

## 5.2. Impacts of pH

To further verify that the effect of  $\text{CO}_2$  saturation on the sedimentation and densification of tailings is due to the change of pH, settling tests were performed

using acid or base to adjust the tailings pH and results are compared with those obtained using CO<sub>2</sub> saturation.

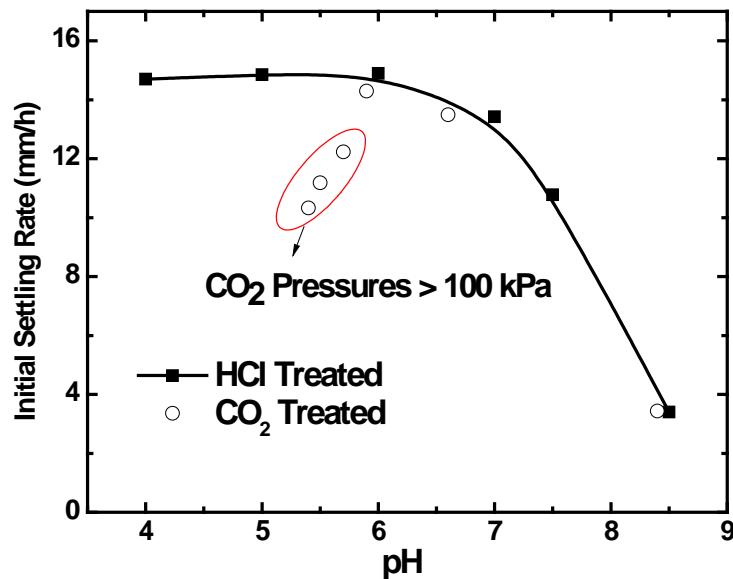


Figure 5-3 Effect of pH on the initial settling rate of tailings.

Figure 5-3 shows an increase in ISR from 3.4 to 14.9 mm/h when HCl was used to change pH from 8.5 to 6 and leveled off with a further decrease in pH. To some extent, this trend corresponds to the effect of pH on coagulation kinetics of kaolinite (Kretzschmar et al. 1998). The sedimentation of oil sands tailings saturated with CO<sub>2</sub> at pressures lower than 100 kPa followed the same responses to pH as that adjusted by acid, confirming that proper action of CO<sub>2</sub> treatment for enhancing sedimentation of oil sands tailings is by reduction of pH and hence particle surface charges, leading to an enhanced coagulation. However,

saturation of CO<sub>2</sub> at pressures above 100 kPa to bring tailings pH below 6 led to a substantial reduction in ISR. In contrast, sedimentation of tailings over the same pH range of 6 to 5, adjusted by acid, maintained at the higher level of 14.9 mm/h. It appears that the use of CO<sub>2</sub> could lead to an overdose, which will be discussed later.

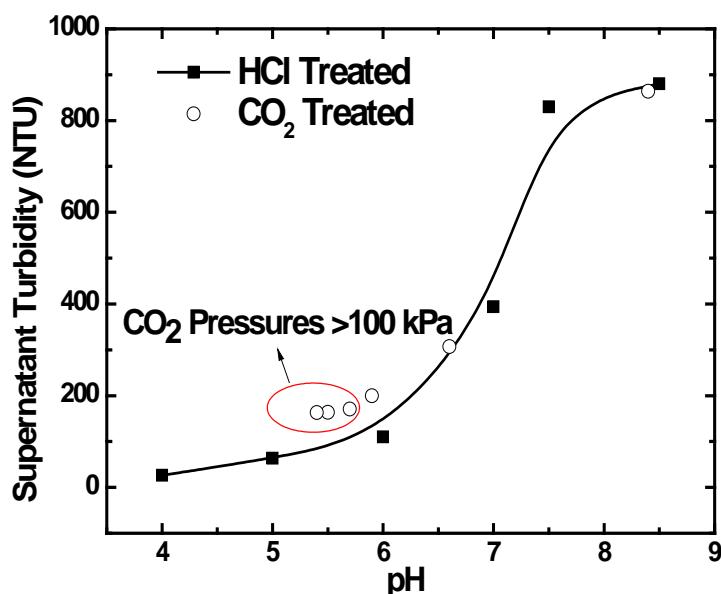


Figure 5-4 Effect of pH on the supernatant turbidity of tailings after 6 hours.

It is interesting to note that the effect of CO<sub>2</sub> and HCl on turbidity of supernatant followed a similar trend as shown in Figure 5-4. The supernatant turbidity of tailings decreases sharply with decreasing pH to 7 adjusted by either CO<sub>2</sub> or acid. A further decrease in pH by acid addition caused additional reduction in turbidity of supernatant although to a less extent, indicating more effective coagulation of fines with reducing pH by acid. In contrast, reducing pH

below 6 by CO<sub>2</sub> saturation at higher pressure had a negligible effect on supernatant clarity, although it decreases the ISR. This observation confirms that effective coagulation of fines by reduction in surface charge of particles is responsible for improved settling of oil sands tailings by CO<sub>2</sub> treatment.

