Turbidity Mitigation in an Oil Sands End Pit Lake through pH Reduction and Fresh Water Addition

by

Jordan Thomas Brandon

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ABSTRACT

The remediation of oil sands wastes such as fluid fine tailings (FFT) and oil sands process-affected water (OSPW) are of increasing concern in the oil sands industry. End pit lakes are one remediation option currently being researched at commercial scale in Base Mine Lake (BML) operated by Syncrude Canada Ltd. BML contains a bottom layer of FFT, averaging 45 m, and a top layer of OSPW and fresh water with a depth of 8.5 m in 2014. BML has experienced high turbidity in the water layer throughout its lifetime, hindering sunlight penetration into the lake which is essential to the development of a healthy ecosystem that in turn drives the remediation of FFT and OSPW. Two research questions were studied during this series of experiments: (1) Can lowering the pH increase water clarity and (2) how does water composition affect water clarity.

Addition of 500 L to 4000 L of CO_2 to the water layer of a 160 L column lowered the pH from 8 to 6 with no initial improvement in Secchi disk depth (0.2 m) in 80% OSPW (20% fresh water), 60% OSPW (40% fresh water) and 20% OSPW (80% fresh water). The addition of HCl in 80% OSPW lowered the pH from 6 to 3.5 and resulted in an increase in water clarity as measured by Secchi disk depth from 0.2 m to 0.8 m within five days. A secondary improvement was seen between 30 and 60 days with Secchi depth improving from 0.8 m to 1.6 m. This time lag was unexpected and mirrored in 60% OSPW with CO_2 addition. Secchi depth improved in 60% OSPW from 0.2 m to 1.2 m between day 78 and day 113 with no significant improvement before day 78. 60% OSPW (Control) without CO_2 addition and 20% OSPW with CO_2 addition did not show an improvement in water clarity in the same time frame. The reason the time lag is present in not readily apparent but may be due to the reaction kinetics of the dissolution of $CaCO_3$ and the cation exchange on suspended clay particles.

Turbidity was reduced in 60% OSPW (300 NTU to 10 NTU), 60% OSPW (Control) (300 NTU to 57 NTU) and 20% OSPW (200 NTU to 57 NTU). Turbidity of 23 NTU corresponded to Secchi depth of 1.2 m in 60% OSPW, exceeding the goal of 1 m and indicating sufficient water clarity for the development of a healthy ecosystem. Decreasing the pH is a possible way to increase water clarity but is affected by the ionic strength of the water layer.

Experiments on 2 L columns over three months with 90% OSPW, 81% OSPW, 54% OSPW, 36% OSPW, 18% OSPW, 5% OSPW and 100% BCR and no pH adjustment resulted in no discernible effect of water composition on water clarity. Only 5% OSPW showed turbidity values (24 NTU) similar to the 23 NTU indicated as sufficient for water clarity. No pattern was found relating water composition to final turbidity.

The relationship between light penetration depth (0.01 light intensity) and Secchi depth was also explored and yielded an experimental equation of light penetration depth = 1.45 * Secchi depth + 0.1.

DEDICATION

To my parents, Erna and Max Brandon, whose support made this thesis possible. They did everything they could to help me, including feed me, encourage me and give me that extra push of motivation when required. I cannot thank them enough for everything they have done for me, both during this study and throughout my life.

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LIST OF ABBREVIATIONS

AER – Alberta Energy Regulator

AFD – Atmospheric Fines Drying

BCE – British Columbia Ministry of Environment

BCR – Beaver Creek Reservoir

BML – Base Mine Lake

CT – Composite or Consolidated Tailings

DDL – Diffuse Double Layer

EPL – End Pit Lake

ERCB – Energy Resources Conservation Board

ESRD – Alberta Environment and Sustainable Resource Development

FFT – Fluid Fine Tailings

MLSB – Mildred Lake Settling Basin

OSPW – Oil Sands Process-affected Water

TDS – Total Dissolved Solids

TRO – Tailings Reduction Operation

TSS – Total Suspended Solids

CHAPTER 1: INTRODUCTION

Alberta houses the third largest proven reserve of crude oil in the world and much of this is contained in the oil sands (Stringham 2012). The oil sands are considered an unconventional source of oil that requires additional refinement before it can be made into commercial products (Humphries 2009). Oil recovery methods used in the oil sands industry are more energy intensive and resource heavy as compared to traditional oil recovery techniques (Humphries 2009). As such, these methods present technical, environmental and social challenges. In particular, the environmental impact of oil sands extraction has come under increased scrutiny due to increased production and a greater international interest in the oil sands.

1.1 Oil Sands Industry

Oil sands are composed of a sand, clay, water and bitumen mixture that is not as readily extracted as other oils (Humphries 2009). Bitumen can be recovered from the deposits in two general ways: surface mining and in situ methods. Surface mining includes removing the overburden (muskeg, glacial till and clay shale) and digging out the oil sands. The mined oil sands are crushed and the bitumen is extracted from the oil sands using variations of the Clark Hot Water process. The Clark Hot Water process combines the mined oil sands with heated water or steam, forming a bitumen froth that floats to the top of the mixture (Clark 1929; Alberta Culture and Tourism 2015). At its most basic, in situ recovery uses steam to mobilise the bitumen while still in the oil sands deposit. Steam is pumped into the deposit through an injection well and the mobilized bitumen ‘flows’ to a recovery well (usually a second well drilled into the deposit) (Humphries 2009). The bitumen becomes mobile by raising its temperature and therefore lowering its viscosity. The bitumen recovered by both methods is then upgraded to synthetic crude oil.

Surface mining and in situ methods are used for different oil deposits based on the depth of the deposit. Each also has its unique advantages and disadvantages. Surface mining is economically feasible in shallow deposits where the overburden is less than 75 m deep (Humphries 2008). This type of oil sands recovery is similar to other types of mining mineral extraction methods although the bitumen extraction methods are unique to the oil sands industry (Larter and Head 2014). Surface mining has a greater total surface land disturbance than in situ methods (Alberta Energy Regulator (AER) 2015b). In situ methods are preferred for deeper oil sands deposits and require extensive knowledge of geology in the area (to maximize bitumen recovery and prevent catastrophic failure) and the in situ method used. Different methods have different advantages and disadvantages, for example Cyclic Steam Stimulation requires a stronger overburden cap because the operating pressures are higher than in Steam Assisted Gravity Drainage) (Alberta Energy Regulator 2015b). In addition to greater depths and more knowledge of the overburden, in situ methods also require natural gas to convert water into steam use in the extraction process. In general, surface mining is less energy intensive than in situ methods although in situ methods can be used to access more oil sands deposits (Humphries 2009).

The Canadian oil sands are mainly based in Alberta with some of the deposits straying into Saskatchewan. In Alberta, the oil sands were first commercially developed by The Great Canadian Oil Sands Company, established by the company now called Suncor Energy Inc., in 1967 (Humphries 2009). In the past two decades, higher oil prices and improvements in technology have made the oil sands more economical to develop resulting in greater production. Currently, oil sands development in Alberta is based in three areas, Peace River, Fort McMurray and Cold Lake (AER 2014). In 2013, total production of unconventional oil, encompassing both mined and in situ bitumen, was 121 million cubic metres, with in situ totalling 64 million cubic metres (AER 2014). The remaining established reserves are estimated to be 26 565 million cubic metres, approximately eighty percent of which is accessible though in situ methods (AER 2014). However, the growth of the oil sands industry has been accompanied with many challenges, including environmental impacts. One of the major issues still on-going is the storage or handling of by-products produced by oil sands extraction.

Two major by-products produced in mining oil sands are oil sands process-affected water (OSPW) and fluid fine tailings (FFT). OSPW is water used in the extraction process, some of which is recycled. OSPW is typically alkaline (pH 8-8.4) with total dissolved solids (TDS) between 2000 to 2500 mg/L, the majority of the TDS coming from sodium, bicarbonate, chloride and sulphate (Allen 2008). OSPW also contains a number of organic compounds such as bitumen, phenols, polycyclic aromatic hydrocarbons, benzene, toluene and naphthenic acids (Allen 2008). OSPW acute toxicity is generally attributed to the presence of the naphthenic acids (Toor 2012; Brown and Ulrich 2015). However, the effect and interactions of all the constituents of OSPW is not fully understood and constituents other than naphthenic acids also contribute to the toxicity of OSPW (Brown and Ulrich 2015). FFT are a combination of water and fines (silt and clay) with an initial solids content (based on mass throughout this thesis) of 10-20%w/w that reaches ~30%w/w in 2-4 years through settlement, but takes decades to reach >60%w/w (Siddique et al. 2014; Scott et al. 2013; Chalaturnyk et al. 2002). The fine particles in FFT form a stable colloidal suspension that hinders settlement (Siddique et al. 2014). In addition to fine particles, FFT also contains unrecovered bitumen and some diluent (Siddique et al. 2014; Funk 1979). Diluent composition varies by company with naphtha solvents being most common and paraffinic solvents (linear, branched and cyclic aliphatics) also being used (Small et al. 2015). Handling and managing these by-products in an economically feasible and environmentally sound manner continues to challenge the industry. Historically FFT is placed in out-of-pit or in-pit tailings impoundment structures (Chen et al. 2013). Out-of-pit tailings structures are large open areas ringed with dams, usually made with compacted sand from the ore, that allow coarse solids to settle and accumulated water to be reused the extraction process (Chen et al. 2013; Mikula 2013). However, FFT settling and dewatering in a tailings impoundment takes many decades and the area required to hold increasing volumes of FFT in tailings impoundments increases also. In 2013, the total active tailings area including all tailings impoundment structures was 220 km^2 (Alberta Environment and Sustainable Resource Development (ESRD) 2015).

1.2 FFT and OSPW Management

In 2009, Alberta’s Energy Resources Conservation Board (ERCB) issued Directive 074 to manage the volume and characteristics of oil sands tailings (ERCB 2009). At least 50% of the fines in oil sands must be disposed of in a dedicated area by 2013 with a strength of 5 kPa after one year and 10 kPa after five years (ERCB 2009). In addition to Directive 074, oil sands operators must comply with their government approvals, which have not included discharge of treated or untreated OSPW at the present time. This results in containment and storage of OSPW on site. The implementation of the containment and storage and Directive 074 has spurred innovation and research in oil sands tailings management and encouraged oil sands operators to combine their knowledge and expertise to find and fund the most promising tailings remediation techniques (Read 2014). Some of techniques currently being studied are centrifuging, consolidated or composite tailings, overburden mixing, polymer addition, rim ditching (accelerated dewatering), thickener technology, thin-lift dewatering and water capping (end pit lakes (EPLs)). These techniques are explained further in Chapter 2 but none of these remediation methods alone can solve the challenges of FFT and OSPW in oil sands mining, but may form part of the solution (Read 2014). The focus of this thesis is EPLs and optimizing the health and performance of EPLs as a remediation strategy in the oil sands industry. On March 13, 2015, AER (successor to the ERCB) officially suspended

Directive 074 with further information forthcoming under the Tailings Management Framework for Mineable Athabasca Oil Sands with the stated understanding that the oil sands operators will continue to manage their tailings responsibly until the new government policy is outlined (AER 2015a).

1.3 End Pit Lakes

The mining industry has used pit lakes as a remediation strategy for many years (Mikula 2013). They have been used for storage of mine by-products, recreational activities, metal recovery, as a water supply and as a habitat for aquatic life (Gammons et al. 2009). The Lusatia region in Germany contains over 500 pit lakes, with other pit lakes in Australia, USA and Spain (Castendyk 2012). In Alberta, East Pit Lake near the town of Wabamun is a pit lake that supports recreational fishing (Gammons et al. 2009). East Pit Lake was constructed from a pit created by dragline mining of coal and replaces two small water bodies drained for a mining operation (Gammons et al. 2009). It was filled using groundwater; grass and trees were planted around the lake to promote revegetation (Gammons et al. 2009). Castendyk (2012) summarises over 36 peer reviewed journals and conferences that publish data on EPLs from 1982 to 2010 as graphically represented in Figure 1.1.

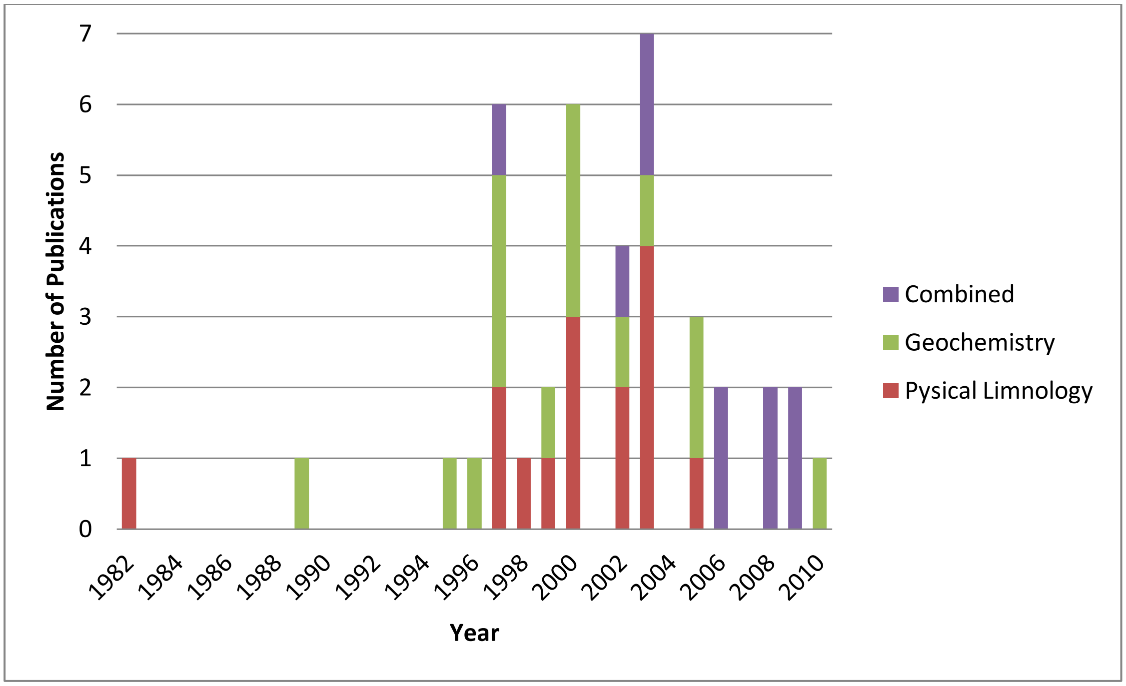

Figure 1.1: Number of publications on non-oil sands EPLs from 1982-2010 as summarized by Castendyk (2012). Combined refers to studies on both geochemistry and physical limnology.

In an oil sands context, EPLs will consist of a bottom layer of FFT and a top layer of water likely composed of a combination of OSPW (released from settling FFT and also originally present after being used as an in-pit tailings impoundment) and fresh water., An EPL may be used to:

1. *Manage surface water flows (hydrology)*
2. *Ensure acceptable water quality*
3. *Store tailings and bioremediate process-affected waters*
4. *Function as a sustainable aquatic ecosystem*
5. *Support other economic, ecological, and societal uses* (McKenna and Hrynyshyn 2012)

Precursor studies on how EPLs might be used by oil sand mining operations has been conducted by Syncrude Canada Ltd. since 1980 (Read 2014). Ten small ponds and one larger pond were constructed in 1989 to examine the feasibility of EPLs in an oil sands context (Read 2014). The smaller ponds had an approximate size of 50 m by 15 m by 7 m depth with a fine tails layer between 4-5 m and a capping layer of 2.5 m (MacKinnon and Boerger 1991). The smaller ponds included one control (fresh water only, no FFT), four contained FFT capped with fresh water with different nutrient loadings, one contained FFT capped with OSPW from a tailings pond and one with FFT, capped only with released water from the FFT and precipitation (MacKinnon and Boerger 1991). FFT settling and dewatering occurred in these ponds but at a slower rate than was expected based on lab results (Fine Tailings Fundamentals Consortium 1995). The cap water was only minimally affected by porewater released from the settling FFT in terms of ions (MacKinnon and Boerger 1991). While porewater released as FFT settled (i.e. OSPW) was acutely toxic the pond water was non-toxic based on Microtox testing (MacKinnon and Boerger 1991). After one year, aquatic ecosystems were forming in the ponds with the emergence of both plants and animals in the cap water and increases in microbiological activity in both the FFT and the cap water (MacKinnon and Boerger 1991). Other research was done by Lawrence et al. (1991) focussing on the resuspension of FFT using theoretical equations and applying them for use on Syncrude's Mildred Lake site. Their results show that resuspension of settled particles due to wave action is minimized by a sufficient cap water depth: 6.1 m depth is sufficient for a lake with a fetch of 5 km, using site wind direction, magnitude and duration data. .

The success of the small scale ponds have led to the inclusion of EPLs in many oil sands reclamation plans with the approval of the Alberta Energy Utilities Board (formally the ERCB, now AER), pending the successful demonstration on a large scale (McKenna and Hrynyshyn 2012). Syncrude pioneered the research on EPLs on a small scale and similarly operates the first large scale EPL. Base Mine Lake (BML) is the first oil sands EPL that will be a test case and a benchmark for future oil sand EPLs (Read 2014).

1.3.1 Study Site – Base Mine Lake (BML)

BML is the first full scale demonstration of EPL technology in oil sands, commissioned in late 2012 (Read 2014). It is located in the former West Mine of Syncrude's Mildred Lake site (Read 2014). Since 1999, BML has been filled with 186 M m^3 FFT to an average depth of 45 m (Dompierre and Barbour 2014; Geoffrey Halferdahl, personal communication, 2015). Initial cap water was comprised of OSPW (released from FFT placed in BML over the years plus an additional volume added) with some fresh water from Beaver Creek Reservoir (BCR) which was added in 2013 to achieve an average depth of approximately 8.5 m in 2014 (Dompierre and Barbour 2014). BML stretches approximately 3 km north/south and 2 km east/west (Geoffrey Halferdahl, personal communication, 2015). BML officially opened in late 2012 (Read 2014). An aerial view of BML is shown in Figure 1.2.

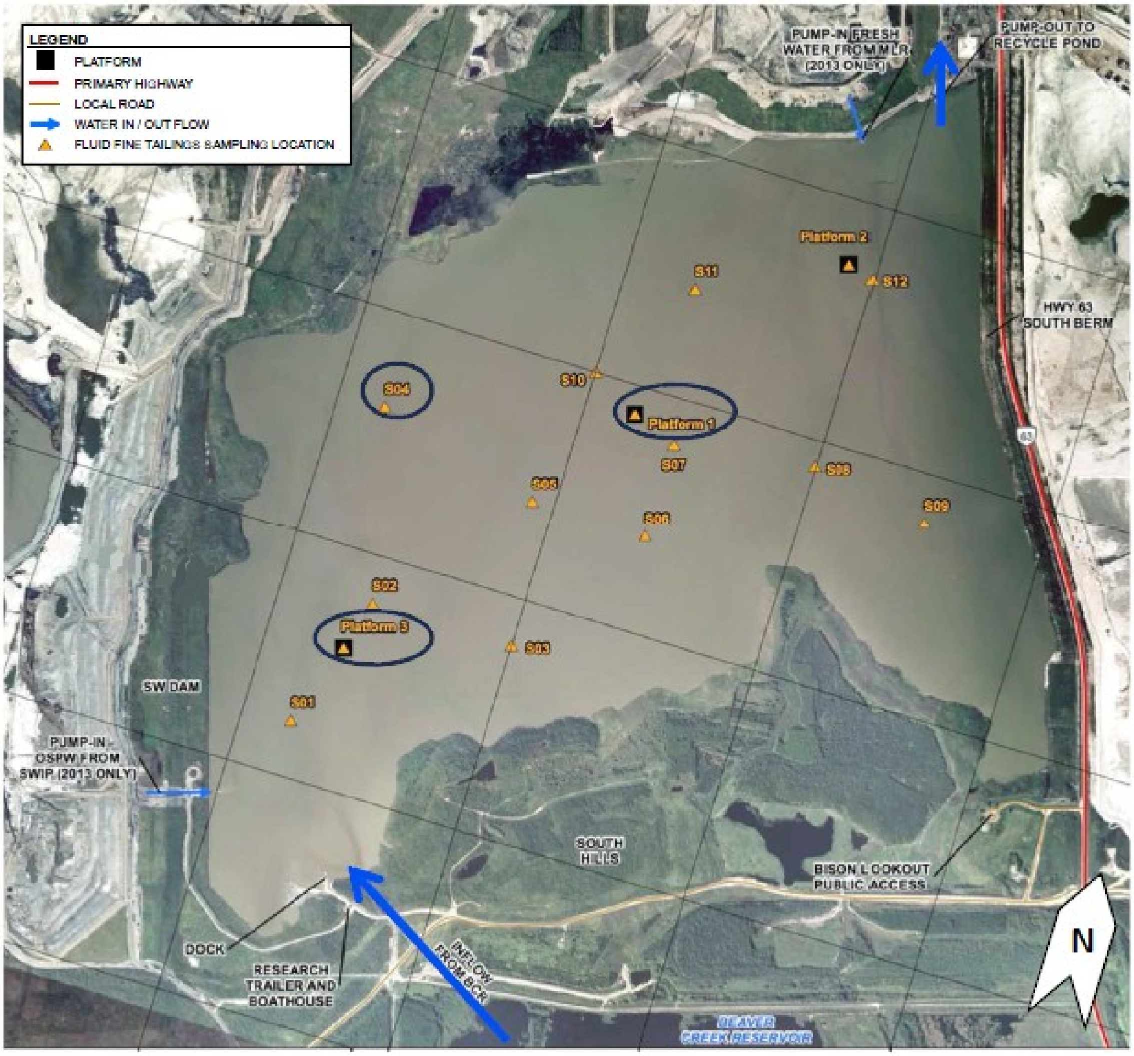

Figure 1.2: Aerial view of BML modified from Dompierre and Barbour (2014).

1.3.1 Important Parameters in Base Mine Lake

One of the key long term objectives of the BML is to function as a sustainable aquatic ecosystem. Many factors affect the health of an aquatic ecosystem such as dissolved oxygen concentration, toxicity levels, water chemistry, nutrients present, the littoral zone and water clarity (Charette and Mooder 2012). Dissolved oxygen levels must be sufficient to support an ecosystem although these levels will fluctuate seasonally, with low oxygen levels common in Alberta's winters (Charette and Mooder 2012). Toxicity levels must be low and the water chemistry and nutrients present determine the type ecosystem that can develop in the EPL. The littoral zone of a lake is the area from the shoreline to the edge where plants are present and encompasses the greatest ecosystem diversity (Charette and Mooder

2012). The littoral zone is extremely important because it houses the plants that regulate dissolved oxygen levels, provide food for animals and stabilize the sediment at the bottom of the lake (Charette and Mooder 2012). The maximum depth of the littoral zone is determined by the maximum depth that sunlight penetrates: ideally this is between 2-3 m (Charette and Mooder 2012). Water clarity is a factor of light penetration.

Water clarity is affected by different parameters. Suspended particles can lower the water clarity, phytoplankton and other organic material can absorb and scatter photons and coloured dissolved organic materials can affect water clarity (Capuzzo et al. 2015). In addition to these parameters, there are other factors that can directly or indirectly affect water clarity as well. Turbulence in the water (from wave action), the temperature regime dominating a pond or lake and the water chemistry can all play a role in water clarity. Turbulence can resuspend particles decreasing water clarity as well as slowing the settling process of suspended solids. Spring and Fall mixosis (mixing events) caused by thermal stratification breakdown and winds can suspend previously settled solids, reducing water clarity.. Water chemistry of a lake or pond can have effects on settling as well, due to the interaction of the charges in the water with the surface charges on materials that are settling. This is explained in more detail in Chapter 2.

BML is currently exhibiting very high turbidity and low sunlight penetration and low water clarity. The low water clarity of BML is not fully understood but the suspended clay particles in the cap water as well as factors such as water chemistry, turnover of the lake (temperature regime) and turbulence from wave action are likely part of the problem. As stated previously, sunlight penetration is essential for plant growth in the littoral zone, which in turn is important to the overall health of the ecosystem. Increasing sunlight penetration is one of the first steps to establishing a healthy ecosystem in BML.

1.4 Research Objectives

The overall objective of the research is to understand what water chemistry factors influence the settling of fines and therefore the water clarity in an EPL scenario. More specifically the research questions that are investigated include:

1.4.1 Can Lowering the pH Increase Water Clarity?

It is hypothesized that fine clay particles make up the bulk of the turbidity in BML. These particles are very fine (oil sands definition of fines is less than 45 μm) and take many decades to settle out by gravity (Scott 2003). These fines also do not flocculate, because of their surface charges, thus hindering settling. Flocculation of clay particles is controlled by the thickness of the double diffusive layer (DDL) surrounding each clay particle, which in term is controlled by the charge potential on the surface of the clay particle (Siddique et al. 2014). Lowering the pH of the water will help positive charges to develop on the edges of clay particles, neutralizing the inherent negative charge of the clay particles and promoting edge-to-edge flocculation and decreasing the thickness of the DDL (Proskin et al. 2012). Another proposed mechanism for increased flocculation is lower pH dissolves more carbonate materials, releasing more divalent calcium and magnesium ions (Siddique et al. 2014). Divalent cations are known to neutralize the negative charges of clay particles better than monovalent cations, decreasing the thickness of the DDL and allowing more flocculation to occur (Siddique et al. 2014). Higher flocculation results in faster settling of particles. Carbon dioxide can be used to lower the pH because it is already part of the natural buffering system, it is non-toxic and the lower limit of the pH reduction should be 5.7 based on $10^{-3.5}$ atm carbon dioxide partial pressure, 25°C in deionized water (Lower 2014).

1.4.2 How Does Water Composition Affect Water Clarity?

OSPW contains high concentrations of sodium while natural waters contain higher concentrations of calcium (Allen 2008). As stated before, divalent cations promote more flocculation and faster settling. Changing the composition of the cap water from higher sodium content (OSPW) to higher calcium content (natural water) could lead to a change in the flocculation and settling behaviour of the fines in BML. Another factor identified by Siddique et al. (2014) affecting flocculation is ionic strength. Ionic strength has a direct impact on the size of the DDL: higher ionic strength decreases the thickness of the DDL (Siddique et al. 2014). OSPW has a much higher ionic strength than natural water thus a balance must be found between increasing divalent cation concentration and ionic strength to find the optimal flocculation and settling range for clay particles.

1.5 Thesis Outline

This thesis contains five chapters organized in the following format: Chapter 2 contains the literature review and background information, Chapter 3 explores the relationship between pH and water clarity and Chapter 4 explores the relationship between water composition and water clarity. Chapter 5 contains the summary and conclusions of the research presented in the preceding chapters.

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CHAPTER 2: LITERATURE REVIEW

As discussed in the introduction, the oil sands industry drives the economy in Alberta but also presents many technical, social and environmental challenges. Environmental challenges of the oil sands include emissions, land use and by-products produced in the recovery of oil from the oil sands. Focussing on the storage and remediation of these materials, there are a number of different methods being researched and used in the oil sands industry today.

2.1 Review of Remediation and Storage Strategies

Traditionally FFT is placed in tailings impoundments commonly called ponds. The FFT is left to dewater mostly through gravity, with the water recycled. Because FFT is slow to dewater and also because operators do not have approval to discharge water back to the environment, a growing tailings containment volume is required. This increasing containment volume requirement, combined with new government regulations to reduce volumes of FFT (e.g. Directive 074), has accelerated research into FFT dewatering and remediation strategies.

2.1.1 Tailings Ponds

Placing tailings in impoundments is the conventional strategy employed by open pit mining operations (Delamaide et al. 2011). In oil sands open pit mining, fresh tailings from oil sands operations are discharged into an impoundment where the coarse solids settle quickly and the fine solids runoff with the water in the tailings slurry into an internal pond and form FFT. (Delamaide et al. 2011). Tailings sand, the coarse solids, is compacted and used to build containment for the FFT (Delamaide et al. 2011). FFT must be contained because it is not solid enough without containment and takes a very long time to dewater (Delamaide et al. 2011). In the first few weeks in a tailings impoundment, FFT solids content are typically 10-20%w/w and can reach ~30%w/w in 2-4 years, but it may take many decades for settlement to take place to increase the solids content to >60%w/w solids if left alone in a tailings impoundment (Siddique et al. 2014; Scott et al. 2013; Chalaturnyk et al. 2002).Tailings ponds are economically preferred in oil sands mining and mining operations in general, because they provide some key benefits:

- Increased development of the mine provides increased building material for the tailings ponds, reusing material that would otherwise be considered waste and reducing the overall cost.
- Staged development is possible allowing operators to build their tailings ponds as needed and as material becomes available from their mining operations.
- Liquid-solid separation happens over time with no additional mechanical input. This allows the operator to recycle water and increase the density of the solids deposited, which leads to a lower overall footprint in which their waste is deposited. (Kerr and Ulrich 2011)

However, tailings ponds have drawbacks and, in their operational form, cannot be used for permanent storage of FFT in site remediation plans. Issues with tailings ponds include:

- Tailings ponds have a large footprint. As stated before, in 2013 tailings structures covered 220 km^2 (Alberta Environment and Sustainable Resource Development (ESRD) 2015).
- Residual bitumen will float to the top of the tailings ponds. This is advantageous as the bitumen can then be recovered, but also poses an environmental hazard to animals, especially birds (Kerr and Ulrich 2011).
- Tailings ponds do not follow the guidelines set out by Directive 074.
- Underground seepage from the tailings ponds has been demonstrated, and counteractions must be employed to prevent contaminated groundwater from reaching water bodies (Kerr and Ulrich 2011; Yasuda et al. 2010).
- Tailings ponds in non-oil sands mining operations have failed, increasing the public awareness and hostility to tailings ponds (Kerr and Ulrich 2011). A recent Canadian breach of a tailings dam occurred at the Mount Polley Mine, BC (British Columbia Ministry of Environment (BCE) (2015). On August 4, 2014 the breach occurred, releasing approximately 17 million m^3 of water and eight million m^3 of tailings (BCE 2014). Independent Expert Engineering Investigation and Review Panel (2015) determined the failing of the dam was due to a foundation failure.

Tailings ponds are essential to the operations of a surface oil sands mine but cannot be the sole storage and remediation strategy employed by oil sands operators. Oil sands operators are actively looking for new and better storage and remediation strategies to be used in conjunction with tailings ponds.

2.1.2 Polymer Addition

While not a standalone FFT remediation strategy, industry has been researching and implementing polymer addition as an alternative to chemical additives (Read 2014). Chemical pre-treatment is essential to many remediation strategies (Mikula 2013). Chemical addition can create a buildup of ions in the water, especially if there is water recycling back to operations (Mikula 2013). The use of polymers can help mitigate this issue. Remediation strategies such as thin-lift dewatering and rim-ditching use polymers instead of chemical additives to increase the strength and dewatering of the FFT (Read 2014). Polymers and their dosages are researched and tested to find the optimal injection and mixing rates (Oil Sands Tailings Consortium 2012). Some polymers and dosages are listed in Table 2.1. More research is being conducted to find more efficient polymers, which aid in remediation and are also economically beneficial to the oil sands operators (Oil Sands Tailings Consortium 2012).

Table 2.1: Optimal polymer applications for FFT dewatering: dosage, pH and temperate ranges.

