# Ozone-Assisted Settling of Diluted Oil Sands Mature Fine Tailings: A Mechanistic Study

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# REPORT SUMMARY

The accumulation of mature fine tailings (MFT) in tailings ponds with very slow natural consolidation rate has been a concern for decades. Previous studies and current practices for tailings consolidation focus on the addition of various inorganic and organic additives to reduce MFT production and accumulation. It is highly desirable to develop more efficient and effective techniques for MFT consolidation to reduce the potential environmental impacts of oil sands tailings.

In this study, the performance and mechanisms of a novel ozone-assisted MFT dewatering method were evaluated. MFT with different solids contents were ozonated for 15, 30, and 60 minutes to determine the optimal ozonation treatment conditions for MFT consolidation. The volume and turbidity of release water, and the solids content of settled sludge (i.e., solids) were measured to evaluate the performance of ozone on MFT consolidation. MFT initial settling curves were developed by monitoring the change of the water and sludge interface positions over time. To investigate the surface interaction mechanisms involved in the process, major ions of MFT release water and the surface charge of MFT fine particles were characterized. Specifically, these parameters included pH, ion concentrations, acid extractable fraction (AEF) concentration of MFT release water, zeta potentials, and surface functional groups of fine particles. Additional experiments were performed to investigate the roles of pH and ion concentrations in ozone assisted MFT consolidation.

Our results showed that ozonation treatment effectively accelerated diluted MFT particle settling at all treatment conditions tested in this study. MFT quickly settled after short (15 minute) ozonation treatment, leaving clear brown water and compact settled sludge. The volume and turbidity of release water and the solids content of settled sludge were comparable at 1 wt% MFT under different ozonation times (15, 30 and 60 minutes). At 3 wt% and 5 wt% MFT, a longer ozonation time improved MFT settling. Therefore, we conclude that the ozonation time needed for MFT settling varied depending on the solids content of MFT suspensions.

Additional studies showed that the ozone-accelerated settling of MFT particles probably results from a change in MFT particle surface properties and the weakening of repulsive forces among fine particles through at least four mechanisms: (1) the desorption of stabilized organic matter on MFT surfaces, which reduces the steric or electrostatic stabilizing effects among fine particles; (2) the release of organic acids (such as oxalic and acetic acids) into the water, which decreases the pH of the MFT suspensions and neutralizes MFT surface charges; (3) ozone breakage of organometallic complexes in MFT, leading to the release of oxidized metal ions such as $Fe^{2+}$, $Mn^{2+}$, and $Al^{3+}$ that can act as coagulants; and, (4) an increase in cations and carboxylic groups that facilitate the generation of metal humate complexes, leading to an accelerated precipitation of fine particles.

Compared to the chemical additives currently used or studied to accelerate MFT consolidation, ozone-based processes have several advantages: (1) The process is economical because even a low ozone dose appears to be sufficient to destabilize tailings fine particles; (2) The process is environmentally friendly because ozone decomposes rapidly; and (3) The excess ozone can decompose organic compounds in tailings and thus improve the water quality.

Despite the promise observed in the present study, a cost analysis and a life cycle analysis should be performed to determine the feasibility of this treatment process. The effectiveness of ozonation treatment for undiluted MFT settling should be evaluated. The toxicity of the release water should be evaluated to examine the environmental impact of the process. Additional research on the long-term impact of ozone-assisted MFT settling processes on MFT reclamation is also needed.

# ACKNOWLEDGEMENTS

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# 1 INTRODUCTION

Alberta holds the largest oil sands reserve and the third largest (next to Saudi Arabia and Venezuela) proven crude oil reserve in the world. This oil sands reserve contains an estimated 2.5 trillion barrels of recoverable bitumen entrained in a mineral matrix of sand, clay, and water (Penner and Foght 2010). It is estimated that the Alberta oil sands contain over 1.6 trillion barrels of crude oil with over 178 billion barrels recoverable under current economic conditions. In 2008, the rate of oil production reached approximately 1.2 million barrels per day (Giesy et al. 2010), and it is anticipated that production will increase five-fold within the next two decades (Siddique et al. 2008).

At present, the most commonly used method for producing bitumen from mined oil sands ore is Clark Hot Water Extraction (CHWE) (Clark and Pasternack 1932). This technique requires large amounts of water and produces large volumes of slurry waste (tailings); approximately 12 $m^3$ of water is used and approximately 4 $m^3$ of slurry waste is generated to produce 1 $m^3$ of crude oil (Mikula et al. 2009). The tailings slurry consists of water, sand, fine particles (silt and clay <44 $\mu$m in diameter), residual bitumen (0.5% to 5% mass), and naphtha diluents (< 1% mass) used in the extraction process (Chalaturnyk et al. 2002). Mature fine tailings (MFT) are the remaining materials suspended in the large on-site recycle water ponds after the coarse sand fraction rapidly settles (Penner and Foght 2010). Greater than 90% of MFT solids are fine particles to which aqueous organic matter is usually attached (Adegoroye et al. 2010). It has been shown that the adsorption of organic matter onto particles leads to an increase in their negative surface potentials, contributes to colloidal stability, and consequently inhibits the aggregation of particles in an aquatic environment (Chandrakanth et al. 1996, Farvardin and Collins 1989, Jekel 1986). As a result of these properties, it is estimated that the fine clay will require hundreds of years to reach full consolidation (Headley et al. 2010, Mikula et al. 1996).

## 1.1 Motivation

Ozone has been widely used as a powerful oxidant and disinfectant in water and wastewater treatment. Our previous research demonstrated that ozonation is an effective treatment of oil sands process-affected water (OSPW). Through this research, ozone caused rapid settling of the fine particles in the tailings water. After ozonation, OSPW became clearer and a layer of fine particles was generated on the bottom of the container. It has previously been demonstrated that a suitable dose of ozone can assist in particle destabilization and aggregation. For decades, ozone-induced particle destabilization mechanisms have been widely investigated. Accordingly, it seemed promising that ozonation could be successfully applied for MFT aggregation. However, the in situ ozone-assisted consolidation and remediation process for oil sands tailings has never been systematically tested.

Motivated by the lack of knowledge on the impact of ozonation on oil sands fine particle settling, the present study was performed to investigate the controlling mechanisms leading to tailings particle aggregation by ozone treatment. Information obtained from the present study can then be utilized to help in developing proper reactors for oil sands tailings consolidation using ozone treatment.

### 1.2 Objectives

Our research addresses one of the most pressing issues facing continued and sustainable development of the oil sands resource in Canada: management of mature fine tailings and associated process-affected water. Our research is developing a novel, low-cost, and environment-friendly ozone-assisted consolidation and remediation process to increase the settling rate of the fine solid particles and remove organic components in MFT. This will allow less turbid water to be generated for recycling in the oil sands extraction process or its safe return to the environment. We measured the impact of ozone on MFT aggregation and investigated the mechanisms involved. The specific objectives were to:

1. Determine the effect of ozone on diluted MFT settling;
2. Measure the impact of ozone on MFT release water chemistry;
3. Evaluate the influence of ozonation on the surface properties of MFT particles; and,
4. Elucidate the mechanisms involved in the ozone-assisted MFT fine particle settling process.

### 1.3 Report Organization

The proposed theories and experimental design of the MFT ozonation process are discussed in sections 2 and 3. The effectiveness of ozone on MFT consolidation is evaluated under different experimental conditions and is discussed in section 4. Section 4 also investigates the mechanisms involved in the ozone-assisted MFT consolidation process.

## 2 BACKGROUND

### 2.1 Mature Fine Tailings (MFT)

During the water-based extraction of bitumen from the oil sands, a large quantity of tailings is produced. The tailings contain residual bitumen, quartz sands, clays, and silts (Long et al. 2006b). The slurry is transferred to a tailings pond where the coarse sands settle rapidly leaving a stable suspension of fine solids in the middle and relatively solid-free water on the top. It is estimated that the middle layer will take several hundred years to consolidate without any treatment due to its extremely poor water releasing property (Headley et al. 2010, Mikula et al. 1996). This stable suspension is called mature fine tailings (MFT). The constant accumulation of MFT requires more and more ponds for storage. The economic and environmental concerns created by the proliferating ponds containing MFT have become one of the most critical challenges to the oil sands industry.

## 2.2 Existing Technologies for MFT Dewatering

Many physical, chemical, and biological methods have been investigated to improve consolidation and enable reclamation of MFT (BGC Engineering Inc. 2010, Li et al. 2003, Matthews et al. 2002, Mpofu et al. 2004, Proskin et al. 2010, Sworska et al. 2000, Wang et al. 2010), however, the current technologies cannot overcome the environmental and economic concerns. The chemical-assisted process gives tailings a fast dewatering efficiency and produces sediments with high solids-content, thus it has been the major MFT treatment of interest to researchers and industries for several decades (Caughill et al. 1993, Matthews et al. 2002). In addition, centrifuge technology involves putting tailings through vessels where a spinning action separates out the water; however, centrifugation is an energy intensive approach for tailings management (Mikula et al. 2009). Here we mainly focus on the review of inorganic and organic additives and ozone treatment.

### 2.2.1 *Inorganic Additives*

The gypsum addition method has been widely used in industries to accelerate tailings densification. At dosages between 900 and 1,200 g/m$^3$, gypsum ($CaSO_4 \cdot 2H_2O$) was considered to be the most effective and economically-accessible coagulant for the consolidation of tailings (producing CT – consolidated tailings or composite tailings) (Matthews et al. 2002). However, this process may detrimentally affect the efficiency of bitumen extraction due to the continuous accumulation of calcium and sulfate ions in the recycled water (Redfield et al. 2003).

Alum ($Al_2(SO_4)_3 \cdot 14.3H_2O$, 50% solution of aluminum sulfate) is another option for tailings consolidation. Alum, at dosages of about 1,000 g/m$^3$, performs comparably to gypsum. Compared with gypsum, alum addition leads to lowered salinity and pH of recycled water (MacKinnon et al. 2001). However, inorganic coagulant aids used in the CT process have an undesirable impact on the resulting water, from both operational and reclamation aspects.

Carbon dioxide ($CO_2$) assisted densification of oil sands tailings was investigated (NEDAPAC Co. Ltd. 1973, 1974, Zhu et al. 2011). It was found that lowering the pH with $CO_2$ caused the MFT to coagulate. However, the low solubility of $CO_2$ in saline water limited the $CO_2$ sequestration of oil sands tailings.

### 2.2.2 *Polymer Additives*

High molecular weight anionic polymers (e.g., polyacrylamides and their derivatives) have been used commercially for tailings treatment (Sworska et al. 2000). Xu et al. (2008) studied the filterability of the paste obtained after oil sands tailings were flocculated with polymers. The filterability of the paste was found to be two orders of magnitude higher than that of the untreated tailings (Xu and Cymerman 1999, Xu et al. 2008). It was demonstrated that strong adhesion forces were detected between fine solids in aqueous solutions in the presence of partially hydrolyzed polyacrylamide (HPAM) which acted as a flocculant (Long et al. 2006a). More recently, hybrid $Al(OH)_3$-polyacrylamide (Al-PAM) was shown to be even more effective than HPAM in assisting filtration of MFT (Alamgir et al. 2012, Wang et al. 2010).

Although polymers can enhance the flocculation of fine clay particles, the excessive dosage required may cause destabilization of clay particles (Mpofu et al. 2004). Moreover, these polymer-based processes often incur high operational costs and their long term environmental implications are still unknown (Pourrezaei et al. 2011).

## 2.3 Ozone-Assisted Particle Aggregation

The oxidizing property of ozone is well known and it is used widely as a disinfectant and oxidant in water and wastewater treatments (Li et al. 2009, von Gunten 2003, Yan et al. 2007). The ability of ozone to assist particle destabilization and aggregation has also been noticed for decades. Several mechanisms have been proposed by Reckhow et al. (1986):

1. Ozone may release oxidized metal ions, such as iron, manganese, and alum, from organometallic complexes formed on solid surfaces, leading to an in situ production of coagulant;
2. Ozonation may lead to an increase of carboxylic acid content on solid surfaces, resulting in greater aluminum, magnesium, and calcium associations followed by precipitation of metal humate complexes;
3. Ozone can desorb the stabilized organic matter coatings from particles by converting the organics from high to low molecular weight and thus reduce the steric and electrostatic repulsive forces;
4. Ozone may induce polymerization of natural organic matter, leading to aggregation via bridging reactions; and
5. Algal/bacterial cell lysis caused by ozone can liberate biopolymers that may have been acting as coagulating polymers (Thanomsub et al. 2002).

For decades the mechanisms of ozone-induced particle destabilization have been widely investigated (Chheda and Grasso 1994, Farvardin and Collins 1989, Grasso and Weber 1988, Jekel 1983, Paode et al. 1995, Saunier et al. 1983).