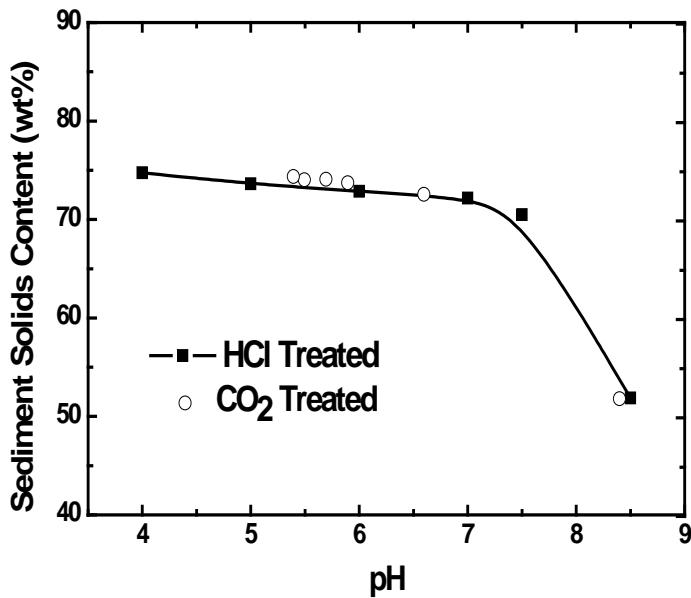


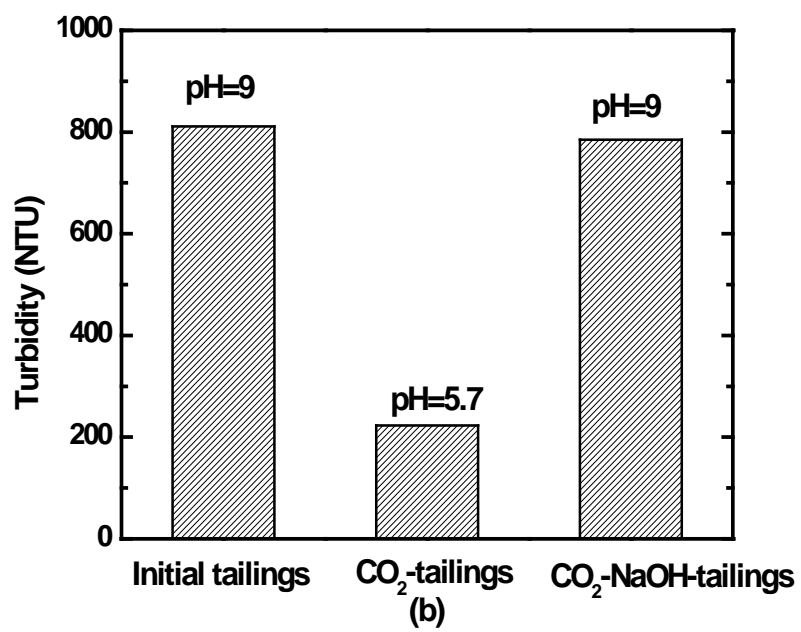
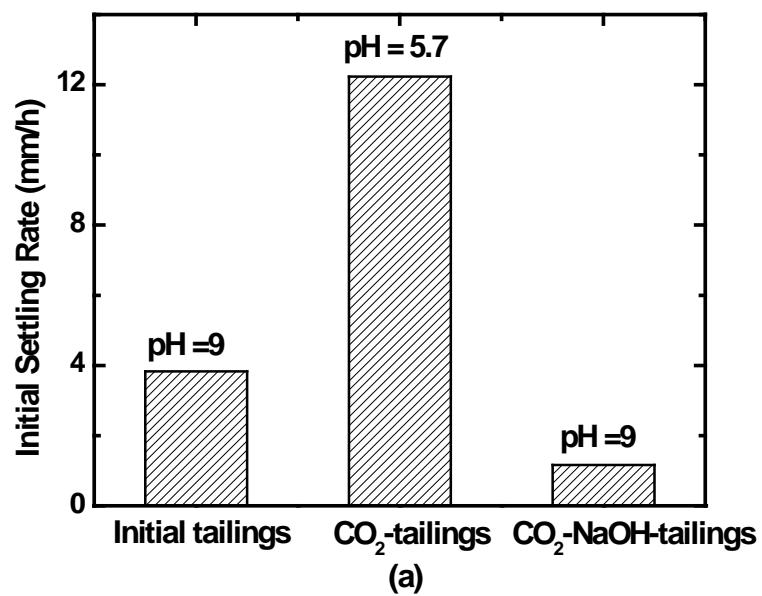
Figure 5-5 Effect of pH on the solids content of final sediment of S tailings.

Figure 5-5 shows the solids content of final sediment of tailings treated by CO<sub>2</sub> and HCl as a function of pH. The solids content of the final sediments was found to increase with decreasing pH, reaching a constant value of 72 wt% at pH 7. Below pH 7, a further reduction in pH only increased the solids content of final sediment marginally. It is evident that reduction of electrostatic repulsion between particles by reduction of surface charge with decreasing pH assists densification of solid sediments. Meanwhile, the use of CO<sub>2</sub> or acid to adjust pH does not make

any difference in terms of increasing solids content of final sediments, confirming that reducing pH by CO<sub>2</sub> saturation is the key for enhancing solids densification.

In addition, the impacts of CO<sub>2</sub> on the tailings settling were found reversible with adjusting pH. The experiment was performed with a procedure of pressurizing the tailings with 400 kPa CO<sub>2</sub>, adding NaOH to increase the lowered pH of tailings back to the initial pH before pressurization and observing the settling of the tailings. As shown in Figure 5-6(a), (b), and (c), the ISR, supernatant clarity and solids content of final sediment of the CO<sub>2</sub>-NaOH-tailings were all as poor as those of the blank tailings while the settling performances of the CO<sub>2</sub>-tailings was remarkably enhanced.

To sum it up, the results above suggest that the improvement in settling and densification of tailings by CO<sub>2</sub> treatment is mainly due to a reduction in tailings pH. Excessive treatment with CO<sub>2</sub> saturation above 100 kPa was found detrimental to sedimentation of oil sands tailings and to release of high quality process water, but had no effect on solids densification. Since massive bubbles were observed to be generated in the tailings when a high pressure of CO<sub>2</sub> was applied, it is natural to assume that the effect of CO<sub>2</sub> bubbles would outweigh the effect of pH, which is discussed below.



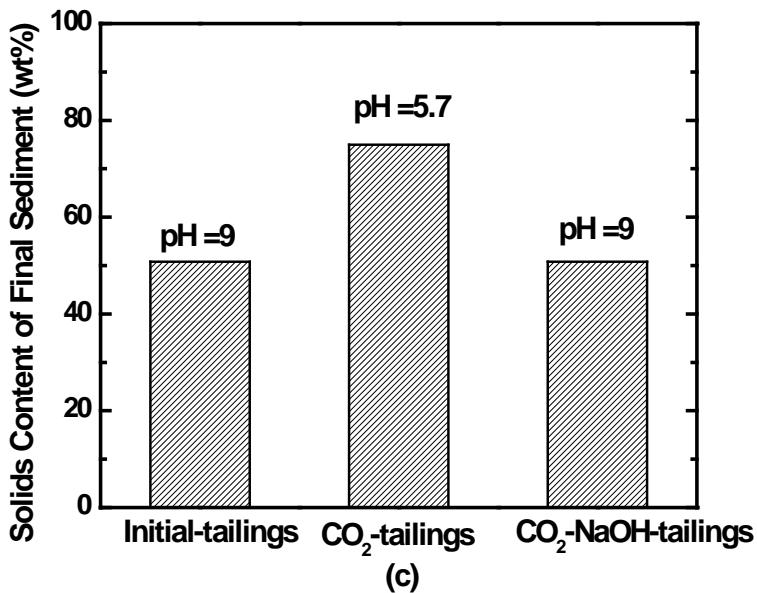


Figure 5-6 Reversibility of the effect of CO<sub>2</sub> on tailings as a function of pH. Tailings was first pressurized with 400 kPa CO<sub>2</sub> and then added with NaOH. The responses of (a) the ISR, (b) the supernatant turbidity after 6 hours of settling, and (c) the solids content of final sediment are correlated with pH.