Polymer	pH Range	Dosage	Temperature	Density Improvement	Source
0.71×10^6 g/mol poly(N-isopropylacrylamide)	5	20 mg/L	25°C	50%w/w solids to 60%w/w solids in 24 hrs	O'Shea et al. (2010)
Percol 727	8.6	20 mg/L	Not stated (assumed room temperature)	~15%w/w solids to ~26%w/w solids in 5 min	Sworska et al. (2000)
95 mol% N-isopropylacrylamide, 5 mol% *N*-[3-(Dimethylamino)propyl]methacrylamide	8.5	100 mg/L	Room temperature	15%w/w solids to 30%w/w solids in 24 hrs	Osborn (2015)

2.1.3 Centrifugation

Centrifugation involves spinning FFT to produce two effluents, (1) supernatant water that can be recycled and a (2) a cake made of partly dewatered solids that can be used as a base for reclamation soil after one year of freeze-thaw cycle if placed in lifts that fully freeze (Read 2014). Following these processing steps, the cake usually contains 50-60%w/w solids and can be deposited without fluid containment (Mikula 2012). Centrifuging is an attractive option because partial dewatering of FFT can occur in minutes rather than the weeks or years required by other methods, and in the process produces two useful effluents (Read 2014). Centrifuged and partially dewatered FFT can be placed in tailings impoundments, increasing the tonnes of solids placed in a given volume compared to FFT not centrifuged. Syncrude has built a $1.9 billion centrifuge plant that will take FFT from Mildred Lake Settling Basin and produce cake that will be placed in-pit in the North Mine in a deep 40 to 45 m deposit and capped. The supernatant water will be pumped back to Mildred Lake Settling Basin and reused in extraction operations (Read 2014; Syncrude 2014). The high initial capital cost of centrifuging facilities as well as properly controlling the polymer dosage in response to varying clay contents in the FFT are two drawbacks of centrifuging and partially dewatering FFT (Mikula et al. 2007; Mikula 2013; Read 2014).

2.1.4 Composite or Consolidated Tailings (CT)

The CT process combines FFT (30%), amended with gypsum to reduce the amount of water it retains, with coarse sand (70%) (Delamaide et al. 2011; Mikula 2013). Gypsum, alum, lime or a polymer is also added as a flocculant to improve dewatering of the FFT (Delamaide et al. 2011; Kasperski and Mikula 2011). Properly made CT produces a solid sand matrix and recycles water typically within a month (Delamaide et al. 2011). However, tailings sand is also used to build FFT containment so there is a continually adjusting balance between use of sand in CT and other uses (Delamaide et al. 2011). Because the porewater in CT can have elevated ion concentrations (sodium is often a concern), it can pose challenges for vegetation growth (Delamaide et al. 2011). Wu et al. (2011) reported CT calcium concentrations above optimal for plant growth (reported: 242 ppm and 235 ppm, optimal: 80-200 ppm), but also showed wheatgrass growth during their experiments. Syncrude continues studies on incorporating CT into the stratigraphy of reclamation landforms. In the former East Mine at Syncrudes' Base Lease operations, CT forms the foundation covered with a sand layer for a fen research water shed (Syncrude 2014). Results to date indicate the sand layer and reclamation soil provide a viable stratigraphy for wetlands development (Syncrude 2014).

2.1.5 Overburden Mixing (Co-Mix)

Overburden mixing mixes extremely low moisture content Clearwater clays with FFT to make a geotechnically workable clay. Overburden (Clearwater) clay, removed to access ore, is mixed with FFT, to make a clay mixture of varying strength, depending on the ratio of Clearwater clay to FFT used, with a minimum target of about 10 kPa undrained shear strength (Read 2014). The strength of the resulting mix can support placement of reclamation soils and vegetation development (Read 2014). No chemicals are added in overburden mixing and it is insensitive to FFT density, unlike other methods such as centrifuging (Read 2014). Overburden mixing underwent significant study in the 1980s at Syncrude and has recently re-emerged to be studied again. A demonstration pilot was conducted in 2014, mostly focused on how best to mix extremely low moisture Clearwater clays with FFT (Syncrude 2014). Overburden mixing has certain advantages over CT including no added chemicals (polymer or other) and no tailings sand (Read 2014). Disadvantages include issues around mixing two very dissimilar materials to produce a quality controlled clay material and challenges around transporting it and placing it (Read 2014).

2.1.6 Rim (Perimeter) Ditching (Accelerated Dewatering)

The Florida phosphate industry uses rim ditching as a dewatering technique; it has been studied for dewatering FFT (Read 2014). In rim ditching, a flocculant is added to the FFT, which is pumped to a containment area (Mikula 2012). A perimeter ditch in the FFT is progressively deepened to remove FFT porewater as the FFT slowly dries as it is exposed to the sun, shrinks and a cracked surface crust develops (Lorentz et al. 2014; Read 2014; Mikula 2012). The perimeter ditch collects and allows both expelled FFT porewater and any rainwater to efficiently be removed, allowing the self-weight loading of the crust to continue to drive FFT dewatering (Read 2014; Mikula 2012). Rim ditching requires a chemical aid such as a flocculant to be added to the FFT at the start of the process and, on a commercial scale, it may take 2-5 or more years to fill a deposit with treated FFT and then rim ditch it, depending on the size of the deposit (Mikula 2012). The length of time to fill the deposit may be contrary to Directive 074, which has one and five year time limits for strength that would not be met if time is counted from the start of depositing (Mikula 2012). A Syncrude pilot deposit has produced about a 50% FFT volume reduction in five years (Read 2014).

2.1.7 Thickener Technology

The thickening technology process first takes FFT from the extraction process through a hydro-cyclone instead of straight to a settling basin, producing two effluents, the underflow and overflow (Sobkowicz 2012). The underflow is typically composed of 50%w/w solids and contains most of the coarse sand (Sobkowicz 2012). This underflow can be used for constructing terrestrial closure landforms (Read 2014). The hydro-cyclone overflow, containing most of the water and fines, is amended with flocculants in a thickener designed to use gravity sedimentation to produce two effluents also: an underflow a dense fluid with virtually all the solids and an overflow composed mostly of water (Read 2014). The overflow of the thickener is recycled back to the extraction process while the underflow is deposited in a containment area (Sobkowicz 2012). This deposited material has variable solids content from 10%w/w to 55%w/w with flow rates in the thickener sometimes decreasing the solids content of the deposited material as more water is needed to keep the material flowing (Read 2014; Sobkowicz 2012). Thickeners may offer the opportunity to recover thermal energy if the overflow water is put through a heat exchanger. Although the underflow material produced by thickeners can be pumped and is denser than untreated FFT and may continue to dewater, operational challenges can result in variable results (Sobkowicz 2012). Commercial application of thickeners have resulted in unreliable results causing some operators to miss their fines capture targets (Energy Resources Conservation Board (ERCB) 2013). Improvements can be made in the flocculant dosage and the consistency of the product (Sobkowicz 2012).

2.1.8 Thin-lift Dewatering (Tailings Reduction Operation (TRO) or Atmospheric Fines Drying (AFD))

Thin-lift dewatering forms the main process of two differently named processes, TRO (Suncor Energy Inc.) and AFD (Shell Canada Limited) (Read 2014). Thin-lift dewatering relies on polymer addition (anionic polyacrylamide flocculent produced by SNF Floerger) (Oil Sands Tailings Consortium 2012; Sobkowicz 2012). Polymers are added during the pumping of FFT to the disposal site starting initial mixing and flocculation during transport (Oil Sands Tailings Consortium 2012). The FFT and polymer mixture is then discharged on a small slope in a thin layer (10-30 cm) to dewater through evaporation (Mikula 2013; Oil Sands Tailings Consortium 2012). Results in a pilot plant by Suncor indicated that the initial mixture has enough strength (5 kPa) to maintain the slope, promoting dewatering and reducing the impact of rainfall (Mikula 2013). When the material has sufficiently dewatered (approximately 60%w/w solids), it may be kept in place or trucked to other locations for final disposal (Oil Sands Tailings Consortium 2012). Thin-lift dewatering is limited by the land area or footprint area required and the length of the drying season that year (ERCB 2013). Originally, the operations planned on an annual deposition rate of 3 t/m^2 to 5 t/m^2 but large field trials only treated 1 t/m^2 consistently (Sobkowicz 2012).

2.1.9 End Pit Lakes (EPLs) or Tailings Water Cap Technology

Water capping is the process of storing FFT under a layer of water (Read 2014). The water may be OSPW, fresh water or a combination of both. The resultant water body is called an EPL. EPLs store FFT as it slowly dewaters over time, while the water layer houses a healthy ecosystem (Oil Sands Tailings Consortium 2012). EPLs can serve as a long term place for FFT and also a place where natural remediation of FFT and OSPW with no flocculants can happen (Mikula 2013; Read 2014). Syncrude began preliminary studies on EPLs in the 1980s with 11 small pilot ponds constructed in the late 1980s and early 1990s (Read 2014). Seven of these ponds were presented on by MacKinnon and Boerger (1991). The ponds were 50 m by 15 m by 7 m deep and filled with FFT (4-5 m) and then capped with fresh water with various nutrient loadings (MacKinnon and Boerger 1991). One pond contained FFT only and the control pond contained fresh water only. No major ionic concentration shifts in the pond waters were found in the first 18 months and there was no evidence of an increase in acute toxicity (MacKinnon and Boerger 1991). After one year, the ecosystem developed in the water layer of the small ponds was similar to that of the control (MacKinnon and Boerger 1991). Some of these results contributing to Syncrude being granted permission to proceed with a commercial-scale demonstration EPL. In late 2012, BML was established officially as the first commercial scale demonstration EPL in the oil sands industry (Syncrude 2014). EPLs are explored more in depth in Section 2.2.

2.2 EPLs

EPL technology has been used in non-oil sands mining operations for many years (Castendyk 2012). EPLs in a mining context are often called pit lakes, mining lakes, mine lakes or mine pit lakes (Geller et al. 2013). For this section, pit lakes will refer to lakes in a general mining context and EPLs will refer to lakes in an oil sands context specifically.

2.2.1 Pit Lakes in Non-Oil Sands Context

Pit lakes are found in a variety of surface mining industries employing open pit mining (Geller et al. 2013). These mines are only economical for shallow deposits, but with technology development increasing the depth at which surface mining is feasible (up to several hundred meters) (Geller et al. 2013). In general and traditionally, pit lakes are formed in depleted open pits where groundwater and surface water runoff collects after mining operations have ceased (Castendyk and Eary 2009).

2.2.1.1 Formation of Pit Lakes

The size and depth of pit lakes are governed by how the deposit is harvested and the stability of the surrounding ground (Castendyk and Eary 2009). Mines in hard rock are often deep with steep sidewalls while mines in areas with fractured rock and deep soil cover have gentler slopes (Geller et al. 2009). The resultant pit lake is also affected by how much the mining pit is refilled with overburden and waste rock and if any additional land formation work is completed before water is allowed to fill the pit (Geller et al. 2013). The filling rate and general hydrology of a pit lake is affected by climate, surface water inputs and, most importantly, groundwater hydrology (Castendyk and Eary 2009; Geller et al. 2013). Usually the bottom of mining pits and their resultant pit lakes are below the natural water table and the cessation of pumping groundwater naturally leads to a rebounding of the water table and filling of the mining area (Castendyk and Eary 2009).

2.2.1.2 Water Quality in Pit Lakes

The water quality of pit lakes is influenced by the water source (Castendyk and Eary 2009), type of mining, surrounding geochemistry (Gammons et al. 2009), evaporation,, that may increase concentrations of contaminants, and ecological processes taking place in the pit lake (Castendyk and Eary 2009). Finally, seasonal lake turnovers and thermal stratification can affect pit lake water chemistry (Van Zyl 2009).

Most water in pit lakes is groundwater seeping through the sides of the mined out pit (Castendyk and Eary 2009). Sulfide ore, in particular pyrite (FeS_2), exposed by mining, in combination with water and oxygen, produces sulfuric acid (Gammons et al. 2009; Van Zyl 2009). The formation of sulfuric acid lowers the pH of the pit lake water producing acid mine drainage. Pyrite is commonly found in gold, coal, phosphate, metals, solid fuels and sometimes uranium mining and the acidification of pit lakes is a common issue throughout the world (Gammons et al. 2009; Geller et al. 2013). Mining industries in relatively inert material (clay, limestone, sand and gravel) and surroundings do not, in general, produce acidified pit lakes (Gammons et al. 2009). Subsurface materials in the oil sands region mostly contain clay, shale, silt and fine grained sands with some variability, especially in glacial tills (Mooder 2012).

Evaporation in a pit lake, especially a terminal lake, may increase concentrations of contaminants over time (Castendyk 2012). Terminal lakes are pit lakes with no groundwater or surface outflow, water loss is through evaporation only (Gammons et al. 2009). Flow-through lakes usually have both groundwater inflow and outflow and are less affected by increasing ionic concentrations due to evaporation (Gammons et al. 2009).

A number of ecological processes influence the water quality in pit lakes while water quality often determines the ecological process possible. Photosynthesis in pit lakes helps to increase dissolved oxygen concentrations and reduce carbon dioxide concentrations (Gammons et al. 2009). For pit lakes with an established littoral zone, the plants in this zone contribute the majority of the dissolved oxygen found in the pit water (Charette and Mooder 2012). Planktonic algae and cyano-bacteria will also photosynthesize (Gammons et al. 2009).

Pit lakes exhibit vertical stratification depending on the depth of the lake (Castendyk and Eary 2009). Turnover in a lake may mix different water layers and qualities (Van Zyl 2009). The temperature regime in the lake and the surrounding climate also helps govern the turnover behavior in a lake. Turnover is driven by atmospheric temperature changes in fall and spring where the epilimnion (shallow water) cools/warms changing the density of the layer, causing vertical water movement (Castendyk 2012). Wind and turbulent conditions contribute to mixing of the epilimnion and hypolimnion (deep water) but do not cause complete turnover without atmospheric temperature changes (Castendyk 2012). The epilimnion is saturated with oxygen and hypolimnion has low oxygen saturation (Castendyk 2012). Holomictic lakes exhibit both layers and show turnover at least once annually (Castendyk et al. 2015). Meromictic lakes have a third layer (monimolimnion) under the hypolimnion that exhibits anoxic conditions and never comes in contact with the surface (not affected by turnover) (Castendyk et al. 2015).

Turnover carries oxygen rich water from the surface to deeper parts of the pit lake while carbon dioxide rich water from deeper layers is carried to the surface, which can affect the pH of the surface layer (Castendyk et al. 2015). Oxygen levels will generally determine the makeup of the aquatic. Turnover also causes movement of other dissolved and suspended materials and can affect the settling of these materials, in turn affecting the turbidity in the lakes.

2.2.2 EPLs in an Oil Sands Context

EPLs are a relatively new remediation strategy in the oil sands industry compared to other types of mining. Since pit lakes are the basis of EPLs they share many objectives such as: water flow management, controlling water quality, encouraging a healthy aquatic ecosystem and accommodating recreational activities (if water quality passes surface water quality guidelines) (McKenna and Hrynyshyn 2012). Figure 2.1 shows a conceptual drawing of an EPL, which contains a bottom FFT layer and a top water layer. One major difference between EPLs and pit lakes is the ability to store and remediate FFT in EPLs.

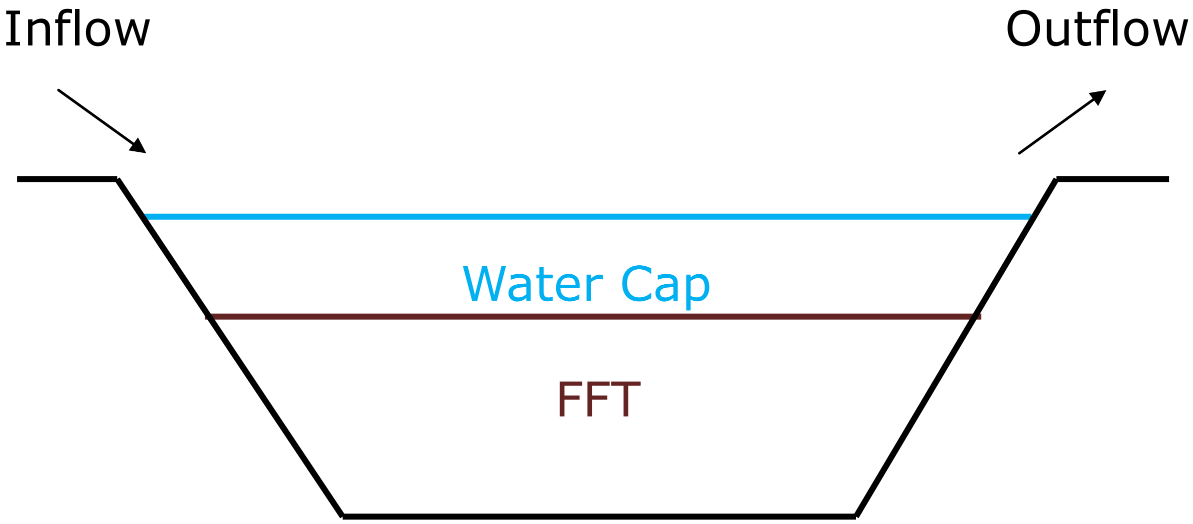

Figure 2.1: Conceptual EPL figure with a bottom FFT layer and water layer on top (which can be comprised of OSPW, fresh water or a combination).

In more detail the key objectives of EPLs are outlined below. An EPL is part of the water flow management on a site since it is the dominant hydraulic structure, collects surface run-off, and is likely connected to the groundwater (Hrynyshyn 2012). EPLs are designed with an outflow where water will be discharged if quality meets standards and is approved by the Alberta government. Biodegradation processes within the EPL will hopefully achieve these water quality standards. The development of a healthy aquatic ecosystem is a key objective of EPLs. They are designed to provide habitat for flora and fauna, especially fish species (Hrynyshyn 2012). The Alberta government requires EPLs to be constructed to fill a similar ecological role to lakes present before mining disturbance (Hrynyshyn 2012). The main objective of EPLs that make them unique from pit lakes is the storage and remediation of FFT. EPLs store FFT in a dedicated area while bacterial activity reduces contaminants such as naphthenic acids, polycyclic aromatic hydrocarbons and salts (Hrynyshyn 2012). The storage of FFT in EPLs will impact the water layer because the FFT will continue to dewater. Porewater expressed from the FFT will contribute chemistry to the water layer. Other uses of EPLs are secondary to the four objectives listed before (Hrynyshyn 2012). Recreational uses as well as access for aboriginal uses and aesthetics are all considered but the Alberta government mandates they must not conflict with the ecology of the EPL and the water quality (Hrynyshyn 2012).

2.2.2.1 Formation of EPLs and BML

Oil sands mines in general have large surface areas (0.6 to 13 km^2) and relatively low depth (6-55 m) similar to pancake shapes while non-oil sands mines are often more carrot shaped but heavily depends on the mining operation and deposit area (Castendyk 2012). The water depth of EPLs is reduced depending on how much FFT is disposed in the bottom of the mine pit.

2.2.2.2 Water Quality in EPLs

Water quality in EPLs is affected by water source, geochemistry of the surrounding area, evaporation, ecological processes in the lake and lake turnover. To facilitate the majority of natural remediation occurring in EPLs, bacterial and other ecological processes will break down NAs and other harmful contaminants in the water layer. Organic debris from the ecosystem will settle and eventually form a cap on top of the FFT, potentially sealing any contaminants migrating from the FFT into the water layer.

The water layer for all planned EPLs is to partially come from surface water (Vandenberg 2012). As indicated, the water layer for BML was initially OSPW augmented with fresh water from BCR. Groundwater inflow has relatively less influence on EPLs compared to pit lakes because of the surface water inflow. In addition, pyrite oxidation and the chance of acidification of EPLs is also relatively low because while pyrite is present in the Clearwater Formation that forms part of the overburden, the predicted relative effect on EPL water quality is low (Castendyk 2012; Mooder 2012).

In terms of lake turnover, EPLs are likely to behave similarly to natural lakes in the area. Industry is favouring the development of holomictic lakes (complete turnover in two-layered lakes) to aid in the remediation of OSPW and deposition of contaminants (Castendyk 2012). The development of a stagnant third layer (meromictic lakes) represents a risk because it is difficult to control the formation of these lakes and the reactions and ecosystem in the deepest, stagnant layer are very difficult to control or adjust (Castendyk 2012).

2.3 Water Clarity

Water clarity is an important parameter in EPLs because many other aspects of a healthy EPL ecosystem are dependent on the depth of sunlight penetration. Water clarity directly determines the depth of sunlight penetration, which in turn determines the depth of the littoral zone.

2.3.1 The Littoral Zone

The littoral zones (from the shore to the deepest part sunlight penetrates to the bottom of the lake) are essential to the health of the aquatic ecosystem in any EPL (Engel 1990). The littoral zone provides shelter and food for aquatic species. It helps to regulate the nutrient concentrations of an EPL as well as dissolved oxygen concentrations. The littoral zone also helps to stabilize bottom sediment on the edges of the EPL where it is more prone to erosion. Stabilizing the bottom sediment contributes indirectly to water clarity, preventing resuspension of sediment.

2.3.2 Factors Affecting Water Clarity

Water clarity is affected by many factors including erosion and resuspension of sediment and FFT, nutrient and organic matter concentrations, and salinity and chemistry of the water (Küpper 2012). Erosion of the banks of an EPL creates loose sediment that may be suspended or resuspended in the water layer. Suspended particles hinder light penetration and lower water clarity. Preventing resuspension of sediment and FFT is of particular importance in EPLs because the fines in FFT take a very long time to settle out by gravity. Resuspension of these materials will hinder the growth of a healthy aquatic system for many years. The littoral zone helps to prevent resuspension of sediment and FFT on the edges of the EPL where it is shallow enough. The design of EPLs must have a sufficient water depth at the centre to prevent surface inputs such as wind, waves and/or precipitation from affecting the bottom sediment and FFT. Turbidity standards for turbid surface waters for Alberta set by ESRD limit increases in turbidity over background levels to 8 NTU (background levels 8-80 NTU) or 10% of background level (background level >80 NTU) (ESRD 2014). For aesthetic purposes, recreational use turbidity guideline is <50 NTU (ESRD 2014). Fish tolerance to turbidity varies and is explored and summarized in Birtwell et al. (2008). Table 2.2 summarizes the risk of impairment of fresh fish to turbid waters.

Table 2.2: Summary of risk of impairment of clear water fish exposed to turbid waters (adapted from Birtwell et al. 2008).

Risk of Significant Impairment	Turbidity (NTU)	Duration
None	<3	
Low	3-8	3 weeks to 10 months
Moderate	9-20	5 days to 3 weeks
Significant	21-100	3 hours to 5 days
Unacceptable	>100	<3 hours

Nutrient levels must be kept stable and high enough to encourage growth of a healthy ecosystem. Usually phosphorus and nitrogen are the most important nutrients. Nutrient limits for lakes indicate no rise in either nutrient concentration is permitted over background levels (ESRD 2014). For nitrate - N the long-term surface water limit is 3.0 mg (as N) /L over 30 days and the instantaneous limit is 124 mg (as N)/L (ESRD 2014). However, these limits may be adjusted based on chloride concentrations (ESRD 2014). Background levels of nutrients in EPLs are hard to determine because EPLs are constructed but old (and withdrawn) guidelines of 0.05 mg/L for total phosphorus and 1.0 mg (as N)/L for total nitrogen may provide a guideline for nutrient levels.

2.3.2.1 Clay Behaviour in Water

Clays are usually made up of tetrahedral or octahedral units with oxygen atoms at the corners and cations at the centre. This structure creates charged regions in the clay with positive charges focussed at the centre and negative charges at the surface. Stacked layers of clay units have cations in between the layers to offset the negative charges. (Appelo and Postma 2005)

In a water solution, because of the surface charges, clay particles develop a layer around each particle called the diffuse double layer (DDL) according to the Stern model (as shown in Figure 2.2). The surface charges attract ions to the water surrounding the clay particle (Tripathy et al. 2004). A first layer of adsorbed ions is called the Stern plane and these ions are considered immobile (Masliyah and Bhattacharjee 2006). For clays in neutral and basic pH, the negative surface charges attract cations to fill the Stern plane. A second, more mobile layer surrounds the Stern plane. The DDL starts at the Stern plane to the end of the mobile, more diffuse layer (Masliyah and Bhattacharjee 2006). Also indicated on the figure is the Debye length (κ^{-1}). The Debye length is often considered the thickness of the

DDL but this is not technically the case: the DDL usually extends beyond the Debye length (Masliyah and Bhattacharjee 2006). The Debye length occurs at the point where the electrical potential is 33% of the surface potential (Masliyah and Bhattacharjee 2006). Within the DDL there is the shear plane that occurs one to two hydrated ions radii away from the surface of the clay particle (where the no-slip fluid flow boundary occurs) (Masliyah and Bhattacharjee 2006). The zeta potential of a particle is measured at this point (which is often used to show the surface charge of a particle), because the charge at this point determines the stability of a particle in solution and it is the only measurable charge of a particle.

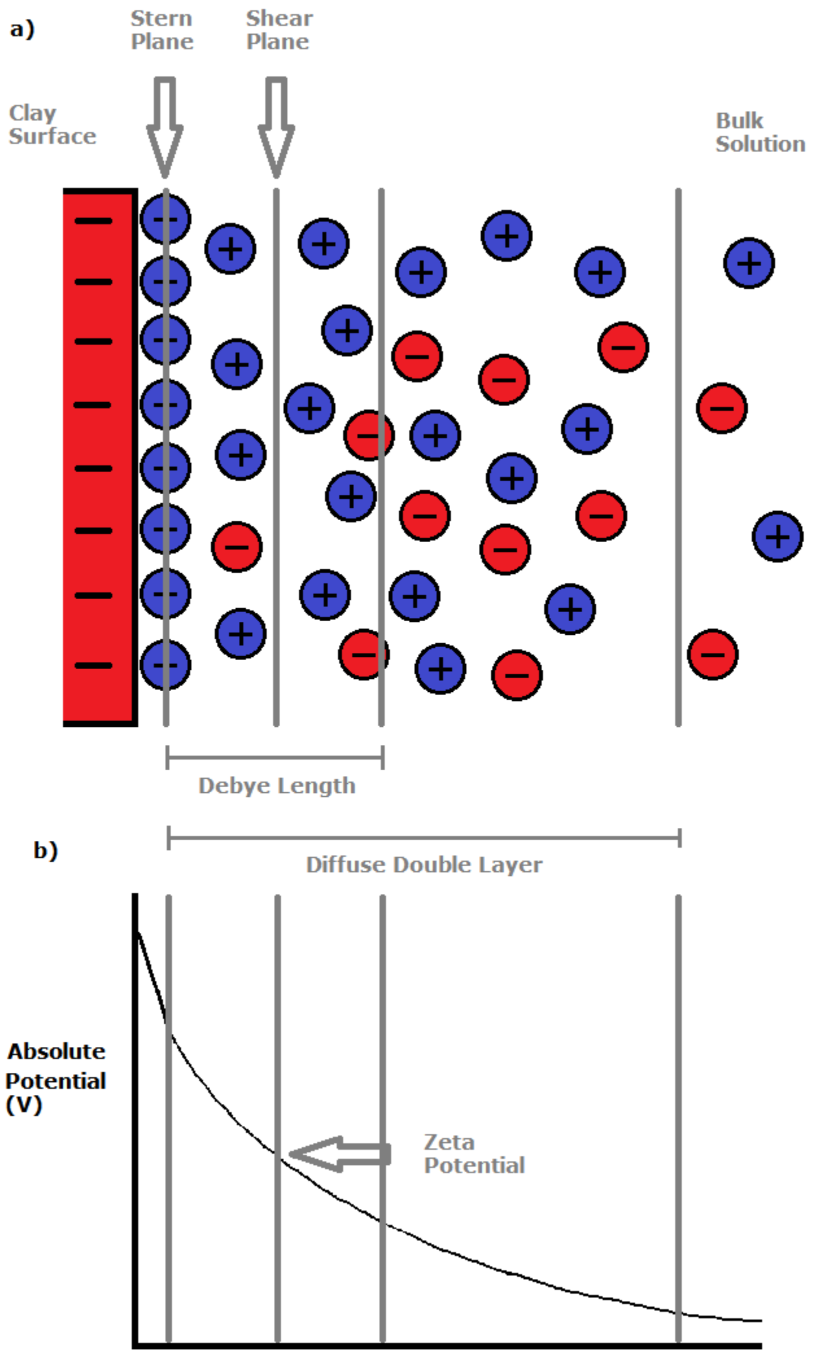

Figure 2.2: a) Representation of the Stern model showing a clay particle with negative surface charges and a cation dominated Stern plane. b) The absolute electric potential and where zeta potential is measured. Both the Debye length and DDL extent are shown. Modified from Masliyah and Bhattacharjee (2006).

The thickness of the DDL (represented as the Debye length) is determined by the ionic strength (equation 2.1) of the water solution and the average mean charge of the cations by the clay surface as shown in equation 2.2 (Siddique et al. 2014). Decreasing the thickness of the DDL increases flocculation (Siddique et al. 2014). Based on equations 2.1 and 2.2, decreasing the thickness of the DDL can be achieved by increasing the ionic strength of the solution or by increasing the absolute value of the average charge of the ions in the solution. Increasing ionic strength can be achieved through addition of ions and increasing the average charge can be achieved by adding divalent and multivalent ions.

$$\mathrm{I} = \frac{1}{2}\sum_{\mathrm{i}}(\mathrm{M_i Z_i^2}) \qquad (2.1)$$

Where, I = ionic strength (mol/L)
M_i = concentration of species i (mol/L)
Z_i = charge of species i (Siddique et al. 2014)

$$\kappa^{-1} = \frac{3.042 \text{ x } 10^{-8}}{\mathrm{ZI}^{0.5}} \qquad (2.2)$$

Where, κ^{-1} = Debye length (cm)
Z = average mean charge of exchangeable cations
I = ionic strength (mol/L) (Siddique et al. 2014)

Zeta potential is a measure of the net electrical charge at the shear plane as shown in Figure 2.2 (Masliyah and Bhattacharjee 2006). Larger positive or negative values indicate more stable particles and DDLs (Vercellone et al. 2015). Clay particles have negative zeta potentials at neutral pH, increasing as the pH is decreases (Vercellone et al. 2015). Moayedi et al. (2013) states that stable solutions have particles that typically have a zeta of greater than 30 mV or less than -30 mV. A number of research papers have been published on zeta potential of clay particles with Table 2.3 showing some of their results. According to Saka and Güller (2006), zeta potential is the primary factor in determining the dispersion and flocculation behaviour of clays and is affected by temperature, pH, ionic strength and the types of ions present.

Table 2.3: Published Zeta potentials.

Research Area	Material	Zeta potential (mV)	Comments	Source
Zeta potential	Urrbrae McLaren Claremont Keilira	-38 -42 -19 -25.6	Natural soils	Marchuk et al. (2013)
Zeta potential and pH	Montmorillonite	-16 -20	pH 2.5 pH 12	Saka and Güller (2006)
Zeta potential, pH and Turbidity	Urrbrae	-25.1 -46.7 -58.1 -61.2	pH 3.4; 517 NTU pH 6.7; 2680 NTU pH 9.8; 3830 NTU pH 11.4; 4170 NTU	Marchuk et al. (2013)
Zeta potential, pH and Turbidity	Claremont	-15.6 -21.7 -28.6 -38.8	pH 6.9; 200 NTU pH 7.7; 1230 NTU pH 9.3; 3047 NTU pH 11.6; 9760 NTU	Marchuk et al. (2013)
Zeta potential and Ca^{2+}	Montmorillonite	-15 -5	10^{-5} mol Ca/L 10^{-2} mol Ca/L	Saka and Güller (2006)
Zeta potential and flocculation with bioflocculant	Kaolin	-14.8 -20.4 -22.1 -25.2	D[1]: 0 FA[2]: 94.99% D[1]: 1.2 FA[2]: 96.27% D[1]: 4.1 FA[2]: 96.53% D[1]: 11.6 FA[2]: 92.14%	Liu et al. (2015)

[1] D: Bioflocculant dosage (mg/L)

[2] FA: Flocculant activity

Cation exchange capacity (CEC) is a measure of how many cations originally on the surface of clay particles can be replaced by other cations. Cations in solution can exchange with the ones currently on the surface of the particle based on the concentration of the cation in solution and the preference of cations on the particle (Appelo and Postma 2005). There is a balance between all cation concentrations in solution and cation concentrations on the clay particle (Appelo and Postma 2005). A change in the concentration in any of the cation concentrations affects this equilibrium (Appelo and Postma 2005). For four of the main cations in OSPW and fresh water, the preference order for the clay surface is as follows $K^+ > Ca^{2+} > Mg^{2+} > Na^+$ (Appelo and Postma 2005). Holden et al. (2012) investigated four different methods of determining CEC (Lithium chloride, Silver Thiourea, Methylene Blue and sodium acetate +ammonium acetate) in glacial sediments sampled from northern Alberta and concluded Methylene Blue is the least affected by carbonate salts present in this area. Their research supports the use of Methylene Blue for CEC determination in the oil sands industry, which operates in the same area. Osacky et al. (2014) and Kaminsky et al. (2009) investigated the CEC of oil sands materials using both Methylene Blue and copper(II) trieylenetetramine. Table 2.4 summarizes their results. Kaminsky et al. (2009) did not report overall CEC values, which are lower than the values reported.