The impact of pre-ozonation on coagulation and particle stabilization was studied through investigating the properties of flocs (Li et al. 2009). It was observed that pre-ozonation could increase the negative charge of particles and the polarity of ozonated water. The optimal dose was found to depend on the total organic carbon (TOC) in the water.

Bonneville and Smith (2001) demonstrated that pre-ozonation with small doses of ozone, when used in conjunction with alum or polyaluminum chloride (PACl), may slightly improve the flocculation of particles and facilitate their subsequent removal in a dissolved air flotation unit. However, it was also found that high ozone doses impeded flocculation.

The type of natural organic matter (NOM) coated on particles and the presence of calcium were shown to play roles in colloid destabilization (Chandrakanth and Amy 1998). It was found that ozone can break high molecular weight organic matter into smaller and more polar compounds (e.g., carboxylic acids) which are repelled from the mineral surface (Chandrakanth and Amy

1996, Yan et al. 2007). The desorbed organic particles destabilized the colloidal system (Yukselen et al. 2006).

In summary, it has been demonstrated that a suitable dose of ozone can assist in particle destabilization and aggregation (Beltran et al. 1999, Chandrakanth et al. 1996, Chang and Singer 1991, Chheda and Grasso 1994, Liu et al. 2007). Thus, ozonation may help in MFT particle aggregation and consolidation.

# 3 METHODOLOGIES

## 3.1 MFT Settling Test

### 3.1.1 *Sample Conservation and Preparation*

MFT from oil sands sites in northern Alberta having a solids content of 38 wt% was used throughout the experiments. MFT samples were sealed well and stored in a refrigerator at 4°C. The stable gel-like structure of MFT does not allow proper mixing of ozone using the available laboratory reactors. Ozone treatment of raw MFT (38 wt% solids) did not show any improvement on settling of the MFT. Even a dilution of MFT to 10 wt% solids did not exhibit any visible enhancement in settling rate in comparison to the untreated samples. Dewatering at measurable rates was observed only when the MFT was diluted to 7.5 wt% solids or less. Further, since both organic and inorganic compounds can react with ozone and impact the consolidation behavior of particles in a suspension, deionized (DI) water was used for MFT dilution to eliminate the impact of dilution water on the MFT settling. This will allow us to better understand the mechanisms of the ozone assisted MFT settling.

Therefore, in the present study, MFT was diluted with DI water to mimic fresh fine tailings suspensions with solid contents of 1, 3, 5, and 7.5 wt% prior to ozonation (Alamgir et al. 2012). MFT suspensions were freshly prepared for each ozonation.

### 3.1.2 *Ozone Application*

Ozone was produced by a laboratory generator (Wedeco GmbH® D-32051) using USP-grade oxygen, and was applied to the diluted MFT suspensions using a semi-batch method. The gas flow rate was set to 2.38 ± 0.1 L/min with an ozone concentration of 71.14 ± 0.64 mg/L. Thereafter, samples of 120 mL of MFT suspensions were transferred to 1 L jars to allow immersion of the entire ozone diffuser (Figure 1). The samples were then ozonated for three different durations (15, 30 and 60 minutes) and were compared with the control (no ozonation).

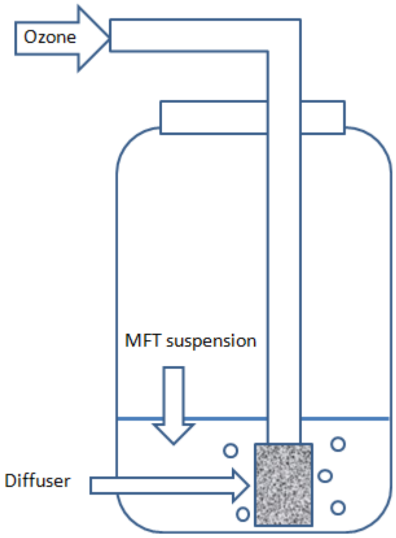


Figure 1. Schematic of MFT ozonation apparatus.
MFT suspensions with 1, 3, 5, and 7.5 wt% solid content were treated by ozonation for 0 (control), 15, 30, and 60 minutes.

### 3.1.3 *MFT Settling*

After ozonation, the 1 L jar was sealed and thoroughly shaken for 1 minute. 80 mL of the MFT sample was then transferred quickly to 100 mL volumetric cylinders to initiate settling. The height of the water-solid interface was recorded every 15 minutes for the first three hours of settling as well as at the 24-hour end point.

## 3.2 Settling Effectiveness Assessment

The performance of ozonation on MFT settling was evaluated through four parameters:

1. Volume of release water,
2. Initial settling curves,
3. Turbidity of the release water, and
4. Solids content of the settled sludge.

The initial settling curves were created by plotting the solid-liquid interface positions over time for the first three hours of settling. After 24 hours, about 20 mL of release water was drained gently by a pipette and then transferred to a disposable scintillation vial to measure turbidity using an Orbeco-Hellige® digital direct-reading turbidimeter. If the volume of release water was insufficient for measurement, a certain amount of DI water was added to dilute it and make it to 20 mL. After removing some of the release water for the turbidity measurement, the remaining supernatant was discarded by pipette without introducing significant disturbance.

To determine the settled sludge's solid content, approximately 1 mL of settled sludge was transferred to a crucible and dried at 105 °C overnight to remove all water content. The weight of dried settled sludge was measured after the crucible had been cooled to room temperature in desiccators.

## 3.3 Chemistry of MFT Release Water

### 3.3.1 *Ion Concentration Measurement*

To determine ion concentrations, MFT released water was centrifuged at 3,750 rpm for 10 minutes to remove suspended particles. The supernatant obtained from the centrifugation process was then filtered through 0.45 μm filters to remove any remaining particles. The cations (sodium, calcium, magnesium, manganese, aluminum, and iron) were evaluated by an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) (Thermo Scientific ICAP6300) and the anions (chloride and sulfate) were assessed by Ion Chromatography (IC) (Dionex DX600).

### 3.3.2 *Acid-Extractable Fraction (AEF) Concentration Measurement*

The acid-extractable fraction (AEF) concentration in MFT release water was measured by Fourier Transformed Infrared Spectroscopy (FT-IR). Suspended particles were removed from the release water by the centrifugation and filtration processes described above. To improve organic acids extraction, the pH of the supernatant was adjusted to 2.0 ± 0.1 using concentrated hydrochloric acid to precipitate organic acids. Dichloromethane (DCM) was used to extract organic compounds from the MFT release water by separatory funnels; 250 mL of DCM was required for every 1 L of release water. To purify the extracts, the extraction process was repeated twice. DCM was then evaporated overnight in a fume hood to obtain only the organic compounds. On the second day, a certain amount of DCM (~6 g) was added to dissolve the AEF, and the AEF concentrations were determined by a PerkinElmer® FT-IR spectrometer (Spectrum 100) operating in transmission mode. The spectra were acquired and processed by PerkinElmer® Spectrum software. Carboxylic acids have two peaks at 1,743 and 1,706 $cm^{-1}$ (Yen et al. 2004), and therefore the absorbances at these two points were targeted. Thirty-two co-added scans were obtained for each spectrum. The spectral resolution was 4 $cm^{-1}$ and the spectral range was 4,000 to 400 $cm^{-1}$.

### 3.3.3 *Chemical Oxygen Demand (COD) Measurement*

The ability of ozone in removing organic compounds in MFT was determined by measuring the chemical oxygen demand (COD) of MFT. Before measuring COD, the MFT suspensions were shaken thoroughly for at least 1 minute to ensure they were well mixed. Different degrees of dilution were made before measurement according to the solids content of MFT samples. The COD of MFT is expressed in mg COD/g MFT.

## 3.4 MFT Surface Characterization

### 3.4.1 *Zeta Potentials of MFT Fine Particles*

The MFT suspensions were prepared and ozonated as previously described. The MFT suspensions were centrifuged at 3,750 rpm for 10 minutes to obtain solid-free release water. A small amount of settled sludge was added to the solid-free release water to generate a solution with 1 to 5 mg particles/mL to measure the zeta potentials. Zeta potentials of the MFT particles before and after the ozone treatment were measured by a Malvern® Zetasizer Nano-ZS.

### 3.4.2 *MFT Surface Chemical Bondings*

X-ray Photoelectron Spectroscopy (XPS) was applied to determine the surface chemical bondings of MFT fine particles. To perform the XPS experiments, several droplets of well-mixed MFT suspensions were dried at 60℃ for 48 hours on a piece of aluminum foil. A Kratos Axis spectrometer with monochromatized Al Kα ($h\upsilon = 1{,}486.71$ eV) was used to perform XPS experiments to investigate chemical bonding on the MFT particles' surfaces at room temperature. The pressure of the analysis chamber during the experiments was greater than $6.5 \times 10^{-8}$ Pa. A hemispherical electron-energy analyzer working at the pass energy of 20 eV was used to collect core-level spectra, while a survey spectrum within a range of binding energies from 0 to 1,100 eV was collected at an analyzer pass energy of 160 eV. A Shirley background was applied to subtract the inelastic background of core-level peaks. Non-linear optimization using the Marquardt Algorithm (Casa XPS) was used to determine the peak model parameters such as peak positions, widths, and intensities. The model peak to describe XPS core-level lines for curve fitting was a product of Gaussian and Lorentzian functions. Different chemical bonds were corrected by using a C 1s peak at 284.8 eV through Casa XPS.

## 3.5 Statistical Analysis

One-way analysis of variance (ANOVA) was used to validate data differences. Microsoft Excel® software was used to perform ANOVA and results were reported as p-values; p-values of less than 0.05 suggested that differences were statistically significant.

# 4 RESULTS AND DISCUSSION

## 4.1 The Effect of Ozone on MFT Settling

### 4.1.1 *MFT after 24-hour Settlement*

Figure 2 shows images of MFT suspensions after 24 hours of settling. As shown in Figure 2, MFT with no ozone treatment did not settle in 24 hours. However, after only 15 minutes of ozonation, the MFT suspensions showed a well-demarcated sedimentation. The volume of water released in a sample containing 1 wt% MFT remained the same for all durations of ozone treatment.

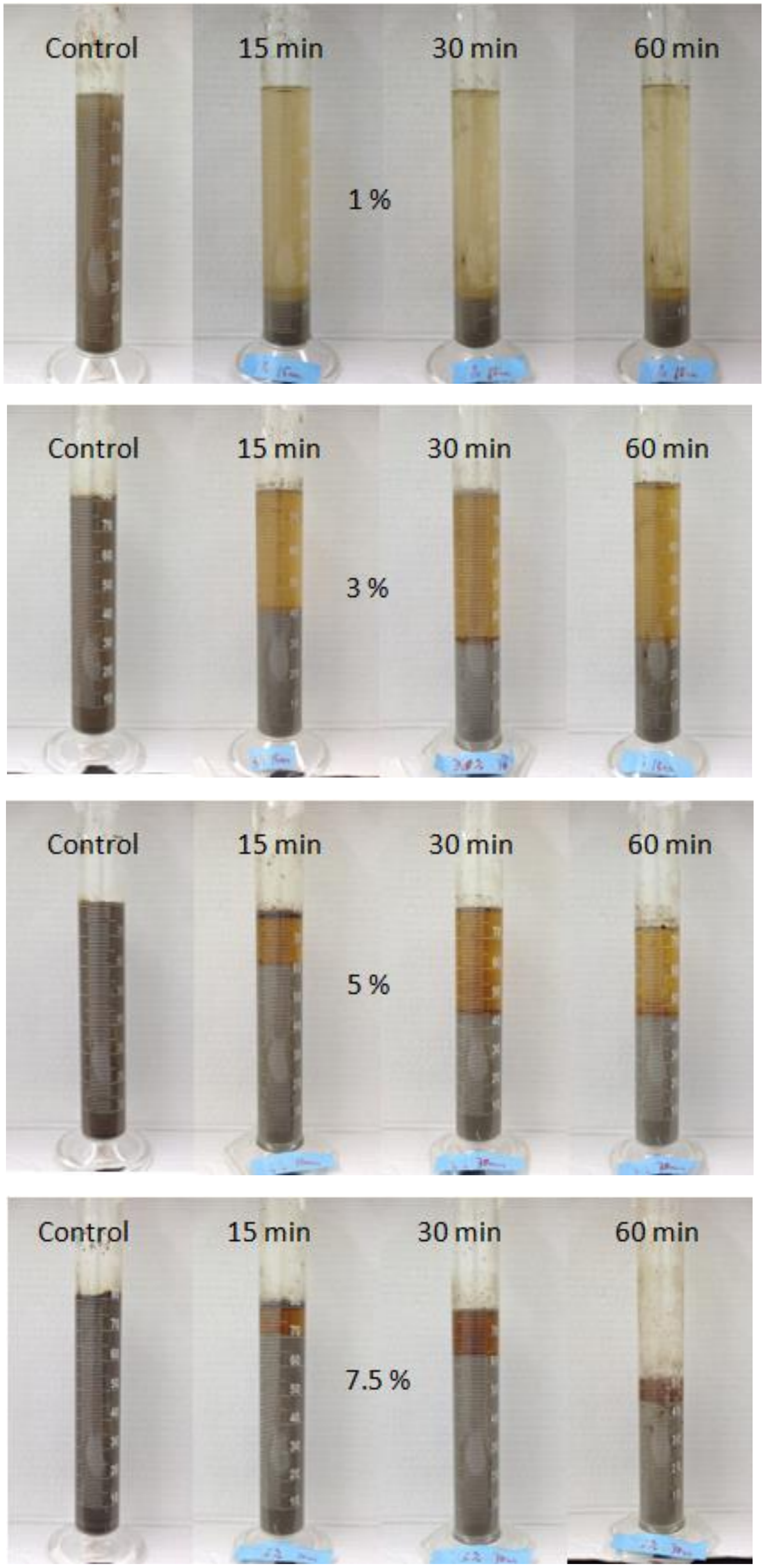


Figure 2. Photographs of MFT suspensions after 24 hours of settling.
MFT suspensions with 1, 3, 5, and 7.5 wt% solid content were treated by ozonation for 0 (control), 15, 30, and 60 minutes.