### 5.3. Effect of CO<sub>2</sub> gas bubbles

While the pH reduction is a driving force to improve sedimentation of tailings, the gas hold up in tailings may have an adverse effect on sedimentation. After CO<sub>2</sub> saturation, the tailings are transferred from a pressurized autoclave to an open cylinder for settling. During this process, the inevitable pressure drop causes the solution to be supersaturated with dissolved CO<sub>2</sub> and hence to cause formation of CO<sub>2</sub> gas bubbles. Although bigger bubbles formed by collision and coalescence of smaller bubbles rise quickly to the top of the slurry, smaller bubbles suspended in the solution would interact with solid particles. Furthermore, residual saturated

gases may precipitate on hydrophobic solids contaminated by bitumen components. These processes are quite similar to the situation encountered in conventional dissolved air flotation as widely used in water treatment (Crittenden et al. 2005). The total volume of bubbles can be estimated by mass balance and ideal gas law as described by equations (5-8) and (5-9):

$$[CO_2(aq)]_{in} + [HCO_3^-]_{in} + [CO_3^{2-}]_{in} = [CO_2(aq)]_{atm} + [HCO_3^-]_{atm} + [CO_3^{2-}]_{atm} + \frac{CO_2(g)}{V_l} \quad (5-8)$$

$$P_b \cdot V_b = CO_2(g) \cdot R \cdot T \quad (5-9)$$

where  $[CO_2(aq)]_{in}$ ,  $[HCO_3^-]_{in}$ ,  $[CO_3^{2-}]_{in}$ ,  $[CO_2(aq)]_{atm}$ ,  $[HCO_3^-]_{atm}$ , and  $[CO_3^{2-}]_{atm}$  represent the concentrations of carbonic species of the solution inside the pressure vessel or under atmosphere, respectively (mol/L);  $CO_2(g)$  = molar amount of the  $CO_2$  gas released from the supersaturated solution (mol);  $V_l$  = volume of the tailings solution (assume 1 L);  $P_b$  = pressure of  $CO_2$  gas in the bubbles (assume atmospheric pressure of 101 kPa);  $V_b$  = total volume of the  $CO_2$  gas bubbles formed in the solution ( $m^3$ );  $R$  = ideal gas constant ( $\approx 8.314 \text{ J/(mol} \cdot \text{K)}$ ). When the  $CO_2$  partial pressure applied is above 100 kPa,  $[HCO_3^-]_{in}$ ,  $[CO_3^{2-}]_{in}$ ,  $[CO_2(aq)]_{atm}$ ,  $[HCO_3^-]_{atm}$ , and  $[CO_3^{2-}]_{atm}$  are negligible as compared to  $[CO_2(aq)]_{in}$ . Therefore we know that the total volume of bubbles that would form at atmospheric pressure is only dependent on  $[CO_2(aq)]_{in}$  and hence directly proportional to the  $CO_2$  partial pressure in the headspace of pressure vessel.

To study the effect of bubble generation on solid sedimentation and densification without the effect of water chemistry change, such as pH change, inert nitrogen gas ( $N_2$ ) was used to pressurize the tailings. The pH was indeed found unchanged after  $N_2$  pressurization. According to the analysis on  $CO_2$  above, the total volume of  $N_2$  bubbles formed after pressurization must also be directly proportional to the  $N_2$  pressure. The settling of tailings was compared at a given pH with and without  $N_2$  pressurization.

The results in Figure 5-7 show a steady decrease in ISR of oil sands tailings with increasing  $N_2$  pressure from 78 to 900 kPa, more pronounced at pH 7 than at pH 6. However, the extent of decrease in ISR caused by  $N_2$  saturation is much less than that by  $CO_2$  saturation. This difference is attributed to the differences in number and size of  $N_2$  and  $CO_2$  bubbles generated due to their different solubility. Nevertheless, the reduction in ISR is common for both gases, and it is a result of the presence of gas nuclei on solid particles, which was also observed by other researchers (Yianatos et al. 1986; Smuk et al. 1991). For the flocculated suspensions with high solid concentrations as in the current case, however, factors such as the attachment or entrainment of bubbles within the aggregates and flocs also contribute to the decrease in ISR (Crittenden et al. 2005).

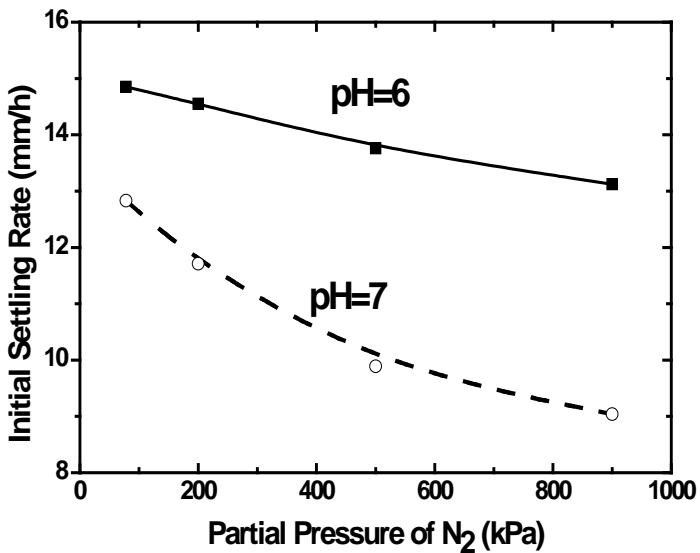


Figure 5-7 Effect of N<sub>2</sub> pressure on the ISR of tailings at pH 6 and pH 7.

The turbidity of the supernatant at the end of the initial settling period increases with increasing nitrogen partial pressure, particularly at a higher pH of 7, as shown in Figure 5-8. Since the chemistry and hence the aggregation of solids at a given pH are the same for suspensions saturated with nitrogen at different pressures, the observed increase in supernatant turbidity with increasing pressure of nitrogen saturation of tailings appears to be the results of the disturbance and interference of the re-suspended sediments and aggregates by bubbles. The rising bubbles would carry fines and flocs up to the supernatant and drop them off when collapsing, contributing to the increase in supernatant turbidity (Scardina and Edwards 2001; Scardina and Edwards 2002). This observation explains the

negative effect of CO<sub>2</sub> gas bubbles in supersaturated solution on solid removal from the supernatant.

It should be noted that no significant effect of nitrogen pressurization on the solid content of the final sediments was detected, suggesting that gas bubbles only affect the settling but not the densification of oil sands tailings.

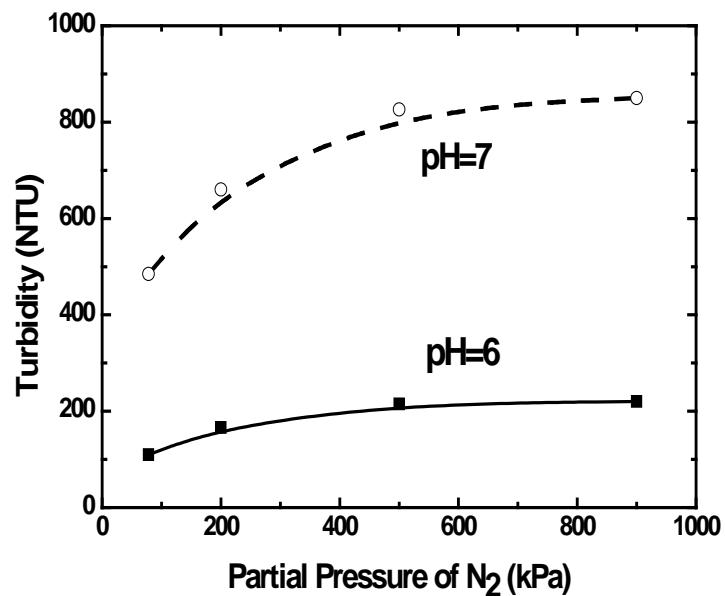


Figure 5-8 Effect of N<sub>2</sub> pressure on the supernatant turbidity of tailings .