Table 2.4: Summary CEC of oil sands materials using both Methylene Blue and copper(II) trieylenetetramine.

Material	Particle Size Fraction	Methylene Blue Index (meq/100g)	copper(II) trieylenetetramine (meq/100g)	Source
Marine Sand	bulk	1.4	3.1	Osacky et al. (2014)
Marine Clay	bulk	6.5	5.8	Osacky et al. (2014)
Estuarine Clay	bulk	7.2	7.1	Osacky et al. (2014)
Estuarine Sand	bulk	0.7	0.8	Osacky et al. (2014)
Tailings	<0.2 μm	38	33	Kaminsky et al. (2009); Hooshiar et al. (2010)
Tailings	0.2 - 2 μm	9	11	Kaminsky et al. (2009); Hooshiar et al. (2010)

2.3.2.2 Clay Settling

Clay settling can be increased through a number of methods: (1) addition of divalent or multivalent cations, (2) increasing the ionic strength of the solution and (3) changing the pH of the solution.

The dominant cation in OSPW and FFT is sodium. The exchange sites on clay particles in OSPW or FFT are usually saturated with sodium ions. The addition of divalent cations in water solution leads to the exchange of sodium for divalent cations in the DDL based on the cation preference ($K^+ > Ca^{2+} > Mg^{2+} > Na^+$). Increasing the concentration of divalent cations in the DDL increases the average charge of the cations in the DDL and decreases the thickness of the DDL as shown in Equation 2.2 (Lyons and Plisga 2005; Siddique et al. 2014). Decreasing the DDL thickness leads to greater flocculation and increased settling of the clay particles. Figure 2.3 a) and b) show a likely scenario of a clay particle stable in OSPW or FFT and Figure 2.3 c) and d) show how the addition of divalent cations might affect the DDL around the clay particle. Decreasing the DDL thickness decreases both the Debye length and shear plane but does not affect the Stern layer.

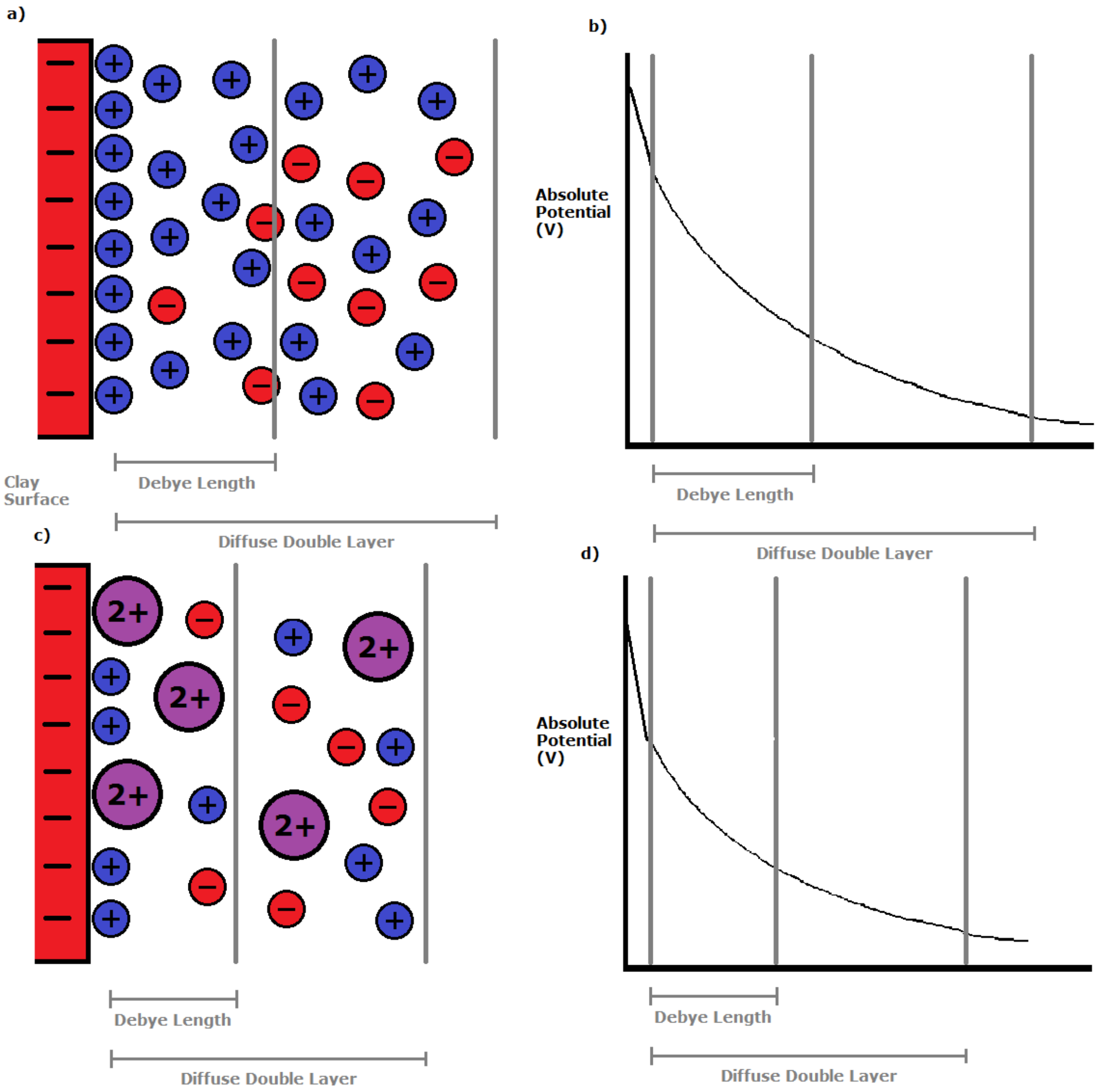

Figure 2.3: a) Clay particle in equilibrium with OSPW and predominately Na+ surrounding the particle with b) showing the electric potential graph similar to Figure 2.2 (modified from Masliyah and Bhattacharjee (2006)). c) Clay particle with divalent cations showing a decreased Debeye length and DDL thickness and d) showing the corresponding electric potential graph.

Following Equation 2.2, increasing the ionic strength is another method of decreasing the thickness of the DDL. Increased ionic strength in the solution helps to shield the negative charges from clay particles, decreasing their effect (Siddique et al. 2014). With more charged ions in the water solution, there is more interaction between different ions and charged clay particles. All these interactions help to mask the negative charges of the clay particles and reduce the effect it has on the surroundings.

Surface charges of clay particles are pH dependent (Appelo and Postma 2005; Kim and Nestmann 2009). Oxygen atoms in the clay can bind or unbind with hydrogen ions depending on the solution pH (Appelo and Postma 2005). In neutral and basic pH, oxygen atoms in clays are generally not bound to hydrogen atoms and a negative surface charge results (Appelo and Postma 2005). Lowering the pH results in higher hydrogen ion concentration in the solution and more bonding of oxygen and hydrogen on the clay surface (Appelo and Postma 2005). Figure 2.4 a) and b) show a clay particle in neutral pH and Figure 2.4 c) and d) show a clay particle with bonded hydrogen ions showing some positive surface charges in acidic pH. This results in less cations in the DDL to compensate for the clay surface charges.

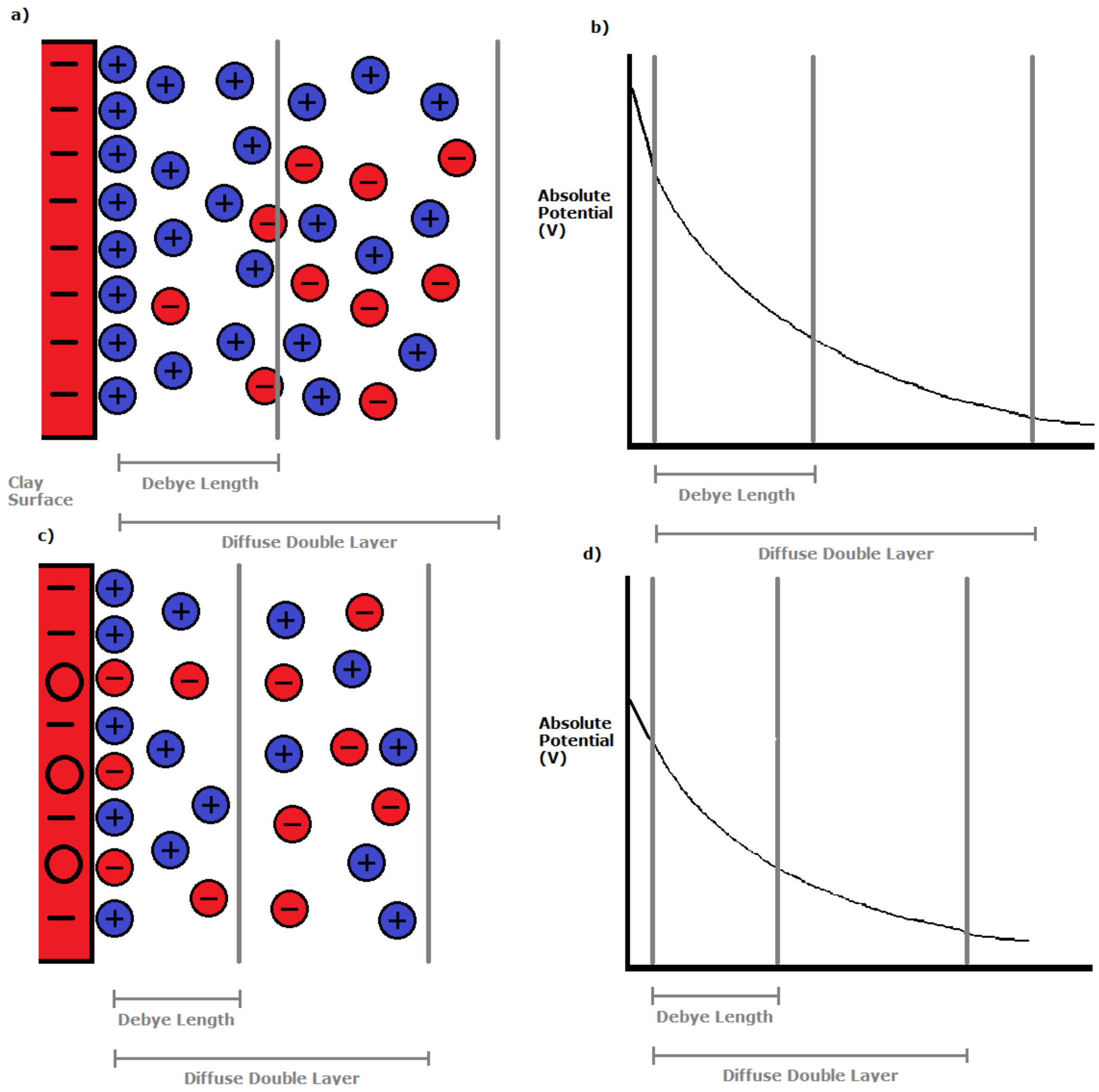

Figure 2.4: a) Clay particle in neutral pH with b) showing the electric potential graph similar to Figure 2.2 (modified from Masliyah and Bhattacharjee (2006)). c) Clay particle in acidic pH showing more neutralsurface charges and corresponding lower cations in the DDL. d) Electric potential graph of a clay particle in acidic pH with lower surface charges compared to the clay particle in neutral pH (b)).

2.4 Proposed Modifications to Increase Water Clarity

Two practical ways have been proposed to increase water clarity in BML: (1) adjusting the pH of the water layer and (2) changing the ionic composition of the water layer.

2.4.1 pH Adjustment

Decreasing the pH of the water layer is hypothesised to increase flocculation and settling and, therefore, water clarity as explained in Section 2.3.2.1. Mietta et al. (2009) experimented on clay flocculation in varying pH and found the floc length increased from approximately 30 μm at pH 9 to 40 μm at pH 6 and just over 80 μm at pH 4. Sutherland et al. (2015) gives an equation for settling velocity, partially based on clay size (Equation 2.3). Settling velocity is the maximum speed of a particle moving by gravity and depends on a number of different variables, both based on the medium and the particle. Based on this equation, small particles settle slower and the radius of a particle has more effect on settling velocity than other variable.

$$w_s = \frac{2g' r_p^2}{9v} \tag{2.3}$$

Where, w_s = settling velocity (cm/s)

g' = reduced gravity $g\,(\rho_p - \rho_w)/\,\rho_w$

ρ_p = particle density (g/cm^3)

ρ_w = water density (g/cm^3)

r_p = particle radius (spherical particle) (cm)

v = kinematic viscosity of water (cm^2/s)

pH adjustment can be achieved through various means such as acid addition and CO_2 addition though biogenic gas produced by bacteria or direct bubbling. The addition of a strong acid will lower the pH at the fastest rate. A study done by Hesslein et al. (2009) on an experimental lake indicates that HCl addition for nine years to a low of 5 pH resulted in an alkalinity drop from 60 μeq/L to -10 μeq/L during acid addition with a return to previous levels eight years after stopping acid addition. Sulfate concentration during the same time frame increased from 50 μeq/L to 150 μeq/L back to 75 μeq/L, respectively (Hesslein et al. 2009).

Siddique et al. (2014) experimented with pH reduction in FFT and found maximum dewatering in FFT at pH 1 and concluded the surface charges of clays were changed from negative to positive to increase dewatering. Siddique et al. (2014) concluded biogenic CO_2 gas contributed to settlement, in part by lowering the pH of the pore water in FFT. CO_2 dissolved in water forms carbonic acid that can lower pH. Arkell et al. (2014) stimulated microbial activity in FFT and found similar results to Siddique et al. (2014). Increased microbial activity led to increased CO_2 and CH_4 production that in turn led to lower pH and increased dewatering of FFT (Arkell et al. 2014). Zhu et al. (2011) demonstrated the use of non-biogenic CO_2 addition to FFT leads to decreased pH and increased dewatering as well. Using an autoclave and 100 kPa CO_2 pressure, solids content of FFT was increased from 52%w/w to 72%w/w for Syncrude Canada Ltd. FFT and 37%w/w to 49%w/w for Canadian Natural Resources Ltd. FFT in 24 hours (Zhu et al. 2011). In deionised water, the theoretical lower limit for pH reduction is 5.7 at 25 °C and $10^{-3.5}$ atm carbon dioxide partial pressure (Lower 2014). Carbon dioxide is also non-toxic and mimics the carbon dioxide equilibrium present in natural lakes.

2.4.2 Changing the Water Layer Composition

The source water of BML is both OSPW and fresh water from BCR. OSPW is high in ionic strength (30 mmol/L) and sodium concentration (700-800 mg/L) and BCR is low in ionic strength (7 mmol/L) and sodium concentration (33 mg/L). OSPW and BML have about the same concentration of divalent cations (100 mg/L calcium and 10 mg/L magnesium). It is hypothesized that higher ionic strength of OSPW helps to increase settling. In addition, the lower sodium concentration of natural waters will help to exchange some sodium ions on clay particles with divalent ions. The effect of both ionic strength and cation exchange will be studied together by varying the water composition of OSPW and BCR in this thesis.

Sutherland et al. (2015) experimented with salt concentrations and found that high ionic concentrations increased settling significantly. In fresh water, clay particles settled 5 cm in about 6.5 hours. In contrast, settling in solution with 11 g NaCl added (ionic strength approximately 190 mmol/L), clay settled 5 cm in 15 min. Sutherland et al. (2015)

Lower sodium concentrations in the water layer should lead to increased divalent cations on the clay surface as sodium is exchanged from the clay surface to keep equilibrium. Addition of divalent cations is used in water treatment where calcium is used to increase settling (Chen et al. 2013). In FFT, addition of CaO at 2 g/L at 70 °C dewatered the FFT by half in two hours (Chalaturnyk et al. 2002). Addition of $Ca(OH)_2$ and CO_2 combined led to 70% dewatering of tailings in 50 hours (60% without CO_2 addition) (Chalaturnyk et al. 2002).

2.5 Summary of Literature Review

Remediation in the oil sands is complex and no optimal solution has been found yet for the remediation and storage of FFT and OSPW. Research continues with many strategies, including EPLs. The EPL remediation strategy derives from a similar strategy in other mining activities called pit lakes. Pit lakes have long been used in mining various commodities . Now, using some information from small test ponds, BML has been established as the first commercial demonstration EPL in oil sands. The development of a healthy aquatic ecosystem in and EPL depends to some degree on the remediation of OSPW by various in-situ processes. .

BML exhibits high turbidity and low water clarity since commissioning. High turbidity inhibits the formation of a healthy aquatic ecosystem because it limits the formation of a littoral zone in the EPL. The littoral zone drives the production of dissolved oxygen, stabilizes soil making it vital to the health of an aquatic ecosystem. Increasing water clarity can be achieved through increasing settling of clay particles. Due to surface charges, clay particles do not flocculate well. Neutralising the surface charges through pH adjustment or increasing divalent cations and ionic strength promotes flocculation and settling.

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CHAPTER 3: LARGE COLUMN EXPERIMENTS[1]

3.1 Introduction

The third largest proven reserve of crude oil in the world is in Alberta, most of which is contained in the oil sands (Stringham 2012). The Alberta oil sands deposits are found in three main regions: Cold Lake, Fort McMurray and Peace River (Alberta Energy Regulator 2014). Oil sands consist of a mixture of bitumen, water and sand or clay and were first commercially developed in Alberta in 1967 (Humphries 2009). Compared to conventional crude oil, additional upgrading and extraction techniques are used in the recovery of oil from the oil sands, requiring specialized equipment and techniques (Humphries 2009).

Because of historically high oil prices and advances in technology, Alberta has seen rapid expansion in the oil sands industry in the past decade (Humphries 2009). This expansion has driven the economy, but also created a number of issues. Currently, one of the major issues in the oil sands industry is the storage and remediation of by-products produced during the extraction process. Two major streams of by-products produced in the extraction of bitumen are oil sands process-affected water (OSPW) and fluid fine tailings (FFT). OSPW contains many inorganic (sodium, chloride and sulfate) and organic compounds (naphthenic acids, benzene, toluene and polycyclic aromatic hydrocarbons) (Small et al. 2015). OSPW has been shown to be toxic, with the toxicity mostly attributed to the naphthenic acids (Garcia-Garcia et al. 2011; Morandi et al. 2015; Toor 2012). FFT contains fine clay and silt particles, which form a stable colloidal suspension that takes an extremely long time to dewater. Also included in FFT is bitumen not recovered in operational processes, and some solvent used in recovery of the bitumen from oil sands (Siddique et al. 2014). The solids content in FFT is typically 10-20%w/w directly after disposal with settlement increasing solids content to ~30%w/w in 2-4 years (Chalaturnyk et al. 2002). It takes decades for the solids content to reach >60%w/w (Chalaturnyk et al. 2002). Increased settlement leads to decreased storage needs and increased water recycling.

Traditionally, tailings ponds are used for FFT settling and water recovery for reuse in oil sands operations (Chen et al. 2013; Mikula 2013). More recently, less time-consuming techniques have been investigated such as centrifugation, thin-lift dewatering, rim ditching, consolidated tailings and thickener technology (Mikula 2013; Kasperski and Mikula 2013; Read 2014). In addition, end pit lakes (EPLs) have been researched to both store and

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[1] All work completed in chapter by Jordan Brandon except 60% OSPW (Control) with testing completed by Xiaoxuan (Lily) Yu

remediate OSPW and FFT (Read 2014). EPLs are an attractive option because they address the need for storage and remediation and do not require chemical or polymer additives, unlike the previous techniques listed (Read 2014). EPLs consist of a bottom layer of FFT and a top layer of water. The water layer can be OSPW, fresh water or a combination of both. The water layer provides the habitat for a healthy aquatic ecosystem while the FFT is allowed to naturally dewater over time (McKenna and Hrynyshyn 2012). The main objectives of an EPL are to store and remediate tailings and OSPW to form a healthy ecosystem. In order for EPLs to succeed as a remediation tool, it is essential that the water cap sustain a healthy aquatic ecosystem.

The health of an aquatic ecosystem is determined by many factors including dissolved oxygen concentration, toxicity, nutrients present and the littoral zone of the lake (Charette and Mooder 2012). The littoral zone is defined as the area where plants are present, from the shoreline to the deepest part of the lake where sunlight can still penetrate to the bottom of the lake (Charette and Mooder 2012). Ideally sunlight penetration is 2-3 m for a healthy littoral zone (Charette and Mooder 2012). The littoral zone is important because it contains the highest biodiversity in the lake and the plants in the littoral zone help to regulate dissolved oxygen, stabilize bottom sediment and provide food for animals in the lake (Charette and Mooder 2012).

Syncrude pioneered research on the use of EPLs starting in the 1980s with the construction of small ponds testing the effect of FFT storage with different OSPW:fresh water ratios in the water layer (MacKinnon and Boerger 1991; Read 2014). Their research indicated that aquatic ecosystems formed in the ponds after one year with increased microbial activity in both the water layer and FFT (MacKinnon and Boerger 1991). The water fractions showed dissolved oxygen levels between 7 and 9 mg/L and plant growth in the littoral zone of the pits (MacKinnon and Boerger 1991). These positive results, although on a small scale led to the Alberta government's approval of the construction of a full size EPL by Syncrude called Base Mine Lake (BML) (Read 2014). BML opened in late 2012 and is rigorously monitored to see if EPLs are a feasible remediation option for the oil sands industry. More EPLs will be approved pending a successful demonstration in BML (McKenna and Hrynyshyn 2012). BML contains FFT from Syncrude operations and the water layer was initially comprised of only OSPW with fresh water from the Beaver Creek Reservoir (BCR) added over time until a desirable water depth was achieved (exact depth to be determined pending monitoring of BML).

Initial measurements at BML indicate that high turbidity of the water layer is a concern and sunlight penetration is very low. Fine particles in the FFT and OSPW are often suspended, increasing turbidity and decreasing sunlight penetration (Oil Sands Tailings Consortium 2012). These suspended particles are often clay particles. High turbidity in the water cap is of particular concern because of the effect it has on the formation of the littoral zone in an EPL. There are a number of different ways to reduce turbidity. In water treatment, aluminum sulfate, polyaluminum chloride, ferric chloride, ferric sulfate and polyacrylamide-based polyelectrolytes are often used as coagulation/flocculation agents that help small particles form flocs and settle out, reducing turbidity (White et al. 2011). Rhoton and Bigham (2009) used natural ferrihydrite to promote flocculation of clay and silt from the Mississippi delta. They found that turbidity was significantly reduced (percent transmittance increased by as much as 15% compared to control) within 24 hours of addition of 10 mg/L, 25 mg/L and 50 mg/L ferrihydrite (Rhoton and Bigham 2009). In addition, pH was found to affect turbidity with pH 5 showing the best results (highest percent transmittance: 83.5%) and pH 6 and 7 showing increased turbidity (79% and 69% respectively) (Rhoton and Bigham 2009). At pH 8, the control samples showed highest transmittance (45%) (Rhoton and Bigham 2009). Other aluminum and iron flocculants used in water treatment have also been used in lake settings (Özkundakei and Hamilton 2006). These studies showed a dependence on pH for flocculation and are consistent with our understanding of the characteristics of clay particles in suspension (Hogg 2000).

Because pH dependence is shown in almost all studies on clay flocculation, in this study pH adjustment is proposed to reduce turbidity in BML. Lowering the pH of the water alters the surface charges of the suspended particles and promotes edge-to-edge flocculation (Proskin et al. 2012). Flocculation of particles increases the size of the particles and their settling rate. One method found to be effective for lowering pH is the addition of carbon dioxide (CO_2). This method is preferable to other methods because CO_2 is a natural part of the lake pH regulation system (through the bicarbonate equilibrium system) and CO_2 supersaturation occurs in nature (Lazzarino et al. 2009). Using CO_2, the effect on the ecosystem is thought to be minimized while still being effective in reducing turbidity. The following experiments attempt to validate the theory that pH adjustment is a feasible method for mitigating high turbidity in EPLs; in particular, whether CO_2 addition can sufficiently lower the pH of the aquatic system to improve sunlight penetration. From these previous studies, we expect that CO_2 addition will lower the pH and that this reduction is sufficient to increase water clarity in BML water.

3.2 Materials and Methods

Four large scale column tests were performed with different water compositions as summarized in Table 3.1. The water compositions varied for the different experiments and were chosen to mimic the water composition of BML over time where fresh water is added over time diluting the OSPW. Two sources of water, provided by Syncrude, were used in this experiment: BML water collected in 2013 containing approximately 90% OSPW and 10% fresh water and Beaver Creek Reservoir water (BCR), the fresh water source for BML collected in 2013 and 2014. The 80% OSPW treatment was completed as a preliminary experiment to test the feasibility of dropping the water pH (using CO_2 and HCl) with a subsequent reduction in turbidity. Since these results were favorable (discussed in Section 3.3.3) a more thorough experimental set-up was completed as outlined in Table 3.1.

Table 3.1: Experimental treatments and their water composition based on % volume

	Composition (%)	
Treatment	OSPW	BCR
80% OSPW[a]	81	19
60% OSPW	60	40
60% OSPW (Control)[b]	60	40
20% OSPW	20	80

[a] Preliminary treatment to test the feasibility of the idea.

[b] 60% OSPW (Control) treatment has no CO_2 addition.

3.2.1 Column Set-up

Two Townsend acrylic columns were constructed at 2.5 m tall, 0.305 m diameter and 0.635 cm wall thickness (shown in Figure 3.1). Ten sampling ports were installed, two each at heights of 0.40, 0.80, 1.20, 1.60 and 2.00 m, controlled by Swagelok SS Quarter-Turn Instrument Plugs, model SS-4P6T4. To stabilize the columns a wood and metal base support was constructed. A Globe Workshop halogen work light (250 Watts, model no. 60568) was fixed above each column facing downward and the sides of the columns were covered with a curtain (Suede Image Curtain with Grommets, 140 x 245 cm, 100% polyester). An effort was made to center the lights and face them straight down the columns but the lights could not be set up in an identical fashion. Reporting of relative light intensity minimizes the direct impact of non-identical set ups.

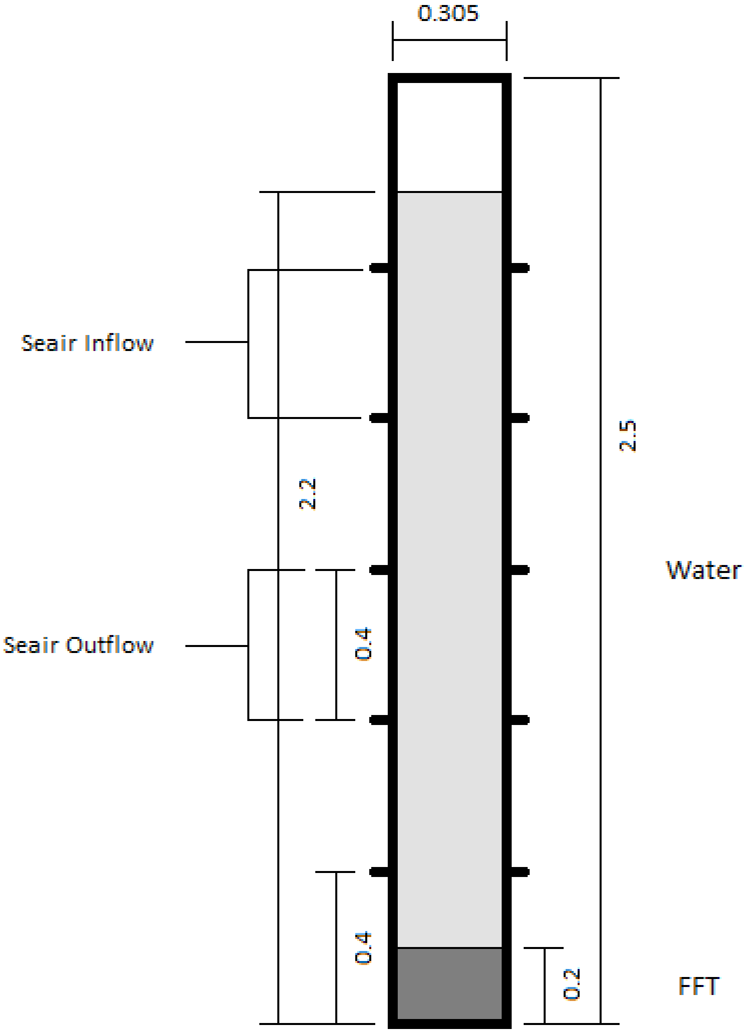

Figure 3.1: Diagram of column dimensions (all dimensions in m).

Using a funnel and tubing, FFT was added to the bottom of the columns to a height of approximately 0.20 m. The water layer was then gently added using a variable peristaltic pump to minimize mixing of the FFT and water layers. The water layer depth was initially just over 2 m for a total depth of just over 2.2 m. The 80% and 60% OSPW treatments were left open to simulate lake conditions during the entire experiment and 48 days, respectively. However, evaporation loss was significant as shown in Table 3.2 thus the 60% OSPW column was covered after 48 days resulting in decreased evaporation. The 60% OSPW (Control) and 20% OSPW treatments were covered during the entire experiment except during sample analysis. 22 L of BCR was added to 60% OSPW on day 48 to compensate for the water lost due to evaporation. The headspace in 60% OSPW, 60% OSPW (Control) and 20% OSPW was approximately 22 L when covered. 750 mL of FFT was added to 60% OSPW, 60% OSPW (Control) and 20% OSPW to increase turbidity to closer represent field turbidity values of 200 to 400 NTU; no additional turbidity was added to the 80% treatment.

Table 3.2: Evaporation losses and rates comparing covered and uncovered columns.

Treatment	Evaporation Loss (L)	Time Period (Days)	Evaporation Rate (L/day)
80% OSPW (Uncovered)	8.0	34	0.24
60% OSPW (Uncovered)	7.1	48	0.17
60% OSPW (Covered)	1.3	62	0.01
60% OSPW (Control) (Covered)	1.9	94	0.02
20% OSPW (Covered)	2.5	153	0.02

3.2.2 Secchi Depth

The Secchi disk used in this experiment is a 20 cm diameter disk with a black and white pattern (Science First 78-010 Fieldmaster Secchi disk) shown in Figure 3.2a. Secchi depths were measured with an opaque curtain covering the side of the column and by the same person throughout the experiment for consistency. Deeper Secchi depths indicate higher water clarity as shown in Figure 3.2b. Secchi depth is a field measurement used by Syncrude in BML making comparisons easier between field and lab data.

