Diluted MFT Settling by Ozonation; A Mechanistic Study

by

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Abstract

The oil sands tailings generated after bitumen extraction are permanently contained in lake-size ponds. Primarily the tailings ponds are used to settle the solid particles so the cap water could be recycle back to the extraction operations, while the tailings with higher concentration of suspended particles, like Mature Fine Tailings (MFT), need to be treated by other means. Different methods have been developed to accelerate the dewatering of MFT, such the use of different polymers and gypsum. Chemical treatments like ozonation could treat diluted MFT to release the trapped water, as a novel method for the settlement of MFT particles and recovery of water. Ozonation of MFT led to a substantial pH change (from 8.4 to ≤ 4.0) that helped the fine particle to be settled. Formation of small organic acids after the oxidation process led to this pH drop. The objective of this research was to study the substantial pH change during the ozonation of diluted MFT, and its possible correlation to MFT particle settlement. During the ozone treatment an increment in the concentration of ions was observed, as well as the formation of carboxylic bonds on the surface of MFT particles, and the release of humic acids to form metal humate complexes. The increment on conductivity, salinity, and ionic strength during the ozone treatment suggested that the drop of the pH could influence the settlement mechanism. Changes on the particle surface properties improve the settlement of particles and led to the release of trapped water. It was concluded that changes in particle conformation and suspension caused by a drop in the pH were major factors in MFT aggregation.

Dedication

To my kids & their Dad and my Mom

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Table of Contents

Table of Figures and Tables

Chapter 1

Introduction

1.1 Background

Canada hosts the world’s third largest crude oil reservoir. Bitumen is extracted from the Alberta oil sands using the Clark Hot Water Extraction method (Allen, 2008). The rapid generation and slow consolidation of oil sands tailings (> 100 years) (Headley et al., 2010) have made their management a pressing research topic. Large amount of water is trapped in the “mature fine tailings” (MFT), a layer of the tailings that contains a mixture of bitumen (~ 1–5% mass), naphtha, other aromatic compounds, sand, silt, and fine clay particles (< 44 μm in diameter) (Chalaturnyk et al. 2002). The MFT management goal is to release the water that was used in the extraction process so that it can be reused in bitumen extraction or safely disposed in the source of origin. MFT particle surfaces contain organic matter (e.g., humic acids, asphaltenes) along with residual bitumen and hold a high negative charge that inhibits the settling process (Gutierrez and Pawlik, 2014; Kessick, 1979a; Ignasiak et al. 1983, Kotlyar et al. 1990, J. Chalaturnyk et al. 2002).

1.2 Rationale

The constant accumulation of oil sands tailings represents a big challenge for the management of the MFT. There have been numerous research efforts in order to find a solution to enhance the consolidation process of MFT. Traditional methods to dewater the MFT are mechanicals such as centrifugation, filtering, freeze and thaw method, etc., are expensive. Dewatering process using chemical methods need less energy and could treat larger volumes, although some of these methods could introduce new species in the water difficult to remove afterwards. (OSRIN Report, 2010, 2014). During the ozonation of oil sands process-affected water (OSPW) (Perez-Estrada, et al. 2011); it was observed that the particles settle faster. Therefore, it seems feasible that ozone could improve the consolidation of MFT. Liang et al. (2014) reported that the ozonation of MFT improved the consolidation and a first mechanism was proposed. During the treatment the pH dropped, from pH 8.4 to 4±0.2, this acidification could cause important changes in the water chemistry, for instance, heavy metals to dissolve. However, during the ozonation process the generated radicals oxidize water soluble organic compounds, perhaps leading to the formation of carboxylic acids which may cause the reduction of the pH.

1.3 Objectives

There are various hypotheses that may explain the observed decrease of pH during the ozonation of diluted MFT. The present study has the general objective of clarify the reasons for the observed pH reduction and explore possible correlations between the pH and the particle settlement. Specific objectives to pursuit in this study are:

I. Find the possible cause for the pH drop after the ozonation treatment
II. Correlation between pH drop and particle settlement behavior
III. Propose a mechanism for the particle settlement.

1.4 Organization of the Thesis

This thesis paper is organized in five major chapters. Chapter 1 Introduction, describing the background, motivation, objectives of the research. Chapter 2 covers the literature review. Materials and methodologies are described in chapter 3. Chapter 4 explains the results observed with detailed analysis and Chapter 5 contains an overall conclusion with proposed recommendations.

Chapter 2

Literature Review

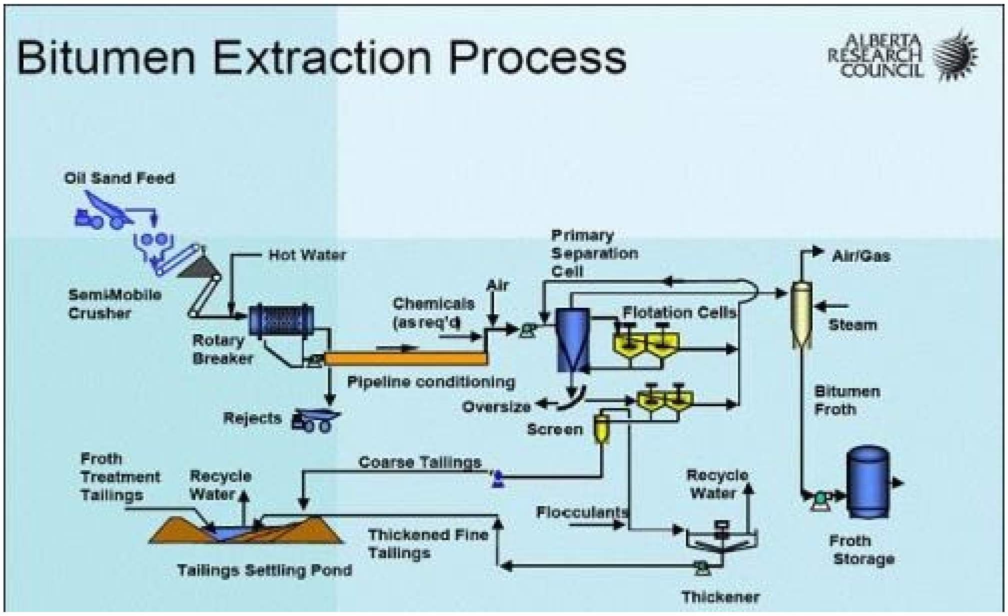
2.1 Brief Overview of Oil Sands in Canada and Properties of Bitumen in Oil Sands

Canada is one of the largest hydrocarbon deposits having the bituminous sands that are called oil sands. There are three major oil sands deposits in Alberta: Athabasca (the largest), Peace River and Cold Lake. Canada is the world's third largest crude oil reservoir after Saudi Arabia and Venezuela. The Government of Alberta has set a goal for bitumen production of 3.8 million barrels per day by 2022 in order to fulfill the increasing demand of oil (Alberta energy 2014). From the 300 billion cubic meters contained in the proved reserves, around 21 billion m^3 can be extracted by surface mining; the rest could be extracted by in-situ technologies due to the difference in thickness of the mining area. (AER –ST98, 2012).

2.2 Bitumen Extraction Process from Oil Sands

There are mainly two different types of bitumen extraction process from oil sands: Hot water extraction process (Clark process) and In-situ recovery process (SAGD). Nevertheless, the extraction process that generated most of the tailings is the hot water extraction process.