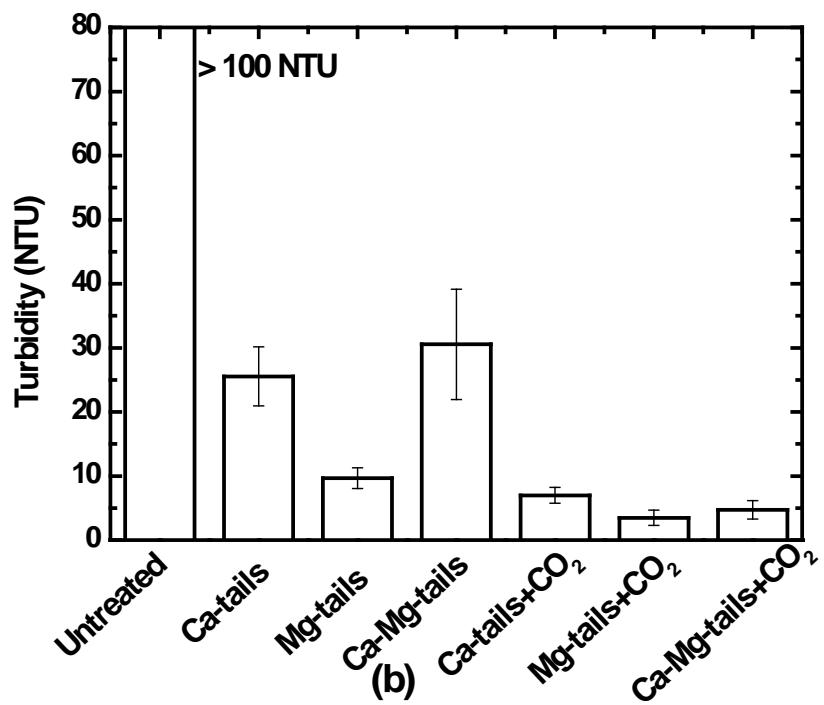
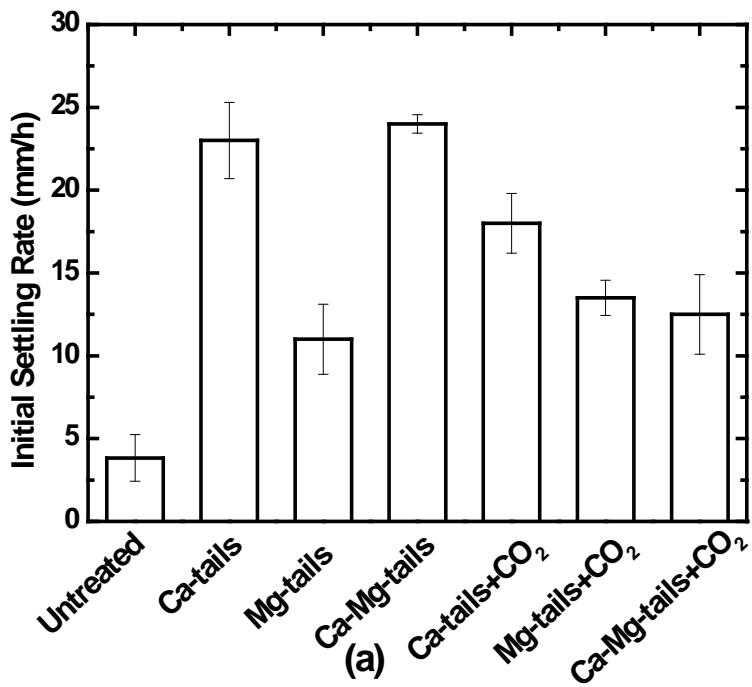
## **Chapter 6      Synergy of CO<sub>2</sub> with Cationic Coagulants on Densification of Tailings**

In this chapter we will explore the synergy of CO<sub>2</sub> with divalent cationic coagulants, such as Ca(OH)<sub>2</sub> lime and Mg(OH)<sub>2</sub> brucite, on settling and densification of oil sands tailings. The experiments were performed on S tailings whose composition was given in Table 3-1. The treatment details were described in section 3.3.2.

### **6.1. Synergy on settling and densification of tailings**

The settling performances of the tailings resulted from various chemical treatments are shown in Figure 6-1 with respect to the ISR, the supernatant turbidity and the solids content of final sediment. For the samples without treatment of CO<sub>2</sub>, the addition of cationic coagulants significantly increased the ISR as shown in Figure 6-1(a) and decreased the supernatant turbidity as shown in Figure 6-1(b). The effects of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> on the settling performance were different. As shown in Figure 6-1(a), Ca(OH)<sub>2</sub> appeared more effective on increasing the ISR of tailings than Mg(OH)<sub>2</sub> did. However, as shown in Figure 6-1(b), Mg(OH)<sub>2</sub> gave the tailings a better supernatant clarity than Ca(OH)<sub>2</sub> did.

On the other hand, as shown in Figure 6-1(c), the solids content of final sediment of tailings decreased when treated with Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub>.



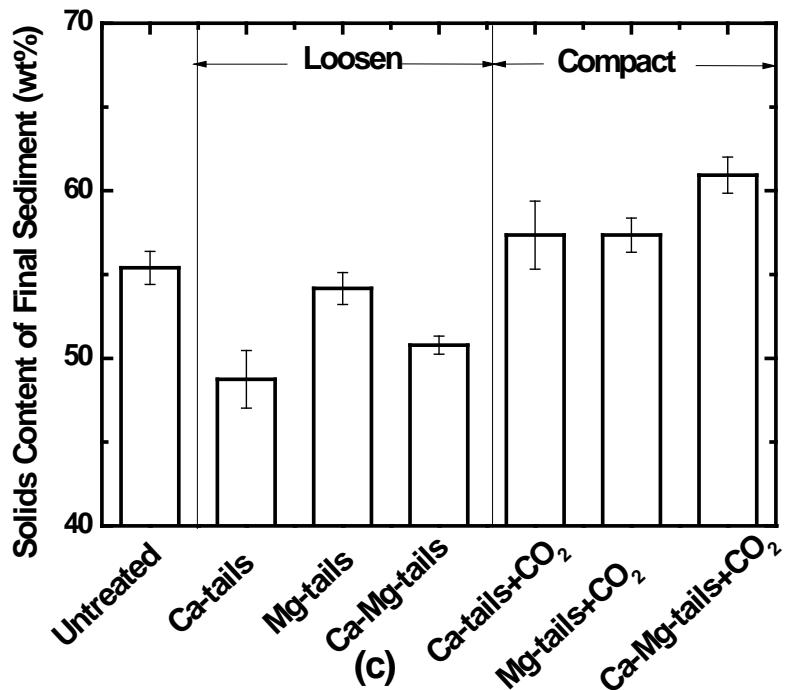


Figure 6-1 Effects of CO<sub>2</sub> and cationic coagulants on (a) ISR, (b) supernatant turbidity at the end of 24-hour settling, and (c) solids content of final sediment of tailings.