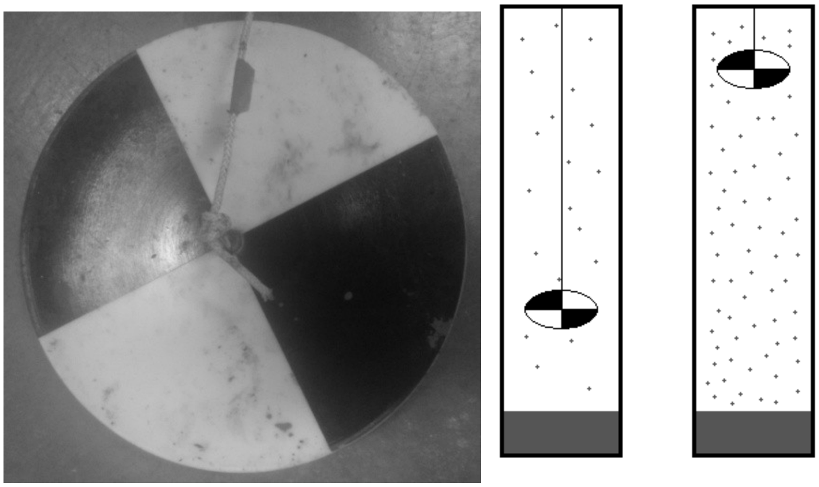

Figure 3.2a and b: (a) A Secchi disk with nylon lowering rope attached used to determine Secchi depth. (b) Representation of Secchi depth in low turbidity (left) and high turbidity (right). Deeper Secchi depths indicate higher water clarity.

3.2.3 Light Intensity

Light intensity was measured at the surface of the water and various depths, including the Secchi depth. Measurements were performed using a LI-COR LI-192SA Underwater Quantum Sensor (pointed towards the surface) mounted on a modified lowering frame and read by a LI-1400 datalogger (Figure 3.3). This sensor records light intensity in the photosynthetically active radiation range of wavelengths 400 to 700 nm (Li-COR 2006; Alados and Alados-Arboledas 1998). Light intensity measurements were recorded with an opaque curtain covering the side of the column to ensure that light measured was entering the column from the surface only. Light intensity is a relative measurement comparing the light intensity at a given depth to the light intensity at the surface. The light penetration depth is considered to be the depth at which the light intensity is 1% of the surface light intensity (Luhtala and Tolvanen 2013).

Figure 3.3: LI-COR light sensor set in a modified lowering frame and datalogger used for measuring light intensity.

The relationship between Secchi depth and light intensity is complicated and varied for different waters, but the accepted approximations are that (1) Secchi depth occurs at 10% of surface light intensity and (2) sunlight penetration depth is twice Secchi depth (Aas et al. 2014).

3.2.4 Water Characterization

General water parameters were tested at the start of the experiment and every 1-2 weeks, with later measurements taken at increasing time intervals to not lower water amounts significantly and to minimise disturbance of the water in the column. Samples were taken at each sampling port depth (5 samples for each sampling point) and the results were averaged unless stated otherwise. General parameters recorded include pH, conductivity, alkalinity, dissolved oxygen and turbidity. Certain water parameters were conducted at different intervals including total dissolved solids (TDS), total suspended solids (TSS), naphthenic acid concentrations, total organic carbon and dissolved organic carbon. Anions and cations were also tested for the samples taken following procedures listed in Abolfazlzadehdoshanbehbazari et al. (2013). HCO_3^- concentrations were calculated based on the measured alkalinity. An Accumet AR50 Dual Channel pH/Ion/Conductivity meter was used to measure pH while an Exstik II EC500 portable meter was used to measure conductivity. Alkalinity was measured using an automatic titrator and 0.02 N sulfuric acid and dissolved oxygen was measured using an YSI Incorporated Model 50B DO meter and checked using Winkler titration modified for smaller sample volumes (ISO 5813-1983, 1983). Turbidity was measured after five seconds in an Orbecco-Hellige Digital Direct-Reading Turbimeter. Following ASTM standard D5907 (2013), TDS and TSS were measured with overnight drying. Naphthenic acid concentrations were determined using GC-FID and procedures listed in Miles et al. (2014). Dissolved organic carbon and total organic carbon were measured using a Shimadzu Model TOC-L with an ASI-L Shimadzu autosampler.

3.2.5 FFT Characterization

FFT was characterized at the start of the experiment. Parameters tested include Zeta potential, water/solids content, methylene blue index (MBI), pH and particle size distribution. Zeta potential was measured using a Malvern Zetasizer Nano ZSP and folded capillary cells DTS1070 at 25°C using electrophoretic light scattering. Water/solids content was determined following procedures listed in ASTM Standard D5907 (2013). Kaminsky (2014) lays out the CONRAD method for MBI determination. Particle size distribution was determined using a 152H hydrometer and procedures in ASTM D422 (2007). A sample of settled solids was taken in situ at the end of the 60% OSPW and 20% OSPW using 50 mL centrifuge containers. The samples were spun at 1500 rpm for 5 minutes, the excess water drained and frozen at -80 °C until DNA analysis could be performed. Microbial quantification was performed using qPCR procedures listed in Brown et al. (2013) with 35 cycles.

3.2.6 CO_2 Addition

CO_2 (PRAXAIR, 99.9% purity) addition was achieved through different methods. CO_2 addition for 80% OSPW was achieved initially by bubbling through a 4 mm Seal Plastics polyethylene tube (44D-1/4 OD) and, later, through a sparger (Corning, 39533-12C, pore size 40-60 μm). Initial flow measured by a flow meter (Dwyer Cat. No. VFA-22) was 0.1 to

0.3 L/min with the CO_2 released 0.14 m above the water/FFT interface. The release point for the CO_2 was raised to 1 m above the water/FFT interface, in order to prevent disturbance of FFT with the 0.3 L/min flow rate. A sparger was introduced to increase dissolution of the CO_2, lowering the release point to 0.9 m above the FFT. With the addition of the sparger the flow rate was increased to 1 L/min.

CO_2 addition to the 60% OSPW and 20% OSPW treatments were achieved through the use of Seair microbubbling technology. Seair microbubbling was used to increase dissolution of the CO_2 into the water layer, resulting in a faster pH drop and a lower stable pH. Three external stacked units were connected to the sampling ports. Water was taken from the column through the 4 highest sampling ports (2 each at 1.40 m and 1.80 m above the water/FFT interface) pumped through the Seair system and returned to the sampling ports at 0.60 m and 1.00 m above the water/FFT interface. Gas flow rate through the system was approximately 4 L/min. As discussed in the results, the pH for 60% OSPW rose necessitating follow up CO_2 addition on day 48 with BCR water added to make up for evaporation loss (as mentioned in Section 3.2.1).

3.2.7 HCl Addition, 80% OSPW treatment only

After nine days of CO_2 addition, HCl was added to the top of the water layer in 80% OSPW while CO_2 addition with the sparger was used to mix the HCl and water. Day 0 is considered the end of the CO_2 phase and the start of HCl addition. The equivalent of 165 mL of 12 N HCl was added between day 0 and day 28 as shown in Table 3.3.

Table 3.3: Summary of HCl addition for 80% OSPW.

Day	HCl added (mL)	Concentration (N)	Equivalent 12N volume (mL)
0	71	0.1	0.6
1	83	6	41.5
2	105	12	105
5	2	6	1
9	2	6	1
12	5	6	2.5
16	5.5	12	5.5
26	4	12	4
28	7	6	3.5
Total			**164.6**

3.3 Results and Discussion

3.3.1 Water Composition in BML

Different water compositions were chosen for these experiments based on the projected compositions for BML. BML initially contained 100% OSPW from Syncrude operations with only BCR added over time. Performing experiments on decreasing OSPW fractions mimics the projected trend in BML. Rough preliminary calculations indicate 80% OSPW, 60% OSPW and 20% OSPW might occur in 2014, 2015 and 2017, respectively.

3.3.2 Initial Water and FFT Characterization

Initial water quality parameters, porewater ions and FFT characterization are shown in Table 3.4, Table 3.5 and Table 3.6, respectively and the particle size analysis is shown in Figure 3.4. The initial water parameters follow expected downward trends in conductivity, alkalinity and TDS with decreasing OSPW percentages. Initial turbidity values show highest turbidity in 60% OSPW and lowest in 80% OSPW which can be explained by the addition of turbidity to the 60% OSPW, 60% OSPW (Control) and 20% OSPW. Additional turbidity was added to 60% OSPW, 60% OSPW (Control) and 20% OSPW to better mimic the field turbidity measured (200-300 NTU). TSS values are shown but experimental data displayed great variability throughout the experiment and some negative values were recorded for some visibly saturated filters.

Table 3.4: Initial water parameters for experiments performed with one standard deviation shown.

Parameter	80% OSPW	60% OSPW	60% OSPW (Control)	20% OSPW
pH	7.92 ± 0.02	8.26 ± 0.07	7.85 ± 0.06	8.03 ± 0.04
Conductivity (mS/cm)	2.92 ± 0.08	2.12 ± 0.03	2.29 ± 0.06	1.05 ± 0.04
Turbidity (NTU)	88 ± 9	299 ± 9	301 ± 17	208 ± 12
Alkalinity (mg $CaCO_3$/L)	588 ± 5	561 ± 7	468 ± 10	267 ± 4
TSS (mg/L)	29 ± 6	384 ± 145	-	422 ± 43
TDS (mg/L)	1940 ± 60	1818 ± 101	-	985 ± 106
Cl^- (mg/L)	-	396 ± 16	337 ± 3	143 ± 1
SO_4^{2-} (mg/L)	-	203 ± 1	185 ± 2	51 ± 1
Na^+ (mg/L)	-	574 ± 10	523 ± 38	210 ± 38

Parameter	**80% OSPW**	**60% OSPW**	**60% OSPW (Control)**	**20% OSPW**
Mg^{2+} (mg/L)	-	13.9 ± 0.3	11 ± 1	10 ± 2
K^+ (mg/L)	-	14 ± 3	10 ± 1	15 ± 3
Ca^{2+} (mg/L)	-	29 ± 1	24 ± 3	34 ± 7
Total Organic Carbon (mg/L)	-	-	37.6 ± 2.3	35.0 ± 1.3
Dissolved Organic Carbon (mg/L)	-	41.7 ± 3.0	38.5 ± 1.6	28.5 ± 1.6
Naphthenic Acids (mg/L)	53.2 ± 4.3	33.1 ± 3.5	32.2 ± 2.0	12.2 ± 1.5

Table 3.5: Initial porewater anions and cations with one standard deviation shown.

Cl^- (mg/L)	**1296 ± 10**
SO_4^{2-} (mg/L)	**354 ± 4**
Na^+ (mg/L)	**1118 ± 135**
Mg^{2+} (mg/L)	**24 ± 2**
K^+ (mg/L)	**10 ± 2**
Ca^{2+} (mg/L)	**15 ± 1**

Table 3.6: Initial FFT parameters for experiments performed with one standard deviation shown.

MBI (meq/100g)	3 ± 2
Solids Content (% by mass)	37 ± 7
Zeta potential (mV)	-28 ± 2
Microbial quantity (rpoB gene copy number/mL) (35 cycles)	$3.92 * 10^3$

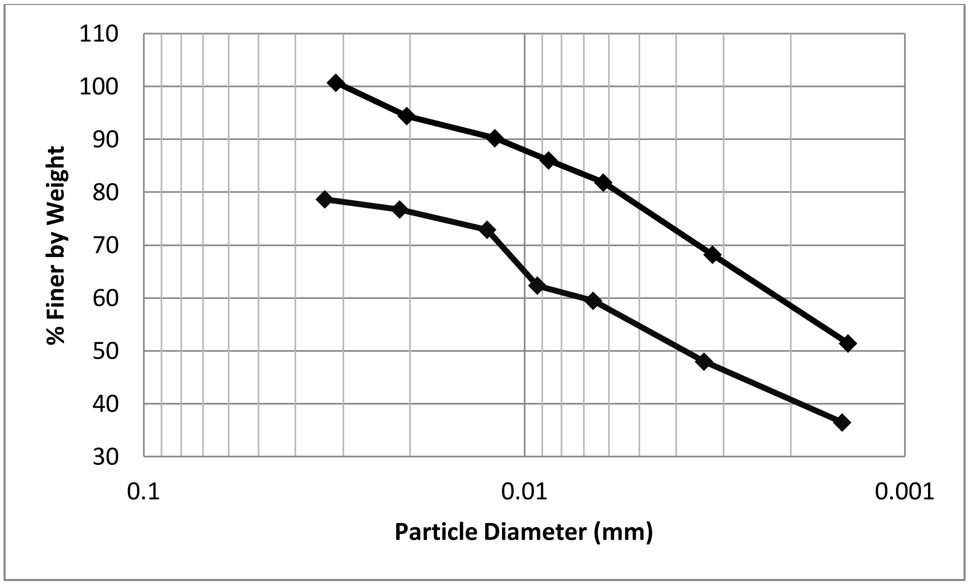

Figure 3.4: Particle size distribution of two samples of FFT.

Initial FFT analysis shows the FFT used in this experiment is within the ranges reported for typical FFT. Osacky et al. (2014) reports the MBI of the original (before processing) bulk materials to be 0.7-7.2 meq/100 g. Kaminsky et al. (2009) and Hooshiar et al. (2010) report MBIs of 9 meq/100 g (particle size 0.2 μm - 2 μm) and 38 meq/100 g (particle size <0.2 μm) for tailings material with no bulk MBI reported. FFT used in this experiment is within the MBI range of the original bulk material.

The solids content of the FFT indicates it is likely 5-6 years based on typical solids content ranges provided by Siddique et al. (2014) and Chalaturnyk et al. (2002): 10-20%w/w initially and ~30%w/w in 2-4 years. FFT used in this experiment is at least 2 years old, up to 15 years. The estimate of 5-6 years based on solids content falls well within this range.

Zeta potential was measured to find the stability of FFT particles. Moayedi et al. (2013) reports that -30 mV is the boundary between stable and unstable clay particles in suspension (<-30 mV being stable, -30 mV to 30 mV being unstable). The FFT used in this experiment is close to the boundary and more susceptible to changing conditions such as pH and ionic concentrations that influence their settling behavior (Saka and Güller 2006).

The particle size analysis shows two samples of FFT. Data reported by Sorta (2015) of different FFT samples taken from Albian Sands Energy Inc. and Syncrude show that our data falls within the ranges measured by Sorta. Dompierre et al. (2016) gives an overall guideline of typical FFT: at least 90%w/w finer than 0.044 mm and 30% finer than 0.002

mm. Using this guideline, the FFT used in this experiment is finer than typical FFT with ranges of 80-100%w/w finer than 0.044 mm and 40-60%w/w finer than 0.002 mm. In oil sands, "fines" are usually used to describe material with particles sizes equal to and smaller than 0.044 mm. These fines are more susceptible to suspension and creating turbidity in water bodies such as EPLs. As indicated, 80-100%w/w of FFT used in this experiment is defined as fines that may degrade water clarity.

3.3.3 80% OSPW: Relationship Between pH and Water Clarity

The 80% OSPW treatment was a preliminary test to determine if a reduction in pH results in an improvement of water clarity. Water clarity was tracked using Secchi depth. No improvement in water clarity was seen in the first nine days (day -9 to day 0) of 80% OSPW with the intermittent addition of 500 L CO_2 as shown in Figure 3.5. During this time period, the lowest pH achieved was 5.97 and pH stabilized after about 2.2 days. The Secchi depth did not significantly change (0.18 – 0.19 m). CO_2 was used as an additive because it is part of the carbonate buffering system that is present in natural waters. Using carbonate equilibrium constants of $pK_H = 1.47$, $pK_1 = 6.35$, $pK_2 = 10.33$ and $pK_w = 14.00$ at 25°C (Lower 2014) and $4*10^{-4}$ atm of CO_2 partial pressure (Tans and Keeling 2015), CO_2 influence alone would lead to a pH of 5.61 in pure water. To explore the relationship between pH and water clarity further, HCl was added to the 80% OSPW treatment to further reduce the pH. HCl addition reduced pH to a low of 3.53 on day 19.

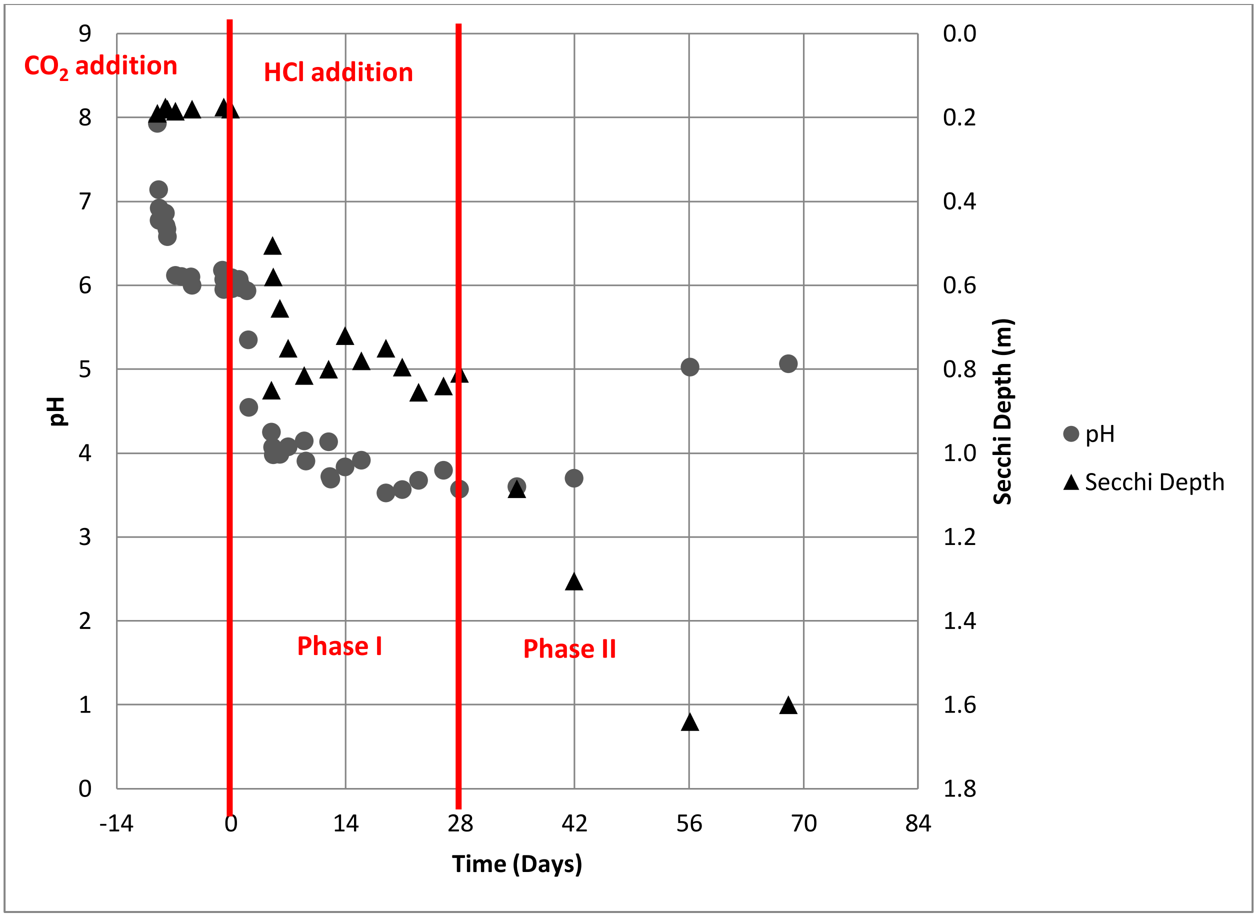

Figure 3.5: 80% OSPW with both CO_2 addition (days -9 to 0) and HCl addition (day 0 to 28). Secchi depth did not show improvement during CO_2 addition but increased in response to HCl addition and stabilized between day 9 and day 28 around 0.80 m (Phase I). Between day 28 and day 56, Secchi depth increased from 0.80 m to 1.64 m with pH increasing from 3.57 to 5.03 (Phase II). pH is shown on the left axis and Secchi depth on the right with the axis inverted.

Secchi depth showed an initial increase from 0.19 m to approximately 0.80 m after HCl addition and stabilized there until day 28 (Phase I in Figure 3.5). In Phase I, pH decreased from 6 to 3.5-4 and stabilized at this range until day 42. In Phase II (day 28 onwards), Secchi depth improved from 0.80 m to 1.64 m (day 56) while pH increased from 3.57 to 5.04 (day 56) showing the opposite behavior from Phase I. No additional HCl was added during Phase II. This secondary improvement of Secchi depth after stabilization was unexpected and may be related to the scale of the experiment. Najafi et al. (2013) and Zhu et al. (2011) experimented with CO_2 addition to FFT at vastly different scales and found the response times to vary as well. Zhu et al. (2011) added CO_2 to 100 mL columns of FFT using an autoclave and 100 kPa pressure of CO_2. The pH was dropped from 8.4 to 5.8 for Syncrude tailings and 8.2 to 6.2 for Canadian Natural Resources Ltd. (CNRL) tailings. In six hours, the expressed porewater turbidity was dropped from 850 NTU to 200 NTU for Syncrude tailings and 825 NTU to 750 NTU for CNRL tailings. In 24 hours, the standardized FFT/water interface for Syncrude tailings for CO_2 treated FFT dropped to 0.52, compared to 0.90 for untreated FFT. CNRL tailings showed an interface drop to 0.69 and 0.95, respectively. Zhu et al. (2011) used the standardized interface to report all their findings which allows comparisons of similar experiments with slightly different interface heights but makes comparisons between experiments of different scales extremely hard. Najafi et al. (2013) added CO_2 directly to FFT going into the external tailings facility at CNRL, which contains 8-10 m of FFT and is a field scale operation. CO_2 was added starting in October 2009 at which time expressed porewater from the FFT had a TSS of 15,000 mg/L. During the addition of CO_2, TSS values initially increased to 21,000 mg/L and then dropped off to 4000 mg/L in two months and <500 mg/L in five months. The different scales of these experiments may have an effect on the time period until improvement is seen and may also play a role in our experiments. In addition, both Zhu et al. (2011) and Najafi et al. (2013) added CO_2 directly to FFT while our experiments added FFT to the water layer, making direct comparisons difficult.

To better explore the lag period in our experiments and to identify the behavior of BML over time, 60% OSPW, 60% OSPW (Control) and 20% OSPW treatments were set up with water compositions to mimic those in BML in the future.

3.3.4 Buffering Capacity

80% OSPW, 60% OSPW and 20% OSPW show that CO_2 addition can lower pH to around 6. To get to ph 6, 500 L of CO_2 was added to 80% OSPW through an open tube and sparger and 4000 L and 1000 L were added through Seair microbubbling to 60% OSPW and 20% OSPW, respectively. Figure 3.5 shows the lowering of pH in 80% OSPW as well as the increase in pH after HCl addition from 3.5 to 5. 80% OSPW showed there is a significant buffering capacity in the BML cap water with 500 L of CO_2 needed to lower the pH to 6 and the equivalent of 165 mL of 12 N HCl needed to lower the pH further to 3.5 (Figure 3.5). The pH then rebounded to 5 on day 56 showing more buffering capacity in the water, either from the FFT or the CO_2 in the atmosphere. The 60% OSPW treatment needed 4000 L of CO_2 to lower the pH to 5.9, due to higher flow rates of the Seair system compared to a sparger. After CO_2 addition was halted, 60% OSPW showed an increase in pH (Figure 3.6a). The pH steadily increased to 7.4 on day 43 while alkalinity slightly increased as well from 561 mg $CaCO_3$/L to 591 mg $CaCO_3$/L on day 43 as shown in Figure 3.7. During this rise in pH, the columns were uncovered. The columns were then covered to limit the impact of evaporation. The covered water mixes (all of 20% OSPW and 60% OSPW after 48 days) showed small to no increase in pH. The 20% OSPW treatment showed a small but steady increase in alkalinity from 267 mg $CaCO_3$/L to 340 mg $CaCO_3$/L over 161 days. On day 48, CO_2 addition to the 60% OSPW treatment corresponded to a decrease in pH and alkalinity as clearly shown in Figures 3.6a and 3.7, respectively.

Using Seair microbubbling as opposed to a sparger in the 60% OSPW and 20% OSPW treatments resulted in a faster pH drop and lower resulting pH (6 (80% OSPW) vs. 5.9 (60% OSPW) vs. 5.8 (20% OSPW)), with 20% OSPW showing the fastest pH drop (24 hours (80% OSPW) vs. 16 hours (60% OSPW) vs. 5 hours (20% OSPW)) and the lowest pH (5.8) (not shown in Figure 3.6a). As expected, the 60% OSPW control treatment with no CO_2 addition maintained a consistent pH varying only between 7.7 and 8. It is unclear how much the water composition contributes to the rate of the pH drop and how this difference would affect any field application of this method, but it is clear that CO_2 addition can change the pH of the water layer, regardless of the water layer composition.

3.3.5 Turbidity

Turbidity fluctuations for the 60% OSPW with CO_2, 60% OSPW Control and 20% OSPW with CO_2 treatments are shown in Figure 3.6b. Turbidity readings steadily decreased over the duration of the experiment for the 60% OSPW treatment from 300 NTU on day 0 to 3 NTU on day 113. The 60% OSPW (Control) showed a quicker decrease in turbidity from 301 NTU on day 0, but then stabilized by day 87 at 70 NTU. The 20% OSPW treatment showed a decrease from 208 NTU on day 0 to the lowest turbidity measured at 55 NTU on day 133. Both 60% OSPW and 20% OSPW show increased turbidity 10-15 days after CO_2 addition. We are not sure about the cause of these increases. Some disturbance of the columns is inevitable while measuring Secchi depth but there was no unusual disturbance on these days. These experiments show that CO_2 addition does help to lower turbidity over time but also highlights the uncertainty in turbidity values. CO_2 addition did not show a significant change in total organic carbon, Dissolved Organic Carbon and naphthenic acid concentration in 60% OSPW or 20% OSPW (data not shown).

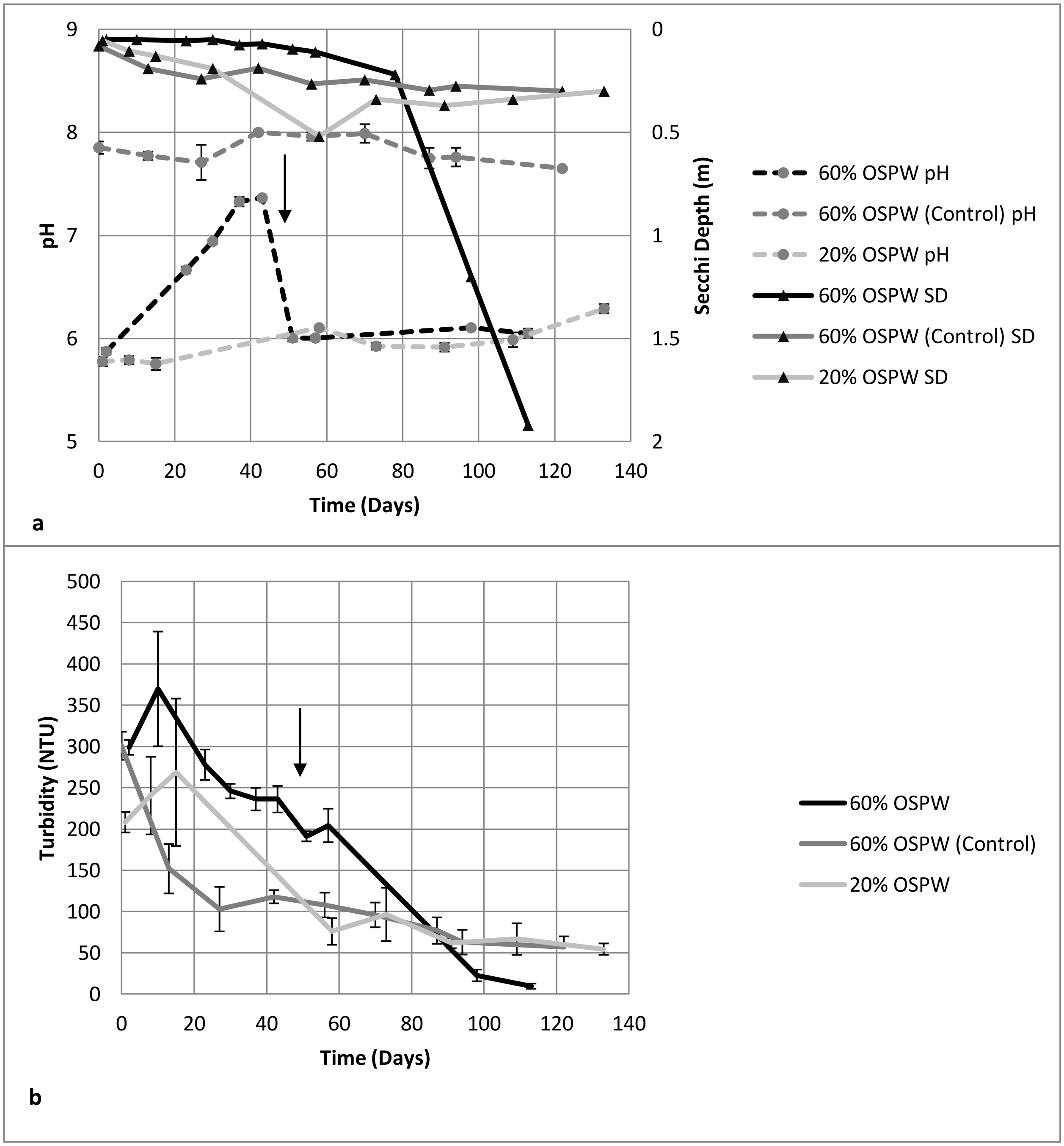

Figure 3.6 a and b: pH and Secchi depth (SD) over time for 60% OSPW with CO2, 60% OSPW (no CO2 addition) and 20% OSPW with CO_2 (6a) and turbidity over time (6b). pH is shown on the left axis and Secchi depth on the right axis with the axis inverted to show Secchi depth closer to how it is measured. Additional CO_2 was added to the 60% experiment on day 48 (indicated by the arrows) to lower the pH back to 6. Data points are an average of 5 and the deviation bars indicate one standard deviation for that sample.