Volumes of release water were greater in samples containing 3 wt% MFT that received 30- or 60-minute ozone treatment compared to 3 wt % MFT samples that received a 15-minute ozone treatment. The difference in volume of release water between MFT suspensions treated with ozone for 30 and 60 minutes and those treated for 15 minutes was greater for 5 wt% MFT samples than for 1 wt% and 3 wt% MFT suspensions. However, no change in volume was found between 30- and 60-minute conditions.

In 7.5 wt% MFT suspensions, 30 minutes of ozonation generated more release water than 15 minutes of ozonation. However, foam produced during ozonation began to overflow the sample container after 30 minutes. As a result, some MFT suspensions were lost in the 60-minute ozonation condition.

Our experiments showed that 15 minutes of ozonation is sufficient to settle 1 wt% MFT, whereas 3 wt% and 5 wt% MFT suspensions require a longer period of ozonation to obtain increased release water volume. The brown colour of the release water may be caused by the presence of organic acids that are produced during ozonation; this experimental outcome will be discussed further in later sections of this report.

### 4.1.2 *Initial Settling Curves*

The initial settling curves in Figure 3 illustrate the positions of the interface (normalized interface position h/H) over the first three hours of ozonation, where h is the height of settled sludge and H is the total height of the MFT suspension. Figure 3 reveals that, except for the 7.5 wt% MFT condition, MFT settled faster at higher ozone doses. This trend was the most significant in the 5 wt% MFT suspensions. The settling rate of 7.5 wt% MFT during the 60-minute ozonation was significantly affected by sample overflow due to foaming during ozonation.

As mentioned above, 15 minutes of ozonation was sufficient to settle a 1 wt% MFT sample but not long enough to settle a 5 wt% MFT sample. Differences between settling curves among samples ozonated for different times were not substantial in the 1 wt% MFT samples but were more evident in the 5 wt% MFT suspensions. These data demonstrate that higher MFT solid concentrations require higher ozone doses to accomplish MFT settling, and that the optimum ozonation time for 5 wt% MFT is longer than 15 minutes.

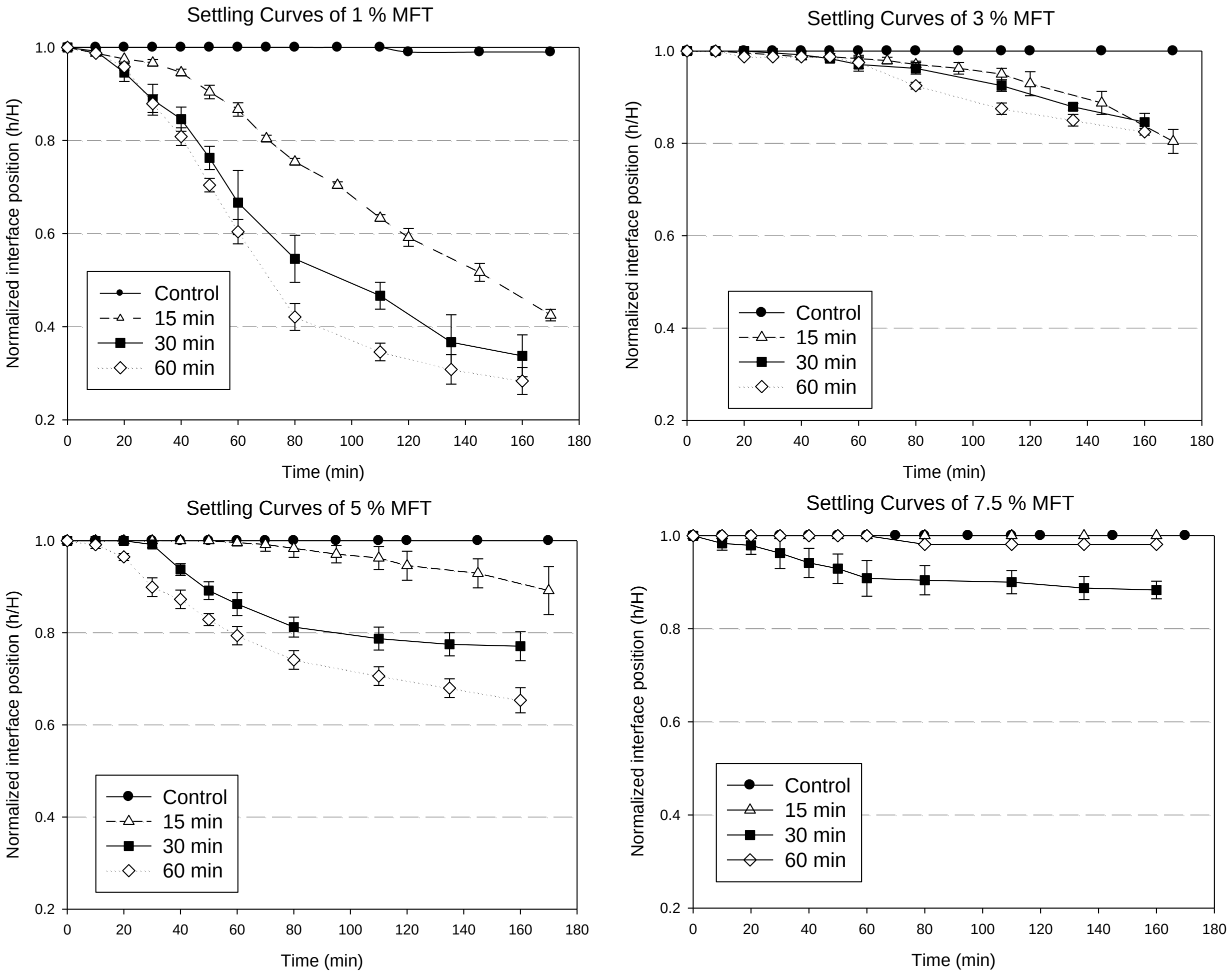


Figure 3. Settling curves of MFT suspensions under different ozonation conditions. MFT suspensions with 1, 3, 5, and 7.5 wt% solid content were treated with 0 (control), 15, 30, and 60 minutes of ozonation. H is the total height of the suspension; h represents the height of the solid-liquid interface. Error bars represent standard deviations of triplicate samples.

### 4.1.3 *Turbidity of Release Water*

Figure 4 shows the turbidities of release water in the 1, 3, 5, and 7.5 wt% MFT suspensions after different times of ozonation (release water in 1, 3, 5, and 7.5 wt% MFT suspensions that did not receive ozonation remained too turbid to measure (over 1,000 Nephelometric Turbidity Units (NTU)) and these values are not shown in Figure 4). The release water turbidities in the 1 wt% suspensions were reduced as the ozonation time increased (from 122.0 ± 16.8 to 44.6 ± 13.2 NTU). The 3 wt% and 5 wt% MFT suspensions showed similar trends (from 66.5 ± 8.2 to 10.8 ± 3.3 NTU, and from 75.7 ± 9.9 to 22.8 ± 6.8 NTU, respectively), but there was no difference in turbidity between those receiving 30 and 60 minutes of ozonation ($p > 0.05$). For the 7.5 wt% MFT sample, there were large variations in replicate experiments, and no significant differences were observed among all ozonation conditions (103.0 ± 39.6, 99.0 ± 18.6, and 83.2 ± 20.9 NTU for 15-, 30-, and 60-minute ozonation, respectively; $p > 0.05$).

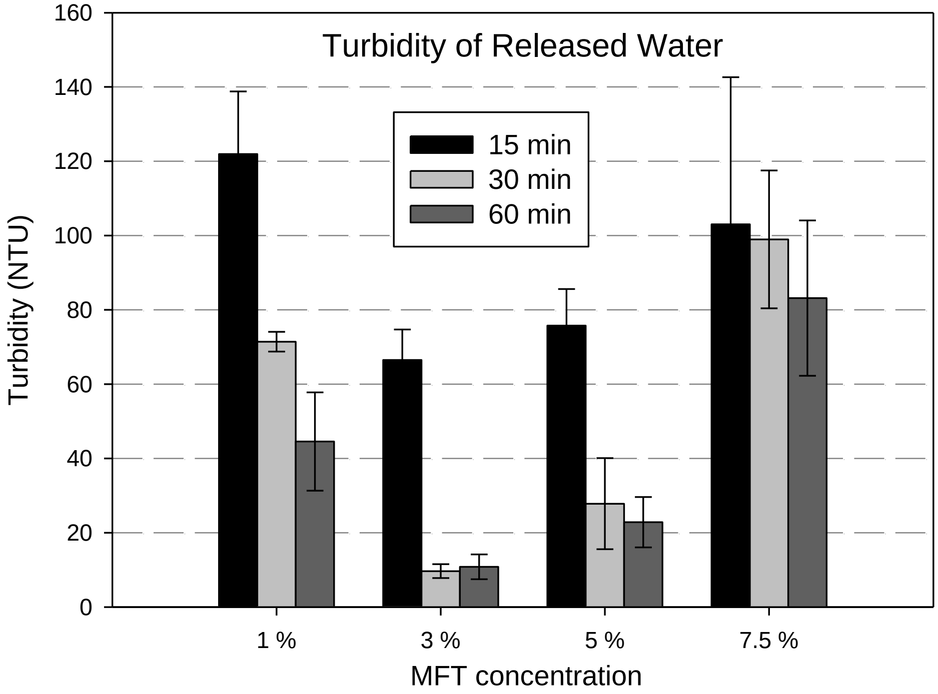


Figure 4. Turbidity of MFT release water generated by ozonation.
MFT suspensions with 1, 3, 5, and 7.5 wt% solid content were treated by 15-, 30-, and 60-minute ozonation. Release water was obtained gently after 24-hour settling without causing turbulence. Error bars represent standard deviations of three measurements.

### 4.1.4 *Solids Content of Settled Sludge*

Figure 5 summarizes the solids content of settled sludge in each experimental condition. The solids content of the settled sludge in the 1, 3, 5, and 7.5 wt% MFT samples without ozonation were 0.96 ± 0.07 wt%, 2.8 ± 0.24 wt%, 4.7 ± 0.30 wt%, and 7.6 ± 0.21 wt% respectively, values similar to the initial solids content, indicating that no settling occurred without ozonation.

The solids content of settled sludge increased significantly after ozonation and reached greater than 5, 6, 10, and 12 wt % in 1, 3, 5, and 7.5 wt% MFT samples, respectively. Similar to the turbidity results, there were no significant differences between 30- and 60-minute ozonation conditions for MFT at all wt% ($p > 0.05$). The benefit from the longer (60 minute) ozonation compared to the 15-minute ozonation was most evident for the 5 wt% and 7.5 wt% conditions, demonstrating that these conditions may need a longer ozonation time ($p = 0.01$) to achieve settling.

The above results suggest that ozone can assist in MFT consolidation, but its performance is not improved greatly by longer ozonation times. The results for the 7.5 wt% MFT sample were unstable, probably due to the overflow of sample during ozone treatment as discussed above. Thus the 7.5 wt% MFT condition was excluded from our other analytical experiments.