The different solids contents of final sediment were attributed to the different mechanisms of sedimentation. Without coagulation, a compact structure of sediment with a random clay particles association forms by accumulation sedimentation of tailings. With the presence of excessive coagulants, a porous structure of sediment with DLA fractal aspect forms by coagulation sedimentation of tailings (Pierre et al. 1995; Ma et al. 1998; Pierre et al. 1999). In addition, as shown in Figure 6-1(a), (b), and (c), the synergies of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> together on ISR, supernatant turbidity, and solids content of final sediment were similar as the effects of Ca(OH)<sub>2</sub>, but different from the effects of Mg(OH)<sub>2</sub>,

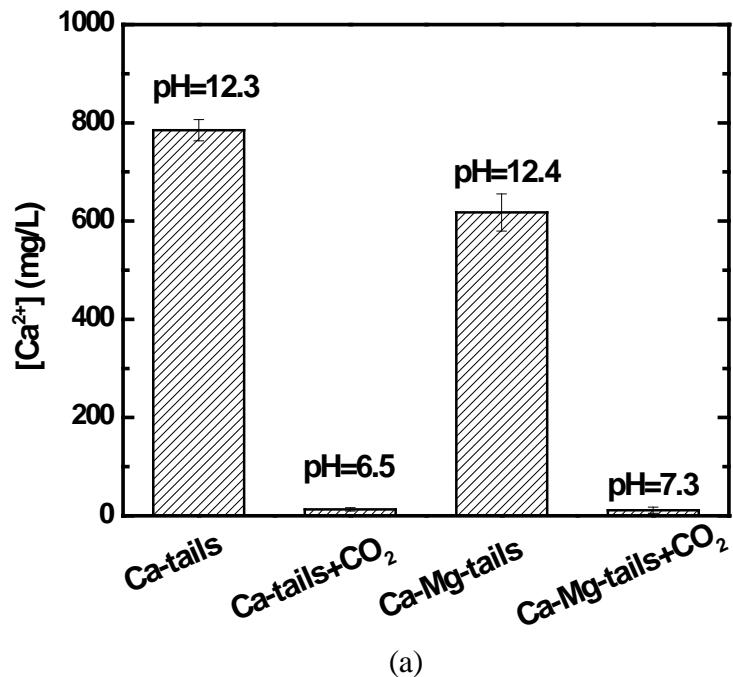
indicating  $\text{Ca}(\text{OH})_2$  dominates the coagulation of tailings when  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  are present in the tailings simultaneously.

The effects of  $\text{CO}_2$  on the Ca-tails and Mg-tails are then evaluated. As shown in Figure 6-1(a), the pressurization with  $\text{CO}_2$  had no significant improvement and even an adverse effect on the ISR of coagulated tailings with cationic coagulants. However, as shown in Figure 6-1(b), the addition of  $\text{CO}_2$  obviously improved the supernatant clarity of Ca-tails and Mg-tails. Moreover, as shown in Figure 6-1(c), the addition of  $\text{CO}_2$  increased the solids content of final sediment of Ca-tails and Mg-tails resulting in compacted sediments. In other words, the densification of the final sediment of tailings, which could not be done by  $\text{Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$ , was now achieved by the addition of  $\text{CO}_2$ . This improvement was likely attributed to either pH or zeta potential which are two factors determining the sedimentation mechanism (Ma and Pierre 1998).

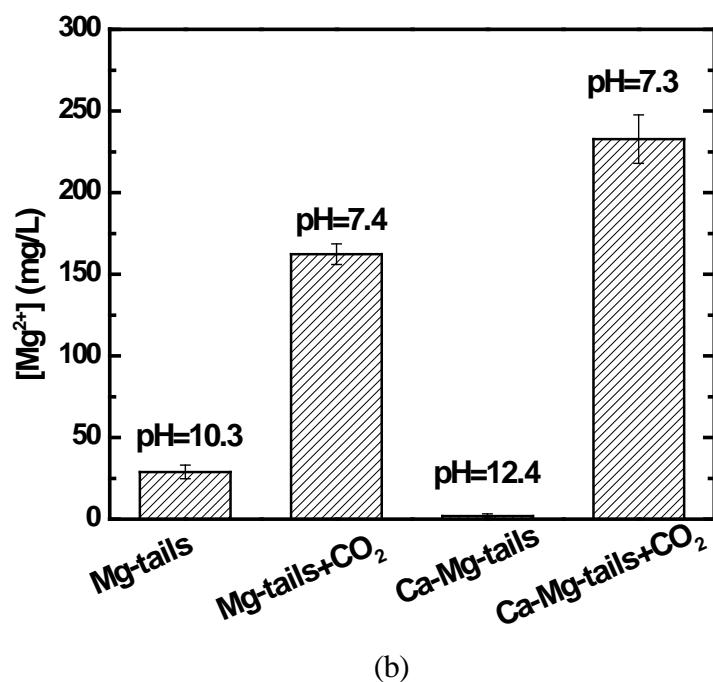
## 6.2. Effect of $\text{CO}_2$ on hardness of tailings water

The water recovered from the tailings treated with lime or gypsum has an excessive calcium ions concentration which is harmful to the subsequent bitumen extraction process. With the presence of abundant fines and clays, the calcium ions, inducing the slime coating, are known to have an adverse effect on bitumen recovery and froth quality in flotation (Kasongo et al. 2000; Fong et al. 2004).

Introduction of CO<sub>2</sub> to the calcium-involved process is anticipated to precipitate the free calcium ions. The concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> of the treatment-affected water were measured by AAS. As shown in Figure 6-2(a), a remarkable decrease in the concentration of calcium by 600 – 800 mg/L occurred when CO<sub>2</sub> was added into the tailings previously coagulated with Ca(OH)<sub>2</sub>. However, the concentration of magnesium of the tailings treated with Mg(OH)<sub>2</sub> increased by 100 – 200 mg/L with addition of CO<sub>2</sub>. Although the addition of CO<sub>2</sub> improved the settling and densification of both Ca(OH)<sub>2</sub>-tailings and Mg(OH)<sub>2</sub>-tailings to certain extent, the opposite effects of CO<sub>2</sub> on Ca<sup>2+</sup> and Mg<sup>2+</sup> indicate the different working mechanisms behind the different synergies of CO<sub>2</sub> with Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> on densification of tailings.



(a)



(b)

Figure 6-2 Effect of  $\text{CO}_2$  on the concentrations of (a) calcium ions and (b) magnesium ions in the released water from tailings. The pH of each filtrate is on the top of each corresponding column.

To understand the different effects of CO<sub>2</sub> on the concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup>, the solution chemistry particularly regarding the solubility of carbonates and hydroxides is analysed. As discussed in section 5.1, for an open system, such as in autoclave with a constant CO<sub>2</sub> pressure, the carbonate ions are supplied continuously by the dissolved CO<sub>2</sub> by a series of reactions as shown in equation (5-3) – equation (5-6). The carbonate ions would precipitate calcium and magnesium ions by reactions (6-1) and (6-2), respectively.