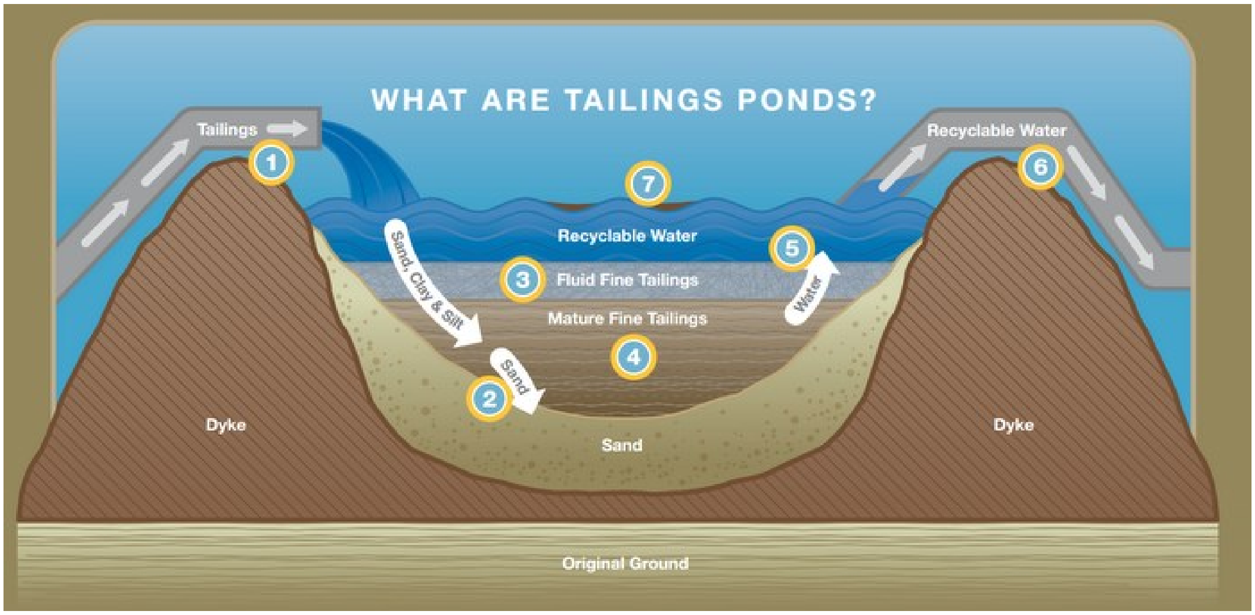
2.2.1 Hot water extraction process: Out of all the methods currently hot water extraction process in being used in bitumen extraction in Alberta. This process was first developed by Dr. Karel Clark in the year 1939. Caustic hot water is passed through one channel that helps in swelling of the clay matter loosen the bondage and help in the easy separation of Bitumen. This technique requires large amounts of water and produces much slurry waste; 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).



Source: Sustainable Development of Oil Sands – Challenges in Recovery and Use, John R McDougall, Alberta Research Council, presentation to Western US Oil Sands Conference, 21 September 2006, www.arc.ab.ca

2.3 Oil Sands Tailings

The hot water extraction process uses from 3 to 5 barrels of water to recover 1 barrel of bitumen. Thus, this process constantly generates large amount of tailings that are deposited and contained in lake-size tailing ponds. The accumulation of these tailings has become the most pressing issue for the oil sands industry due to the toxic nature of these tailings, which makes the land reclamation a challenging step to accomplish.



Source: A schematic of a typical tailings pond. (Image of Government of Alberta, 2009) (www.keystonexl.info/envionment/tailing-ponds)

In the ponds the tailings are stratified into different layer. In the bottom, just above the sand, are the so called mature fine tailings (MFT). This layer it is composed by clay particles, sand, silt and residual bitumen with 45-55 percent of solid content (Chalaturnyk, et al. 2002). In tailing ponds particles get settled with their size and specific gravitational force, due to the presence of different conformational particle in oil sands as well the mixture of different component, different layers are been formed in the tailing ponds.

2.3.1 Matured fine tailings (MFT): Out of different layers the MFT (Matured Fine Tailing) part is currently a major concern due to its unusual settling behavior. After first few years of settling these tailings consisting of almost 30% of solids trapped, this gives liquid slurry without consistency. It has been reported that its consolidation could last for decades up to few hundreds of years (Johnson, et al., 1993, Kasperski, 1992). MFT part comprises of sand, silt and very fine clay particles, as well some residual bitumen with a solid content of approximately 30-40%. Due to different chemical and physical properties a suspension with very slow settling behavior can be described as follows (Chalaturnyk, et al., 2002):

I. Ultrafine clay particle (size even less that 0.22 µm) can hold a huge amount of water by forming the gel like structure

II. In MFT part the water-soluble asphaltic acid (present due to the residual bitumen) can decrease the surface tension as well the interfacial tension of water to act as clay dispersants.

III. Due to the existence of organic matter a strong card house structure is formed that inhibit the particle settlement behaviour, which only can be distorted at pH above 10 or below 6.

These are the most important characteristics of MFT particles with a very slow settling behavior and holds large amounts of water. MFT contents significant amounts of metal ions, as well as organic and inorganic ions such as Na, Cl, K, Ca, Mg and SO_4. Moreover during the hot water extraction process large amounts of NaOH are added to maintain the required pH (8.2-8.6).

2.4 Different Methods for Oil Sands Tailings Management

Different technologies and methods are being adapted for the tailings management. Although, other processes and strategies are still under investigation in order to improve the current management.

Generally most of the management strategies include the following processes (OSRIN review report for tailings management, 2010):

I. Chemical or biological processes
II. Physical or mechanical processes
III. Natural processes
IV. Mixture or co-disposal
V. Permanent storage

2.4.1 A brief description of currently developed and adopted techniques:

Chemical or biological processes: It uses different additives for enhancing the flocculation, various thickeners, coagulants or polymers are used in these processes. Flocculations of tailings have been also suggested by removing the colloidal-sized particles with the use of common flocculants/coagulant reagents (Barbour and Wilson, 1993). These processes showed to be effective for the settling process. Although, due to some environmental issues particularly the lower quality in the released water and its cost impeded that these methods were adopted.

Physical/Mechanical processes: Centrifugation and filtration are methods also have been used for tailings management. Filtration requires diluted MFT (5-10 wt%) to have successful implement (Alamgir, et al., 2012). They are effective for dewatering relatively amount of water, but they are extremely expensive to implement in filed for the tailings ponds scale.

Natural processes: Some natural processes such as freeze-thaw, which is a very common ancient method for dewatering, can be used. It is an effective method and relative inexpensive, with increment of solid content from 30% to 50% (Johnson et al., 1993) but it would need an intense labour work.

Mixtures or co-disposal: Currently the method referred as Composed Tailing (CT) is been adapted by most of the oil company to manage the tailings. This method actually solidifies fine tailing by adding the flocculants, where the newly formed suspension is less durable and the coarse particles settle faster (Caughill, et al., 1993). The process is still under investigation in order to reduce the costs for a large-scale implementation.

Permanent storage: This method involves the usage of fresh water over the top of the stored fine tailings in order to create a lake body which is already been successfully demonstrated in the tailing ponds of Alberta. The fluid fine tailings geotechnically and hydrogeologically get secured in the deposits. Eventually MFT will be capped with the capping of sufficient depth allowing stable self-sustaining lake ecosystem (OSRIN Report, 2010).

2.5 Novel Method for MFT Particle Settlement by Ozone Treatment

Recent studies have shown that fine particles in tailings can be quickly settled after the tailings were ozonated at a 3.5mg/L dose. Other reports describe how low ozone doses, can destabilize colloidal systems and aggregate fine particles (Reckhow et al, 1986; Chang, et al. 1991; Li et al., 2009). The ozonation studies mostly are focus on the treatment are of been conducted using OSPW and ozone treatment considered to be the most efficient one for detoxification and particle aggregation in it.

Previous experiments showed that ozonation accelerate the MFT consolidation (Liang et al., 2014). The basic mechanism might be the alteration of interfacial interaction among the particle by the molecular ozone and generated radicals. The radical species degrade organic compounds by an oxidation process, reducing the size of the original organic molecules and producing carboxylate compounds. These acids appear at the beginning of the oxidation, have a peak when most of the original organic compounds are degraded and diminished towards the end of the oxidation, where mineralization starts. Formation of carboxylic acids might be the reason for the pH change. Therefore, oxidation process can induce chemical and physical changes over the particle surface, improving the consolidation, and introduce changes in the water chemistry of the suspension. The original MFT maintain the same pH as the OSPW, which is between 8 – 9 (Chandrakanth et al., 1996). After the ozonation of MFT a pH drop from 8.4 to 4 was observed (Liang et al., 2014). This drop wasn't explained before but it was considered to have a correlation between MFT fine particle and the settlement mechanism. In the case of river and lake water with high content of clay, it has been reported that Natural Organic Matter (NOM) regulates the surface chemistry to a great extend (Davis and Gloor 1981; Tipping and Cooke 1982; Chandrakanth et al., 1996). Thus, the sorption mechanisms of the NOM onto the particle surface may contribute the particle stability, which could inhibit the aggregation (Chandrakanth et al., 1996).