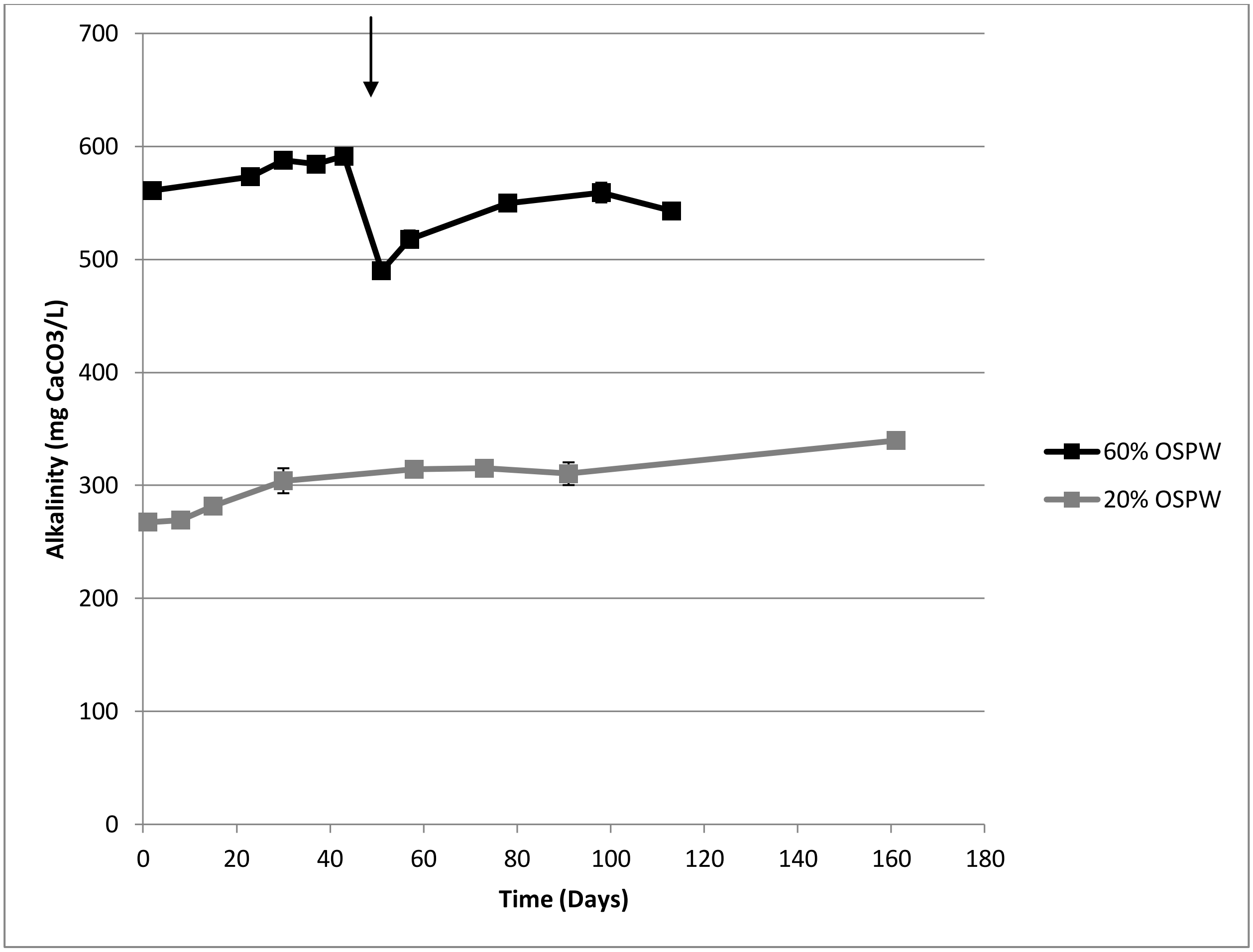

Figure 3.7: Alkalinity data for 60% OSPW and 20% OSPW with the secondary CO_2 addition shown by the arrow for 60% OSPW. No secondary CO_2 addition for 20% OSPW. The error bars indicate one standard deviation.

3.3.6 Water Clarity Lag Time

The 60% OSPW and 20% OSPW treatments showed little Secchi depth improvement in the first 30 days, similar to the 80% OSPW treatment as shown in Figure 3.6a. Initial Secchi depths were less than 0.05 m after turbidity addition. To achieve light penetration of 2 m, Secchi depth must be at least 1 m. The 60% OSPW treatment had a stable Secchi depth of around 0.05 m for 43 days, while the 20% OSPW treatment showed more variability with Secchi depths ranging from 0.10 m to 0.52 m for the duration of the experiment. The deepest Secchi depth reading for the 20% OSPW treatment occurred on day 58, 28 days after the previous reading. This may have influenced the reading as the other Secchi depths were recorded after 14 days usually. The lack of sampling, and associated water disturbance, may have contributed to a deeper Secchi depth reading. The 60% OSPW (Control) treatment showed a gradual increase in Secchi depth from 0.08 m to

0.30 m over 94 days, but this is still short of the target Secchi depth needed for the EPL to thrive. No significant improvement in Secchi depths was found in the 60% OSPW treatment until 98 days after CO_2 addition, at which point the depth increased dramatically, finally reaching 1.92 m after 113 days. This sudden increase after a significant lag period may reflect the same lag period found in 80% OSPW with HCl addition. The lag period in the 80% OSPW treatment was less than 30 days while the lag period in the 60% OSPW treatment was more than triple that time. The pH difference between these two water mixes and the pH adjustment method may account for the different lag periods, but it is important for future studies to note that the lag period is present in both water mixes. Any future water clarity experiments should be run for at least 3 months, depending on the size of the experiment to definitively say if there is water clarity improvement, and field application is unlikely to produce immediate results. The cause of the time lag is unclear but it could be the result of slow coagulation, flocculation and settling.

3.3.7 Ionic Concentrations

To gain a better understanding for the processes occurring in the 60% OSPW, 60% OSPW (Control) and 20% OSPW treatments major cations and anions were monitored over time (shown in Figure 3.8, Figure 3.9 and Figure 3.10 respectively). To control for the effects of evaporation the ion data was normalized with Cl^-, since it acts as a conservative tracer. Both water mixes showed increases in Na^+ and HCO_3^- concentrations over the course of the experiment. The 60% OSPW treatment showed a slight increase in Mg^{2+} and Ca^{2+} concentrations, a slight decrease in K^+ concentration and a decrease in SO_4^{2-} concentration. The 20% OSPW treatment showed slight increases in Mg^{2+} and SO_4^{2-} concentrations and slight decreases in K^+ and Ca^{2+} concentrations. Based on these observations three different mechanisms for the ionic behavior in both water mixes have been explored: (1) cation exchange on the clay particles, (2) diffusion from the underlying FFT and (3) dissolution and precipitation of $CaCO_3$.

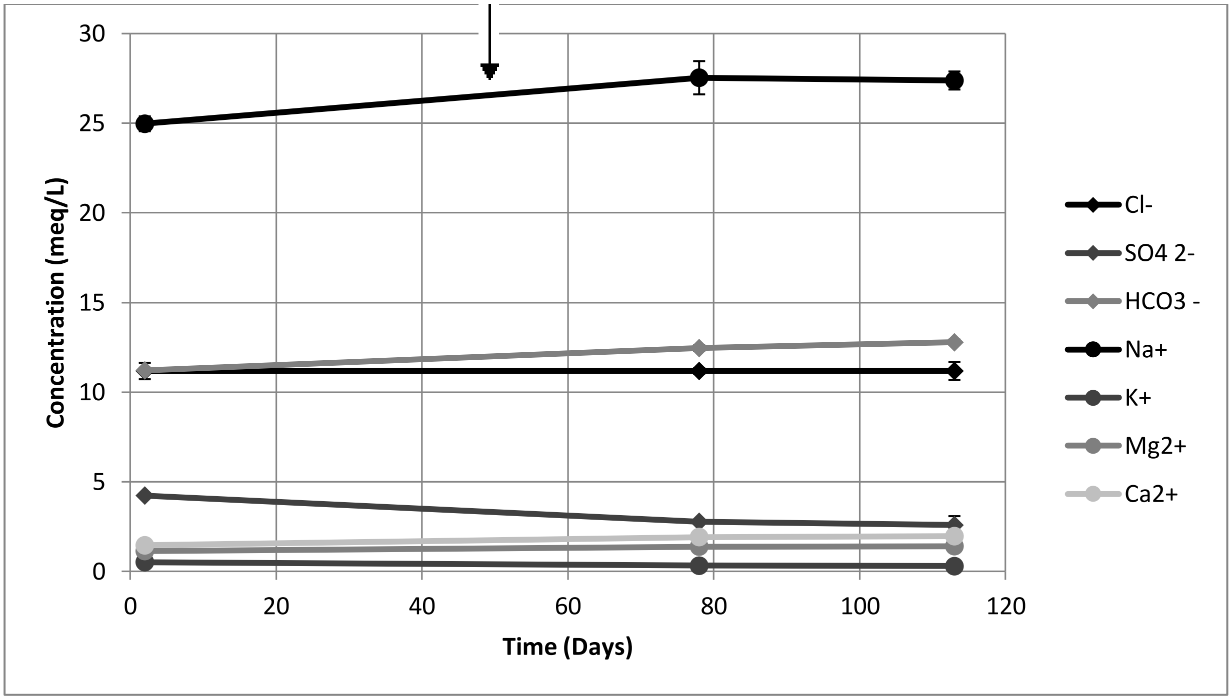

Figure 3.8: 60% OSPW treatment major cations and anions in the cap water layer normalized to Cl^- concentration. The column was filled with 22 L of BCR on day 48 as shown by the arrow. BCR water was added to compensate for water lost to evaporation. The error bars indicate one standard deviation.

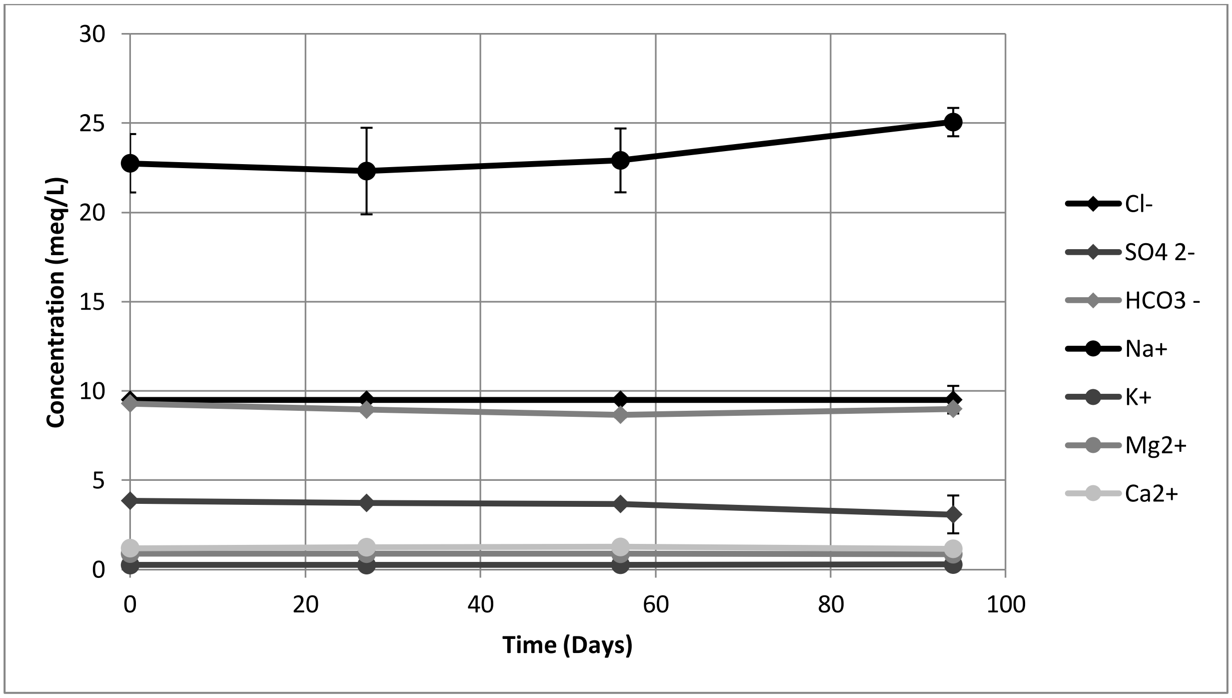

Figure 3.9: Figure 3.8: 60% OSPW (Control) treatment major cations and anions in the cap water layer normalized to Cl^- concentration. The error bars indicate one standard deviation.

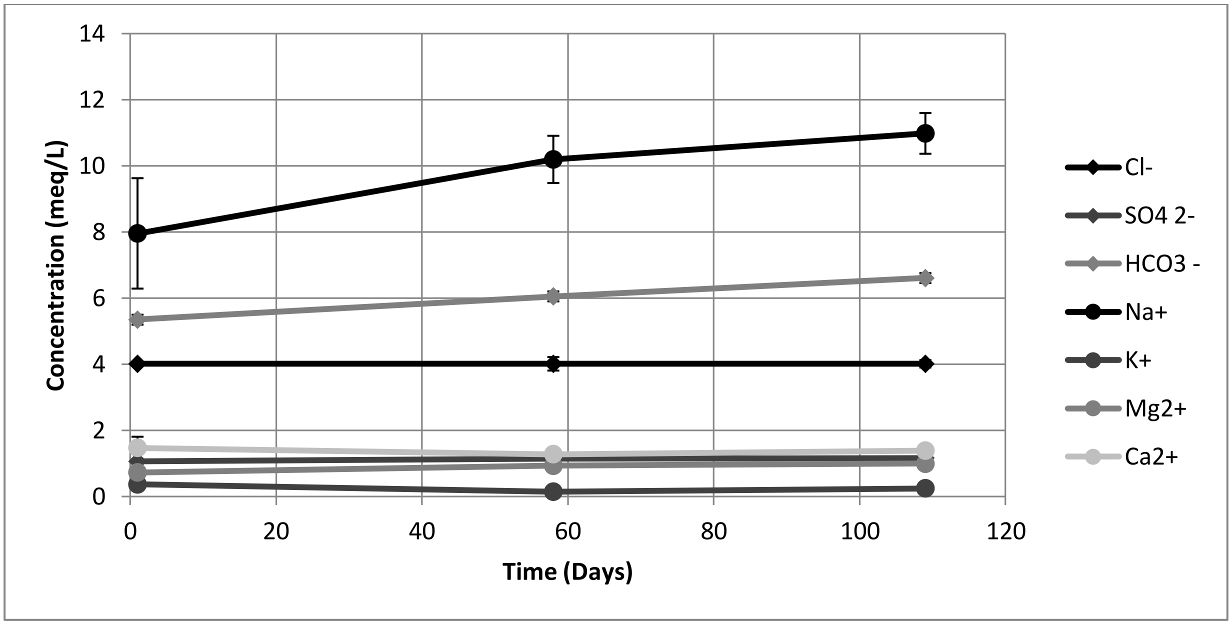

Figure 3.10: 20% OSPW treatment major cations and anions in the cap water layer normalized to Cl^- concentration. The error bars indicate one standard deviation.

Cation exchange on clay particles occurs based on cation preference and concentration in the bulk liquid as explored in Section 2.3.2. Cation preference for clay is K^+ > Ca^{2+}> Mg^{2+} > Na^+. The clay particles found in FFT are originally saturated with Na^+ since they have been in equilibrium with OSPW (Na^+ rich waters). As such, the presence of Ca^{2+}, Mg^{2+} or K^+, based on the order provided above, will preferentially exchange with the Na^+. Therefore, an increase in Na^+ concentration will be observed with a corresponding decrease in Ca^{2+}, Mg^{2+} and K^+. This is not observed for both the 60% OSPW and 20% OSPW treatments. Based on the measured data, it is unlikely that cation exchange is playing a dominant role at these cation concentration levels.

Diffusion of sodium ions from the underlying FFT layer into the water cap can partially explain the increase in Na^+ concentration over time. Initial porewater Na^+ concentration is 49 meq/L, which is much higher than the initial cap water layer concentration of 25 meq/L and 8 meq/L for 60% OSPW and 20% OSPW treatments, respectively. The final Na^+ concentrations measured in the cap water were 27 meq/L and 11 meq/L, for the 60% OSPW and 20% OSPW treatments respectively. Based on the FFT water content and the volumes of the FFT layer and cap water layer, and assuming Na^+ concentration equilibrium is reached between the FFT and water layers, diffusion alone accounts for 60-80% of the increase in Na^+ concentration. However, diffusion is a very slow process and it is unlikely equilibrium would have been reached during the course of this experiment. Some diffusion between FFT and the water layer is likely with other processes (such as water movement due to Secchi depth readings) transported Na^+ from the bottom of the water layer to the top.

Dissolution and precipitation of $CaCO_3$ was also looked at as possible drivers in ionic concentration change over time. Buhmann and Dreybrodt (1987) researched $CaCO_3$ dissolution and found calculated dissolution rates based on Ca^{2+}, $Mg^{2+}$and Na^+ concentrations. Based on 1.5 meq/L of Ca^{2+} and 1 meq/L of Mg^{2+}, the dissolution rate is calculated to be $2*10^{-7}$ meq/cm^2/s. Based on 1.5 meq/L of Ca^{2+} and 10 meq/L of Na^+ (highest concentration tested by Buhmann and Dreybrodt (1987)), the dissolution rate is calculated to be $2*10^{-7}$ meq/cm^2/s as well. This does not take into account the interaction of all species, which will increase the dissolution rate. Dissolution of $CaCO_3$ increases Ca^{2+} concentrations, which could exchange with Na^+ on clay particles as part of cation exchange. It is unclear if this process is happening and more research needs to be done to find out the exact process and if dissolution of $CaCO_3$ provides a significant source of Ca^{2+} for cation exchange. Precipitation of $CaCO_3$ is not expected based on the research by Goss et al. (2007) and the guidelines provided by the American Society of Plumbing Engineers (2010). Goss et al. (2007) reports the solubility of $CaCO_3$ based on pH and atmospheric CO_2 pressure and found increasing solubility of $CaCO_3$ at lower pH (2.6 meq/L at pH 7.5 and 76 meq/L at pH 6). Both solubility concentrations are higher than recorded Ca^{2+} concentrations thus decreasing the pH will not induce precipitation of $CaCO_3$. In addition, the guidelines provided in American Society of Plumbing Engineers (2010) indicate the saturation pH for $CaCO_3$ for our water characteristics (based on the Laneglier Index) is 7.7, with lower pH indicating no precipitation of $CaCO_3$ will occur. Precipitation of $CaCO_3$ is not expected but dissolution of $CaCO_3$ may provide Ca^{2+} for cation exchange in clay particles.

SO_4^{2-} concentration decreased in the 60% OSPW treatment from 4.2 meq/L to 2.6 meq/L, but stayed the same in the 20% OSPW treatment from 1.1 meq/L to 1.2 meq/L. One possible explanation for this difference is sulfate reduction carried out by microorganisms. Fedorak et al. (2002) measured sulfate reduction in mature fine tailings due to sulfate reducing bacteria and found sulfate reduction occurs at higher sulfate concentrations to a low of 0.35 meq/L to 0.42 meq/L when methanogenesis becomes the dominant bacterial mechanism. This small decrease in sulfate could be attributed to sulfate reducing bacteria, even though no significant change in microbial numbers were observed in the FFT in 60% OSPW or 20% OSPW.

3.3.8 Light Intensity

Light intensity measurements for 60% OSPW, 60% OSPW (Control) and 20% OSPW are shown in Figures 3.11a, b and c, respectively. The light intensity curves were very similar thus key dates are shown for ease of comparison. The 60% OSPW treatment (Figure 3.11a) showed a dramatic change in light intensity curves as the Secchi depth increased. Light intensity curves for days 2 through 43 are very similar (correspond to Secchi depths of 0.05 m - 0.07 m) with the first visual deviation occurring at 51 and 57 days (Secchi depth 0.10 m and 0.11 m respectively). Days 98 and 113 showed an increase in light intensity when Secchi depth also increased to 1.20 m and 1.92 m, respectively. Light intensity goal is 0.01 at 2 m, corresponding to 1 m of Secchi depth and 23 NTU based on the turbidity as shown in Figure 3.6b. The light intensity and Secchi depth relationship is explored further in Section 3.3.9. In general these results were expected, light intensity curves were similar for similar Secchi depths. The sharp increase in Secchi depth was mirrored with increased light intensity curves, distinct from the previous light intensity curves. 60% OSPW (Control) (Figure 3.11b) showed very little improvement in light intensity with some improvement between day 0 and day 13. The 20% OSPW treatment (Figure 3.11c) shows a more gradual change in light intensity curves, with the first visual change occurring on day 30. Day 58 showed the deepest Secchi depth (0.52 m) and the highest water clarity curve even though subsequent days showed lower Secchi depths and light intensity curves (e.g. day 133, Secchi depth 0.30 m). The light intensity curves corresponding to Secchi depths from 0.40 m to 1.40 m from days 58 to 133 are very similar.

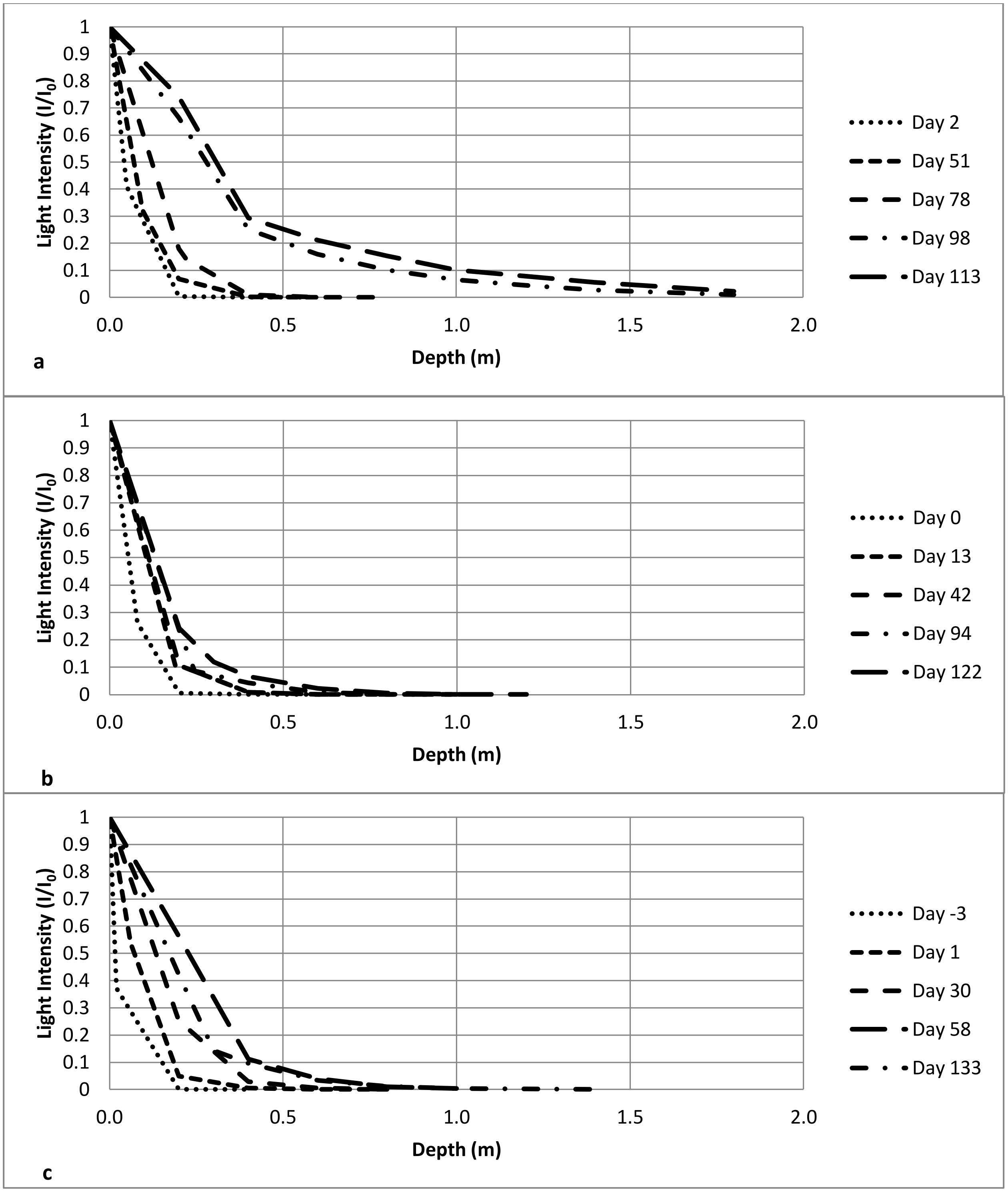

Figure 3.11 a and b: Light intensity curves for selected days for the 60% OSPW treatment (a), 60% OSPW (Control) (b) and 20% OSPW treatment (c). For 60% OSPW, curves were very similar between day 2 and 51. An increase in light intensity at depth is clearly seen at day 98. For 60% OSPW (Control) there is almost no improvement in light intensity. For 20% OSPW there is a gradual increase in light intensity. Similar curves were omitted for clarity.

3.3.9 Light intensity and Secchi depth relationship.

Aas et al. (2014) introduces two approximations that relate light intensity and Secchi depth. The first approximation states that Secchi depth occurs at light intensity of 0.10 (or 10%). Figure 3.12 shows the light intensity measured at the Secchi depth for our experiment with the expected results (0.10) marked with a blue line. The data for three treatments (80% OSPW, 60% OSPW and 20% OSPW) are graphed with the lower Secchi depths showing elevated light intensity, which does not conform with the expected result of 0.10. Koenings and Edmundson (1991) did similar experiments in Alaskan and northern Canadian lakes over a two year period. The average light intensity and standard deviation at the Secchi depth was found to be 0.075 ± 0.043 for clear water, 0.046 ± 0.033 for stained (yellow color due to organic acids) water and 0.212 ± 0.080 for turbid water (Koengins and Edmundson 1991). Koenings and Edmundson (1991) show a similar pattern as shown in our data with elevated light intensity at Secchi depth in lower clarity water. Aas et al. (2014) did similar experiments but related light intensity and Secchi depth differently. They compared their data by taking the ratio of Secchi depth to the depth of 0.10 light intensity (Secchi depth:0.10 light intensity depth) and found it to be 0.92 ± 0.30 (expected result is 1). These results indicate there is variability in the light intensity at the Secchi depth and that clarity does play a factor itself in the relationship.

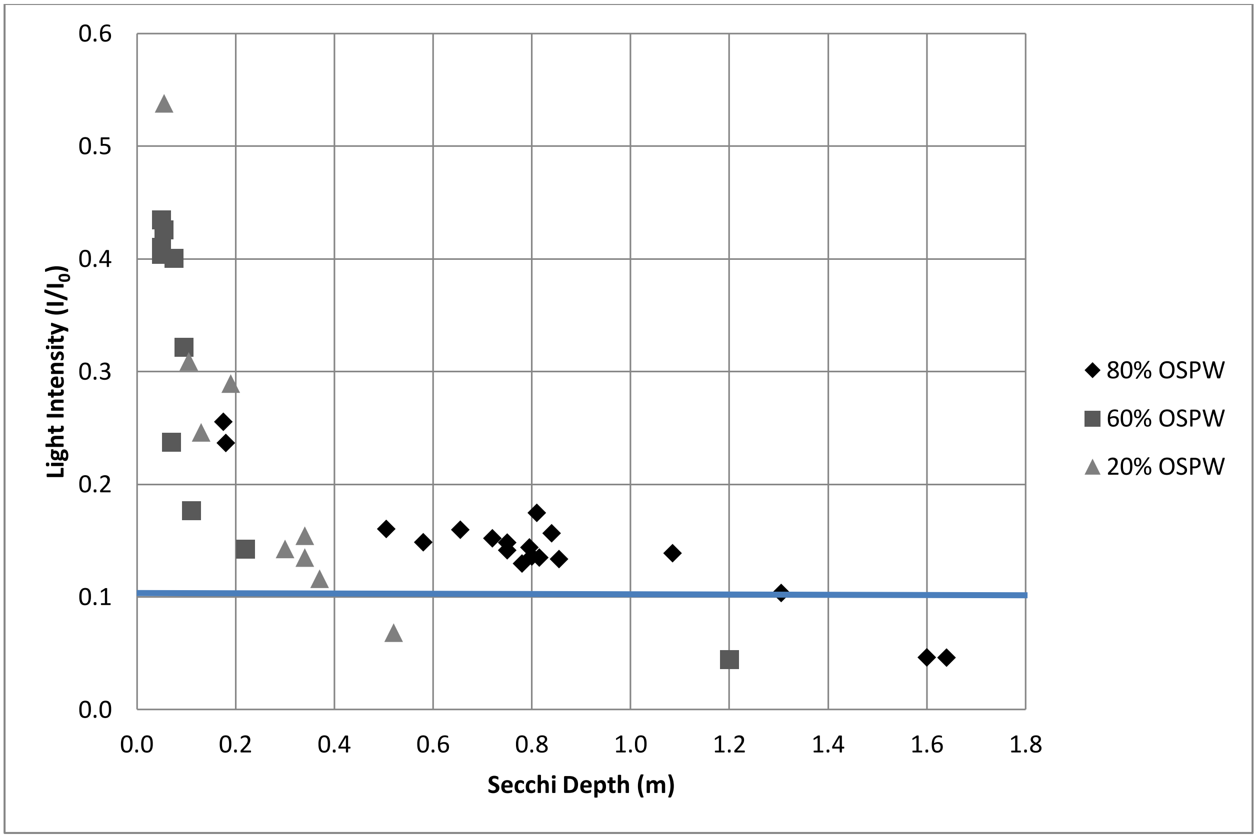

Figure 3.12: Correlation between measured light intensity and Secchi depth for 80% OSPW, 60% OSPW and 20% OSPW. The blue line indicates the first approximation by Aas et al. (2014): Secchi depth occurs at 0.1 light intensity.

Aas et al. (2014) second approximation states that light penetration depth (depth of 0.01 (1%) light intensity) occurs at twice the Secchi depth. This relationship can be generalized using the following equation where the approximation is m =2:

$$\mathrm{LP} = m * \mathrm{SD} + \mathrm{b} \tag{3.1}$$

Where, LP = Light penetration depth (m)
SD = Secchi depth (m)
m = Coefficient
b = LP intercept

Figure 3.13 shows the relationship between Secchi depth and approximate light penetration depth for the 20% OSPW and 60% OSPW treatments. The light penetration depths were interpolated from the light intensity graphs (Figures 3.11a and c). A linear line of best fit of the complete data set resulted in a linear line of best fit of LP = 1.45*SD + 0.17 (expected result LP = 2*SD + 0). Omitting the last data point that may have skewed results, resulted in a linear line of best fit of LP = 1.73*SD + 0.13, closer to the expected value. Figure 3.13 shows both lines of best fit as well as the 95% confidence interval of the regression. Experiments done by other researchers show varying values of *m*. Luhtala and Tolvanen (2013) studied this relationship in the Baltic Sea and found in general *m* is lower in clear water and higher in turbid water. Table 3.6 summarizes their results based on depth and they found the average *m* ranged from 2.35 - 3.32, higher than our initial approximation. Koenings and Edmundson (1991) found average values of *m* to be 2.41±0.61 for clear water, 1.73±0.41 for stained water and 4.97±1.39 for turbid water. This again follows the trend of higher *m* in turbid waters. The data collected in our experiment is for Secchi depths much shallower than those collected by Koenings and Edmundson (1991) and Luhtala and Tolvanen (2013) which should indicate higher *m* but our experiment shows a lower *m*. Further experimentation needs to be done in BML to see if the lake properties and configuration may influence the *m* of this water, as both Luhtala and Tolvanen and Koenings and Edmundson conducted their experiments in open water.