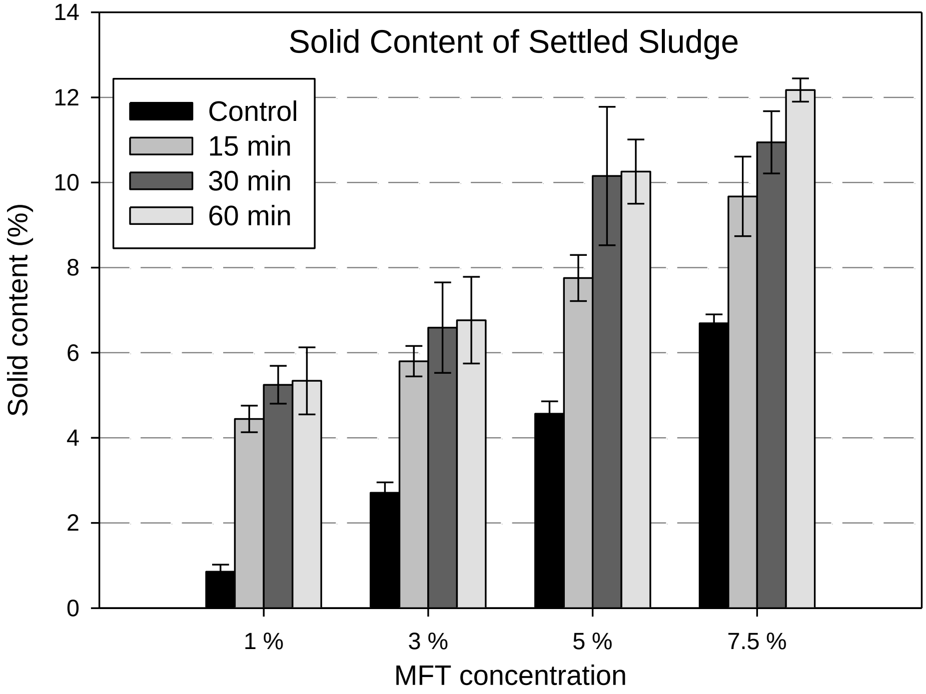


Figure 5. Solids content of MFT settled sludge.
MFT suspensions with 1, 3, 5, and 7.5 wt% solid content were treated by 0-(control), 15-, 30-, and 60-minute ozonation. Settled sludge was obtained from the bottom of the suspensions after 24-hour settling. Error bars represent standard deviations of three measurements.

## 4.2 The Impact of Ozonation on MFT Water Chemistry

### 4.2.1 *pH of MFT Suspensions*

Figure 6 presents pH measurements of MFT suspensions in each experimental condition. The original weakly basic pH (7.7 to 9.0) of the MFT suspensions, due to caustic additions during the extraction process (Siwik et al. 2000), became acidic after ozonation.

The pH of the suspensions dropped substantially (to 4 or below) with any ozone treatment – it fell in small increments with increasing treatment times, and remained fairly comparable among the different MFT concentrations. The significant decrease in pH after ozonation may be attributed to the desorption of organic compounds coating the particles and the production of carboxylic acids (Chheda and Grasso 1994). We measured a much larger decrease in pH than Chheda and Grasso (1994) where the pH was only marginally reduced. Our observations might have been the result of more organic content in the MFT, a low buffering capacity, or a higher ozone dose. The pH of all MFT suspensions decreased as ozonation times increased, demonstrating that more organic acids were detached from the MFT surface and/or more carboxylic acids were produced by the ozone treatment. The brown colour of the release water shown in Figure 2 suggests the presence of aqueous humic substances. Importantly, a pH reduction can lead to other water chemistry changes that are favorable for MFT consolidation.

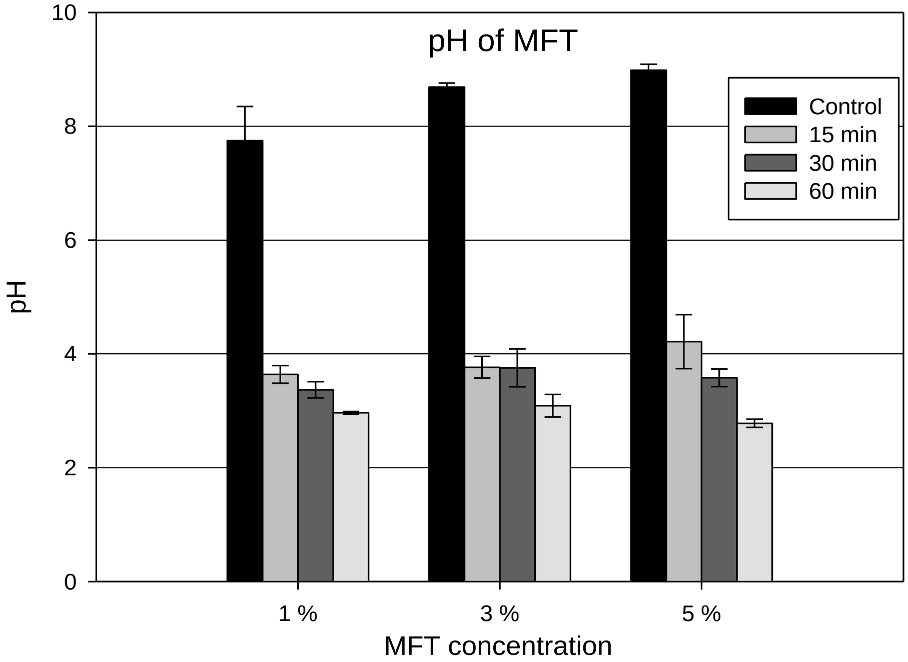


Figure 6. pH of MFT suspensions after 24 hours settling.
MFT suspensions with 1, 3, and 5 wt% solids content were treated with 0-(control), 15-, 30-, and 60-minute ozonation. The pH was measured after 24-hour settling. Error bars represent standard deviations of three measurements.

### 4.2.2 *Ion Concentrations of MFT Release Water*

Table 1 summarizes the major ion concentrations of the MFT release water. Due to caustic additions during bitumen extraction from the oil sands, sodium usually predominates in original MFT suspensions (Chalaturnyk et al. 2002, Clark and Pasternack 1932). The concentration of most ions, except aluminum and chloride, increased 1.5 to 155 times after ozonation and showed a positive dose response. The concentrations of sodium and potassium approximately doubled after 60 minutes of ozonation, but those of magnesium, calcium, iron, and sulfate increased up to 100 times their original value. The increased concentration of cations is likely related to ozone's ability to break up organometallic complexes (Dowbiggin and Singer 1989, Jekel 1994); a decrease in pH can also lead to a release of metal ions as well as an increase in metal solubility into the suspensions, because many metallic oxides can dissolve in acidic environments. The increase in ionic strength (IS) of the MFT suspensions with ozone treatment might cause the surface charges of MFT particles to be suppressed and thus could contribute to their destabilization.

Table 1. Ion concentrations of MFT release water.

| Wt% and Ozonation Time | **Cations** (mg/L) | | | | | | **Anions** (mg/L) | |
|---|---|---|---|---|---|---|---|---|
| | **Na** | **Mg** | **Al** | **K** | **Ca** | **Fe** | **Cl** | **$SO_4$** |
| 1% Control | 22.09 | 0.65 | 9.48 | 2.64 | <0.005 | 2.21 | 8.40 | 6.00 |
| 1% 15 min | 31.61 | 9.34 | 1.80 | 3.18 | 29.5 | 79.82 | 5.50 | 42.80 |
| 1% 30 min | 34.81 | 12.58 | 2.41 | 3.54 | 36.7 | 128.20 | 10.10 | 68.50 |
| 1% 60 min | 38.24 | 12.58 | 2.53 | 3.94 | 39.2 | 151.10 | 9.60 | 98.60 |
| | | | | | | | | |
| 3% Control | 63.39 | 1.49 | 19.60 | 5.61 | 0.8 | 4.47 | 25.20 | 9.80 |
| 3% 15 min | 91.82 | 21.02 | 4.37 | 7.65 | 63.4 | 126.30 | 16.60 | 73.40 |
| 3% 30 min | 92.00 | 26.87 | 5.43 | 8.18 | 80.1 | 261.90 | 33.60 | 153.00 |
| 3% 60 min | 103.70 | 33.59 | 6.83 | 9.49 | 102.4 | 391.70 | 30.60 | 229.00 |
| | | | | | | | | |
| 5% Control | 92.31 | 2.01 | 26.36 | 7.17 | 1.2 | 6.07 | 54.00 | 19.00 |
| 5% 15 min | 146.50 | 28.76 | 6.39 | 10.96 | 84.8 | 138.10 | 40.00 | 170.50 |
| 5% 30 min | 179.00 | 50.83 | 10.43 | 14.18 | 148.6 | 471.70 | 53.50 | 191.50 |
| 5% 60 min | 183.10 | 60.66 | 12.65 | 15.99 | 186.9 | 662.10 | 42.50 | 427.50 |

Control = no ozonation.

The concentrations of aluminum ions were lower after ozonation. For example, the aluminum cation concentration in 3 wt% MFT was reduced from 19.6 mg/L to 4.37 mg/L after 15 minutes ozonation. This reduction in dissolved aluminum is probably due to an enhanced association between the metal and humate molecules induced by ozonation (Edwards and Benjamin 1992, Li et al. 2009). Inorganic compounds can change in composition, and thus in charge, with changes in pH; for example, aluminum hydroxide is a neutral species below pH 6 but at about pH 5.5 to 4.5 it can form positively charged species such as $Al(OH)_2^+$ and $Al(OH)^{2+}$, and become $Al^{3+}$ if the pH is reduced further (pH 3). Positively charged aluminum hydroxide ions are highly capable of trapping negatively charged species. Ozone has also been shown to form carboxylic acid which may also strongly associate with metals (such as aluminum and calcium) (Li et al. 2009), but this does not fully explain the findings shown in Table 1 which indicate that the concentrations of calcium and other cations were not similarly reduced after ozonation and that the aluminum cation concentration in 3 wt% MFT rose (4.37 mg/L to 6.83 mg/L) with longer (30 to 60 minute) ozone treatment.

One explanation for this is that ozone might have released and/or oxidized metal ions from organometallic complexes through the creation of an acidic environment favorable for this release, and generated carboxylic acids. Carboxylic acid groups, having a higher affinity to aluminum hydroxides than to calcium ion, preferentially associated with aluminum resulting in a decrease in the free aluminum ion concentration (Chandrakanth and Amy 1996). Due to a limited number of adsorption sites on carboxylic acid groups for aluminum and the continual release of metals from organometallic complexes, aluminum ions were continuously released into the solution causing the concentration of aluminum to increase during the longer ozone dose.

Electrical conductivity was evaluated for 3 wt% MFT samples (Figure 7). Conductivity is a measure of the ionic activity of a solution in terms of its capacity to transmit current which is correlated to total dissolved solids (TDS). In dilute solutions, the two measures are reasonably comparable, and TDS = 0.5 × EC. As shown in Figure 7, ozonation led to enhanced conductivity in the suspension.

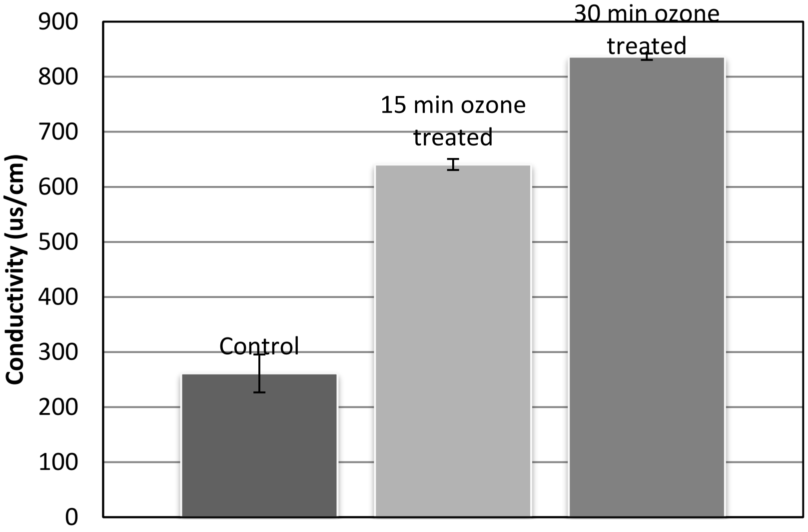


Figure 7. Conductivity of 3 wt% MFT suspensions after 24 hours settling.
MFT suspensions were treated with 0-(control), 15-, and 30-minute ozonation. The conductivity was measured after 24-hour settling. Error bars represent standard deviations of three measurements.

### 4.2.3 *Acid Extractable Fraction (AEF) Concentrations of MFT Release Water*

To examine these proposed mechanisms, additional experiments were performed using FT-IR to evaluate the concentration of the acid extractable fraction (AEF) in the release water. As shown in Figure 8, the concentration of AEF increased 3 to 6 times after ozonation, correlating with the pH results and supporting the AEF as a contributor to the reduction in pH. This effect may be caused by desorption of organic compounds that coat the MFT surfaces and/or conversion of high molecular weight matter to lower molecular weight compounds (such as compounds with hydroxyl and carboxylic groups). Our finding that the AEF in MFT suspensions increased after sample ozonation is consistent with findings in previous studies (Edwards et al. 1993, Jekel 1991, Liu et al. 2009).