Liang et al. (2014) concluded that the ozonation of MFT particle cause the consolidation of the particles through the following steps:

I. Ozone degrades NOM reducing the molecular weight of its organic compounds, forms carboxylic groups that may have less affinity for the mineral particle surfaces. This leads to desorption of the stable, negatively charged, organic matter coating of the MFT particles. Consequently, the zeta potentials of MFT particles become less negative. In addition, the release of organic compounds into the water decreases the pH of the MFT suspension, which may be beneficial for the release of metal ions into the water (Perez-Estrada et al., 2011).

II. Ozone breaks organometallic complexes in MFT, leading to the release of 1.5 mg/L to 600 mg/L cations, such as calcium and iron species, into the suspension. The ionic strength (IS) of the MFT suspension it is increased, which cause that the surface charges of MFT particles were largely reduced (approximately from -50 mV to -30 mV), perhaps due to the compression of their double layers by bi- or trivalent cations. The released cations such as calcium and iron may also act as coagulants.

III. The increase of cations (calcium and iron) and carboxylic groups also facilitates the generation of metal humate complexes (Reckhow et al., 1986). More adsorption of positive cations on the particle surfaces also occurs.

Chapter 3

Materials and Methods

3.1 Selection of Sample Condition

In previous experiments the ozonation conditions of MFT settlement by ozonation were: ozone concentration 72 mg/L with a flow rate of 2.4 L/min, for reaction times of 15, 30 and 60 minutes. Diluted MFT samples were prepared with of 1 wt%, 3 wt%, 5 wt% and 7.5 wt% of the original MFT. An MFT dilution of 3wt% in weight and ozonation times of 15 and 30 minutes were selected for the mechanistic analysis with the following rationale:

I. 1 wt%, too low in solid content

II. 5 wt% and 7.5 wt%, too concentrated to operate the ozonation without losing sample volume due to high bubbling

III. Most of the important changes occur before 30 minutes. Afterwards the changes in settlement were not significant.

3.2 Effect of pH Adjustment in Diluted MFT & Ozonated Samples

The MFT from different tailings has reported solid content over 30% (Chalaturnyk, et al. 2002). Here for the experiment MFT with solid content of 38 wt% was used. The selected MFT dilutions of 3 wt% were prepared using DI water. In the previous work, an increase in ion concentration, accompanied with an important diminished of the pH value, was observed after the ozonation. In order to assess the impact of pH change in the ionic concentration and particle settling, the pH was manually adjusted to pH 3, 4 and 6, and compared with the ozonated samples. The rationale of the selected pH values is:

I. In some experiments the pH value was lower than 4 (3.8). In order to cover a low range pH 3 was selected.
II. In most of the experiment the resulting pH value after the treatment was 4 ± 0.2.
III. At pH values below 6 the surface activity of the clay-organic materials is reduced promoting the particle aggregation.

3.3 Sample Preparation and Initial Settling Measurement

3.3.1 Control sample: Control sample was the diluted 3 wt% sample without application of any treatment. Throughout the analysis, where the analysis required for using the pore/ released water, this untreated 3wt% sample was centrifuged at 10,000 rpm for 10 minutes in a Sorvall LYNX 4000 Superspeed centrifuge.

3.3.2 Ozonated and pH adjusted sample preparation: The ozonation of the samples was carried out using an ozone generator Wedeco GmbH® D-32051, using USP-grade oxygen. The gas flow rate was 2.38 ± 0.1 L/min with an input ozone concentration of 71.14 ± 0.64 mg/L (in gas phase). Prior to ozonation, the MFT sample was diluted with deionized (DI) water to mimic fresh MFT suspensions, facilitate the experimental procedure in lab scale. Samples of 120 mL of MFT suspension were transferred to 1 L flasks to allow immersion of the entire diffuser. The samples were then ozonated during the predetermined times (0 (control), 15 and 30 min).

For pH adjusted sample, they were mixed constantly using magnetic stirrer while adding small drop of 33% by volume concentrated HCl till the desired pH was attained. To have a stable pH even after the adjustment samples were kept for overnight for proper insertion of the acid through the particles. After 24 hours samples' pH was controlled showing a good consistency.

Once the ozonation was completed and MFT suspensions were shaken thoroughly for 1 minute, and then transferred to a 100 mL volumetric cylinder to initiate settling. For pH adjusted sample, after proper shaking were transferred to 100 mL volumetric cylinder as well. The level of the solid interface was recorded every 20 min for the first three hours and after 24 hours.

3.4 Water Chemistry Analysis

3.4.1 Alkalinity, pH, conductivity, turbidity, total dissolved solid (TDS):

Conductivity and pH were measured using pH and conductivity meter VWR® Symphony™ Benchtop Meter. Results were compared with the control samples. Calibration was done using the standard solutions provided by the instrument supplier.

Alkalinity was measured in control and ozonated samples (supernatant) using the HACH Kit Method 10239, where 0.5 ml sample was added to the 2 ml solution supplied and the alkalinity was recorded using a spectrophotometer HACH DR 3900 Benchtop Spectrophotometer.

Turbidity was measured using an Orbeco-Hellige® digital direct-reading turbidity meter, 20 mL aliquot of water released from each ozonated and pH adjusted samples was transferred to a disposable scintillation vial that was introduced in the digital reader.

To determine total dissolved solid a 50 ml aliquot of supernatant from each ozonated and each pH adjusted samples was removed and filtered (0.45 µm pore filter paper) by vacuum filtration. To release the pore water from untreated samples, samples were centrifuged at 10,000 rpm for 10 minutes in a Sorvall LYNX 4000 Superspeed Centrifuge. Supernatants were filtered then heated in pre-weighed evaporating dishes at 105 °C overnight to evaporate the water then weighed to determine the total dissolved solid (TDS).

3.4.2 Ion analysis: Sample supernatants were collected after 24 hours and filtered with 0.45µm pore filter paper (PTFE Fisher Chemical, Canada). Cations in the filtered water were evaluated by inductively coupled plasma—optical emission spectrometry (ICP-OES) (Thermo Scientific ICAP6300) and anions were assessed by a Dionex DX 600 ion chromatography (IC) system.

3.4.3 Inorganic carbon (IC): Total inorganic carbon (TIC) were measured using a TOC-$L_{CPH/CPN}$ Analyzer equipped with an ASI-L Autosampler from Shimadzu Corporation (Kyoto, Japan).

3.5 Organic Parameter Analysis

3.5.1 Total organic carbon (TOC): Supernatants from the control and ozone treated samples were filtered with 0.45µm pore filters (PTFE, Fisher chemical, Canada) and diluted 5× with Milli-Q water (18.2 MΩ) for organic carbon measurement. Non-purgable organic carbon (NPOC) was measured using a TOC-$L_{CPH/CPN}$ Analyzer equipped with an ASI-L Autosampler from Shimadzu Corporation (Kyoto, Japan). Here the volatile carbon was assumed to be negligible and NPOC considered to represent the TOC.

3.5.2 COD measurement: COD of Pore water of untreated and ozone treated samples were measured using the HACH kit following the Reactor Digestion method; after adding the acid digestion solution to 2mL of sample, the vials were kept in digestion reactor at 150 ^{o}C for two hours, afterwards the vials were cooled down to room temperature. Digested sample tubes were placed in the spectrophotometer (HACH DR 3900) and the COD measurements were directly taken from the readings.

COD of the acid extractable fractions (AEFs) of the supernatants was measured using the same method after dissolving the acid extractable fraction in 0.1 N NaOH. For getting AEFs all the filtered samples were acidified to pH 2.0 and organics were extracted by liquid–liquid extraction with portions of dichloromethane (DCM) in a separation funnel. After the separation, DCM was evaporated, leaving the extracted AEFs in the container.