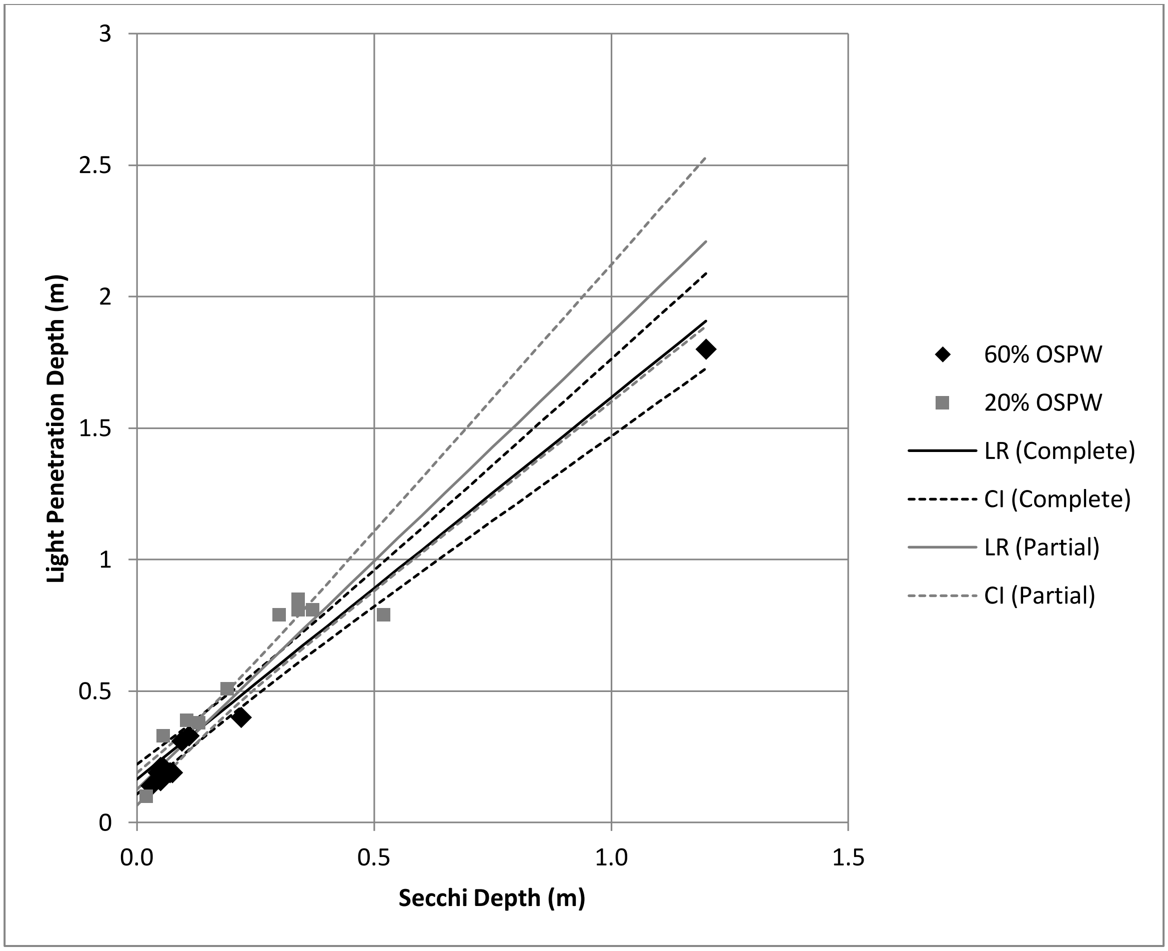

Figure 3.13: Relationship between light penetration depth and Secchi depth to find the correlation. Light penetration depth (depth of 0.01 light intensity) was approximated from the light intensity curves of each experiment. LR refers to the linear regression line of best fit and CI refers to the confidence interval. The complete data set was used in black line of best fit while the last data point (SD = 1.2) was omitted in the grey line of best fit, resulting in a regression closer to the expected value.

Table 3.7: Coefficient m relating light penetration depth and Secchi depth as measured in the Baltic Sea (adapted from Luhtala and Tolvanen 2013).

Secchi Depth (m)	***m***
<2.1	3.32
2.1-3.6	3.08
3.7-4.5	2.69
>4.5	2.35

3.3.10 Mechanisms for Coagulation

Siddique et al. (2014) proposes three main mechanisms for how coagulation may be increased with lower pH. All relate to the double diffuse layer (DDL) surrounding each submerged clay particle as explained in Section 2.3.2. The thickness of the DDL is regulated by the charges on the surface of each particle and the reciprocal charged ions in solution that neutralize the surface charges (Siddique et al. 2014). For clay particles, the surface charges are usually negative with the reciprocal ions in the water being positive. Decreasing the thickness of the DDL increases coagulation and therefore flocculation and settling (Siddique et al. 2014). The first mechanism proposed is increasing ionic strength decreases the DDL. The conductivity for 60% OSPW ranged from 2.09 mS/cm to 2.67 mS/cm, averaging 2.34 mS/cm while conductivity for 20% OSPW ranged from 1.05 mS/cm to 1.16 mS/cm, averaging 1.11 mS/cm. Higher ionic strength combined with pH reduction resulted in increased water clarity. If high ionic strength alone dominated the settling process, the control column would show similar improvement in water clarity which was not shown. The second mechanism proposed is divalent cations exchange the monovalent cations and neutralize the negative charges better resulting in a lower DDL. Cation concentrations are shown in Figures 3.8, 3.9 and 3.10. Na^+ concentrations for 60% OSPW decreased slightly through the duration of the experiment from 574 mg/L to 533 mg/L while Na^+ concentrations for 20% OSPW increased from 183 mg/L to 262 mg/L. Divalent cation concentrations were much lower (<50 mg/L) and stayed the same for the duration of 60% OSPW and 20% OSPW. The lack of change in concentration of divalent cations indicates that there does not seem to be an exchange of divalent cations. The increase in Na^+ concentration in 20% OSPW and not in 60% OSPW may give an indication that ions from the FFT are moving into the water phase, and the ionic concentrations in 20% OSPW are not high enough to suppress the DDL and therefore results in a lack of settling. It does not give an indication what the minimum ionic concentration is for settling to occur. The third mechanism is lower pH dissolves carbonate material and changes the surface charges of clays, leading to a decreased DDL. Addition of HCl to 80% OSPW lowered the pH and resulted in increased water clarity, following the expected outcome for this coagulation mechanism. However this mechanism does not seem to be the primary coagulation mechanism at pH 6, as 20% OSPW does not show the same increase in water clarity found in 80% OSPW and 60% OSPW. This may also be due to lower concentrations of $CaCO_3$ but this cannot be verified as direct measurements of $CaCO_3$ were not carried out in this study. The water clarity improvement in 60% OSPW and not in 20% OSPW may be a direct result of the first proposed mechanism, ionic strength. More studies must be done to find the optimal ratio or range of ratios of OSPW to BCR, with the correct ionic strength, in order to speed up coagulation, flocculation and settling in BML.

3.4 Conclusion

These experiments were performed to determine if (1) pH adjustment helps to increase water clarity in BML and if (2) CO_2 addition can adjust the pH enough to improve water clarity. The 80% OSPW treatment showed that pH adjustment is a feasible technique to increase water clarity but raised an additional question surrounding the time lag observed between pH adjustment and a corresponding increase in water clarity. The 60% OSPW and 20% OSPW treatments were set up to determine if CO_2 addition can improve water clarity and if it also has a time lag. The pH was again dropped to 6 with CO_2 addition and both experiments showed no initial increase in water clarity. The Secchi depths improved suddenly for the 60% OSPW treatment from 0.22 m at 78 days to 1.20 m at 98 days and 1.92 m at 113 days. The 20% OSPW treatment did not show a similar increase after 133 days. The confirmation of a significant time lag is very important for any future studies on coagulation, flocculation and settling in EPLs and for industry working to manage EPLs. Enough time must be budgeted to fully record all effects of any potential method of dealing with coagulation, flocculation and settling. In addition, the water clarity improvement in 60% OSPW and not 20% OSPW shows ionic strength may be the dominant coagulation mechanism at pH 6. OSPW contains higher ionic strength and keeping a high fraction of OSPW to BCR may be key in increasing settling in conjunction with CO_2 addition. More studies need to be done to determine the optimal ratio of OSPW to fresh water in order to optimize coagulation in EPLs. Increasing coagulation, flocculation and settling is essential to increase light penetration and the health of the littoral zone, which in turn affects the health of the EPL in general.

3.5 Chapter 3 References

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CHAPTER 4: SMALL COLUMN EXPERIMENTS

4.1 Introduction

The Alberta oil sands house the third largest proven reserve of crude oil in the world (Stringham 2012). Oil sands mining and extraction is more energy intensive than traditional crude oil and produces waste streams of fluid fine tailings (FFT) and oil sands process-affected water (OSPW) (Humphries 2009). The remediation and storage of both FFT and OSPW are pressing concerns in the oil sands because oil sands operators do not have approval to discharge at the present time. This policy, that prohibits oil sands operators from discharging OSPW off-site, and a newer Directive 074 (suspended as of March 13, 2015 (Alberta Energy Regulator 2015a)), specifying the undrained shear strength disposed FFT must have after one year (5 kPa) and five years (10 kPa), have spurned oil sands operators to increase development of different storage and remediation techniques (Energy Resources Conservation Board (predecessor to Alberta Energy Regulator) 2009). Techniques such as centrifuging (Mikula 2012; Mikula 2013), thin-lift dewatering (Kasperski and Mikula 2011), consolidated/composite tailings (Delamaide et al. 2011), rim ditching (Lorentz et al. 2014) and thickener technology (Read 2014; Sobkowicz 2012) are all being developed for commercial scale use. In addition to these techniques, end pit lakes (EPLs) are also being developed with Base Mine Lake (BML) as the first operational commercial scale EPL in the oil sands industry (Read 2014). EPLs (including BML) consist of a lower layer of FFT storage and an upper layer of water, ideally housing a healthy ecosystem. In BML, the water layer initially consisted of 100% OSPW with fresh water added over time with no discharge and no OSPW added resulting in decreasing OSPW fractions over time.

FFT is a suspension of clay and silt particles (~10-20%w/w solids content), some residual bitumen and some diluent (naphtha or paraffinic solvents) used in the industrial process (Allen 2008; Small et al. 2015). FFT settles slowly with solids content increasing to ~30%w/w in 2-4 years and >60%w/w in decades (Chalaturnyk et al. 2002). Increased settlement of FFT releases more water for recycling in plant operations and reduces the storage footprint of the FFT. OSPW has many constituents including trace metals, naphthenic acids (NAs) and salts mostly composed of Na^+ (700-800 mg/L), Cl^- (500 mg/L) and SO_4^{2-} (250 mg/L) (Small et al. 2015). The toxicity in OSPW is mostly attributed to NAs, with lower NA concentrations corresponding with lower toxicity (Garcia-Garcia et al. 2011; Morandi et al. 2015). However, Toor (2012) shows toxicity is also affected by salinity, which suggests NAs are not the only contributing factor to toxicity.

BML (and EPLs in general) attempt to store and remediate both OSPW and FFT. A key component of EPLs is creating a healthy aquatic ecosystem that aids remediation, in the water layer. Currently, BML is experiencing very turbid waters that hinder the formation of a healthy ecosystem. The high turbidity in BML may be the result of many factors including wave action, lake turnover and clay settling patterns. Wave action introduces stress into the EPL that can lead to the suspension of bottom material. Lawrence et al. (1991) determined the orbital water velocity at which FFT starts to suspend (0.044 - 0.050 m/s) and calculated the minimum water depth for BML to minimize FFT suspension from wave action due to wind: 6.1 m (ten year return period for wind, 2015 BML water depth is 8.5 m (Geoffrey Halferdahl, personal communication 2015)). Lake turnover may take settling particles from the bottom of the EPL to the top as the lake cycles, keeping particles in suspension longer. Clay settling is slow due to their small size and surface charges.

Clay particles suspended in water have negative surface charges that lead to the formation of a diffuse double layer (DDL), repel other clay particles and hinder flocculation and settling (Schofield and Samson 1954; Sutherland et al. 2015). Both high ionic strength and divalent cations are known to suppress the repulsion between clay particles due to the negative surface charges (Druzbicka and Craw 2013; Lyons and Plisga 2005; Schofield and Samson 1954; Siddique et al. 2014; Sutherland et al. 2015). Sutherland et al. (2015) showed a clay suspension in fresh water (0.00 mmol/L ionic strength) settled 5 cm in 6.5 hours while NaCl addition to the clay suspension (190 mmol/L) settled 5 cm in 15 min. Druzbicka and Craw (2013) showed similar results with microscopic evidence of aggregated flocs 2-3 times the size in saline water over fresh water. Salinity, or extra ions in the water layer, interferes with the stability of the DDL (Druzbicka and Craw 2013). The effect of other ions and charged particles acting on the ions in the DDL diminishes the effect of the clay surface charges (Siddique et al. 2014). As a result, the DDL is compressed and other forces such as van der Waal's forces can overcome the repulsion between clay particles and larger flocs can form that settle faster (Druzbicka and Craw 2013).

Divalent cations can also impact the settling of clay particles in solution. Divalent cations destabilize the DDL and allow clay particles to interact and flocculate (Fowler and Morkel 2009). Divalent cations have a higher charge than monovalent cations and neutralize the negative clay charges better (Appelo and Postma 2005). Exchangeable cations may also be in between clay layers, in the interlayer (Appelo and Postma 2005). Divalent cations in the interlayer have larger radii than monovalent cations, which increases the size of clay structures (negative effect on dewatering in FFT) (Appelo and Postma 2005). Divalent cations have been studied in FFT dewatering and other remediation strategies such as composite/consolidated tailings (CT). Gypsum addition to CT at 1 g $CaSO_4$/L tailings is sufficient to flocculate clay particles to form non-segregating CT with Syncrude Canada Ltd. tailings (Chalaturnyk et al. 2002). CaO addition at 1.5 to 2.0 g/L and $Ca(OH)_2$ addition at 2.0 g/L have also been tested and show increased dewatering in tailings (Chalaturnyk et al. 2002). Globa and Barbour (2001) investigated soil stability based on ionic strength and percentage of sodium (based on equivalents of sodium, potassium, calcium and magnesium) and found porewater with >60% sodium and >1 meq/L total dissolved salts are dispersive. This was attributed to clay in the soil and, in particular, the effect of the DDL of clay under different ionic strength (Globa and Barbour 2001). This is contrary to results already discussed where high ionic strength helps flocculation. Globa and Barbour (2001) looked at soils and how the addition of water can create instability while the other research was looking at wetted and dispersed clays and how they flocculate in solution.

The following experiments attempt to determine the effect of ionic strength and divalent cation proportion on clay settling in BML water. Do higher ionic strength and higher divalent cation concentration increase the clay settling in BML? Based on previous research, both higher ionic strength and higher divalent cation concentration should promote clay settling.

4.2 Materials and Methods

4.2.1 FFT, OSPW and Fresh Water

FFT used in these experiments came from the FFT layer in BML, collected in 2013 by Syncrude and stored in 20 L pails at 4°C. The FFT was mixed within the pail and added to the experiment using a funnel. Water for these experiments was also collected by Syncrude and stored in similar pails at room temperature. Water from BML was collected in 2013 and contains 90% OSPW and 10% fresh water (from Beaver Creek Reservoir (BCR)). BCR water was collected in 2013 and 2014 and is the same fresh water that has been added to BML after it opened. Based on the water composition of BML being 90% OSPW and 10% BCR, different mixes of OSPW and BCR were formed with the water compositions of the mixes reported in OSPW (and BCR) percentages.

4.2.2 Experimental Set-up

2 L columns were set up with 200 mL FFT overlain with 1800 mL of water. These ratios were chosen to mimic similar FFT:water ratios as the big column experiments in chapter 3 (1:9 in 2 L column, 1:10 in 148 L column). FFT was added to Trial B columns to increase turbidity in the water layer to the same range of field turbidity values found in BML (200 - 300 NTU was targeted). FFT was added to the water layer in the column using a 25 mL pipette and mixed using the pipette at the top to avoid disturbance of the FFT bottom layer. Water compositions were chosen in decreasing OSPW percentages to identify potential future settling behavior in BML. Water compositions and turbidity additives are listed in Table 4.1. The columns without additives (Trial A) were completed first and columns with FFT additive (Trial B) completed second due to material constraints. Trial A columns were left open to the atmosphere to imitate lake conditions but visually evaporation led to water loss during the 84 day duration (evaporation not specifically tracked). Trial B columns were covered with tin foil during the duration of the experiment except during testing to minimize the impact of evaporation on the parameters tested.

Table 4.1: Water composition of columns.

Treatment ID	Water Composition	Additives	Trial
90% OSPW	90% OSPW, 10% BCR	N/A	A
81% OSPW	81% OSPW, 19% BCR	N/A	A
81% OSPW (D)	81% OSPW, 19% BCR	10 mL FFT	B
54% OSPW	54% OSPW, 46% BCR	N/A	A
54% OSPW (D)	54% OSPW, 46% BCR	10 mL FFT	B
36% OSPW	36% OSPW, 64% BCR	N/A	A
36% OSPW (D)	36% OSPW, 64% BCR	10 mL FFT	B
18% OSPW	18% OSPW, 72% BCR	N/A	A
18% OSPW (D)	18% OSPW, 72% BCR	10 mL FFT	B
5% OSPW	5% OSPW, 95% BCR	10 mL FFT	B
5% OSPW (D)	5% OSPW, 95% BCR	10 mL FFT	B
100% BCR	100% BCR	N/A	A

4.2.3 Water Analysis

Water analysis for Trial A was completed at the start (day 0), day 1, 2, 4, 7, 14, 28, 56 and 84 (end) to try and catch any parameter changes, with changes more likely during the start of the experiment. Trial B water analysis was completed at the start, day 32 and 90 (end) to minimize the volume of water taken from the columns. Water pH and conductivity were measured in the columns with an Exstik II EC500 portable meter, with calibration every week. Other analyses were completed by taking a 33.5 mL sample from the middle of the water layer and tested externally. Dissolved oxygen (DO) was measured with an YSI Incorporated Model 50B DO meter. Modified Winkler titration (for 150 mL instead of 200 mL) was used to check the DO meter for accuracy (average 7% error, Appendix A) (ISO 5813-1983, 1983). Turbidity was measured using an Orbeco-Hellige Digital Direct-Reading Turbimeter calibrated before every measuring day with readings recorded after five seconds (Orbeco-Hellige 2009). Anions and cations were tested using the same samples using ion chromatography with standards run every time and following procedures reported in Abolfazlzadehdoshanbehbazari et al. (2013). To compensate for evaporation, ionic concentrations were adjusted based on chloride. Chloride was assumed to be conservative and all ionic concentrations were adjusted based on the original chloride concentration and the one measured on that day.

4.2.4 FFT Analysis

FFT depth in the columns was measured using a ruler along the side of the columns to the nearest 0.1 cm at the same time as water analysis was completed (days 0, 1, 2, 4, 7, 14, 28, 56 and 84 for Trial A). FFT was sampled from the original bucket and tested for methylene blue index (MBI), solids content, zeta potential and particle size distribution. Sampling FFT at the end of the experiment was not done because of the difficulty of grabbing a good sample from the bottom of the columns. The change in zeta potential would especially be interesting during the course of the experiment if this could be determined. MBI was determined following the CONRAD method listed in Kaminsky (2014) with the methylene blue solution made the same day and soaking and mixing of the sample before a reading was made. Four samples were tested for MBI and the results averaged. Solids content was determined for 5 samples using overnight drying at 105°C as laid out in ASTM D5907 (2013) with their results averaged. A Malvern Zetasizer Nano ZSP with folded capillary cells DTS1070 at 25°C was used to determine the zeta potential of the FFT with one sample tested three times as per instrument procedure (Malvern 2013). Two samples were for FFT particle size distribution using a 152H hydrometer and procedures in ASTM D422 (2007) after mixing the FFT to grab a representative sample. Particle size distribution was determined over 24 hours after overnight soaking and both were completed using the same dispersant solution (4 g sodium hexametaphosphate /L stock solution, 125 mL of solution in 1 L cylinder during test).

4.3 Results and Discussion

4.3.1 Initial FFT Characterization

Initial FFT characteristics are shown in Table 4.3 and Figure 4.1 with initial porewater ions shown in Table 4.2. The MBI values obtained for this experiment are in the same range (0.7 - 7.2 meq/100g) as the bulk materials reported in Osacky et al. (2014). These oil sands materials were tested before oil sands extraction took place and the materials did not specifically came from the tailings ponds. Kaminsky et al. (2009) and Hooshiar et al. (2010) specifically tested tailings ponds FFT but only reported MBI for particle size ranges of 0.2 μm - 2 μm (9 meq/100 g) and <0.2 μm (38 meq/100 g) with no bulk MBI reported. MBI seems to follow a trend of lower MBI at higher particle sizes thus a lower MBI for bulk material than for small particle sizes is expected. However, no direct comparison can be made between the different studies.

FFT solids content is typically 10-20%w/w initially, ~30%w/w in 2-4 years and takes decades to reach >60%w/w (Siddique et al. 2014; Chalaturnyk et al. 2002). A 38%w/w solids content would indicate the FFT tested was likely around 5-6 years old but there was variability between our samples even after mixing to try and get representative samples.

As mentioned in Chapter 2, zeta potential gives an indication of the stability of a clay particle in suspension. Zeta potentials below -30 mV and above 30 mV are considered indicative of a stable particle (Moayedi et al. 2013). The zeta potentials measured are close to the dividing line so it is hard to say if the FFT itself is stable or unstable. Zeta potential can be influenced by pH (Marchuk et al. 2013; Saka and Güller 2006) and ionic strength including the types of ions present in the solution (Saka and Güller 2006). FFT with zeta potentials on the stability boundary are more likely to change their settling behavior if the zeta potential can be adjusted further into the unstable zone. Zeta potential was only measured for the FFT and not for the particles in the water fraction.

Table 4.2: Initial porewater anions and cations with one standard deviation shown.

Cl^- (mg/L)	**1296 ± 10**
SO_4^{2-} (mg/L)	**354 ± 4**
Na^+ (mg/L)	**1118 ± 135**
Mg^{2+} (mg/L)	**24 ± 2**
K^+ (mg/L)	**10 ± 2**
Ca^{2+} (mg/L)	**15 ± 1**

Table 4.3: Initial FFT characteristics with one standard deviation shown.

Methylene Blue Index (meq/100 g)	3 ± 2
Solids Content (%w/w)	38 ± 5
Zeta Potential (mV)	-28 ± 2

Figure 4.1 shows the particle size distribution of two samples of FFT. The samples do not show an exact match, again highlighting the variability also seen in solids content. The finer sample (the top line) had a 100.6%w/w finer than calculation at 0.031 mm, likely caused by rounding. Dompierre et al. (2016) indicates the typical FFT contains at least 90%w/w finer than 0.044 mm and 30%w/w finer than 0.002 mm. Our particles size distribution indicates likely 80-100%w/w finer than 0.044 mm and 40-60%w/w finer than 0.002mm, showing an increased less than 0.002 mm proportion. Sorta (2015) shows the particles size distribution of a number of tailings from both Albian Sands Energy Inc. and Syncrude with our distributions falling within the range measured.

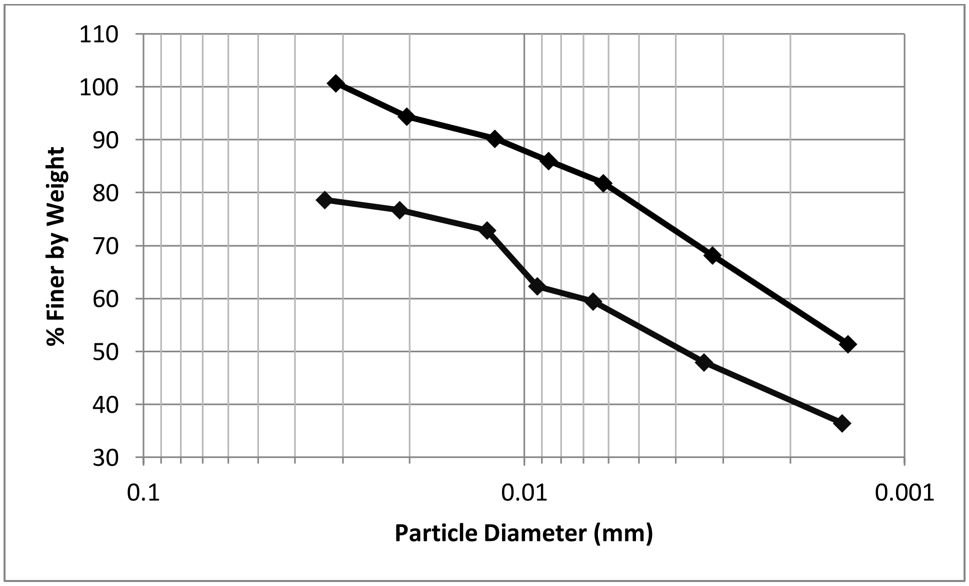

Figure 4.1: Particle size distribution for two samples of FFT.

4.3.2 Evaporation and Ionic Concentration

Trial A columns were left open and Trial B columns covered. Evaporation was not specifically tracked during Trial A and averaged 60 mL after 90 days for Trail B columns (3.3% of original water volume). Ionic concentrations were adjusted based on chloride concentrations as explained in Section 4.2.3. Na^+, K^+, Mg^{2+} and Ca^{2+} concentrations are graphed because of the significance of these cations. The sum of these cations represents 87% (100% BML) to 98% (90% OSPW) of the total cations in the water mix. Figures 4.2 a-d (Trial A) and Table 4.3 (Trial B) show the ionic concentrations changing over time with Na^+ showing an increase over time for all Trial A water mixes while decreasing in Trial B water mixes. K^+, Mg^{2+} and Ca^{2+} show a general decline over time for virtually all water mixes. Increasing Na^+ concentration was the expected result based on assumptions of the clay in the water layer. OSPW is high in Na^+ (as confirmed in Figure 4.2a with initial Na^+ of 34 meq/L in 90% OSPW) and the diffuse double layer (DDL) of the clay particles will be saturated with Na^+. The cation preference in the DDL is $K^+ > Ca^{2+} > Mg^{2+} > Na^+$ as explained in Section 2.3.2.1, thus K^+, Ca^{2+} and Mg^{2+} cations will displace Na^+ cations in the DDL (Appelo and Postma 2005).

However, this explanation does not fully explain the ionic concentration results. If cation exchange is the dominant factor of ionic concentration change, the increase in Na^+ concentration should be equal to the sum of the decrease in K^+, Mg^{2+} and Ca^{2+}. Figure 4.3 shows the cation concentration change in one graph for 54% OSPW for comparison purposes. The increase in Na^+ concentration (5 meq/L) is not equal to the decrease in K^+, Mg^{2+} and Ca^{2+} combined (1 meq/L).

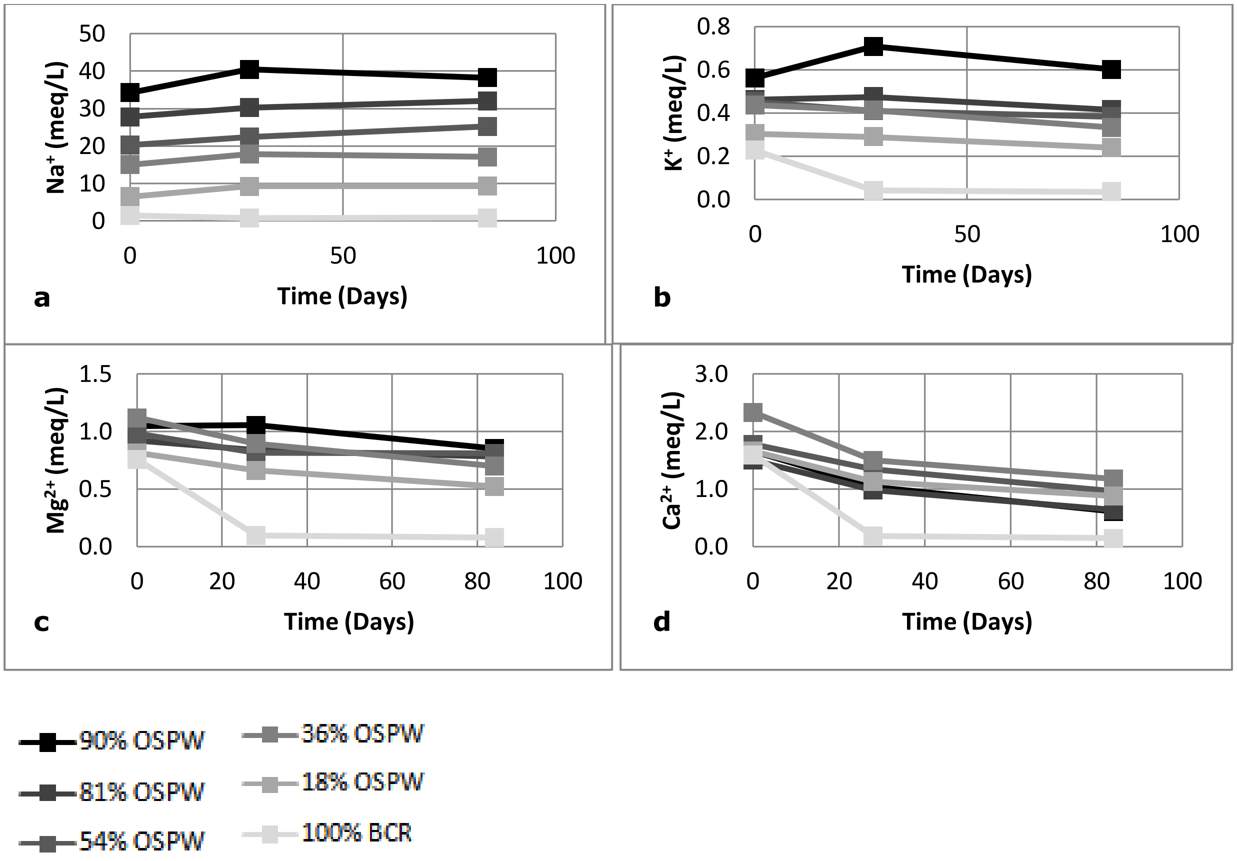

Figure 4.2a through d showing cation concentrations (Cl^- adjusted) over the duration of Trial A.

Table 4.4: Starting and ending cation concentrations (Cl- adjusted) for Trial B.

Treatment ID	Na^+ (meq/L)		K^+ (meq/L)		Mg^{2+} (meq/L)		Ca^{2+} (meq/L)	
	Day 0	Day 90	Day 0	Day 90	Day 0	Day 90	Day 0	Day 90
81% OSPW (D)	30.0	25.3	0.3	0.2	0.9	0.6	0.7	0.4
54% OSPW (D)	20.1	17.2	0.2	0.2	0.8	0.5	0.7	0.3
36% OSPW (D)	14.0	13.2	0.2	0.1	0.8	0.4	0.7	0.3
18% OSPW (D)	7.9	7.6	0.1	0.1	0.8	0.3	0.9	0.3
5% OSPW	8.0	2.9	0.2	0.1	0.6	0.2	0.6	0.2
5% OSPW (D)	3.7	3.1	0.1	0.1	0.8	0.2	1.0	0.2

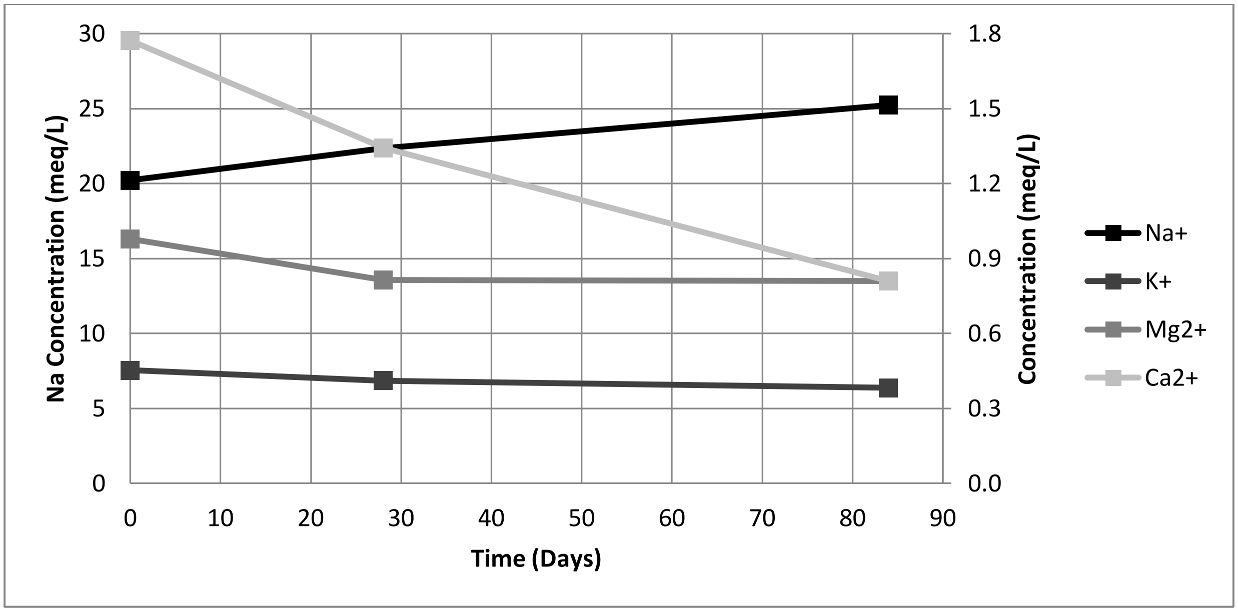

Figure 4.3: Cation concentrations for the 54% OSPW treatment over the duration of the experiment with Na concentration on the left axis and K, Mg and Ca concentrations on the right axis. This shows the increase of Na^+ concentration over the course of the experiment (5 meq/L) is not equal to the sum of the decreases in K^+, Mg^{2+} and Ca^{2+} concentrations (1 meq/L).