Because high molecular weight fractions are destroyed and compounds of higher polarity are formed during ozonation, the resulting organic matter has a lower tendency to be adsorbed on mineral particles such as silicon dioxide and kaolinite (Bonneville and Smith 2001, Chandrakanth and Amy 1996, Farvardin and Collins 1989, Jekel 1991). Consequently, the well-documented steric or electrostatic stabilizing effects of organic compounds on particles are reduced or eliminated (Jekel 1994).

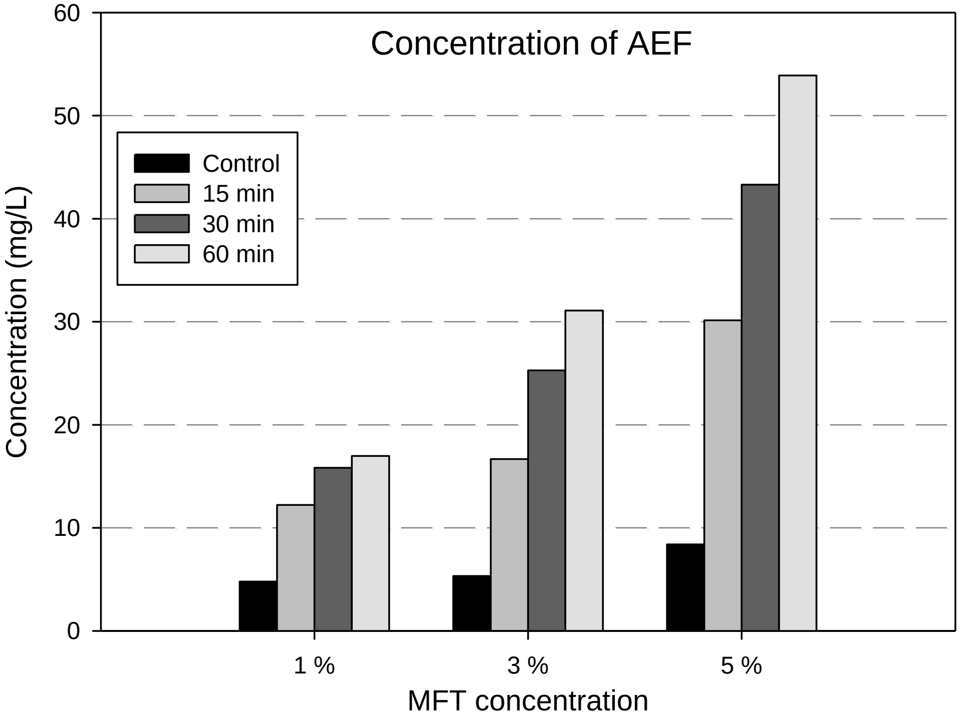
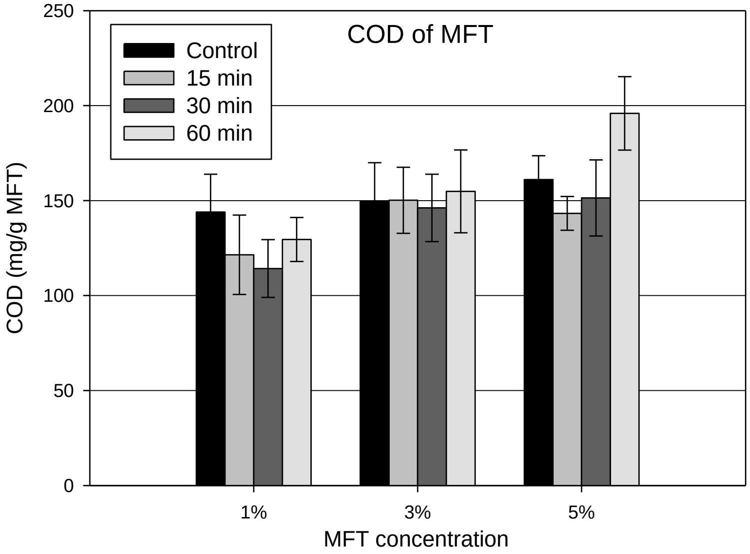


Figure 8. Acid extractable fraction concentration in MFT release water.
MFT suspensions with 1, 3, and 5 wt% solids content were treated by 0-(control), 15-, 30-, and 60-minute ozonation. AEF concentration was measured after 24-hour settling.

The AEF concentrations in 1 wt% MFT suspensions did not increase significantly with longer ozonation time, but notable changes occurred in the 3 wt% and 5 wt% MFT samples. This result suggests that for the 1 wt% MFT suspensions, 15 minutes of ozonation was sufficient to desorb most of the organic compounds from the particle surfaces and/or to convert most of the high molecular weight compounds to carboxylic groups. The 3 wt% and 5 wt% MFT suspensions required longer ozonation times to achieve the desorption/conversion of most organic compounds.

### 4.2.4 *Chemical Oxygen Demand (COD) and Humic Acid of MFT Release Water*

Ozone has been widely applied in water and wastewater treatment because of its advanced oxidative ability. We expected that excess ozone would decompose organic compounds in tailings and thus improve the water quality. However, our results showed no significant change in total chemical oxygen demand (COD) concentrations in MFT samples after ozonation (Figure 9). This might indicate that the ozone doses employed in our experiments are sufficient to achieve MFT fine particle aggregation but insufficient to decompose organic compounds in the samples.



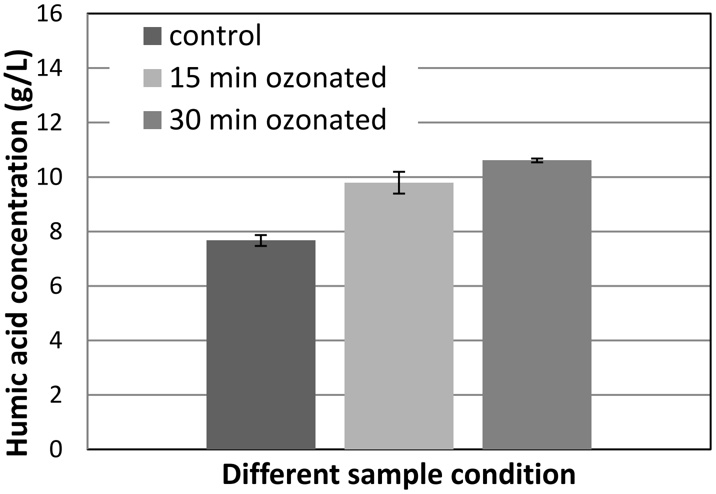


Figure 9. COD and humic acid concentrations in MFT samples before and after ozone treatment.
MFT suspensions with 1, 3, and 5 wt% solids content were treated by 0-(control), 15-, 30-, and 60-minute ozonation for COD measurement. MFT suspensions with 3 wt% solid content were treated by 0-(control), 15-, and 30-minute ozonation for humic acid measurements. COD and humic acid were measured after 24-hour settling. Error bars represent standard deviations of three measurements.

Humic acid concentration increased slightly after the ozone treatment indicating humate substances were released after ozone treatment. Previous studies also showed that ozone may release humic acids from solid surfaces, which may then conjugate with the metal ions to form the metal-humate complexes (Edwards et al. 1993, Jekel 1991, Liu et al. 2009).

## 4.3 The Influence of Ozonation on MFT Particle Surface Characteristics

### 4.3.1 *Surface Charges of MFT Fine Particles*

Based on data acquired from ion chromatography (IC) of anions and inductively coupled plasma – optical emission spectrometry (ICP-OES) of cations, the zeta potentials of the MFT particles were expected to be less negative after ozonation. The increase in ion concentrations in the MFT suspensions as a result of the reduced pH was expected to decrease the surface negativity of the MFT particles through electrical double layer compression and assist in consolidation. The findings shown in Figure 10 support this deduction.

The zeta potentials of 1, 3, and 5 wt% MFT suspensions before ozonation were -46.1 ± 1.2 mv, -47.6 ± 0.8 mv, and -49.7 ± 0.5 mv, respectively. After ozonation, they dropped, as a function of ozonation time, to around -30 mv. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the reduced surface charge should weaken the electrostatic repulsive forces among the particles, enhancing particle aggregation (HidalgoAlvarez et al. 1996).

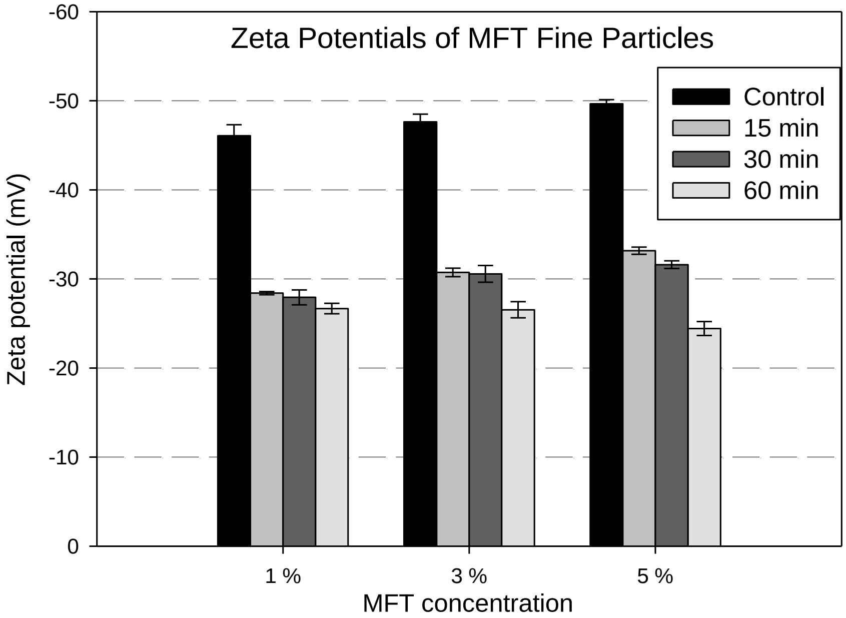


Figure 10. Zeta potentials of MFT fine particles.
MFT suspensions with 1, 3, and 5 wt% solids content were treated by 0-(control), 15-, 30-, and 60-minute ozonation. The zeta potential was measured at 22 ± 1 °C after 24-hour settling. Error bars represent standard deviations of three measurements.

The reduction of particle surface charge by ozonation has been well documented in previous studies (Liu et al. 2007, Yukselen et al. 2006). As shown in section 4.2.3, ozonation can lead to desorption of organic coatings from MFT surfaces (Bonneville and Smith 2001, Chandrakanth and Amy 1996, Farvardin and Collins 1989, Jekel 1991). Moreover, the decreased pH and increased ion concentrations in water released after ozonation could contribute to the charge reduction of the MFT particles.

Consistent with the results from the MFT settling tests, the surface charges of MFT did not decrease to a greater extent after a longer ozonation time in 1 wt% MFT samples ($p > 0.05$). Nevertheless, the MFT particle surface negativity decreased after extended ozonation for 3 wt% and 5 wt% MFT samples ($p < 0.05$). This phenomenon demonstrated that a longer ozonation time is required to lower the surface negativity of particles in MFT suspensions with higher solids content. High dilution of MFT samples can lead to the reduced buffering capacity of the tailings.

### 4.3.2 *Surface Chemical Bonding of MFT Fine Particles*

Spectra of dried MFT suspensions treated with different ozonation times were selected to demonstrate the change of chemical bonding at the MFT particle surfaces before and after ozonation (Figures 11 to 13). The peak heights reflect the relative amount of chemical bonding on MFT surfaces. Before ozonation, it is hard to identify a peak representing carboxylic groups; besides the dominant peak of C-C (graphitic, aromatic, or aliphatic carbon), only a slight peak of C=O (carbonyl groups) is visible. However, after ozonation peaks representing carboxylic and hydroxyl groups became highly apparent.

This result is consistent with previous studies (Chheda and Grasso 1994, Jekel 1994, Valdes et al. 2002). Ozonation of organic matter is known to break high molecular weight organic matter into smaller, more polar, and oxygen-rich compounds, resulting in an increase in the substrate’s contents of hydroxyl, carbonyl, and carboxylic groups (Chandrakanth and Amy 1998, Yukselen et al. 2006). This ozone effect likely contributed to the reduction of the negative surface charge of MFT. Consequently, greater association of aluminum, magnesium, and calcium to the particles is expected, leading to the formation of insoluble aluminum and calcium complexes, or the adsorption of particles to alum flocs (Chandrakanth et al. 1996, Edwards and Benjamin 1992, Yan et al. 2007).