3.5.3 Organic acid quantification and identification: It was assumed that the pH drop in MFT samples during ozonation was a result of the formation of organic acids via the oxidation of larger organic compounds. Analysis using XPS have demonstrated the introduction of carboxylic groups on the particle surface has been reported (Liang et al., 2014). To prove this assumption total organic acid were measured in the MFT's supernatant by Fourier Transform Infrared (FTIR) using the method reported in Hwang et al. (2013) for the analysis of the naphthenic acids. FTIR spectroscopy was adapted for total acid extractable fractions (AEFs) analysis (BioRad, FTS-6000, Cambridge, MA, USA). Prior to FTIR analysis, all the filtered samples were acidified to pH 2.0 and organics were extracted by liquid–liquid extraction with portions of dichloromethane (DCM) in a separation funnel. After the separation, DCM was evaporated, leaving the extracted AEFs in the container. The extracted AEFs were reconstituted with DCM and subjected to FTIR spectral analysis. Sample absorbance was measured at wavelength of 1743 and 1706 cm^{-1}, which corresponds to adsorption bands characteristic of monomeric and dimeric carboxylic groups, respectively. Concentration was measured using a standard prepared with a commercial mixture of naphthenic acid (FLUKA) (Clemente and Fedorak, 2005).

High performance liquid chromatography (HPLC, Agilent 1200 series) using an Aminex 87H column (300 mm × 7.8 mm, Bio-Rad, Mississauga, Canada) coupled to a refractive index detector (Agilent 1200) was used to identify and quantify organic acids. The column was eluted with 5 mM H_2SO_4 at a flow rate of 4 ml/min at 70 °C. Lactate, acetate, ethanol, oxalate, formate, malate, propionate, and butyrate were used as external standards.

After quantification of the detected organic acids (newly formed with oxidation process) in ozonated sample, with the same FTIR method described above, AEF concentration of those known concentration of small organic acids was determined to measure their contribution in total AEF concentration. Moreover it was important to determine the AEF value for those known concentration organic acid using the standard of naphthenic acid.

3.5.4 Humic acid separation: Humic acids were separated from humate substances with a pH dependant coagulation process and then from fulvic acid and other small organic acids (Stevenson 1994). The total humic acid concentration was measured using the CDFA 1999 (California Department of Food and Agriculture) humic acid quantification method followed by gravimetric analysis. Here the whole sample, mixture of solid & supernatant was used and were shaken overnight in 0.5 N NaOH and concentrated HCl (33% by volume) was added to supernatants until the pH dropped to 2 or lower. Samples were centrifuged at 10,000 rpm for 10 minutes in a *Sorvall LYNX* 4000 Superspeed Centrifuge. The pellets were drained and the supernatant was discarded. Pellets were re-dissolved in a 20 ml known volume of 0.5 N NaOH and stored in a pre-weighed evaporating dish at 115 °C until all the water evaporated. The weight of humic acid was obtained by deducting the weight of added NaOH.

3.6 Surface Analysis

3.6.1 X-ray photoelectron spectroscopy (XPS) analysis: X-ray Photoelectron Spectroscopy (XPS) was applied to determine the surface chemical bonding of MFT fine particles. To perform the XPS experiments, several droplets of well-mixed MFT suspensions were dried at 60°C for 48 hours on a piece of aluminum foil. A Kratos Axis spectrometer with monochromatized Al Kα (hυ = 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 ×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.

3.6.2 Particle surface charge: Electrophoretic mobility of particles was measured using MalvernR Zetasizer Nano-ZS, zeta potential analyzer, that uses micro-electrophoresis / electrophoretic light scattering technology to measure zeta potential and electrophoretic mobility. Approximately 1 ml of unfiltered (1–5 mg solid/ml was required for sample measurement) suspensions of each sample was collected and was placed in the plastic cell. An electric field is applied to a solution of molecules or a dispersion of particles, which then move with a velocity related to their zeta potential. This velocity is measured using a patented laser interferometric technique called M3-PALS (Phase analysis Light Scattering). This enables the calculation of electrophoretic mobility, and from this, the zeta potential and zeta potential distribution. The electric field was reversed at a frequency of 250 Hz over a period of 256μs and illumination was provided by a laser beam at wave length of 633 nm.

3.6.3 Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX): Scanning electron microscopy images (SEM, Zeiss EVO MA 15 LaB6 filament scanning electron microscope) of samples were recorded to observe possible particle conformational changes with ozone and pH treatments. All the pictures were taken with the same resolution of 500X with same sample condition.

Energy dispersive X-ray spectroscopy (EDX) was performed to analyse the elemental composition of the particles (spectra were acquired with a Peltier-cooled 10 mm^2 Bruker Quantax 200 Silicon drift detector with 123 eV resolutions).

3.7 Biomass Assay

An indirect objective in the present study was the long term microbial activity over the further consolidation process. The presence of methanogens is a process that is expected in the tailings and may it contribute in further settlement process. Plate counting was conducted using R2A agar to find heterotrophic bacterial. Taking 1 ml sample after 10 minutes sonication (for homogeneous mixing of population as well ensuring the microbial community to be in suspension) serial dilutions were conducted using sample: buffer ratio as 1:9 (10 µL sample added with 90 µL buffer or autoclaved DI water) to make it 10^3 dilution. Making the dilution till 10^7, starting from the most diluted sample three small droplets of 10 µL sample was dropped in the agar plate. After drying the droplets plate was incubated for 24 hours at 31°C temperature and finally kept in room temperature for 3 days. Colony number was counted where was possible with the dilution at that point.

3.8 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.

3.9 Presentation of Error Bars in Graph

Most of the experiment was conducted in triplicated manner for each sample condition so that standard deviation can be measured. Error bar presented in the results actually define the standard deviation among the triplicated sample analysis of same condition.

Chapter 4

Results & Observation

4.1 Ozone/pH Impact on Settling

Figure 1 shows the MFT settlement for both the condition, pH adjustment as well for ozonation. The results for the settling of MFT particles showed an effective consolidation in all the samples (figure 2). Comparison of the normalized interface position with the time revel that samples with adjusted pH consolidates faster. The pH values in the ozone treated samples were 4 ±0.2, showing the important role of pH during the MFT particle consolidation. Ozone treatment led to the pH drop in the sample that can potentially enhance the settling behaviour along with the dewatering process.