Movement of Na^+ from the FFT layer to the cap water layer is one possible explanation of the elevated increase in Na^+ concentrations in all water mixes. Initial porewater Na^+ concentration is 49 meq/L and Cl^- concentration is 37 meq/L, much higher than any initial water mix concentration. Diffusion, assuming equilibrium between the porewater and cap water layer, accounts for 18% (90% OSPW) to 107% (36% OSPW) of the increase in Na^+ concentration in Trial A water mixes. Diffusion of ions from the FFT layer into the water layer also explains the decrease in Na^+ concentration in Trial B columns. For consistency, ionic concentrations were adjusted based on Cl^- concentrations, because Cl^- is conservative and evaporation was not tracked specifically in Trial A columns. Evaporation was tracked in Trial B columns and evaporation adjusted Na^+ and Cl^- concentrations are shown in Table 4.4 showing a slight increase in Na^+ concentration while chloride concentrations increased as well. This is further evidence that diffusion from the porewater in the FFT to the water layer occurs, in line with the ionic gradient between the two layers.

Table 4.5: Initial and final concentrations of Na+ and Cl- showing an increase in both after the evaporation adjustment.

Treatment ID	Na^+ day 0 (meq/L)	Na^+ day 90 (meq/L)	Cl^- day 0 (meq/L)	Cl^- day 90 (meq/L)

81% OSPW (D)	30	30	12	15
54% OSPW (D)	20	21	8.1	10
36% OSPW (D)	14	17	5.9	7.6
18% OSPW (D)	7.9	12	3.0	4.6
5% OSPW	3.7	7.7	1	2.7
5% OSPW (D)	3.7	7.6	1	2.6

4.3.3 Conductivity

Figure 4.4 and Table 4.5 both show increasing trends in conductivity for all treatments. Figure 4.4 shows the conductivity of Trial A columns, however an error in the probe was found on day 56 of the experiment but the same probe was used for consistency for the entirety of Trial A. Conductivity taking with a working probe for days 56 and 84 of Trial A indicate the faulty readings are approximately 3.8 times lower than their actual values. These numbers cannot be compared with Table 4.5 but they do show similar trends. Using Trial B data, the starting conductivity for OSPW is 3.4 mS/cm. Kim et al. (2013) reported conductivity of 4.4 mS/cm for OSPW taken from a Syncrude pumping station. Aged Syncrude OSPW (>15 years) tested by Kavanagh et al. (2011) had a conductivity of 2.0 mS/cm. Our conductivity values fall within this range as expected since the water tested is Syncrude-sourced and aged for at least one year.

The average percentage conductivity increase for Trial A columns is 40% and Trial B columns is 37%. Conductivity can increase through evaporation of pure water (concentrating the remaining ions and resulting in higher conductivity). Evaporation played a larger effect in Trial A columns (as discussed in 4.3.2) and the conductivity in Trial A columns on average increased more than Trial B columns. Interaction with the FFT at the bottom of the columns provides another source of conductivity. Diffusion from the FFT porewater moving into the water layer would explain higher conductivity values over time for almost all columns. As discussed in Section 4.3.2, Cl^- concentrations in Trial B columns increased over time, even after accounting for evaporation, supporting the diffusion of ions from the FFT layer to the water layer.

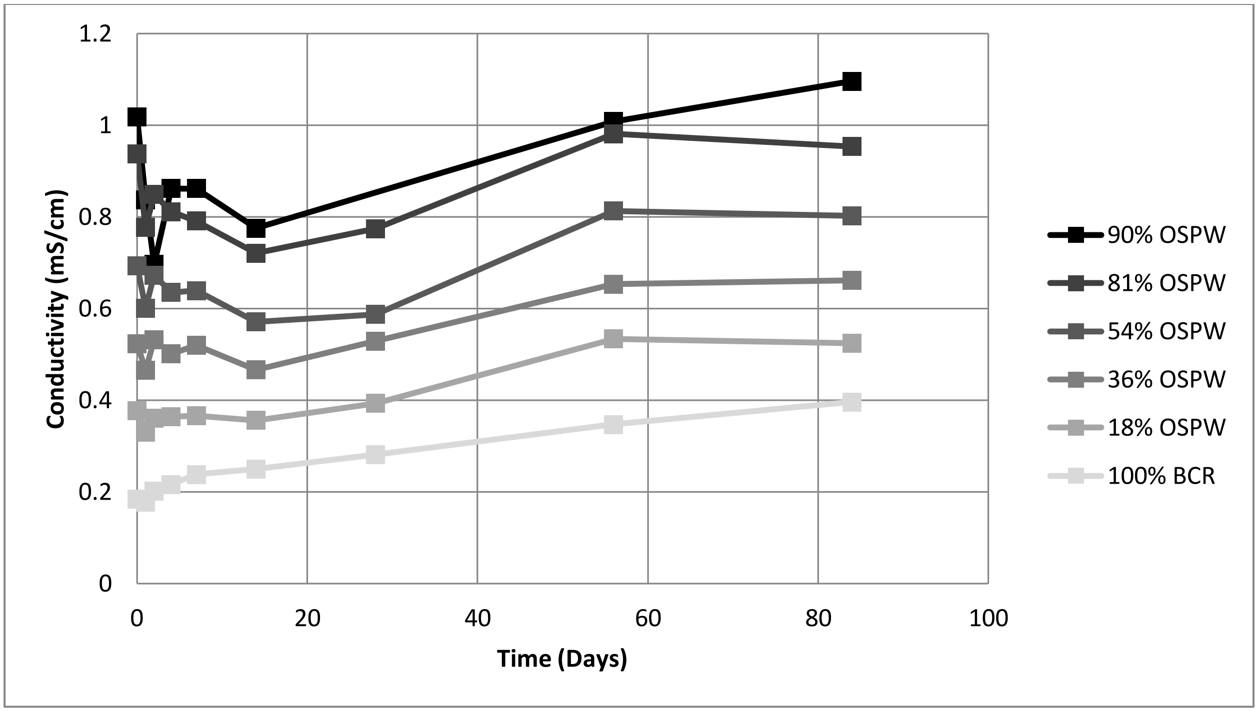

Figure 4.4: Conductivity for Trial A columns. A probe error was found during this experiment on day 56, which resulted in conductivity readings approximately 3.8 times lower than actual values. 90% OSPW day 28 data point was manually removed as an outlier. The original graph can be found in Appendix A.

Table 4.6: Conductivity for Trial B columns showing an increase in all treatments with higher OSPW content showing higher conductivity.

Treatment ID	Conductivity Day 0 (mS/cm)	Conductivity Day 90 (mS/cm)
81% OSPW (D)	2.8	3.0
54% OSPW (D)	2.0	2.2
36% OSPW (D)	1.4	1.7
18% OSPW (D)	0.8	1.1
5% OSPW	0.5	0.8
5% OSPW (D)	0.5	0.8

4.3.4 pH

The recorded pH values of selected treatments are shown in Figure 4.5 and Table 4.6. Starting pH values ranged from 7.90 (100% BCR) to 8.91 (81% OSPW (D)). It is not known why the pH values varied that much even between duplicate samples. It was expected that OSPW would have a pH between 8-8.4 as often reported in literature (Allen 2008; Mohler et al. 2014). The fresh water source, 100% BCR, had a starting pH value of

7.9. Casey (2011) reported on the physical and chemical characteristics of natural lakes in Alberta and found the pH of lakes in the Athabasca watershed, the same watershed that includes Fort McMurray and BML, ranged from 7.6 to 8.7 with an average of 8.3 and standard deviation of 0.3. The pH of 100% BCR falls within the lower range of the recorded natural lakes.

At the end of the experiment, the pH, regardless of starting point and water mix, converged to 8.5 to 9.0, averaging 8.8 with a standard deviation of 0.2. pH increased in general to the upper range of the range of pH values found in the Athabasca watershed as reported by Casey (2011). The convergence of the pH across all water mixes suggests a common influence on all waters. The atmosphere can influence the pH of waters through the diffusion of CO_2 from the atmosphere. The CO_2 interacts with the carbonate/bicarbonate equilibrium system present in most waters. Lower (2014) reported the constants of the carbonate equilibrium system for 25°C to be $pK_H = 1.47$, $pK_1 = 6.35$, $pK_2 = 10.33$ and $pK_w = 14.00$. As of November 2015, the carbon dioxide concentration at Mauna Loa Observatory, Hawaii is 400.16 ppm (Tans and Keeling 2015), which translates to $4*10^{-4}$ atm of partial pressure. Using these numbers, atmospheric influence alone would drive the pH to 5.61 (based on pure water). The pH convergence is well above this and, for many of the water mixes, the pH is rising. Thus it is unlikely that atmospheric CO_2 is having much effect on the pH in the columns. Another common influence for all the mixes is the FFT. The pH of FFT porewater has been reported as 8.33 by Mikula (2013). In addition, experiments done by Mikula (2013) using simulated rainfall on aged FFT, resulted in runoff water with pH of 9.79. However, porewater pH measured from initial FFT in this experiment averages 7.1 with a standard deviation of 0.2, also well below the final pH values recorded in all water mixes. Mikula (2013) did not identify the processes involved in raising the pH of runoff, but a similar increase in pH has been recorded in this experiment and similar processes may be taking place.

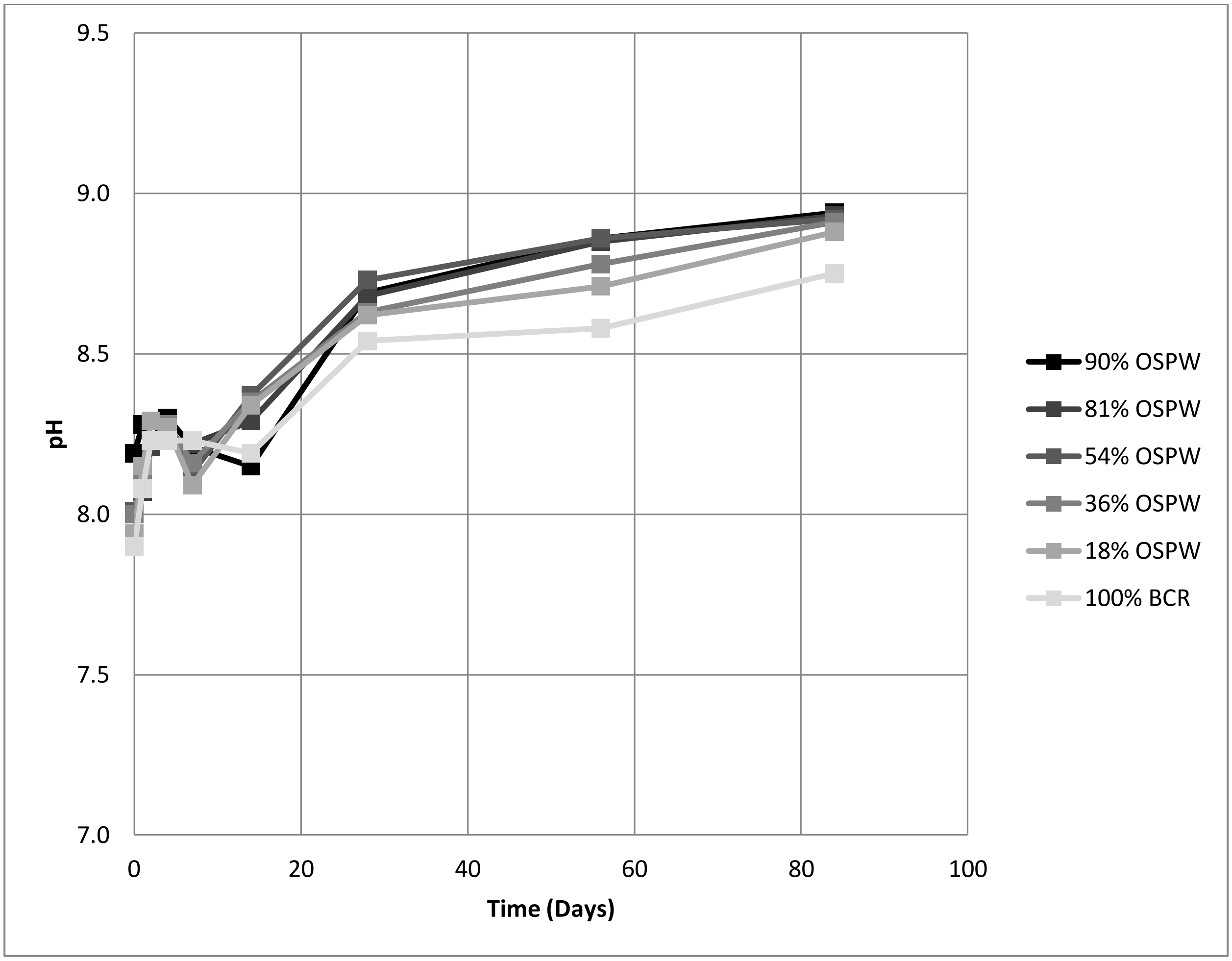

Figure 4.5: pH for the duration of the Trial A with pH converging to 8.5 to 9.0 regardless of the starting pH.

Table 4.7: Starting and ending pH for Trial B columns showing almost no change from the start to the end of the trial.

Treatment ID	pH Day 0	pH Day 90
81% OSPW (D)	8.91	8.83
54% OSPW (D)	8.85	8.80
36% OSPW (D)	8.81	8.81
18% OSPW (D)	8.60	8.64
5% OSPW	8.39	8.47
5% OSPW (D)	8.43	8.48

4.3.5 DO

DO was remarkably similar for all BML/BCR mixes for each trial. DO at the end of Trial A was much higher than Trial B (7.6 mg/L and 5.8 mg/L respectively as shown in Table

4.7) but the variation within each trial was very small. The higher DO in Trial A may be due to the fact the columns were uncovered in Trial A and covered in Trial B. There was approximately 300 mL of headspace in the columns in Trial B but limiting the evaporation in Trial B may also have limited the oxygen available to be dissolved into the water. Temperature and pressure can affect DO levels but are considered to be negligible factors in this experiment with both trials completed in the same place. Microbial activity can also affect DO levels but this was not tested in this experiment (Chen et al. 2013).

Table 4.8: DO values at the start and end of the Trials for BML/BCR mixes. All numbers are averaged for the columns because of the similarity of the values.

	Average ± St. Dev.	Min	Max
Starting DO	6.2 ± 0.5	5.7	6.8
End Trial A	7.6 ± 0.1	7.4	7.8
End Trial B	5.8 ± 0.2	5.5	6.0

4.3.6 Turbidity

All columns showed a significant decrease of turbidity over time as shown in Figure 4.6. Trial B columns included extra turbidity added at the start but end values were similar to Trial A columns. Final turbidity values ranged from 22 NTU (5% OSPW) to 110 NTU (36% OSPW), averaging 56 NTU. As highlighted in Chapter 3, the turbidity goal for 2 m of sunlight penetration is around 23 NTU. Two treatments were close to this goal on day 84: 5% OSPW (22 NTU) and 5% OSPW (D) (26 NTU) suggesting this water composition may produce sufficient water clarity for EPLs without treatment. Turbidity was added to Trial B columns to attempt to highlight the influence of water composition on turbidity. There were significant variations in turbidity in similar samples. The 90% OSPW treatment with no turbidity addition had an initial and final turbidity of 331 NTU and 77 NTU, respectively, while the 90% OSPW (D) treatment with 10 mL of FFT added had an initial and final turbidity of 273 NTU and 44 NTU, respectively. Similarly, 5% OSPW and 5% OSPW (D) treatments each had 10 mL of FFT added but turbidity values were 593 and 316 NTU, respectively at the start of the experiment and final turbidity values of 22 NTU and 26 NTU, respectively. One issue that might have played a role in varying turbidity values is the difficulty of overlaying the FFT with water without disturbing the FFT layer. Increased FFT disturbance leads to higher turbidity values at the start of the experiment. No discernible pattern emerged relating water composition and turbidity reduction. Using MATLAB and a linear regression model with the final turbidity as the dependent variable, no statistically significant relationship could be found for initial turbidity, %OSPW, Na^+ concentration, K^+ concentration, Mg^{2+} concentration and Ca^{2+} concentration ($p>>0.05$).

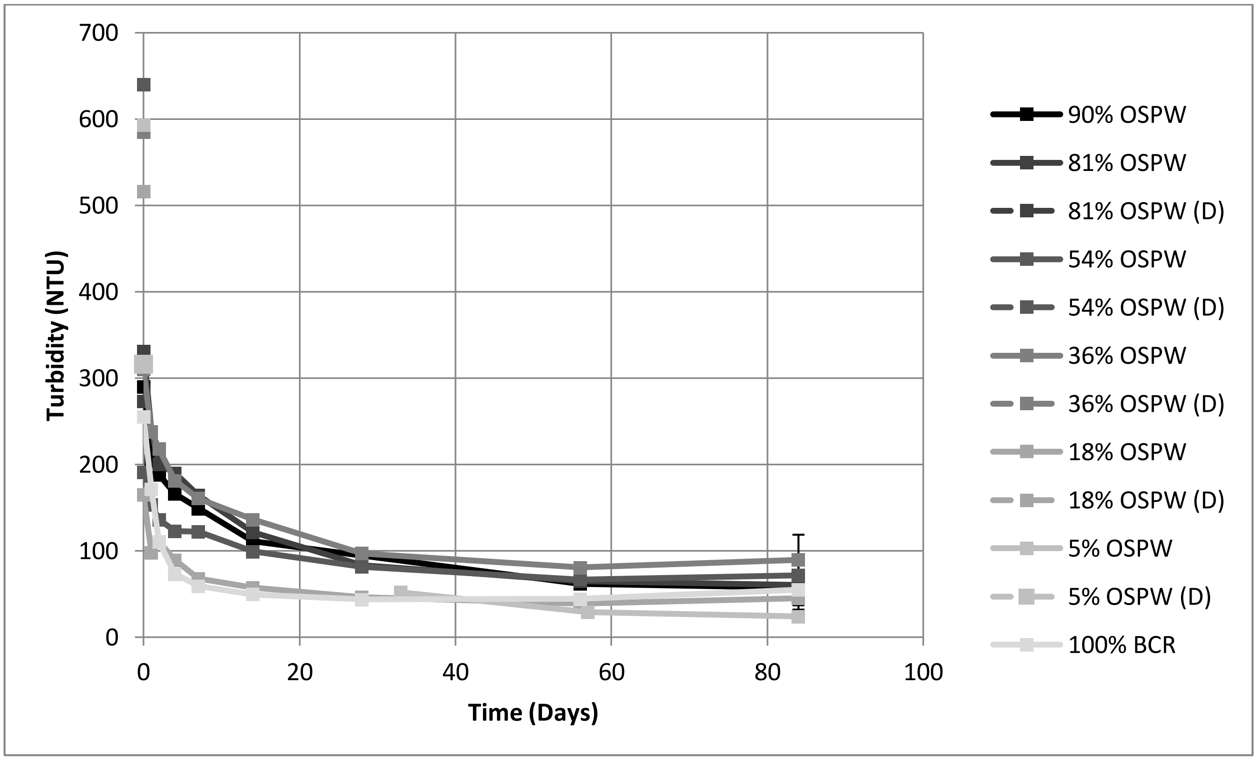

Figure 4.6: Turbidity decrease over time with no additional turbidity added to Trial A columns and 10 mL of FFT added to Trial B columns at the start of the trial. End turbidity values are averaged between same composition water with the error bars showing standard deviation.

4.3.7 FFT Dewatering

The FFT/water layer interface lowered, from its starting depth, over time with a slight increase in some columns in the first seven days. Table 4.8 shows the summary of the depth the interface was lowered and the relative percentage to its original height. A graph provided in Appendix A shows the movement of the FFT/water layer interface over time compared to its original height. Starting depths varied due to varying cylinders used. All columns show dewatering of the FFT layer by the end of the experiment. The 5% OSPW treatments show a FFT reduction by more than 25% while the other columns showed a reduction between 11% and 18%. Curiously 100% BCR had the lowest average reduction of FFT. For 100% BCR, the K^+ concentration, Mg^{2+} concentration and Ca^{2+} concentration all sharply dropped over time in the water layer with Na^+ concentration also showing a decrease. It was assumed that the FFT layer and the clay particles within the FFT would be saturated with cations, however the cation concentration profiles points to a deficit of cations in the FFT and movement of ions from the water layer into the FFT layer. A possible reason for lower dewatering of FFT in 100% BCR is that the cations present in the FFT and water layer are not sufficient in neutralizing the negative surface charge of the clay particles as discussed in Chapter 2. A lack of cations would leave unneutralized negative charges in the FFT, hindering dewatering.

Table 4.9: Lowering of the FFT/water interface in both absolute and relative terms.

	First Column		Second Column		
Treatment ID	Depth Lowered Based on Starting Depth (cm)	% Lowered	Depth Lowered Based on Starting Depth (cm)	% Lowered	Average (%)
90% OSPW	0.8	16	N/A	N/A	16
81% OSPW	0.6	14	0.7	17	15
54% OSPW	1.0	20	0.7	16	18
36% OSPW	0.3	7.1	0.7	18	12
18% OSPW	0.7	16	0.8	15	16
5% OSPW	1.2	29	1.0	26	28
100% BCR	0.5	11	N/A	N/A	11

Globa and Barbour (2001) researched sloughing of cut slopes along a stretch of a canal and found that the clay and porewater chemistry plays an important role in the stability of soil. The dispersion of the clays followed a pattern based on %Na and total dissolved salts (Na + Mg + K + Ca in meq/L) with the different zones shown in Figure 4.7. This research paper showed the importance of knowing the porewater chemistry and how ionic concentrations change the dispersion behavior of clays. It was one of the inspirations of our experiments. Superimposing the data gathered in this experiment on the graph presented by Globa and Barbour (2001) does not show a similar pattern. This may be due to different data being presented: Globa and Barbour (2001) presented porewater data while our experiments show water layer data. However, this figure illustrates that Na^+ concentrations in OSPW are so high that the non-dispersive zone is not going to be reached using a water mix including OSPW. Remediation strategies reliant on Na^+ concentrations may not be effective and research should focus on non Na^+ dependent strategies.

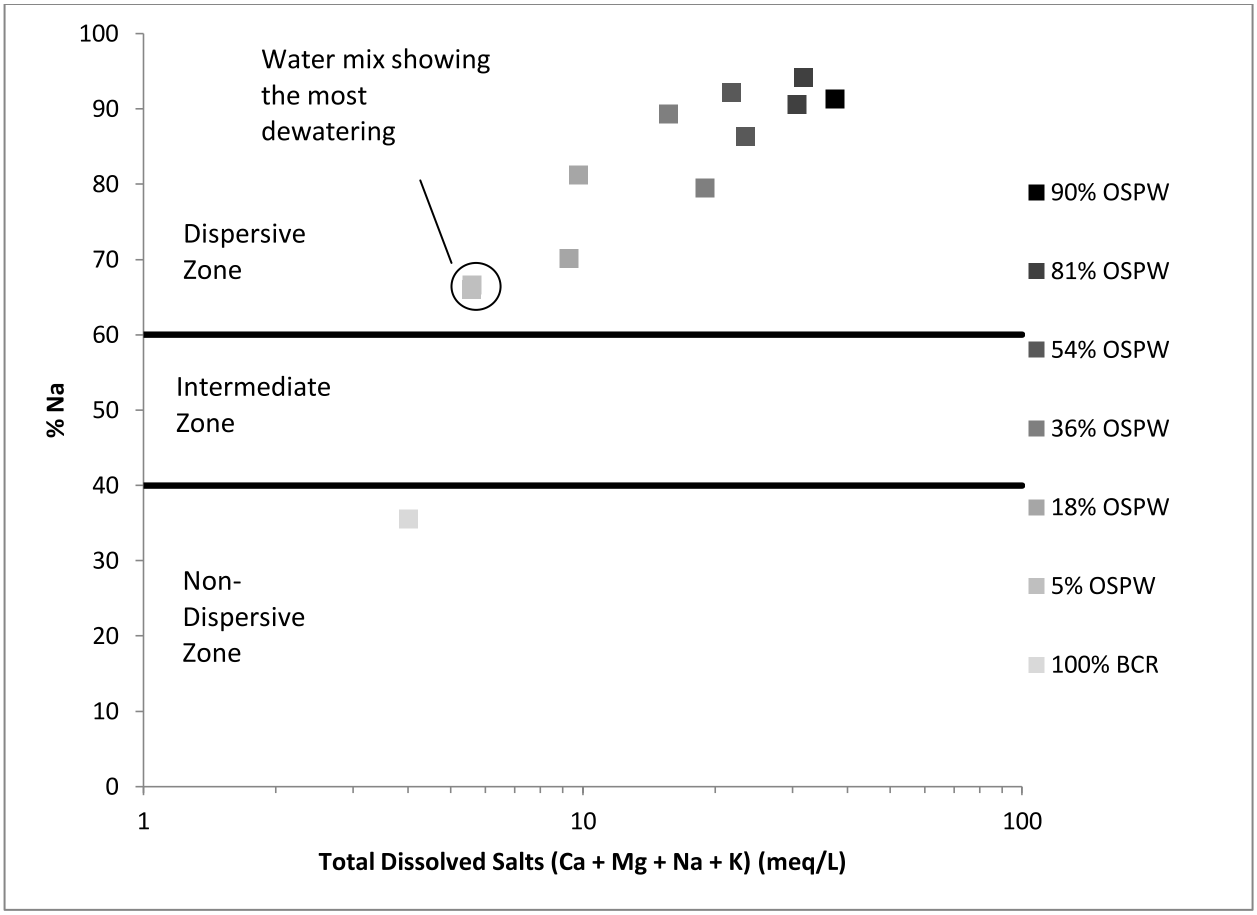

Figure 4.7: Susceptibility to dispersion in clays modified from Globa and Barbour (2001). Important to note is the original figure is based on porewater while water layer data from this experiment is displayed.

4.4 Conclusion

Experiments conducted over 84-90 days on different water compositions indicate that the water composition does not have a large influence on turbidity reduction. All turbidity reduced over time in the columns to below 90 NTU with one exception. Two treatments (5% OSWP and 5% OSPW (D)) have turbidities (22 NTU and 26 NTU, respectively) suggesting water clarity allows for 2 m of light penetration if tested in a large column. From the large column experiment, the 60% OSPW treatment showed Secchi depth of 1.2 m and turbidity of 23 NTU, suggesting the turbidity goal for 2 m of light penetration is 23 NTU. The pH, conductivity and cation concentration results all indicate there is interaction between FFT and the cap water layer, confirmed with a reduction of FFT depth as it dewaters. pH results show a convergence to approximately 8.8 for all columns while conductivity steadily increased by an average of 0.3 mS/cm for most columns over time. Sodium concentrations, the dominant cation, also generally increased over time indicating a flow of Na^+ from the

FFT or FFT porewater to the cap water layer. No significant pattern was found relating the final turbidity to initial turbidity, OSPW%, Na^+ concentration, K^+ concentration, Mg^{2+} concentration and Ca^{2+} concentration. FFT dewatering was highest in 5% OSPW with the lowest dewatering occurring in 100% BCR..

4.5 Chapter 4 References

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CHAPTER 5: CONCLUSION

Studies conducted in this thesis indicate that turbidity reduction (increasing water clarity) in EPLs is a complex process with many variables. Decreasing the pH of the water layer is looked at as one possible strategy to increase the water clarity to 2 m of light penetration, or Secchi depth of 1 m. 500 L of CO_2 addition to 80% OSPW reduced the pH from 8 to 6 but did not show an improvement in water clarity as measured by Secchi depth (0.2 m). Further pH reduction to 3.5 using the equivalent of 165 mL of 12 N HCl produced both an immediate increase in water clarity (Secchi depth 0.8 m) and a secondary increase between 30 and 60 days after HCl addition (Secchi depth 1.6 m). The time lag noted is not fully understood but may be related to the kinetics of the dissolution of $CaCO_3$ and the subsequent exchange of Na^+ with Ca^{2+} of clay particles in the water layer. One pH reduction to 6, due to the addition of 4000 L of CO_2 in the 60% OSPW treatment, showed a dramatic increase in water clarity between 78 days (Secchi depth 0.2 m) and 98 days (Secchi depth 1.2 m). A second treatment (20% OSPW) showed an initial small increase in water clarity (Secchi depth 0.05 m to 0.2 m) after 1000 L of CO_2 addition but not a dramatic increase (deepest Secchi depth recorded 0.5 m). Turbidity improved in 60% OSPW (300 NTU to 23 NTU on day 98), 60% OSPW (Control) (300 NTU to 63 NTU on day 94) and 20% OSPW (200 NTU to 57 NTU on day 122).

It is hypothesised that the difference between the treatments can be explained through the competing factors of ionic strength and divalent cation concentration. Higher ionic strength is beneficial to suppressing the negative surface charges of clay particles, allowing flocculation and settling to occur more readily. Divalent cations are known to neutralise the negative surface charges better than monovalent cations making a higher proportion of divalent cations desirable to increase water clarity. The water sources used in these experiments are OSPW (high ionic strength (70 mmol/L), low divalent cation proportion (10%)) and fresh water (low ionic strength (14 mmol/L), higher divalent cation proportion (59%)). These results indicate that ionic strength has a greater influence on BML water clarity than divalent cation proportions for the water mixes studied. In addition, analysis of ion concentrations in the columns show that diffusion of ions from the FFT to the water layer is the dominant driver of change in ionic concentration, and is more important than cation exchange or dissolution and precipitation of $CaCO_3$.

Increasing water clarity allowed a comparison of different water clarity measurements: Secchi depth and light intensity. Data gathered in the large column experiments indicate that the approximation of Secchi depth occurring at 0.1 light intensity is not an accurate approximation for BML with deeper Secchi depths occurring at lower light intensities. A second approximation stating 0.01 light intensity (light penetration depth) occurs at twice the Secchi depth was more accurate with experimental data yielding an equation: light penetration depth = 1.77 * Secchi depth ($R^2 = 0.82$).

A second study indicates that without pH reduction, the water composition has no real effect on increasing water clarity. Turbidity values measured in small columns with different 0-90% OSPW proportions do not show a discernible trend, except for one water composition (5% OSPW) showing a turbidity reduction to 24 NTU. This final turbidity value is very close to the turbidity value of 23 NTU shown in the large column experiments to correlate to 2 m of light penetration. This leads to the conclusion that 5% OSPW may yield adequate light penetration without pH adjustment. This study also indicates that diffusion of porewater to the water layer and interaction of the FFT layer with the water layer has impact on pH, conductivity and ions present in the water layer. pH converged to approximately 8.8 for all water compositions, regardless of starting pH, which ranged from 7.9 to 8.9. Conductivity increased an average of 39% over the duration of the experiment and a general increase in Na^+ concentration in the water layer was noted of 0-5 meq/L above the starting concentrations.