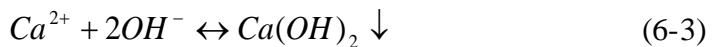


(K<sub>sp</sub> = 3.36 × 10<sup>-9</sup> at 25 °C)

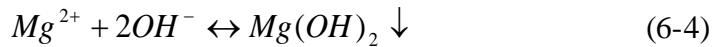


(K<sub>sp</sub> = 6.82 × 10<sup>-6</sup> at 25 °C)

The critical concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> to form carbonates precipitation can be deduced through equations (5-3), (5-4), (6-1) and (6-2) as a function of pH for a given temperature and CO<sub>2</sub> partial pressure. The critical concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> to form hydroxide comply with the reactions (6-3) and (6-4).



(K<sub>sp</sub> = 5.50 × 10<sup>-6</sup> at 25 °C)



(K<sub>sp</sub> = 5.61 × 10<sup>-12</sup> at 25 °C)

The critical precipitation curves of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are given in Figure 6-3(a) and (b). The precipitation forms when  $[\text{Ca}^{2+}]$  and  $[\text{Mg}^{2+}]$  are above the lines in Figure 6-3(a) and (b), respectively. As shown in Figure 6-3(a), the maximum  $[\text{Ca}^{2+}]$  in the initial solution with pH 12.5 is about 1000 mg/L according to the precipitation curve of  $\text{Ca}(\text{OH})_2$ . When  $\text{CO}_2$  is introduced into the solution, the pH decreases to 6.3 – 6.5 at which the maximum  $[\text{Ca}^{2+}]$  is about 10 mg/L according to the precipitation curve of  $\text{CaCO}_3$ . This result satisfactorily explains the decrease of  $[\text{Ca}^{2+}]$  by two orders of magnitude with addition of  $\text{CO}_2$  in Figure 6-2(a). Applying the similar analysis, the increase of critical  $[\text{Mg}^{2+}]$  from pH 10 to 7.4 according to the solubility curves in Figure 6-3(b) explains why  $[\text{Mg}^{2+}]$  increased from 27 to 160 mg/L when  $\text{CO}_2$  was added in Figure 6-2(b).

With the addition of  $\text{CO}_2$ , the calcium ions are converted to calcium carbonate with  $\text{CO}_2$ . The calcium carbonate precipitated on the mineral surface would induce the formation of a new sediment structure different, which is from the coagulated sediment and the accumulated sediment, by adsorbing fines and clays and bridging aggregates and flocs (Chalaturnyk et al. 2002). The special function of calcium carbonate as a bonding agent on the interaction of mineral solids is likely to be responsible for the higher clarity and the solids content of final sediment as shown in Figure 6-1(b) and (c). The increase of  $[\text{Mg}^{2+}]$  by  $\text{CO}_2$  causing the decrease of the magnitude of zeta potential of fine particles

contributed to the improvement on the settling and densification of Mg-tails as shown in Figure 6-1(a) and (c).

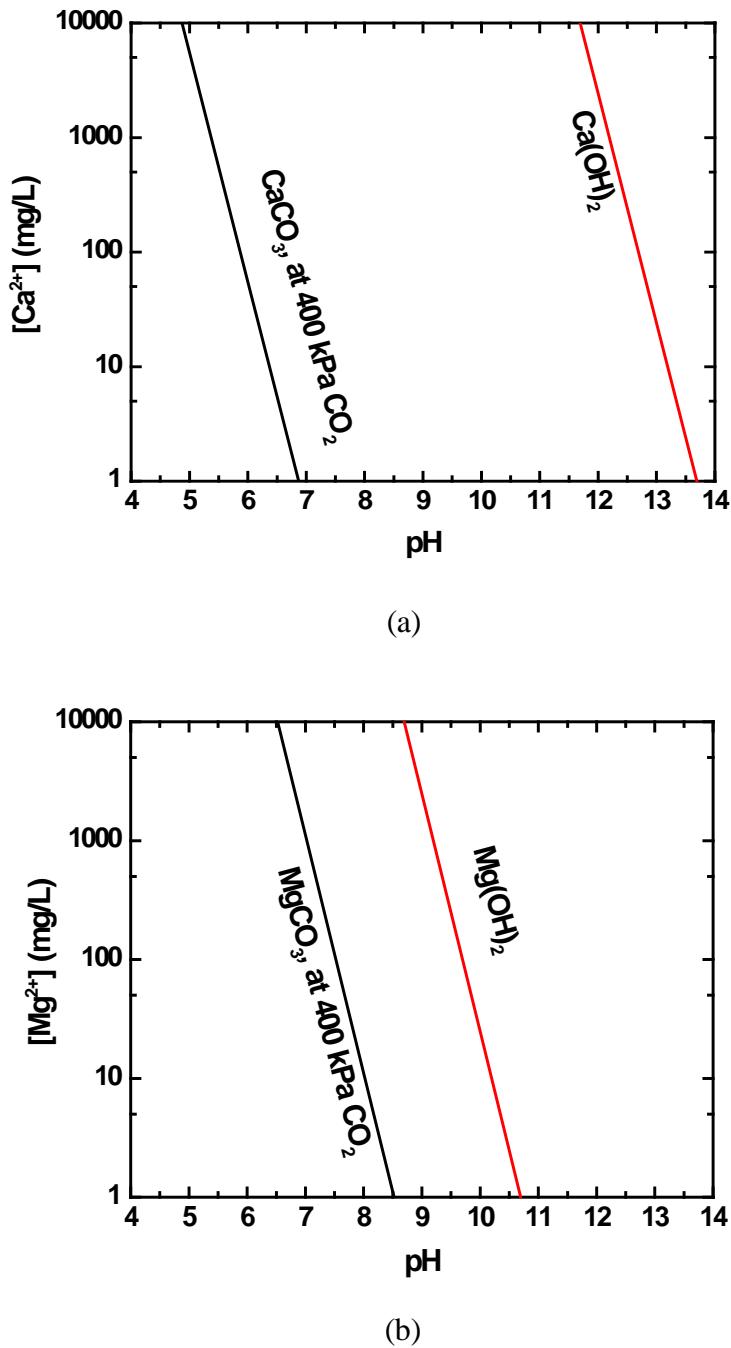


Figure 6-3 Critical precipitation concentrations of (a) calcium ions and (b) magnesium ions as a function of pH.

The analysis on the solution chemistry reveals that the effect of CO<sub>2</sub> on the hardness of the tailings water is governed by the solubility of calcium or magnesium compounds in water and the solution pH. Since the carbonate precipitation favours the fines capture and densification of tailings, the desired formation of MgCO<sub>3</sub> could be achieved by either increasing the CO<sub>2</sub> partial pressure or on-going adjusting the solution pH during reaction.