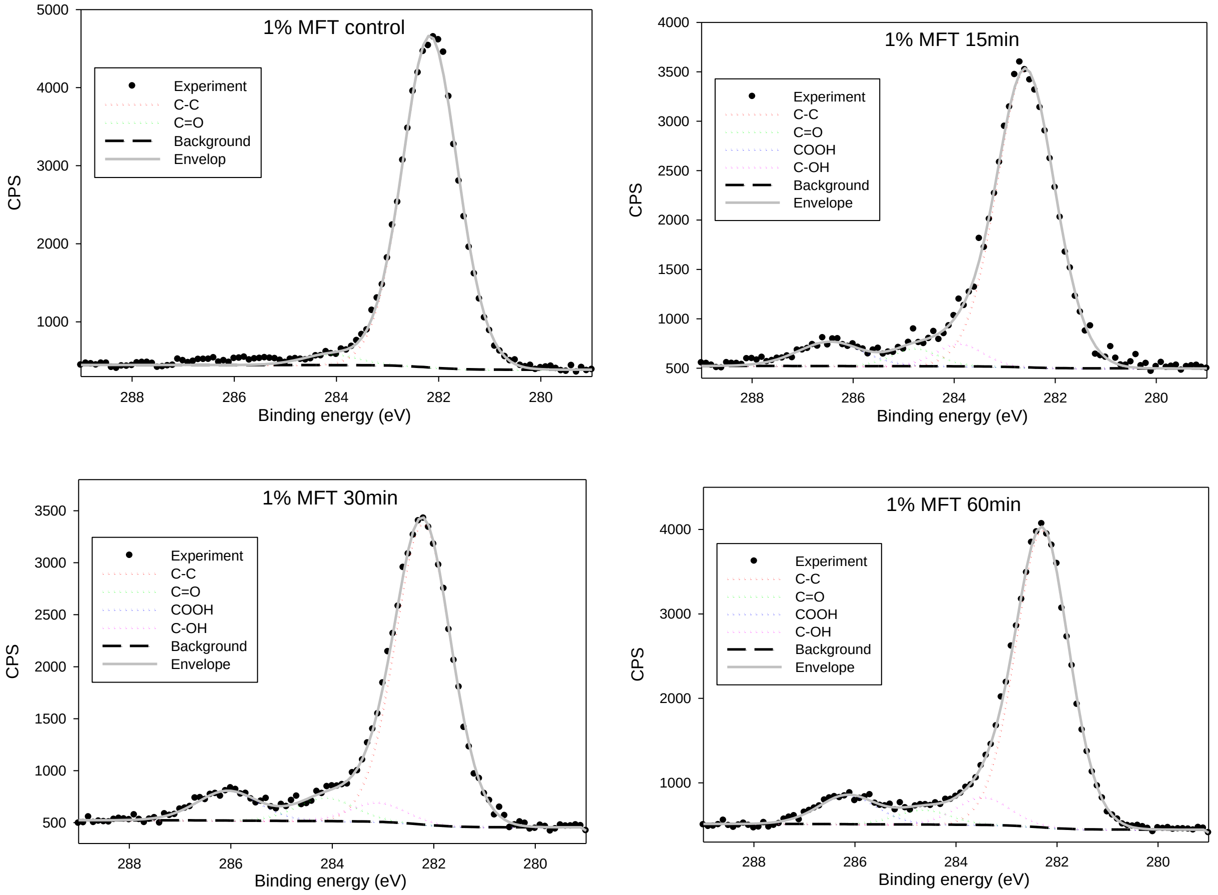


Figure 11. Surface chemical bonding of 1 wt% MFT.
MFT suspensions with 1 wt% solids content were treated by 0-(control), 15-, 30-, and 60-minute ozonation. Counts per second (CPS) represent the strength of signal; a stronger signal reflects a relatively larger amount of chemical bonding. Coloured lines indicate the type of chemical bond.

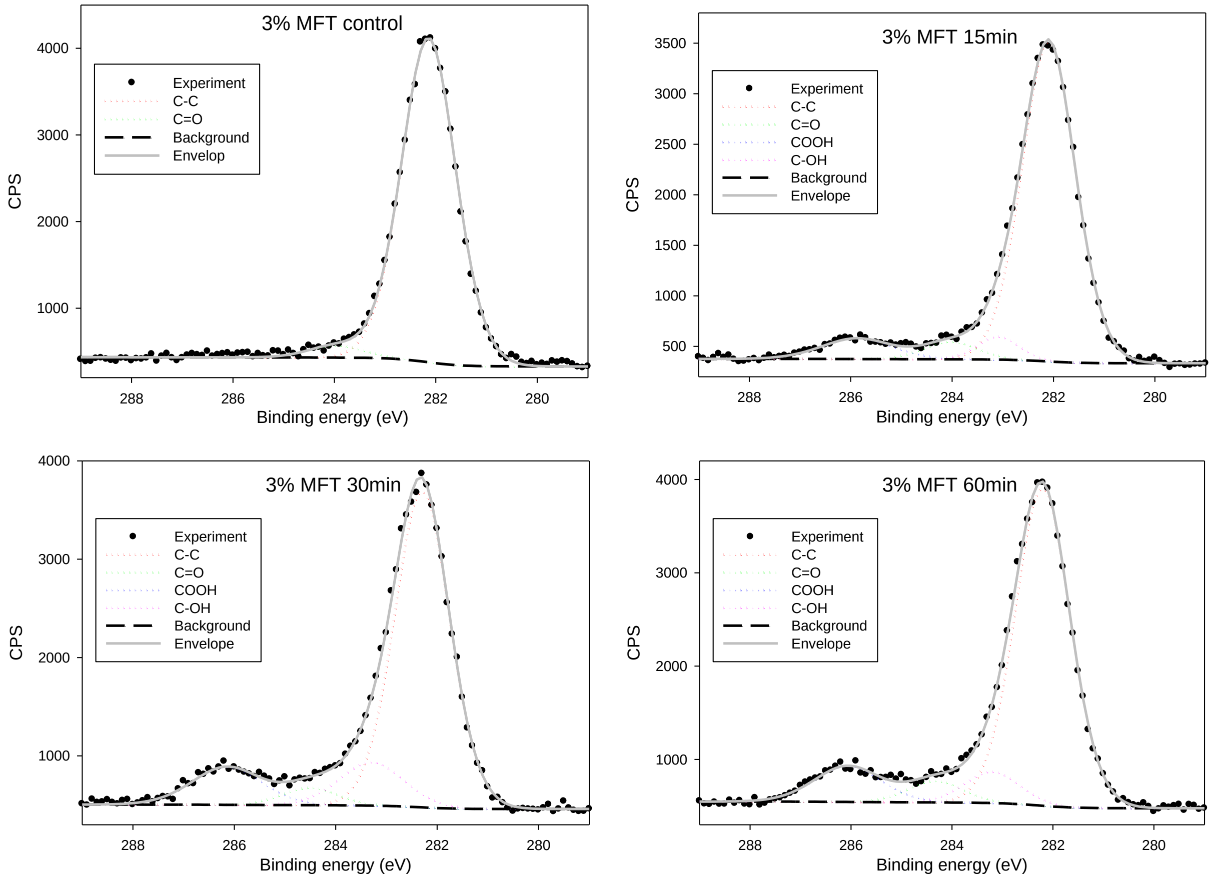


Figure 12. Surface chemical bonding of 3 wt% MFT.
MFT suspensions with 3 wt% solids content were treated by 0-(control), 15-, 30-, and 60-minute ozonation. Counts per second (CPS) represents the strength of signal. A stronger signal reflects a relatively larger amount of chemical bonding. Coloured lines indicate the type of chemical bond.

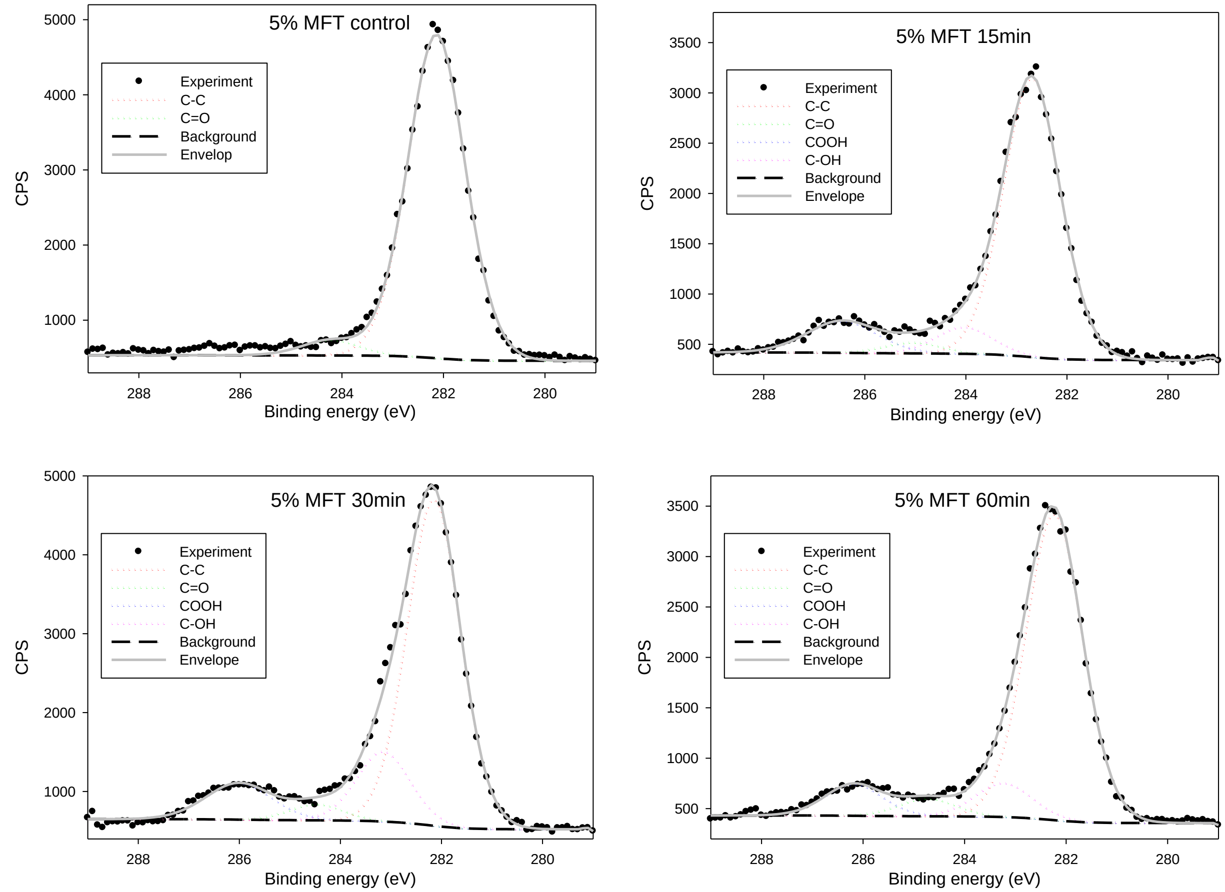


Figure 13. Surface chemical bonding of 5 wt% MFT.
MFT suspensions with 5 wt% solids content were treated by 0-(control), 15-, 30-, and 60-minute ozonation. Counts per second (CPS) represents the strength of signal. A stronger signal reflects a relatively larger amount of chemical bonding. Coloured lines indicate the type of chemical bond.

## 4.4 Investigation of the Mechanisms Involved in Ozone-Assisted MFT Consolidation

### 4.4.1 *The Effect of pH Reduction from Ozonation on MFT Consolidation*

To further investigate the role of the pH reduction that occurred during ozonation, the pH of untreated MFT suspensions was adjusted to 3.8 ± 0.1 (comparable to the pH of ozonated MFT) by adding several drops of concentrated hydrochloric acid before settling the suspensions for 24 hours.

Figure 14 shows that the volumes of release water generated by ozonation or pH adjustment were comparable. However, the colour of the pH-adjusted MFT release water did not change to brown as it did after ozonation. These results indicate that the drop in pH may play a critical role in MFT aggregation, but is not responsible for the brown colour of release water.

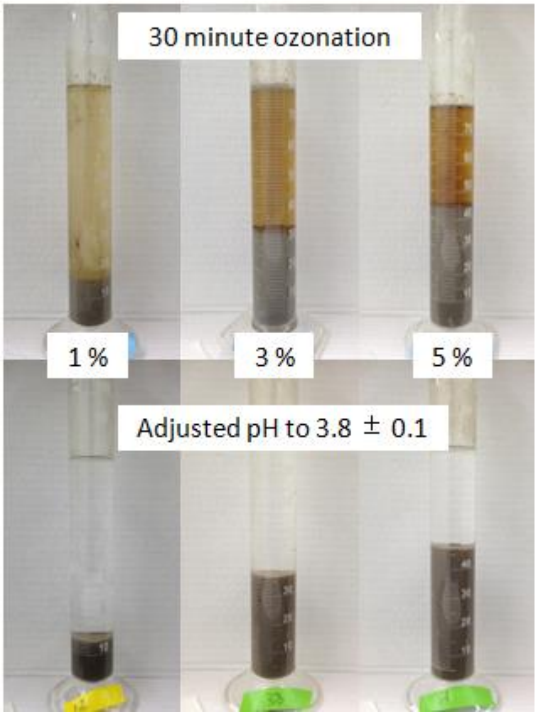


Figure 14. Photographs of MFT after adjusting the pH to 3.8 ± 0.1 using concentrated hydrochloric acid and 24 hours of settling.
The original pH values of 1, 3, and 5 wt% MFT were 7.7 ± 0.60, 8.7 ± 0.07, and 9.0 ± 0.10, respectively. For comparison, images of MFT ozonated for 30 minutes and settled for 24 hours are also shown.