Combining the results of these studies indicates that water clarity is very complex with many factors affecting it. Lowering the pH has a positive effect on water clarity but the effectiveness depends on the water composition. At the same time, water composition on its own without pH adjustment does not seem to have any effect on water clarity, and initial turbidity does not seem to have an effect either. Regardless of the mechanism of water clarity improvment, one common theme found is that the process takes up to three to four months before improvement is seen. This is important for any future research in water clarity improvement, which may show a similar time frame.

Understanding the processes involved in increasing water clarity is extremely important to the health of an EPL. Water clarity directly influences the depth and size of the littoral zone in any lake, including EPLs. The littoral zone regulates DO concentrations in the lake, stabilises soil sediment and provides food and shelter for fish in the lake. It is an essential part of any aquatic ecosystem and, in EPLs, largely determines the effectiveness of the remediation of OSPW.

Finding a successful remediation technique for FFT and OSPW is important for the growth and continuation of the oil sands industry in Alberta. EPLs are part of the research currently being done, with BML seen as a test case to include more EPLs in remediation plans. Many other techniques are also being researched at the moment. Remediation techniques such as centrifuging, thin-lift dewatering and rim ditching are all promising, but have their own drawbacks. A number of techniques have to be commercially viable for the oil sands to continue as a profitable industry.

5.1 Future Recommendations

Research in water clarity in EPLs should be continued in order to promote the development of a healthy ecosystem and lessons learned in this field can be useful in other oil sands remediation techniques. Continuing research should focus on understanding the time lag found in water clarity improvement. This time lag may be influenced by the scale of the experiment as well as the mechanism involved. Time lag may be investigated by HCl addition in the same water composition but different volume columns. This would indicate if the scale of the experiment has an effect on the time lag and may be used to predict how the time lag would affect treatments in the field. In addition, the time lag may be affected by the water movement in a column. Two columns with identical water compositions could be set up, one with Secchi depth monitoring (which will disturb the water) and one without. Water clarity comparisons at the end of the experiment can indicate if water disturbance is a factor in time lag. The FFT layer may also influence the lag time due to ion movement, thus a series of experiments with different amounts of FFT may show the influence or non-influence of FFT on the settling process.

Additional research should be done to see if cation manipulation may encourage coagulation. The addition of divalent cations has been shown to be effective in water treatment flocculation and may increase both ionic strength and the proportion of divalent cations, both of which would stimulate the flocculation of clay particles. Ca^{2+} and Mg^{2+} are two divalent cations that may be added because they are already present in the water. Trivalent cation addition is another possible research area along the same lines. The addition of Al^{3+} is already used in water treatment for coagulation and flocculation and may be beneficial in increasing water clarity in BML.

The interaction of FFT with the water layer is extremely relevant to EPL research. In the small column experiments, 200 mL of FFT had a noticeable impact on the water layer in a number of parameters such as ion concentrations, as well as possibly pH. BML contains a much higher ratio of FFT:water. The effect of FFT on the water layer is likely to be more pronounced with a higher FFT:water ratio. The long term implications of the FFT and water interaction must be studied (especially cation diffusion and exchange from the FFT to the water layer) to ensure that an EPL is a sustainable long-term remediation technique in the oil sands.

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APPENDIX A: SUPPLEMENTARY DATA TABLES AND FIGURES

Table A.1: Winkler titration calibration with DO meter.

DO meter	Winkler	%error	% absolute error
9.17	8.8	4.20454545	4.2
9.02	10.1	-10.693069	10.7
9.09	10	-9.1	9.1
9.09	9.47	-4.0126716	4.0

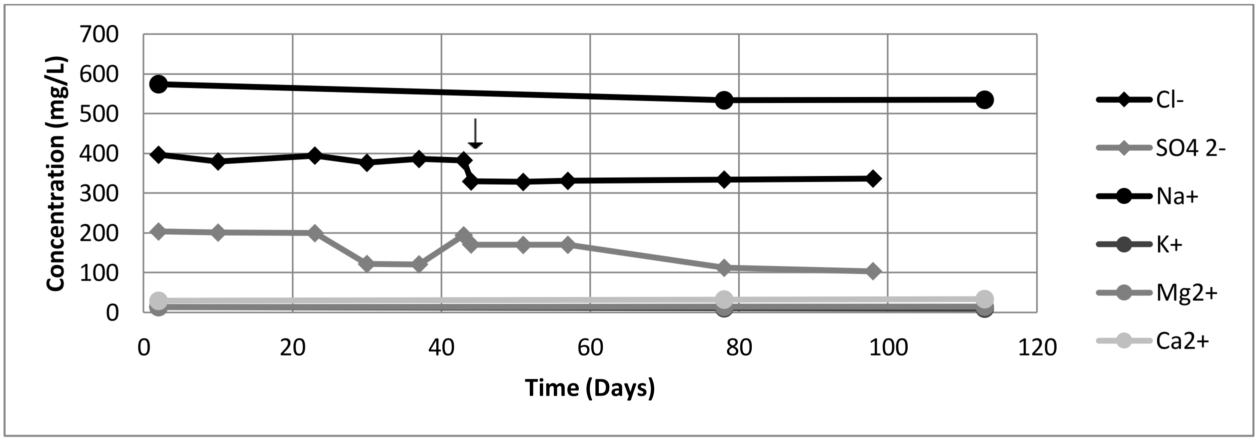


Figure A.1: 60% OSPW ionic concentrations in mg/L with no chloride adjustment. The arrow indicated the addition of BCR on day 43 (after measurements were taken).

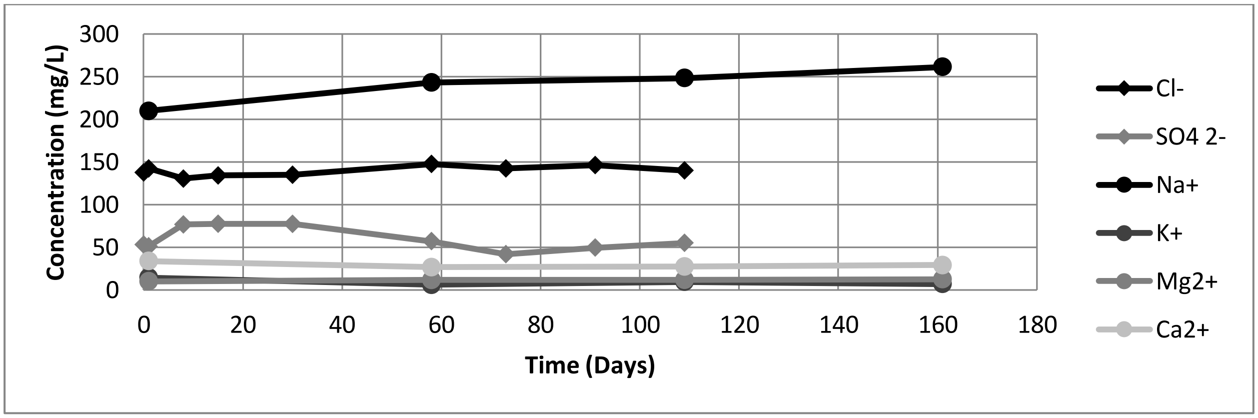


Figure A.2: 20% OSPW ionic concentrations in mg/L with no chloride adjustment.

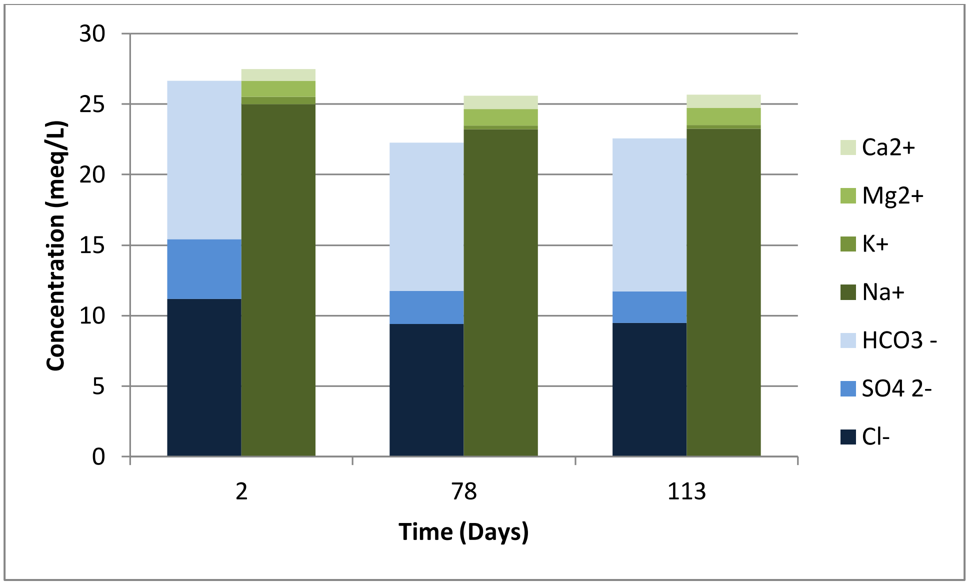


Figure A.3: Ionic balance of cations and anions in meq/L for 60% OSPW with no chloride adjustment.

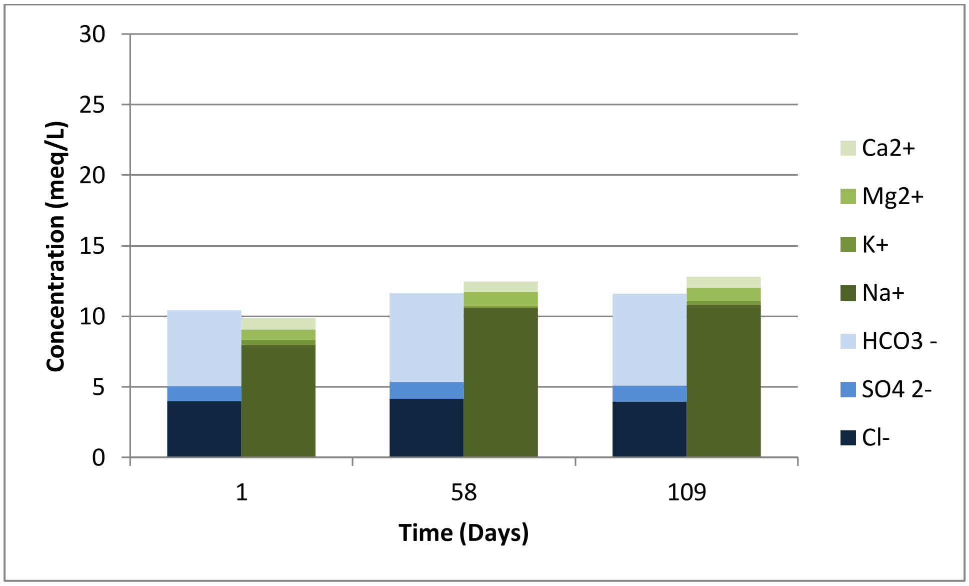


Figure A.4: Ionic balance of cations and anions in meq/L for 20% OSPW with no chloride adjustment.

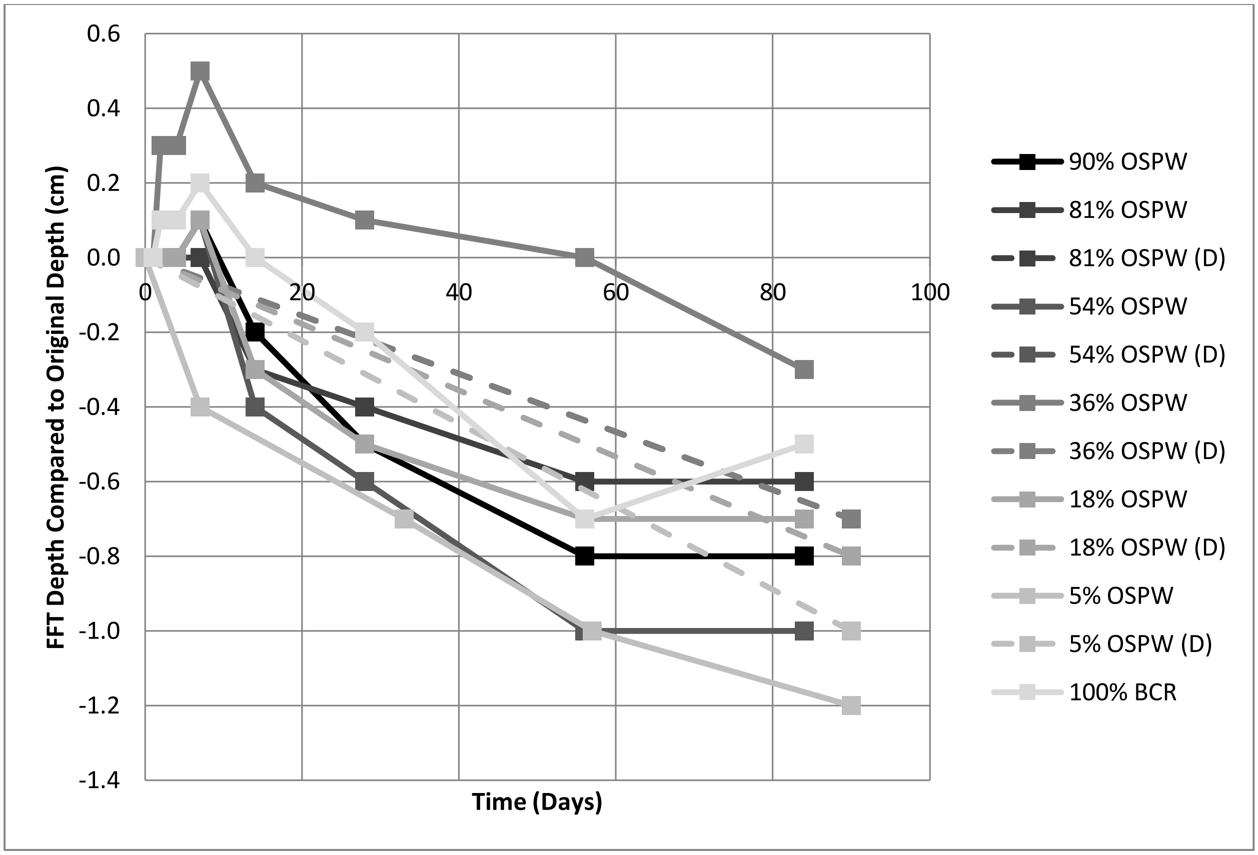


Figure A.5: Change in FFT depth over time for the small columns based on original depth of FFT.

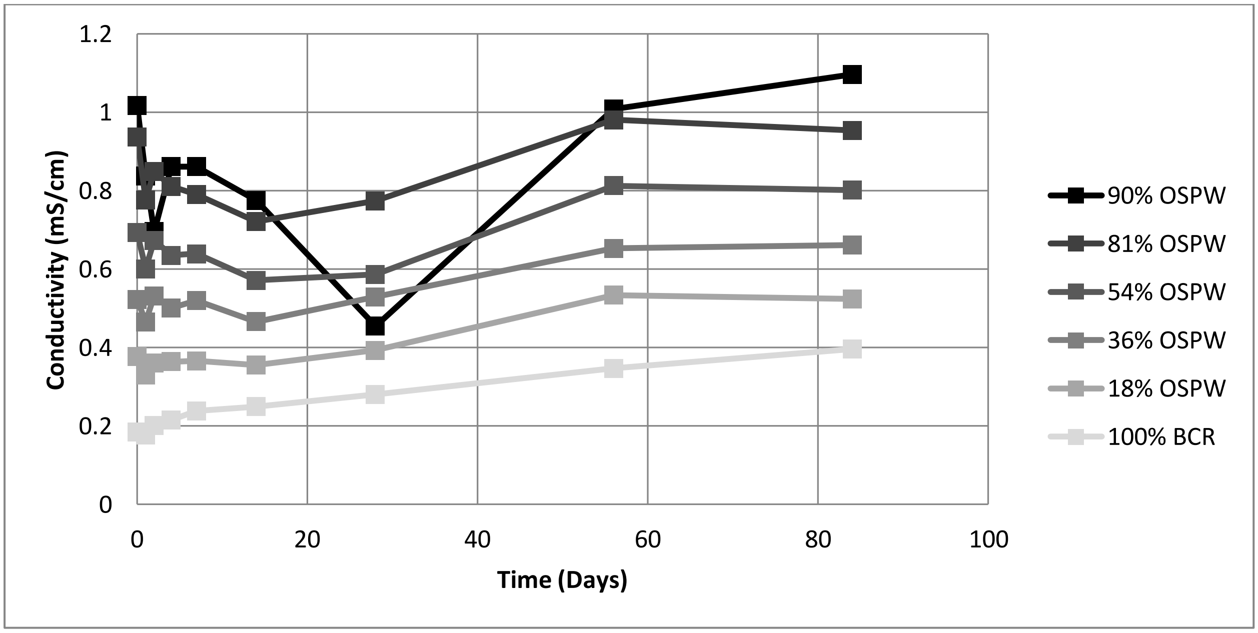


Figure A.6: Raw conductivity data showing an anomaly on day 28 for 90% OSPW.

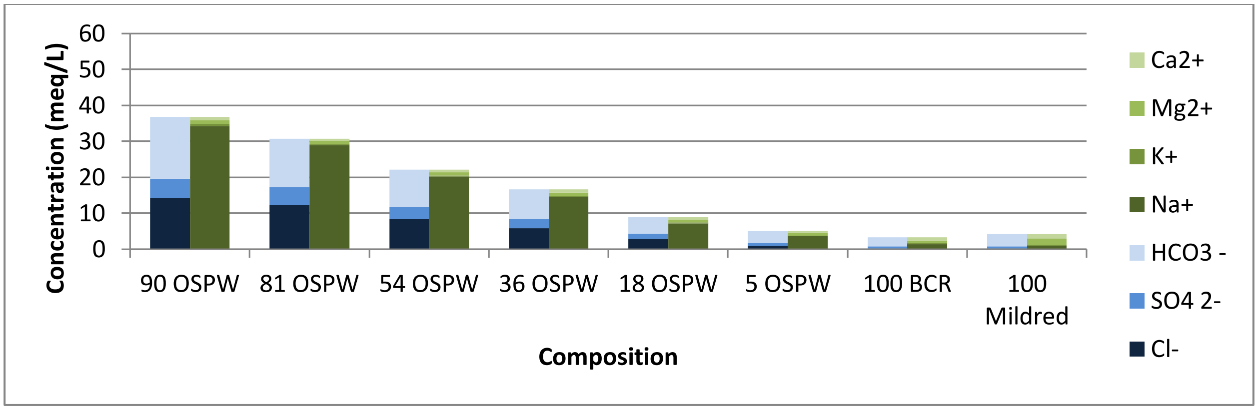


Figure A.7: Ionic balance of cations and anions in meq/L for small columns at the start of the experiment. HCO_3^- concentrations estimated based on ionic neutrality principle.

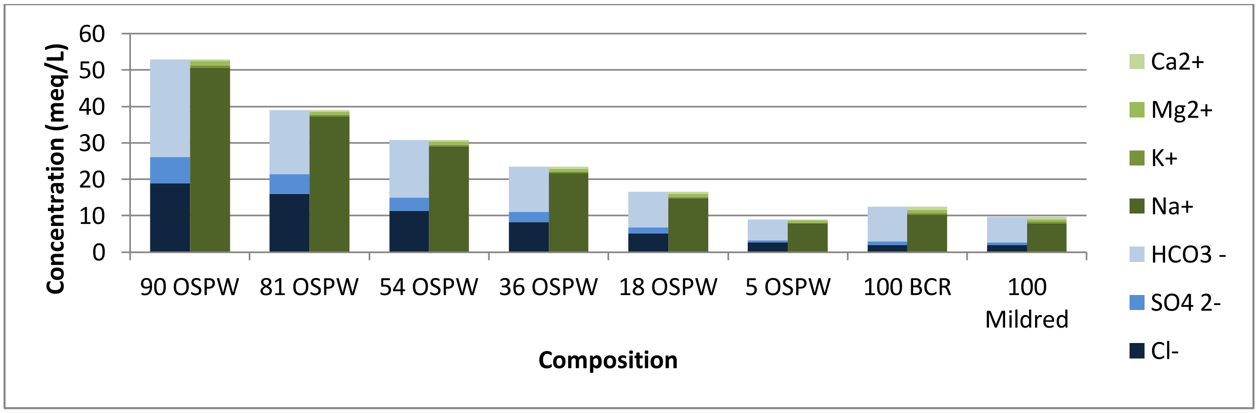


Figure A.8: Ionic balance of cations and anions in meq/L for small columns at the end of the experiment with no chloride adjustment. HCO_3^- concentrations estimated based on ionic neutrality principle.

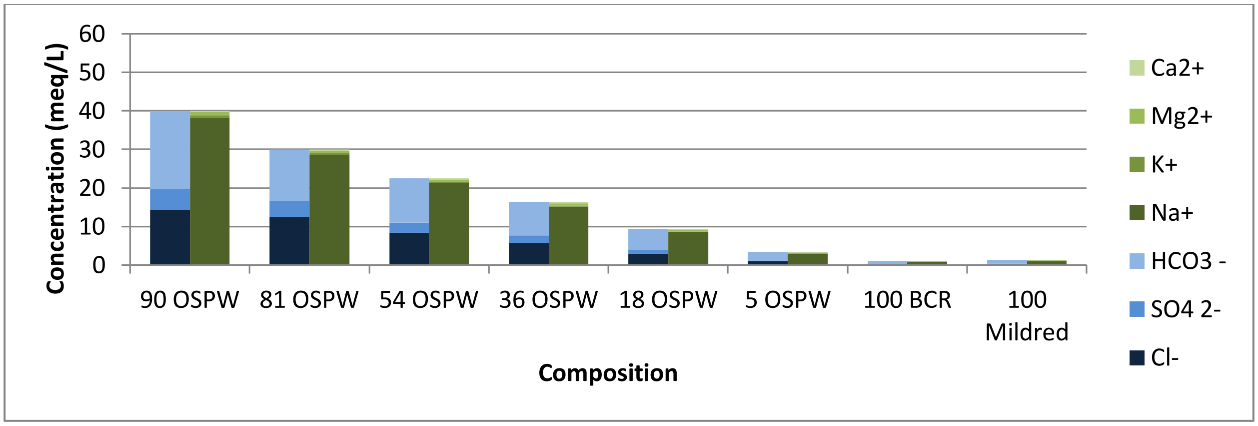


Figure A.9: Ionic balance of cations and anions in meq/L for small columns at the end of the experiment with the chloride adjustment based on starting chloride concentrations. HCO_3^- concentrations estimated based on ionic neutrality principle.

APPENDIX B: COLUMN SET UP AND CLEAN UP

Big column set up

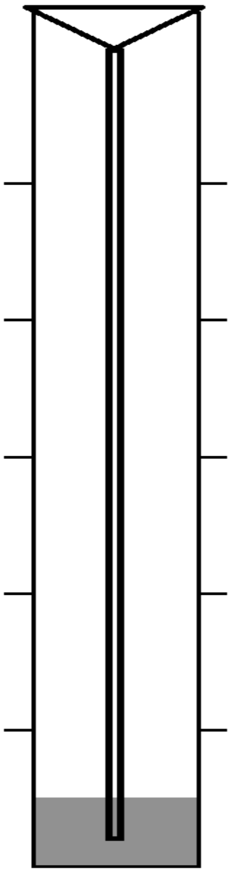
Materials:

- Big column:
    - 2.5 m tall
    - 30.5 cm outer diameter
    - 0.635 cm wall thickness
    - Clear Townsend acrylic tubing
    - Sampling ports (2 each at 40, 80, 120, 160 and 200 cm from bottom)
- Column stand:
    - Length:
    - Width:
- Containment:
    - Length:
    - Width:
- Tie down strap (2)
- Funnel
- Tube (~2.4 m length)
- Long handed trowel
- Peristaltic pump (variable speed)
- Peristaltic tubing
- Bucket
- Marking tape
- Strong tape (packing tape works well)
- Tape measurer
- Curtain
- Light
- Rope
- Lighter (if needed)
- Ladder
- Scissors
- Binder clips
- Carbon dioxide cylinder

- Gas cylinder restraint
- Regulator
- Tubing to attach to system
- Flow meter
- Seair system or sparger and small tube.

Procedure:

1. **Column set up.** Set up containment on an even floor, preferably close to a drain and, if needed and possible near a wall with some kind of restrainment.
2. Place stand in containment, making sure the column sampling ports will be easily accessible (they are perpendicular to vertical brace) and stand is stable.
3. Place column on stand so that the column is snug to the vertical brace and all parts of the base of the column are on the stand. Likely will need 2 people to lift and place column because of length and awkwardness of carrying.
4. Secure column to vertical brace on stand using 2 tie down straps and the holes provided in the stand. Make sure the straps are really tight.
5. Secure stand/column to wall restraint if possible.
6. **FFT addition.** Prepare FFT for addition to column by mixing the FFT in the bucket with a long handed trowel. (FFT buckets stored in 4°C cold room and open by removing locking mechanism and loosening individual sections of lid with hands or bucket opener.)
7. Pour FFT through funnel and tube to bottom of the column as shown in Figure B.1. Try to minimize FFT splattering on the side of the column. If mixed properly, FFT will level out on its own. Filling to the desired level is easiest if marked beforehand.
8. Remove funnel and tube, careful not to smear the sides, especially at the top of the column (some smearing may be unavoidable).



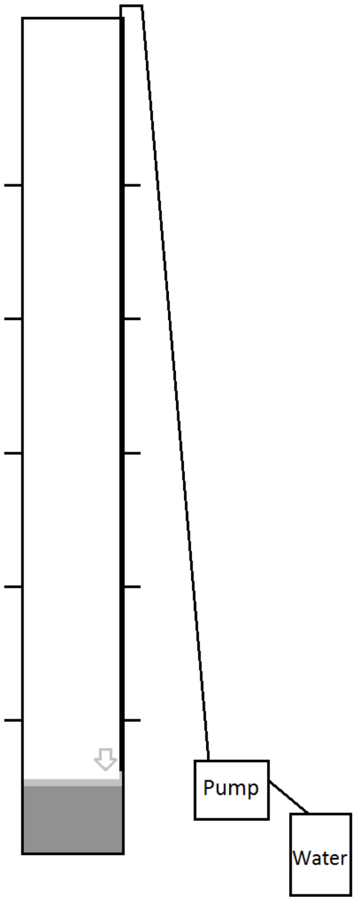


Figure B.1: FFT Addition **Figure B.2: Water Addition**

9. **Water addition.** Mix desired OSPW and fresh water. Easiest is to mark a bucket with desired depths by filling before hand with known volumes of water and filling to the marks.
10. Set up peristaltic pump and tape on end of the tubing on the inside of the column so that is ~5-10 cm above the FFT and touching the side of the column as shown in Figure B.2. Put the other end in the mixed bucket of water. For continuous addition, put mixed water into another container so the marked bucket can be used to mix more water.
11. Add water very slowly at the lowest speed of the pump. Only drops should be coming out. Ideally the drops travel along the side of the column to minimize the disturbance of the FFT.
12. Filling the column takes a number of days, keep the speed as high as it can without disturbance to the FFT but err on the side of caution. Keep raising the tubing to above the water surface. A variable speed pump will allow for gradual increases in pumping. Overfill if using Seair as system will drain some water.

13. **Peripherals set up.** Use a ladder to attach the light above the column. Try to center it over the column and aiming straight down. Use rope and the ceiling bars etc. Use a lighter if needed to melt the ends of the cut rope to stop fraying.
14. Set up curtain around the column using the nuts and bolts of the lid of the column. Start with the end of the curtain of the side where sampling will take place. Hook the second curtain hole over the bolt secured at the top of the column and wrap curtain around the column, hooking the appropriate hole over the bolt on the other side of the column. Hook the last hole over top of the second hole already on the first bolt. Secure he curtain with binder clips both above and below each sampling port to ensure the ports are accessible but no light can enter the column. The curtain can then be opened by opening the clips without having the take the whole curtain off.
15. **Turbidity addition.** Turbidity can be added using FFT and a beaker. Fill the beaker with a set amount of mixed FFT and fill the rest with water from the column. Mix in the beaker as much as possible and swirl into main column, repeating mixing in the beaker as much as needed. Column can be mixed with the carbon dioxide addition or pump only mixing if using the Seair system.
16. **Carbon dioxide addition.** Set up cylinder with restraint and regulator close to the column.
17. Sparger set up: attach regulator to flow meter (short length) and then to sparger (at least 4 m but likely longer depending on set up). Attach sparger and tubing to end of long pipe or similar (could reuse the pipe FFT was poured through). Insert pipe with sparger into the water at the desired height (do not disturb FFT while adding carbon dioxide) and secure at that height by taping a smaller pipe perpendicular to the long one to rest on top of the column forming a cross.

    Seair set up: attach regulator to flow meter mounted on the Seair system. Attach the inlet tubing to the 4 highest sampling ports (160 cm and 200 cm from the ground) and the outlet to the 4 next highest (120 cm and 80 cm). The curtain has to be pulled back to do this. Open sampling ports and let water into system. Open the tubing on the one way valve on top of the system and use a pen to relieve gas pressure to allow water to fill the system completely. Reattach tubing.
18. Add carbon dioxide. Sparger: regulate flow using flow meter and chack regularly as it will drift over time.

    Seair: first turn on pump and let flow through system. After a couple of minutes, open carbon dioxide value. Check all 4 pressure valves. Ideally these should read similar numbers, adjust main water flow on the bottom of the system if this is not the case. Carbon dioxide flow will be constant after initial settling period. Bubbles are very hard to see at the start but can be distinguished using a black background (such as the brace that supports the column). To turn off the system, stop carbon dioxide addition and then turn off pump. If adding carbon dioxide over multiple days, close the sampling ports over night to lower the pressure in the system and reduce the chance and impact of leaks.

19. Stop when desired pH levels are reached (~6) and remove all carbon dioxide systems, making sure the sampling ports are closed.

Big column clean up

Materials

- Cart to transport column
- Waste buckets
- Many people
- Water hose
- Cleaning brush or similar

Procedure

1. Drain water into waste buckets through lowest sampling ports. Slowly open ports because there is a lot of pressure on these ports and water will shoot far.
2. When water is level with lowest sampling port, untie the column from the brace and use multiple people to tip column and drain column from the top. This will leave a streak of FFT on the side of the column. If column cannot be cleaned right away, either do not empty column or refill with tap water to prevent FFT caking unto the column.
3. In an open space, use a hose to refill the column, use water pressure to clean the sides as much as possible and a brush to scrape the sides. Soak column for 2 days or so to get most of the FFT off the column. Using a cart, the column can be moved to NREF 1-057 (with permission) where there is a large drain and hose to help clean up.
4. Tip the column over and use a hose to clean and drain the column at the same time to clean the bottom as much as possible.

Small column set up

Materials

- 2L graduated cylinders
- Small funnel and tubing or peristaltic pump and tubing
- Long stemmed scoop
- Long handed trowel
- Mixing beaker/graduated cylinder

Procedure

1. Mark cylinders to desired FFT and total volumes
2. Prepare FFT for addition to the cylinders by mixing the FFT in the bucket with a long handed trowel. (FFT buckets stored in 4°C cold room and open by removing locking mechanism and loosen individual sections of lid with hands or bucket opener.)
3. Add FFT to cylinders using long stemmed scoop, careful not the touch the sides as far as possible.
4. Mix desired concentration of water using the beaker or spare graduated cylinder.
5. Add water to the cylinders using pump as described in big column set up or use the funnel and tubing. Folding the tubing upwards at the bottom and taping it secure helps to reduce the momentum of the water and the impact on the FFT interface.

Small column clean up

Materials

- Waste bucket
- Cleaning brush

Procedure

1. Empty cylinders into waste bucket and clean right away by adding clean water and letting it soak.
2. Soak and empty until desired and clean with brush and sparkleen.