### **6.3. Effect of CO<sub>2</sub> on zeta potential of solids**

The pressurization with CO<sub>2</sub> decreased [Ca<sup>2+</sup>] and increased [Mg<sup>2+</sup>] of tailings water as mentioned above. It is known that Ca<sup>2+</sup> and Mg<sup>2+</sup> as divalent counter ions affect the zeta potential of mineral solids and hence the interactions between fine particles. Meanwhile CaCO<sub>3</sub> that precipitates on the surface of solids would also change the surface charge of the solids. To understand the effect of CO<sub>2</sub> on the electrokinetics of the solids, zeta potential measurement was carried out on the ZetaPALS and the results are shown in Figure 6-4. The highly heterogeneous nature of the tailings solids could be responsible for the great standard deviation of the measurements. The zeta potentials of the Ca-tails and Ca-Mg-tails were close to zero with values of – 2 mV and – 5 mV, respectively. With addition of CO<sub>2</sub>, the zeta potentials of Ca-tails and Ca-Mg-tails became more negative with values of – 28 mV and – 15 mV, respectively, because of the significant decreases

of  $[Ca^{2+}]$  as shown in Figure 6-2(a). On the other hand, with the addition of  $CO_2$ , the zeta potential of Mg-tails became less negative with the increasing value from  $-25$  mV to  $-16$  mV due to the increase of  $[Mg^{2+}]$  as shown in Figure 6-2(b). Clearly, the zeta potential of solids is dependent of the concentrations of divalent cations in the bulk solution. The effect of  $CO_2$  on the zeta potential of solids is mainly attributed to the effect of  $CO_2$  on  $[Ca^{2+}]$  and  $[Mg^{2+}]$  in the bulk solution.

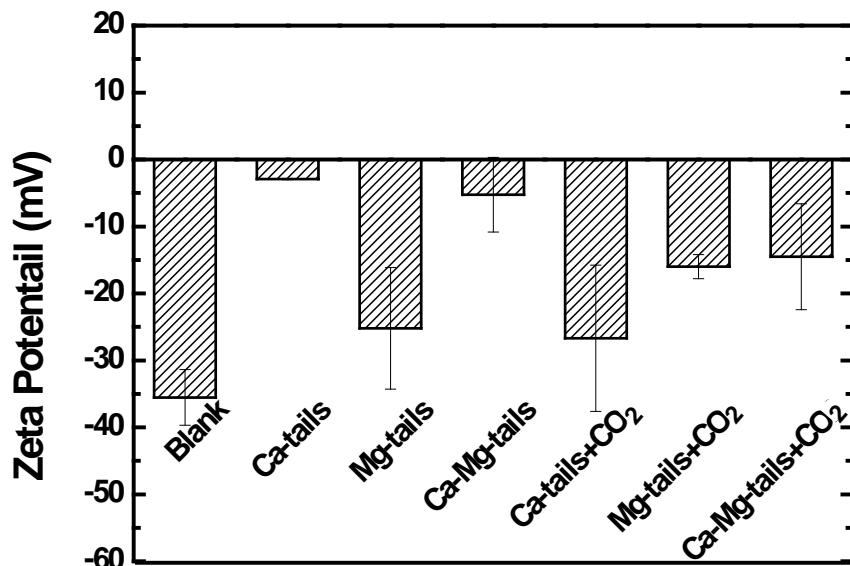


Figure 6-4 Zeta potential of the solids in tailings with various treatments.

In addition, the values of the zeta potential showed a good correlation with the ISR of the tailings as shown in Figure 6-5. The ISR decreased with the increasing magnitude of zeta potential of fines. However, the values of zeta potential showed

no correlation with the supernatant turbidity or the solids content of final sediment.

The effects of  $\text{CaCO}_3$  precipitation generated from the carbonation process on the fines capture and the densification of sediment might outweigh the effects of zeta potential of the solids.

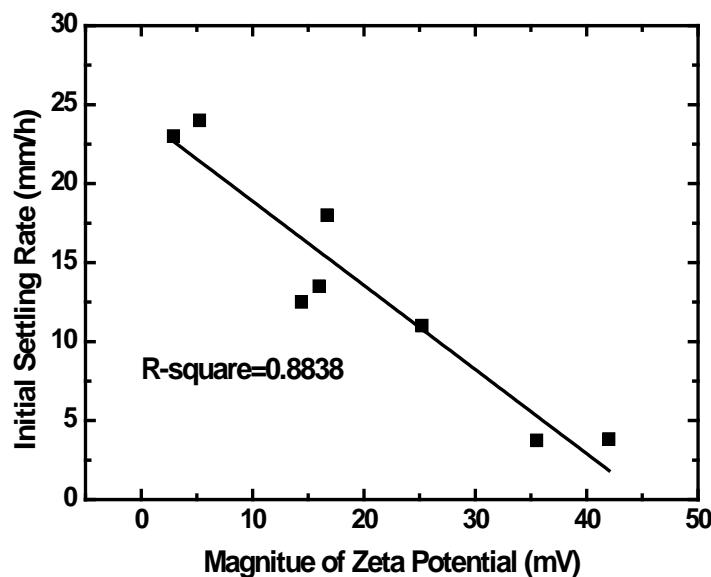


Figure 6-5 Magnitude of zeta potential of fines has a good correlation with ISR of tailings.

## Chapter 7 Potential of CO<sub>2</sub> Sequestration by Tailings \*\*

The three main types of CO<sub>2</sub> sequestration are hydrodynamic (physical), solubility-based (ionic) and mineral sequestration. The latter two are significant for the concept of sequestering CO<sub>2</sub> by oil sands tailings stream based on chemical conversions. In order to evaluate the potential of oil sands tailings to capture CO<sub>2</sub>, a carbon uptake test was carried out on S tailings by using an autoclave. From the experimental procedure described in Section 3.7, the amount of CO<sub>2</sub> absorbed by fluid samples from the headspace in an autoclave until the equilibrium state, n(CO<sub>2</sub>), was obtained. As shown in Figure 7-1, the CO<sub>2</sub> uptake of slurry and solid-free filtrate normalized by the liquid volumes is identical at various CO<sub>2</sub> pressure. In other word, the potential of oil sands tailings to capture CO<sub>2</sub> was mainly attributed to the solubility of CO<sub>2</sub> in the liquids. In addition, the capacity of formation water to ionically sequester CO<sub>2</sub> can also be deduced from equations (5-3) through (5-7) combined with the relationship of carbon mass balance as shown in equation (7-1):

$$n(CO_2) = ([CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] - C_{t0}) \cdot V_l \quad (7-1)$$

where n(CO<sub>2</sub>) = molar amount of the CO<sub>2</sub> captured by fluid samples (mol); C<sub>t0</sub> = total dissolved inorganic carbon concentration of the initial tailings solution

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(mol/L);  $V_1$  = volume of the tailings solution (L).  $C_{t0}$  was measured by dissolved inorganic carbon titration method (DIC). The straight line in Figure 7-1 represents the modeling result of  $\text{CO}_2$  uptake per litre tailings water as a function of  $\text{CO}_2$  partial pressure at equilibrium. The good fit of the experimental result with the modeling prediction further confirms that the solubility of  $\text{CO}_2$  in the saline water is the dominant mechanism and limit of  $\text{CO}_2$  sequestration.