As mentioned in section 4.2.2, the ionic content and thus the charge of inorganic compounds can change with changes in pH. For example, the dominant iron and aluminum species in MFT samples before ozonation were $Fe(OH)_3$ and $Al(OH)_3$, and the pH was around 8. After ozonation, the pH dropped significantly leading to the dissolution of iron and aluminum hydroxide. The formation of positively charged species like $Fe(OH)_2^+$ and $Al(OH)_2^+$ could trap negatively charged particles and thus promote the sedimentation of MFT. Additionally, because of the release of sulfate after ozonation, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ may work as coagulants to assist in MFT settling.

The 1 wt% and 3 wt% MFT suspensions settled faster by adjusting the pH than by ozonation (Figure 15) but the difference between pH adjustment and ozonation became much less significant as the MFT concentration increased from 1 wt% to 3 wt% MFT. In the 5 wt% MFT suspension, pH settling was slightly faster than ozonation settling for the first hour and for the remaining two hours the settling order was reversed. These results suggest that ozonation induced changes in the MFT suspensions unrelated to a drop in pH. These changes may have included organic compound desorption, carboxylic acid production, and surface functional group conversion, each with a potential to facilitate MFT aggregation.

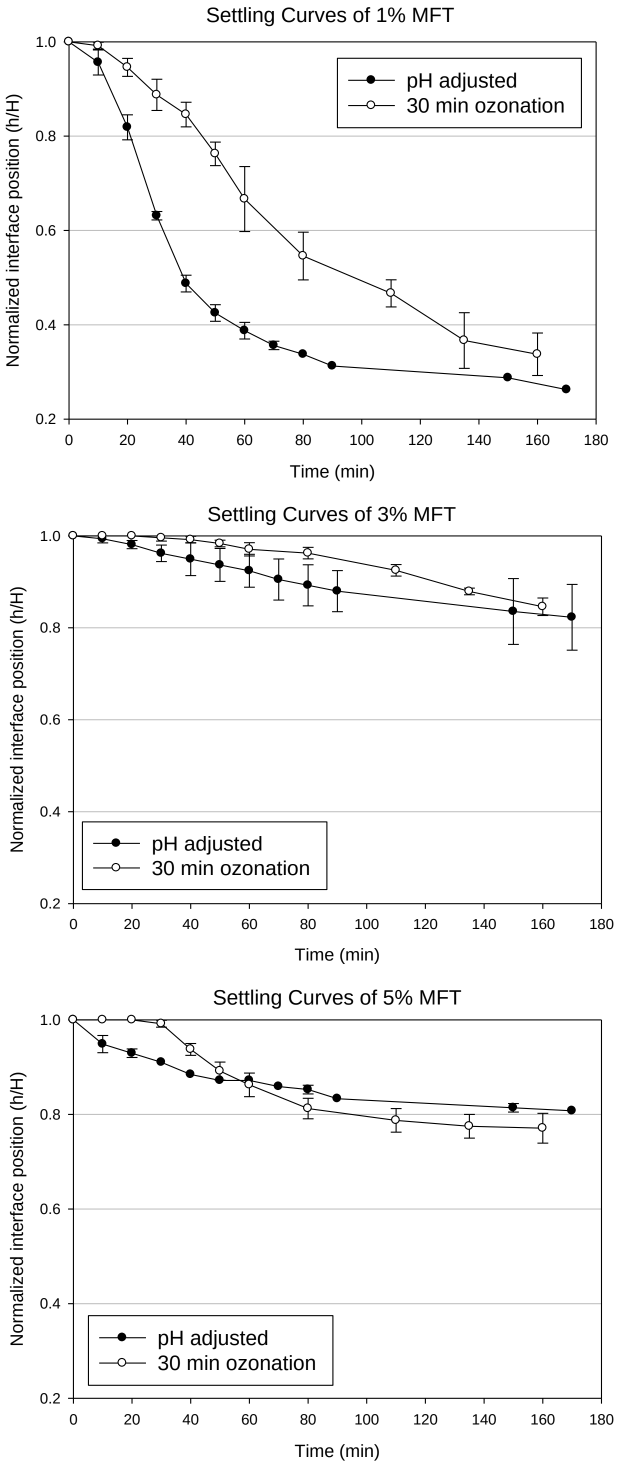


Figure 15. Settling curves of acidified and ozonated MFT.
H is the total height of the suspension and h represents the height of solid-liquid interface. Error bars represent standard deviations of three measurements.

Additional studies on the zeta potential changes due to the pH changes were performed. As shown in Figure 16, the zeta potentials of the pH-adjusted MFT particles were all less negative than those in the ozonated MFT samples. The negativity of zeta potentials dropped to around -15.0 mV in all pH-adjusted MFT samples. Zeta potentials are affected by factors other than ionic strength, such as particle size and surface functional groups, and it was demonstrated here that ozonation can detach organic matter from MFT particle surfaces and alter the surface functional groups. Consequently, the differing zeta potentials of ozonated MFT samples and pH-adjusted MFT samples may have been influenced by these mechanisms. The lower particle surface charges in the pH-adjusted MFT may be responsible for the faster MFT settling.

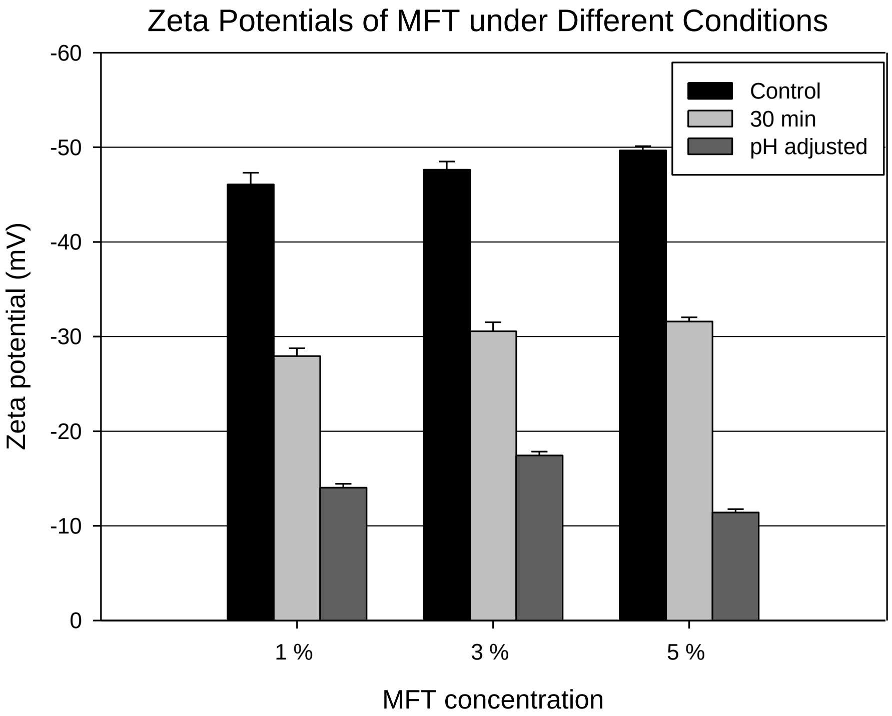


Figure 16. Zeta potentials of acidified and ozonated MFT suspensions.
Zeta potential was measured at 22 ± 1 °C after 24-hour settling. Ozone was applied for 30 minutes. Error bars represent standard deviations of three measurements.

### 4.4.2 *The Effects of Different Metal Ions on MFT Consolidation*

Table 1 shows the significant increases in metal ion concentrations measured in the MFT suspensions after ozonation. Cationic strength in the 3 wt% MFT suspensions increased by about 25 mM after 30 minutes of ozonation. To investigate the impact of each metal cation on MFT aggregation, selected cations sufficient to achieve a 25 mM cation ionic strength increment were added to 3 wt% MFT suspensions. Sulfate salts were selected due to the great increase of sulfate in the MFT release water after ozonation. Specific additions are listed in Table 2. The simulated condition contained the type and amount of metal cations contained in the 3 wt% MFT sample after 30 minutes of ozonation.

Table 2. Cations added to 3 wt% MFT suspensions to achieve an ionic strength increase of 25 mM.
The ionic strength was calculated following the equation $I = \frac{1}{2}cz^2$, where I is ionic strength, c is the molar concentration of ion, and z is the charge of ion.

| **Treatment** | **Cations added (mg/L)** | | | | | **Cationic ionic strength increase** |
|---|---|---|---|---|---|---|
| | **Na** | **Mg** | **Al** | **Ca** | **Fe** | |
| **Na** | 1,150 | - | - | - | - | 25 mM |
| **Ca** | - | - | - | 500 | - | 25 mM |
| **Fe** | - | - | - | - | 311 | 25 mM |
| **Al** | - | - | 150 | - | - | 25 mM |
| **Simulated** | 28 | 25 | - | 80 | 257 | 25 mM |

Figure 17 demonstrates that the addition of cations led to successful settling in 3 wt% MFT suspensions, although the degree of settling differed amongst cations. According to DLVO theory, particle aggregation should be improved more by trivalent metal ions than by divalent and monovalent cations, through a far more effective screening of the electrostatic repulsion (Lee et al. 2012, Schneider et al. 2011). Our results showed that calcium addition produced the most release water, similar to 3 wt% MFT after 30 minutes of ozonation. These findings indicate that calcium ions may have the greatest ability to improve MFT consolidation, and the release of metal ions contributed greatly to the ozone-assisted MFT consolidation.

As shown in Figure 18, the addition of salt, except for sodium, settled the MFT particles faster than ozonation did. Calcium addition led to the fastest settling, followed by the ferric, simulated, and aluminum salts. The simulated condition largely consists of iron, thus it is reasonable that their settling curves are similar.

It should be noted that the release water generated by the salt additions were all colourless in comparison to those produced by ozonation. This phenomenon confirms that ozone not only induced a pH drop and cation release in the MFT suspensions, but also induced other changes in the water chemistry, including desorption of organic contents.

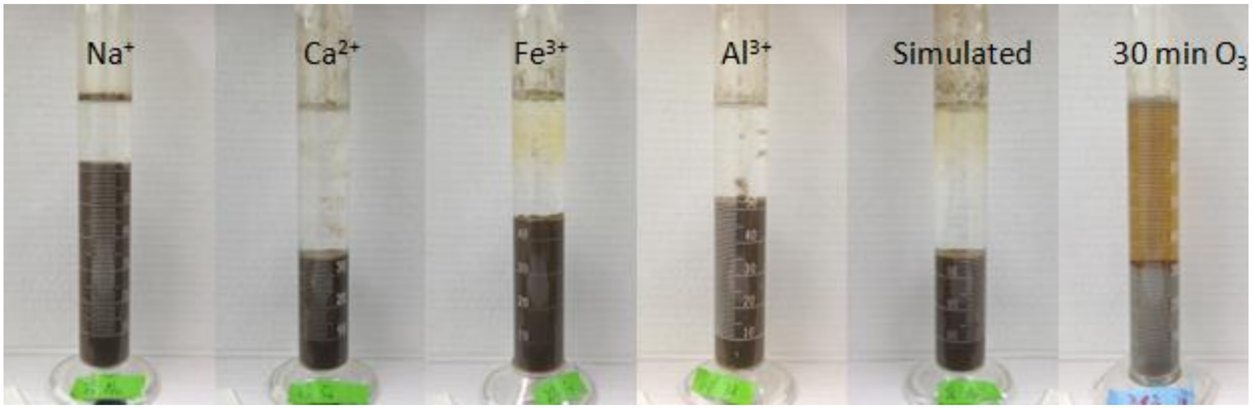


Figure 17. Photographs of 3 wt% MFT after 24 hours of settling by salt addition. 3 wt% MFT was treated with $Na_2SO_4$, $CaSO_4$, $Fe_2(SO_4)_3$ or $Al_2(SO_4)_3$. The simulated condition contains the type and amount of metal cations contained in the 3 wt% MFT sample after 30 minutes of ozonation. 3 wt% MFT settled by 30-minute ozonation is shown for comparison.