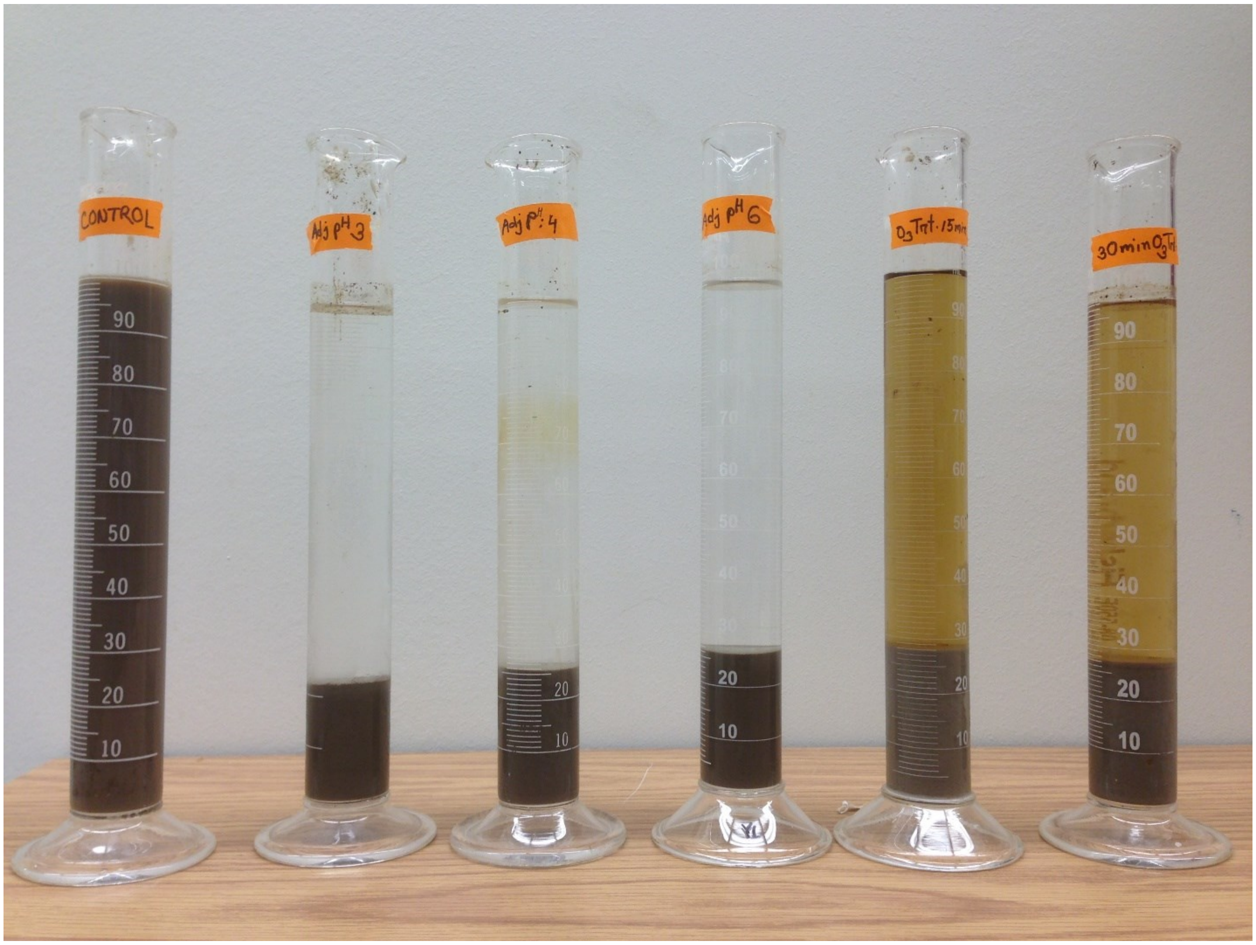


Figure 1: MFT settlement in adjusted pH and ozonated sample after 24 hours of time

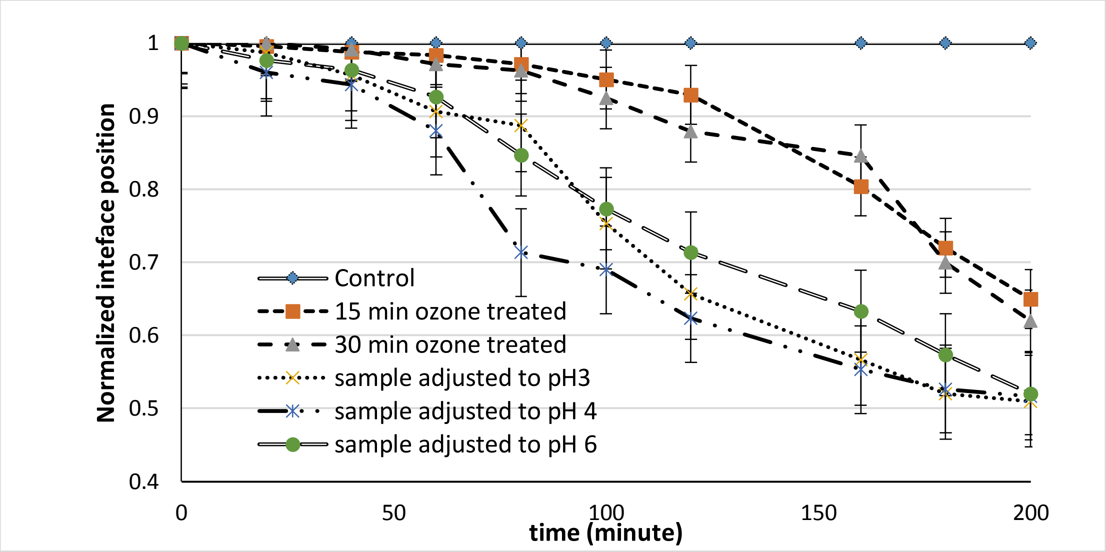


Figure 2: Initial settling curve for untreated, ozone treated (15 minute and 30 minute) and pH adjusted MFT sample

Initial settling rates in pH adjusted samples (figure 2) are higher than those of the ozonated samples ($P < 0.05$); the mud lines were close in either case after 24 hours. Particle settling occurred more quickly in pH-adjusted samples than in ozonated samples. Even though the samples have almost same pH, samples adjusted to pH 4 and the ozonated sample didn't show the same settling behaviour in the initial settling stage ($P<0.05$). The reason could be the addition of concentrated HCl acid that led to the faster suppression of surface negativity than that in the ozone treated sample. Particle settlement was faster in pH adjusted samples, after 24 hours the solid interface level was in the range of 25–30 ml in all the samples except the control. The range mentioned has a normalized interface position value of 0.25–0.3 with close to same volume of released water (figure 1).

4.2 Water Chemistry Change (Inorganic and Metal Ions, pH, Alkalinity, Conductivity, Turbidity, TDS)

Table 1: Measurement of pH, alkalinity, conductivity, TDS concentration in untreated, ozonated and pH adjusted MFT samples

Sample	pH	Alkalinity (mg/L $CaCO_3$)	Conductivity (µs/cm)	Turbidity (NTU)	TDS (mg/L)
Control	8.4	72	261.33	Above detection limit (>200 NTU)	392
15 min ozonated	4.1	38.5	640.66	65	2712
30 min ozonated	3.9	18	830.33	23.4	4868
pH 3	2.9	15.8	1943	15	5520
pH 4	4	18.3	1016	17	4310
pH 6	6.1	49.7	732	19.5	3272

4.2.1 Alkalinity, pH, conductivity, turbidity, and TDS: Table 1 shows the changes in pH after ozone treatment, which is a substantial drop from pH 8.4 to 4±0.2. In a previous study Chalaturnyk et al. (2002) described that the fine clay particle with the conjugation of some organic compounds on the surface of the particle form a non-settling slurry structure termed as the "card-house" effect, which is highly pH dependant and this effect resists particle settlement. They mentioned that either the pH should be below 6 or above 12. Values of pH above 12 will distorted the specific stable card house effect due to the increment of OH^- concentration and same structural distortion happens when pH gets lower than 6. Here the ozone treatment caused the pH to drop below 6, assisting the settling behaviour of MFT particles. The comparable settling behaviour among ozonated and pH adjusted samples (figure 2) suggests that pH played a vital role in particle settlement.

Alkalinity in original MFT samples was high due to the addition of caustic substances (NaOH) during the bitumen extraction process. Table 1 shows that Alkalinity dropped noticeably from 72 mg/L $CaCO_3$ (control sample) to 38.5 mg/L $CaCO_3$ after 15 minute of ozonation and 18 mg/L $CaCO_3$ after 30 minutes. The samples with a pH adjusted to 3 and 4 had a reduction from 72 to 15.8 mg/L $CaCO_3$ and 18.3 mg/L $CaCO_3$ respectively. However, the alkalinity in the sample with a pH adjusted to 6 was reduced until 49.7 mg/L $CaCO_3$. The ozonation proved to be effective in the reduction of the alkalinity, and turbidity, introducing favourable conditions for particle settlement. The increment of ion concentration cause that the conductivity increased 2.5 folds for 15 minute ozonation and 4 folds for 30 minute treatment. Total dissolved solids (TDS) increased in all the samples, in ozonated samples TDS increased 7-folds and 12-fold for 15 and 30 minutes respectively. For the samples with pH adjusted the TDS increased 14-folds, 11-folds and 8-folds for pH values of 3, 4, and 6 respectively than from TDS concentration in control sample. The increment of total dissolved solid in the treated sample may be associated with the drop of pH. Changes in pH caused by ozonation could promote further changes in composition of the dissolved species, for example the conjugates of zinc, sulphate or aluminum can from to different active component with of positively charged ones by oxidation through the change of redox potentiality of the system that can be adsorbed by other newly formed negatively charged molecule on particle surface to go for sedimentation behavior.