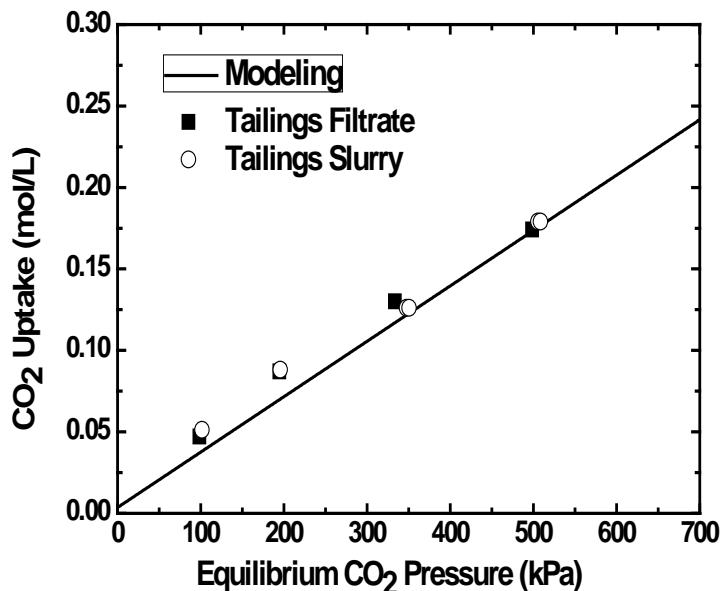


Figure 7-1 Dependence of  $\text{CO}_2$  uptake per litre of liquid on equilibrium  $\text{CO}_2$  partial pressure in the headspace of autoclave.

This result is not surprising from a geochemical perspective. There are extensive studies (Bachu et al. 1994; Maroto-Valer et al. 2005; Bearat et al. 2006) indicating that the ideal aquifers for fixing  $\text{CO}_2$  as carbonates are those with abundant Ca or Mg aluminosilicate minerals, such as olivine, feldspars, and so on.

Even clay minerals containing Ca or Mg ions are not easy to react with CO<sub>2</sub> to form permanent CO<sub>2</sub> sequestration unless more aggressive treatments, such as high temperature and pressure, are applied. However, the major oil sands tailings solids, such as quartz and kaolinite, contain little structural Ca or Mg. Only a marginal amount of Ca or Mg ions are present as substituted ions with Al in the structure of clays, and they are insignificant to CO<sub>2</sub> mineral carbonation sequestration. Our finding further confirms and generalizes the hypothesis of ionic sequestration that was proposed recently by Mikula et al. (2010). Although the increase of bicarbonate in tailings appeared to be linked with increasing amount of clays in terms of cation exchange in which protons replace accessible sodium and calcium ions on clay surfaces, the potential of CO<sub>2</sub> ionic sequestration is ultimately dependent on the equilibrium water chemistry of tailings, specifically the ionic strength of divalent cations. For the case of S tailings (62.5 wt% water), the amount of CO<sub>2</sub> sequestered is estimated to be 135.2 t/Mt of tailings based on the ionic strength and solubility of CO<sub>2</sub> in the sample water.

## **Chapter 8     Conclusions<sup>††</sup>**

In this thesis, the role of CO<sub>2</sub> on the sedimentation and densification of oil sands tailings, and the underlying mechanism have been studied. The synergy of CO<sub>2</sub> with divalent cationic coagulants on tailings treatment has been explored. The potential of tailings to sequestrate CO<sub>2</sub> has been evaluated. The experiments were carried out on two industrial tailings. The followings are the major findings of our study:

1. The effect of CO<sub>2</sub> on the sedimentation and densification of oil sands tailings as a function of CO<sub>2</sub> treatment partial pressure was studied. It was observed that CO<sub>2</sub> effectively improved the ISR, supernatant clarity and solids content of sediment when CO<sub>2</sub> partial pressure was increased from 0.035 to 100 kPa. Above 100 kPa, further improvement with increasing CO<sub>2</sub> pressure was limited.
2. The processing temperature of CO<sub>2</sub>-treatment affected the sedimentation of tailings. The ISR and the supernatant clarity were improved by increasing temperature. The effect of processing temperature was more pronounced when a low CO<sub>2</sub> pressure was applied.

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3. The major mechanism for the CO<sub>2</sub> enhanced settling and densification was pH reduction by CO<sub>2</sub> addition, which led to a decrease in the absolute magnitude of zeta potential of the fines. The effect of pH on the tailings settling and densification was reversible.
4. The adverse effect of bubbles generated from super-saturation of dissolved CO<sub>2</sub> on the ISR and supernatant clarity became apparent at high CO<sub>2</sub> partial pressures. The test using N<sub>2</sub> verified the negative effects of gas bubble on settling rate and supernatant turbidity.
5. Pressurizing the tailings with CO<sub>2</sub> following the addition of Ca(OH)<sub>2</sub> and/or Mg(OH)<sub>2</sub> increased the supernatant clarity and the solids content of final sediment, but decreased the ISR. The effect of CO<sub>2</sub> on the Ca(OH)<sub>2</sub>-tailings could be attributed to the formation of CaCO<sub>3</sub> precipitation that acted as a bonding agent. The effect of CO<sub>2</sub> on the Mg(OH)<sub>2</sub>-tailings was attributed to the increase of [Mg<sup>2+</sup>].
6. The limit to CO<sub>2</sub> sequestration by oil sands tailings was identified mainly by the solubility of CO<sub>2</sub> in saline water.

## **Chapter 9    Recommendations**

### **9.1.    For industry**

In order to maximize the dewatering efficiency and optimize the recycle water quality, the injecting pressure of CO<sub>2</sub> in the pipelines and the temperature of tailings must be controlled. Based on the lab experiments, the optimal partial pressure of CO<sub>2</sub> is around 100 kPa. Excess CO<sub>2</sub> pressure will not be cost-effective, and detrimental to the sedimentation due to the adverse effect of dissolved gas by super-saturation. The temperature of hot tailings from extraction plants which ranges from 50 – 80 °C is beneficial for the settling of tailings. Therefore, an early injection of CO<sub>2</sub> to the hot tailings flowing in the pipelines is recommended.

The synergy of CO<sub>2</sub> with conventional chemical binding agents on the tailings treatment deserves further research and application.

### **9.2.    For future research**

1. Verify the results by using model materials, such as model clays and simulated process water, which would not bring the disturbance of hydrocarbon, surfactants, and other mineral solids into the experiments, to get more fundamental knowledge about the CO<sub>2</sub>-tailings system.
2. Adjust the pH in-situ when Mg(OH)<sub>2</sub>-treated tailings are being pressurized with CO<sub>2</sub> to form magnesium carbonate precipitation.

3. Introduce CO<sub>2</sub> into gypsum-CT to minimize the calcium concentration, enhance the de-watering efficiency, and densify the sediment.
4. Explore aggressive treatments to improve the CO<sub>2</sub> sequestration by oil sands tailings.

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