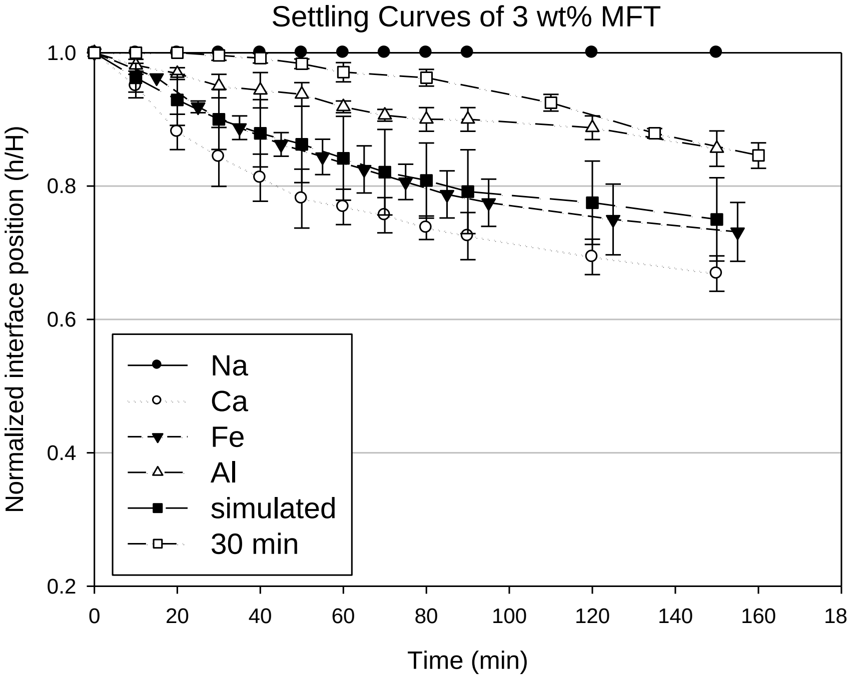


Figure 18. Settling curves of 3 wt% MFT after 24 hours of settling by salt addition. 3 wt% MFT was treated with $Na_2SO_4$, $CaSO_4$, $Fe_2(SO_4)_3$ or $Al_2(SO_4)_3$. The simulated condition contains the type and amount of metal cations contained in the 3 wt% MFT sample after 30 minutes of ozonation. 3 wt% MFT settled by 30-minute ozonation is shown for comparison. Error bars represent standard deviations of three measurements.

The addition of salt reduced the surface charge of MFT particles to different degrees depending on the cation (Figure 19). Consistent with other research, salts having cations with higher valence caused lower zeta potentials (Lee et al. 2012, Marchuk and Rengasamy 2011). However, MFT samples treated with calcium settled faster and generated more release water than MFT samples treated with iron or aluminum. The pH values of ozonated MFT suspensions were around 4, suggesting that positively charged species like $Fe(OH)_2^+$ and $Al(OH)_2^+$ were dominant. However, in the cation addition experiment, the pH was much higher and the neutral hydroxides prevailed. That is, cations may behave in different ways according to the pH. This result strengthens the assertion that pH and surface property/structure are important for MFT aggregation as well as the zeta potentials of the particles. The zeta potentials after adding all the salts, except for sodium salts, were less negative than those reached after ozonation. This may be because the addition of calcium, ferric, and aluminum sulfate reduced the pH of the MFT suspensions due to hydrolysis. This reduced pH would then release some metal ions into the water and increase the ionic strength that would ultimately further compress the electrical double layers (see section 4.3.1) of the MFT particles.

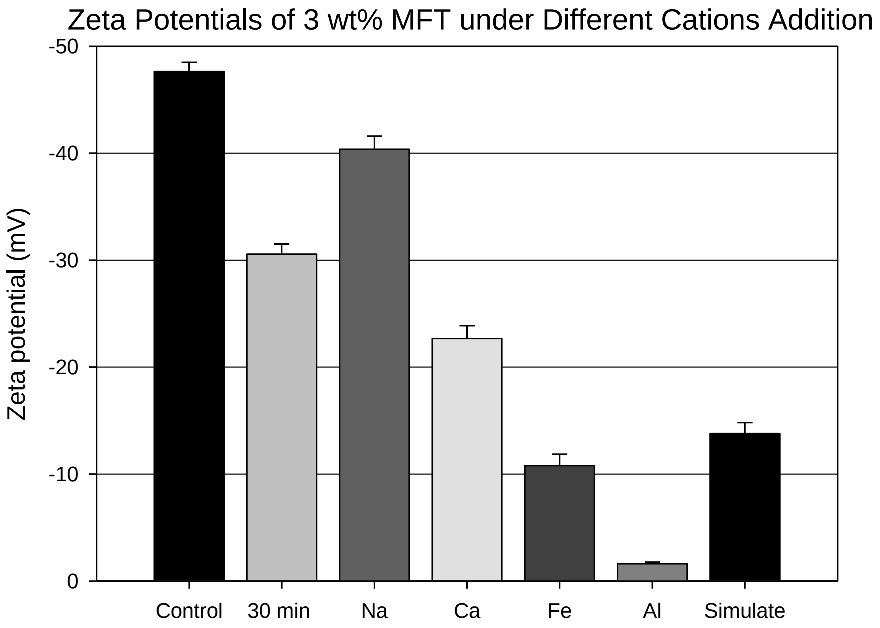


Figure 19. Zeta potentials of 3 wt% MFT samples after salt addition.
The zeta potential was measured at 22 ± 1 °C after 24-hour MFT settling. For comparison, the zeta potentials of 3 wt% MFT with 30-minute ozonation and without ozonation (control) are included. Error bars represent standard deviations of three measurements.

# 5 CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

The findings of the experiments performed in this research are summarized below:

- MFT suspensions of 1, 3, and 5 wt% solids content were successfully settled by ozonation, by lowering pH, or with addition of salt. Samples of 7.5 wt% MFT foamed and overflowed when treated with ozone, thus the results were unstable and further analyses were not pursued. There was no significant settling of 10 wt% MFT samples after 180 minutes of ozonation.
- MFT suspensions with higher solids content required longer ozonation times for settling. The final volume of release water, the turbidity of the release water, and the solids content of the settled sludge were comparable after 15-, 30-, and 60-minute ozonation treatments for 1 wt% MFT, indicating that 15-minute ozonation is sufficient for MFT settling. Significant differences in volume and turbidity of release water, initial settling rate, and solids content of settled sludge between 15- and 60-minute ozone treatments were observed for 3 wt% and 5 wt% MFT suspensions.
- The acid extractable fraction (AEF) concentrations of MFT release water increased 3 to 6 times after ozonation, which can account for the remarkable drop in pH (from 8 to 4) of MFT suspensions after ozonation.
- Changes in water chemistry were detected as a response to the drop of pH after ozonation. Ion concentrations increased dramatically, especially calcium, iron, and sulfate. As a consequence, the surface charges of MFT fine particles were largely compressed so that the repulsive electrostatic forces between particles were weakened.
- Changes in chemical bonding of MFT surface particles were found. Carboxylic groups were generated and their concentration increased as a function of ozonation time.
- After 24-hour settling, pH adjusted MFT samples generated a volume of release water comparable to that of MFT samples treated by ozonation. The zeta potentials of pH adjusted MFT samples were less negative that those of ozonated MFT samples.
- When salts were added to MFT samples, the volume of release water was greatest for calcium salts, followed by aluminum, iron and sodium salts. The zeta potentials of salt-settled MFT samples were the least negative when aluminum salts were added and the most negative when sodium salts were added.

According to the phenomena observed in this study and some related theories proposed by previous researchers, the mechanisms involved in ozone-assisted MFT consolidation can be described as:

1. In MFT suspensions, ozone converts the form and/or reduces the molecular weight of organic matter, forming smaller and more polar organic compounds, such as oxalate and acetate acids. These smaller organic compounds may then detach from the MFT surfaces and lead to the pH reduction of the MFT suspension. As a result, the zeta potentials of MFT particles become less negative and more neutral, reducing the repulsive electrostatic forces among MFT particles (Perez-Estrada et al. 2011).
2. Organometallic complexes in MFT are broken down by ozonation, resulting in the release of cations such as calcium and iron species into the suspensions and increasing the ionic strength of the suspension. Due to the compression of the particles' electrical double layers by bivalent or trivalent cations, the surface charges of particles are significantly reduced (zeta potential reduced from -50 mV to -30 mV). Released cations such as calcium and iron may also play a role in MFT coagulation.
3. The increase of cations (calcium and iron) and carboxylic groups facilitates the generation of metal humate complexes (Reckhow et al. 1986). More adsorption of positive cations on MFT surfaces also occurs.

Large floc production through particle aggregation and substantial MFT precipitation is enabled by the effects of the actions described above.

## 5.2 Recommendations

Before applying ozonation technology in industry, several ramifications of MFT ozonation need to be considered:

1. The increase in salinity and reduction of pH in the release water are potential drawbacks of this process.
2. The cost, feasibility, and toxicity of MFT ozonation need to be investigated.
3. Further study is essential to optimize the MFT ozonation process under batch or flow-through conditions.
4. Long-term studies of the impacts of ozonation on MFT settling and organic compound removal, and the oil sands extraction process should be performed.

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# 7 GLOSSARY

## 7.1 Terms

### Aggregation

Aggregation is the clustering of small particles that attract each other via intermolecular forces.

### Anion

An anion is an ion with a net negative electric charge (e.g., $Cl^-$).

### Cation

A cation is an ion with a net positive electric charge (e.g., $Ca^{2+}$).

### Colloid

A colloid is a substance whose particles are evenly dispersed throughout another substance without settling; the diameter of the colloidal particles is between 1 and 1,000 nanometres.

### Consolidation

Consolidation is an extreme form of aggregation; it involves a decrease in water content and an increase in solid content of a substance.

### Floc

A floc is an aggregation, or flocculation, of fine suspended particles.

### Flocculant

A flocculant is a substance, often an organic polymer, that is used to enhance the aggregation or flocculation of fine particles.

### Initial Settling Curve

The initial settling curves were created by plotting the solid-liquid interface positions over time for the first three hours of settling of the MFT suspensions. They describe the settling status of MFT suspension as a function of time.

### Metal-Humate

A metal-humate is a complex formed by the association between a metal ion and a humic (organic) substance.

### Organometallic Complex

An organometallic complex contains at least one metal-to-carbon bond in which the carbon is part of an organic group.

### Ozone

Ozone is a molecule consisting of three oxygen atoms, with the chemical formula $O_3$.

### Polymer

A polymer is a large molecule composed of many repeated subunits.

### Semi-batch Method

The semi-batch method refers to a process that is neither fully continuous (where substances are continually replaced) nor fully batch (where substances remain fixed); it allows substance addition or removal a certain times throughout the process.

### Stabilized Organic Matter

Stabilized organic matter is matter in which particle surfaces have enough repulsive forces (positive or negative) to resist aggregation and keep them in solution.

### Steric

The spatial arrangement of atoms in a molecule is the molecule’s steric character.

### Supernatant

The supernatant is a precipitate-free liquid remaining above a solid after crystallization, precipitation, centrifugation, or other treatment that causes the aggregation of particles in a solution.

### wt%

Percentage by weight.

### Zeta Potential

The zeta potential is the electrokinetic potential in the interfacial electrical double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface.

## 7.2 Acronyms

| | |
|---|---|
| AEF | Acid Extractable Fraction |
| Al-PAM | $Al(OH)_3$ -Polyacrylamide |
| CHWE | Clark Hot Water Extraction |
| $CO_2$ | Carbon Dioxide |

| | |
|---|---|
| COD | Chemical Oxygen Demand |
| CPS | Counts per Second |
| CT | Composite or Consolidated Tailings |
| DI | Deionized (water) |
| DCM | Dichloromethane |
| DI | Deionized |
| DLVO | Derjaguin-Landau-Verwey-Overbeek |
| eV | Electron Volt |
| FT-IR | Fourier Transformed Infrared Spectroscopy |
| h/H | Normalized Interface Position (H – Total Height of the Suspension; h – Height of the Solid-Liquid Interface) |
| HPAM | Partially Hydrolyzed Polyacrylamide |
| IC | Ion Chromatography |
| ICP-OES | Inductively Coupled Plasma xx- Optical Emission Spectrometry |
| IS | Ionic Strength |
| mM | Millimolar |
| mV | Millivolts |
| MFT | Mature Fine Tailings |
| NOM | Natural Organic Matter |
| NTU | Nephelometric Turbidity Units |
| OSPW | Oil Sands Process-affected Water |
| OSRIN | Oil Sands Research Information Network |
| PACl | Polyaluminum Chloride |
| SEE | School of Energy and the Environment |
| TDS | Total Dissolved Solids |
| TOC | Total Organic Carbon |
| XPS | X-ray Photoelectron Spectroscopy |

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