4.2.2 Impact of important metal ions: After MFT ozonation increment in ion concentration was observed in the MFT released water (Liang, et al., 2014). The increase in ionic strength after ozonation, the probable mechanism might involve is the decrease of pH after the treatment. Figure 3 shows the results of the IC and ICP-MS analysis for ozonated and pH adjusted samples. The total increment in ion concentration in ozonated sample suspension is similar in the pH adjusted samples ($P>0.05$), which indicates that the ionic strength increment could be the result of the pH drop. Protons added to the pH adjusted samples were minor in concentration (1.5-2 ml 33%v HCl to adjust to pH 3 and 4 and around 1 ml to adjust pH 6). At lower pH the solubilisation of metal ions is promoted, however for the metal ions with poly valences only their total-ion concentration was analyzed by the ICP-MS method. Oxidation of certain metal ions (e.g., Fe^{+3}, Mn^{+4} or Al^{+3}) may enhanced the settlement process. (Chandrakanth, et al., 1996; Reckhow, et al., 1986).

Figure 3 also represented a substantial increment of SO4-2 after ozone treatment, almost 2 fold after 15 minute ozone treatment and more than 3 fold after 30 minute ozonation. From the observation of increment in iron ion concentration, this may indicate the formation of iron-sulfate complex which will be dissociated in the observed pH after the treatment with ozone and be more in the suspension.

In current experiment the results showed in figure 3, increase of most of the measures ions in both ozonated and pH adjusted samples. Ionic strength increase after the ozone treatment could be mostly due to the pH drop. The low pH favours ion dissolution and formation of positively charged metal ions complex (e.g., hydroxide of aluminium, iron, and manganese) that can conjugate with MFT particle surfaces and reduce particle surface negativity, at higher pH these metal ions will precipitate.

The concentration of iron and manganese ion increased in the sample suspensions after ozone treatment and pH adjustment (figure 3). The formation of positively charged complexes at low pH 4–5.5 (especially aluminum hydroxide) could contribute to particle destabilization, enhancing settlement. In all samples the concentration of aluminum dropped down to almost 4 fold in ozone treated and pH adjusted to 3 and 4 samples than that in the untreated sample suspension which might be explained by the contribution of aluminum in particle settlement through an adsorption process of positively formed aluminum hydroxide complex in lower pH, over the negatively charged particle surface. Similar results have been observed previously (Li et al., 2009).

To some extent these metal ions might form conjugates with carboxylic groups formed by the oxidation process; such conjugates could accelerate the coagulation process or help in particle settlement (Li et al. 2009). Iron at its higher oxidation level can work as an in-situ coagulator (Reckhow et al. 1986). Iron concentrations measured after sample ozonation were 60 mg/L and 147 mg/L in 15 minutes and 30 minutes ozonated sample respectively whereas untreated sample suspensions has iron concentration as low as 3.5 mg/L. This indicates a 20 to 35 fold increment of released iron ions as a result of oxidation (possibly to higher oxidation states) and as a consequence of the pH drop in the sample. The current results support the proposed mechanism, that is, an increase in metallic ion concentrations through ozonation leads to particle consolidation (Liang et al. 2014). An increment in total ionic strength which is more than 100 times in treated sample, eventually led to the suppression of surface negativity that acts as a barrier to particle settlement. Furthermore, the increased cation concentration will tend to break up organometallic complexes (Jekel et al. 1994; Dowbiggin et al. 1989).

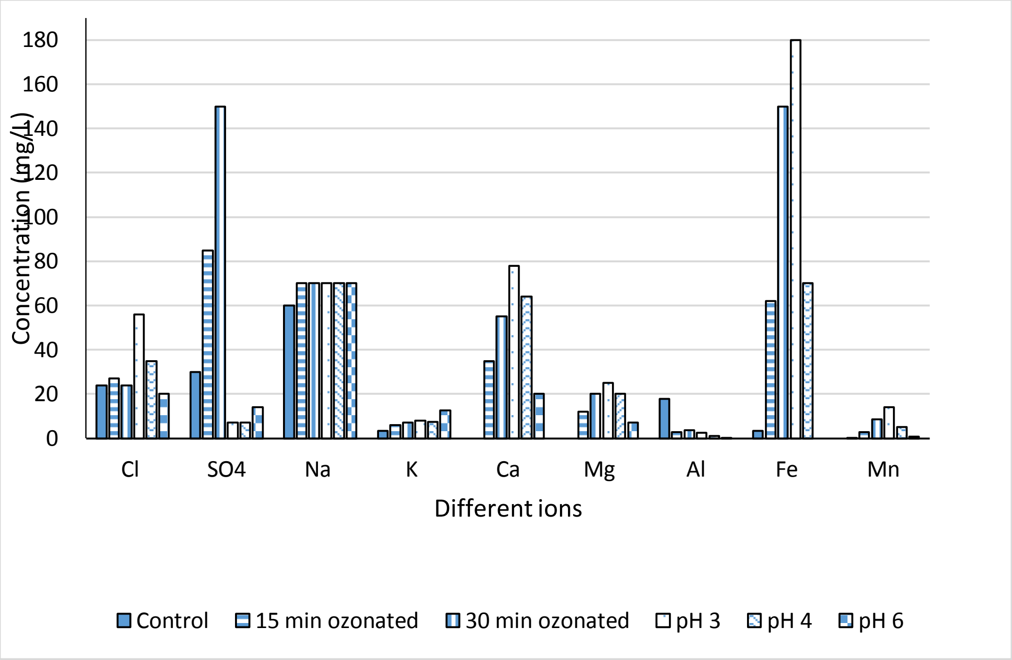


Figure 3: Concentration of different anions, cations and metal ions in untreated, ozonated and pH adjusted sample

The comparative overview of ion concentrations in ozonated and pH adjusted samples it is depicted in the Figure 3. The increment of the ionic strength after the ozone treatment it could be due to the pH drop to acidic condition of pH around 4 from basic pH 8.4. Cationic ion strength increased almost to 25 mM with 30 minute ozonation. Here the increment of Ca^{+2} and Mg^{+2} which is 50% in 15 minute ozonated sample and almost 100% for 30 minute treatment can help in the MFT particle settling process. Polyvalent cations help in particle settlement than the monovalent ones, which was experimentally proved by Liang, et al. (2014).

For particle settlement through oxidation of metal ions, for instance; iron, aluminium and manganese, can contribute, as oxidation of these metal complexes can work as in situ coagulant (Chandrakanth and Honeyman, 1996). From figure 3 Concentration of Iron and manganese increased in suspension after the treatment (for iron increment in concentration was 20 fold in 15 minute ozonation and 35 fold in 30 minute ozonation and for manganese increment observed in concentration was 90 and 210 fold for 15 minute and 30 minute ozone treatment respectively) only a decrease in aluminium, which might be due to the formation of positively charged complexes at lower pH range between 4-5.5 having high affinity for negative charge, and those complex can be adsorbed by the particle surface and contribute in destabilization of particle to enhance the settlement. Similar observation was for the pH adjusted samples. For all the samples aluminum concentration got decreased almost 5 to 9 fold after the treatment of 15 and 30 minute ozonation than from the control sample suspension, indicating contribution of aluminum in particle settlement, may be through the adsorption process over the particle surface as these metal ions might form conjugation with some carboxylic group formed by the oxidation process that can accelerate the coagulation process or help in particle settlement (Li et al. 2009).

From the observation and concentration measured after the ozonation process compared to untreated sample suspension, it can be concluded that the release of substantial amount of iron ions are the result of oxidation process (might be to their highest oxidation level) as well the consequence of pH drop. Thus, the current results proved the first proposed mechanism of increase of metallic ion concentration by ozonation leading to the consolidation (Liang, et al. 2014). Increment in total ionic strength eventually leads to the suppression of surface negativity from -48 mV to -30 mV that could act as the barrier for particle settlement. Furthermore the increased cations concentration which is almost 25 mM higher than the untreated one can help in breaking the organometallic complexes as well (Jekel et al. 1994 and Dowbiggin et al. 1989).

4.2.3 Inorganic carbon concentration decreased with ozonation in MFT sample:

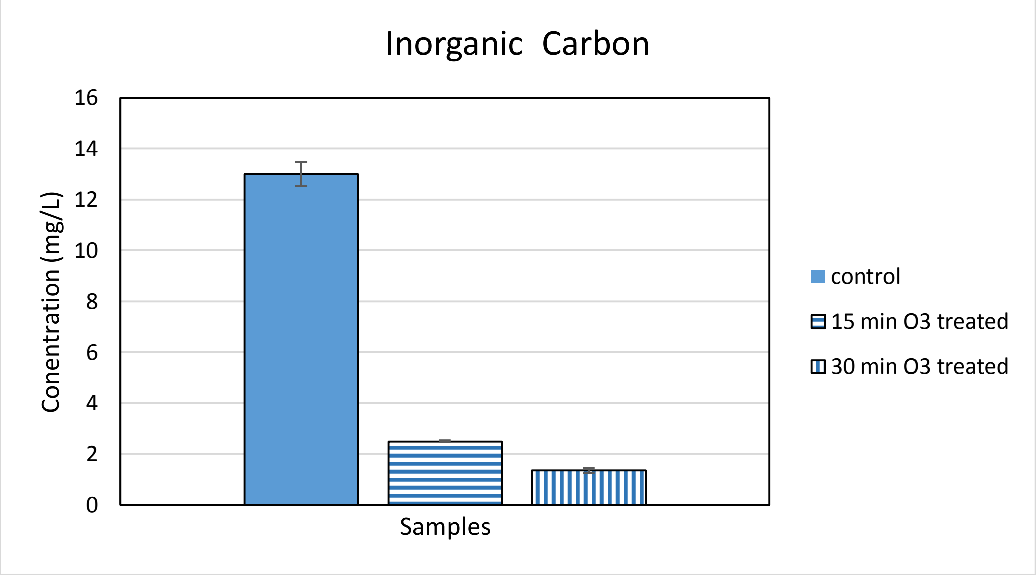


Figure 4: Inorganic carbon measurement in untreated and ozone treated MFT sample

Inorganic carbon (IC) measured in the control sample itself was 13 mg/L and after the ozonation process it was reduced to 2.5 mg/L and 1.5 mg/L in 15 minutes and 30 minutes respectively. Ozonation oxidizes the inorganic carbons to form bicarbonate and eventually carbon dioxide, thus the value of IC got lowered.

4.3 Water Chemistry Changes (Organics)

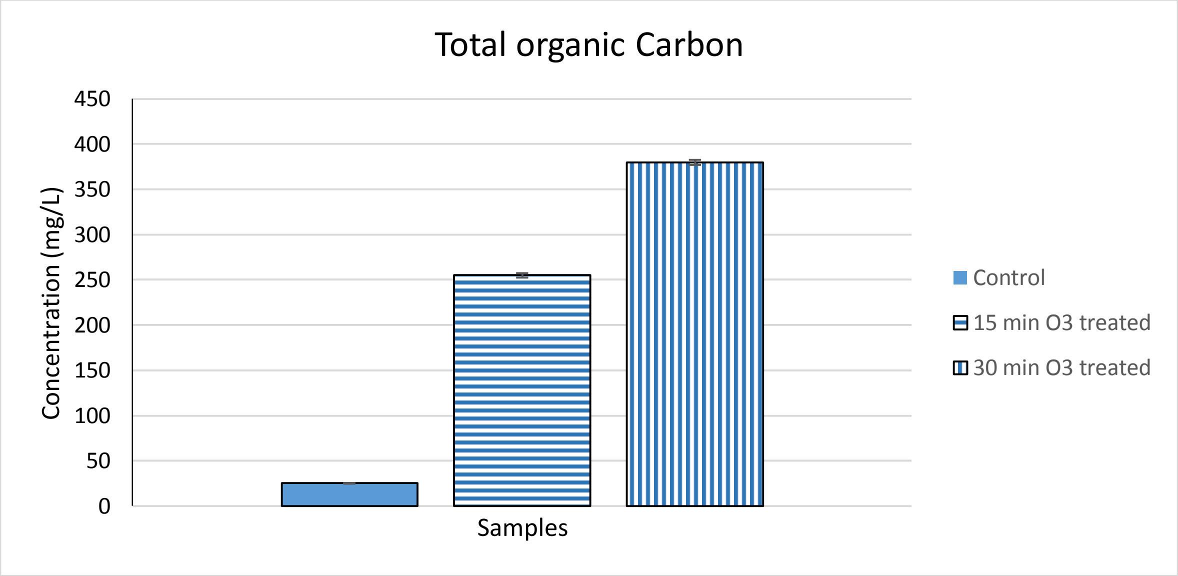


Figure 5: Total organic carbon (TOC) measurement in untreated and ozone treated MFT sample

4.3.1 Total organic carbon increment by ozonation:

Ozonation of MFT samples produce high concentrations of organic compounds. Total Organic carbon was measured to find out the increment and figure 5 represented the data. TOC in MFT suspension increased from 25.07 mg/L in untreated to 255mg/L and 380 mg/L in 15 minute and 30 minute ozone treatment respectively due to the oxidation process. It might be due to the release of organic matter from the particle surface as well the oxidation of trapped bitumen, naphtha in between the MFT particles. During the ozonation process long chain carbon compounds are degraded into smaller compounds and carboxylic groups are formed.

4.3.2 Ozonation lead to increment of COD and organic fraction: The figure 56shows how the COD of the sample suspension increased 250 to 300 fold in concentration after ozone treatment of 15 minute and 30 minute. COD in the untreated MFT sample was 29 mg/L; whereas COD in 15 and 30 minute ozonated sample suspension was 713.5 mg/L and 900 mg/L, respectively. Probable sources of the COD increase could be (1) dissolution of MFT surface bound organics to the released water after ozonation, (2) the release of oxidized organics by the ozone treatment to the released water, and (3) the release of metal ions along with some inorganics present to the released water which can be oxidized and contributed to the measured COD.

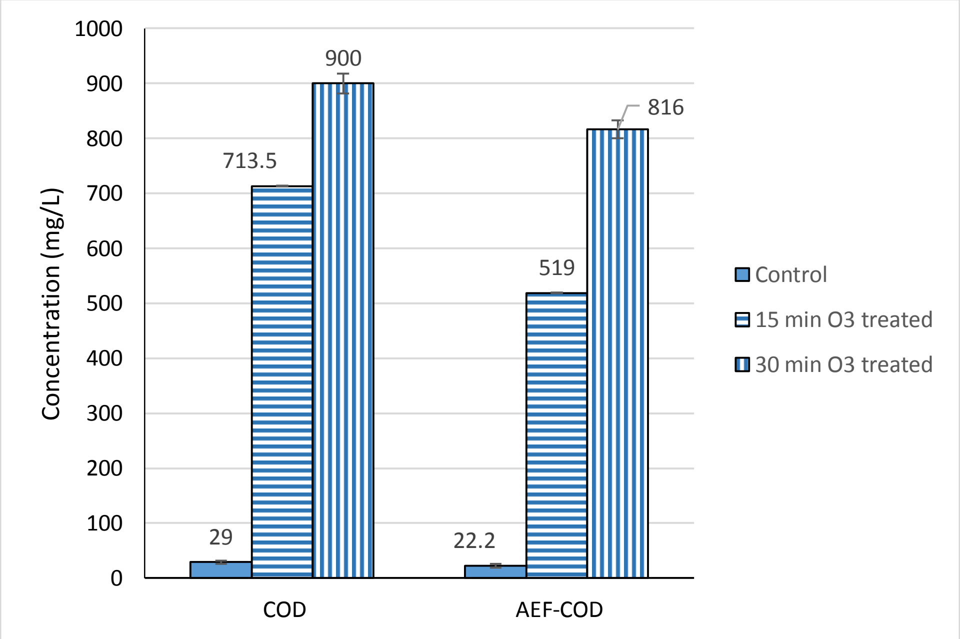


Figure 6: Total COD and AEF-COD measured in untreated and ozone treated MFT suspension

As shown in Figure 6, an increment in AEFs COD was also observed. In the control sample AEFs COD was around 22.2 mg/L. In ozonated samples AEFs COD increased to 519 mg/L and 816 mg/L for 15 and 30 minute respectively. This result describes the increment of organic compounds concentration in the MFT released water after ozonation that mostly contributed to the total COD measured in the released water. The increase in the concentration of organic acids in released water revels that the settlement process will be accompanied with a reduction of the pH in the released water.

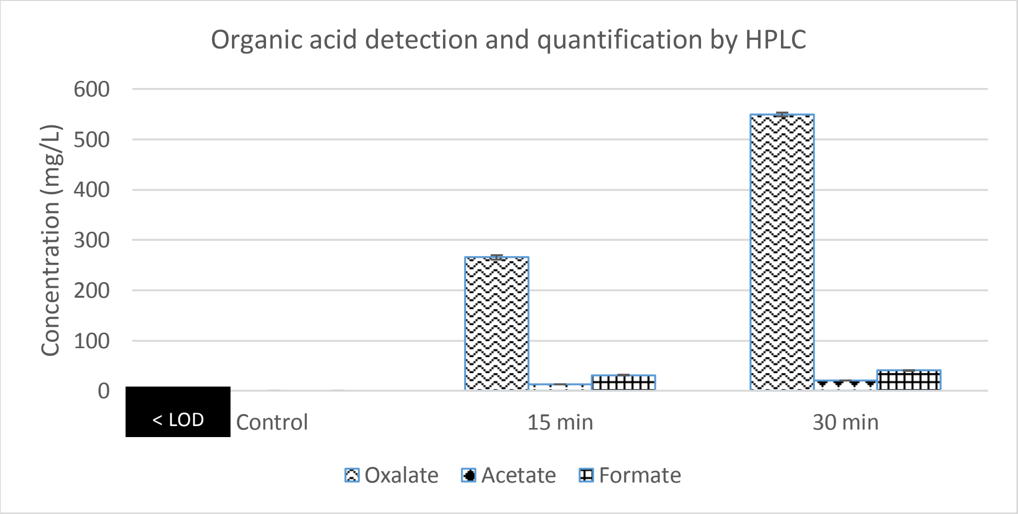


Figure 7: Small organic acid detection and quantification in untreated and ozonated sample

4.3.3 Small organic acid formation by ozonation process: In the figure 7 the formation of oxalic acid, acetic acid and formic acid after ozonation shows that the oxidation of organic compounds takes place. Although, the trend in the oxalic acid concentration appears to increase and the mineralization point it is not achieved, 60% of the COD has been transformed into short chain carboxylic acids that could be easily biodegraded. In the present study, seven small organic acids were tested for identification and quantification by HPLC, acetic acid, formic acid, propionic acid, butyric acid, lactic acid, maleic acid, and oxalic acid. Among the seven tested organic acids, oxalic acid proved to be the prominent carboxylic acid formed after the ozonation process. Concentration measured for oxalic acid in 15 minute ozone treated MFT released water is around 250 mg/L, and in 30 minute ozonation led to the formation of as high as 500 mg/L of oxalic acid. Where as in untreated MFT suspension concentration of oxalic acid as well the rest two (acetic acid and formic acid) were measured to be below the limit of detection.

Ozonation can break up long chain organic compounds, to form small organic acid fragments (Martins, et al., 2013). In previous studies while applying ozone for any disinfection or particle settlement process, it was observed that ozone can lead to the breakage of longer organic molecule to the smaller organic compounds mostly the organic acids through oxidation process (Chandrakanth and Honeyman, 1996; Świetlik, et al., 2004; Martins, et al., 2013). Moreover the introduction of oxygen by ozonation into the larger molecular structure is mostly accompanied by the increase in acidic functional group (Maier, 1979; Breeman, et al., 1979; Reckhow, et al., 1992, Chandrakanth, et al, 1996).

Oxalate has a pKa values of 1.25 and 4.14, and in higher concentrations, it is expected the drop of pH in the system substantially after the ozonation treatment. In a previous study conducted by Chandrakanth et al. (1996) the same acidification and lowering of pH was observed, and it was concluded that the formation of oxalic acid from dissolved organic compound by ozone treatment was the probable cause. Acetic acid and formic acids were also observed in the analysis although their concentrations were marginal in comparison to the oxalic acid.

4.3.4 Contribution of newly forms small organic acid to the total organic acid in released water to change overall pH in the system:

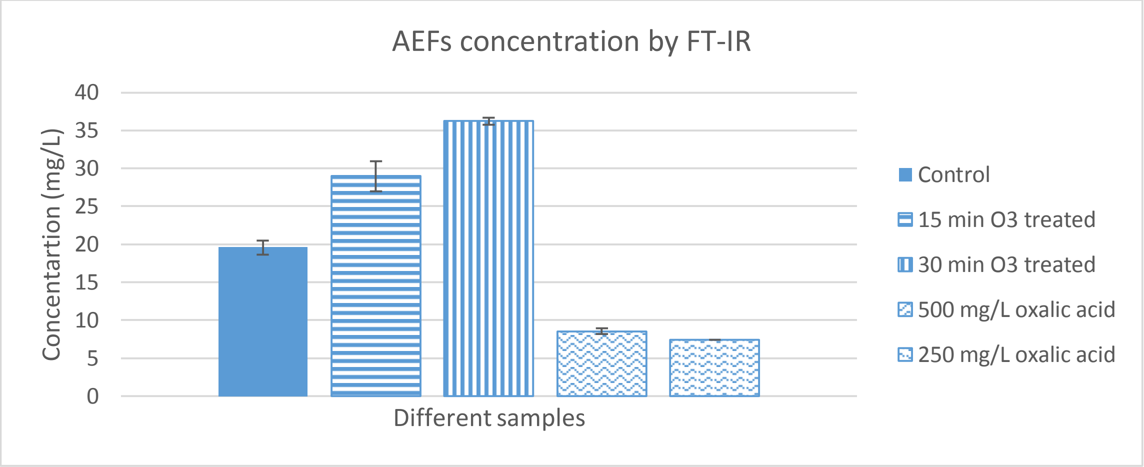


Figure 8: Qualitative representation for AEFs concentration in untreated and ozonated sample along with predetermined concentration of oxalic acid

The FT-IR is the most commonly used technique for the measurement of total organic acid and AEF. It should be noted that FT-IR cannot specify the organic acids present as it represents the total carbonyl group, grouping the carboxylic, aldehyde, and ester group in one measurement. The FT-IR measurement was conducted using a commercial naphthenic acids mixture as a standard. The results in figure 7 showed a 50 % increment in organic acid concentration after 15 minute ozone treatment as well 75% increment for 30 minute ozonation. The AEFs concentration increased from 20mg/L in the control sample to 30 mg/L and 37 mg/L in the 15 and 30 minute ozonated sample respectively.

To evaluate the contribution of the oxalic acids in the overall organic acid concentration changes, oxalic acid solutions at the concentration being detected in the HPLC experiments (250 mg/L and 500 mg/L for 15 and 30 minutes ozone treatment) were prepared in the laboratory to evaluate their corresponding AEFs concentrations using NAs as the standard. Results from this study are shown in figure 8. It was observed that AEFs concentrations of the oxalic acids were 7 mg/L and 8.5 mg/L for 15 and 30 minutes ozone treated samples respectively.

FT-IR method represents the cumulative result for all the carbonyl group (aldehyde, ketone and carboxylic group). Because oxalic acids only possess the carboxylic group, it might reflect a lower value than the origin. Moreover, the background value we used in this study was naphthenic acids, which might impact the FTIR readings as well. Hereby the FTIR results should be used with caution. Here presented results of FTIR represented qualitative than quantitative measurement of the examined sample. (Grewer, et al., 2010). Future studies using different standards for calibration curve (oxialic acid for instance) might be needed to represent the actual AEF concentration for oxalic acids.

The results presented in figure 8 can explain major contribution of oxalic acid to the total measured AEFs concentration of almost 50% of the total that can indicate to be one of the probable reasons behind the pH drop by ozonation which is mainly providing one of the most important mechanisms for settlement of MFT after this treatment.

4.3.5 Increment of humic acid with ozonation:

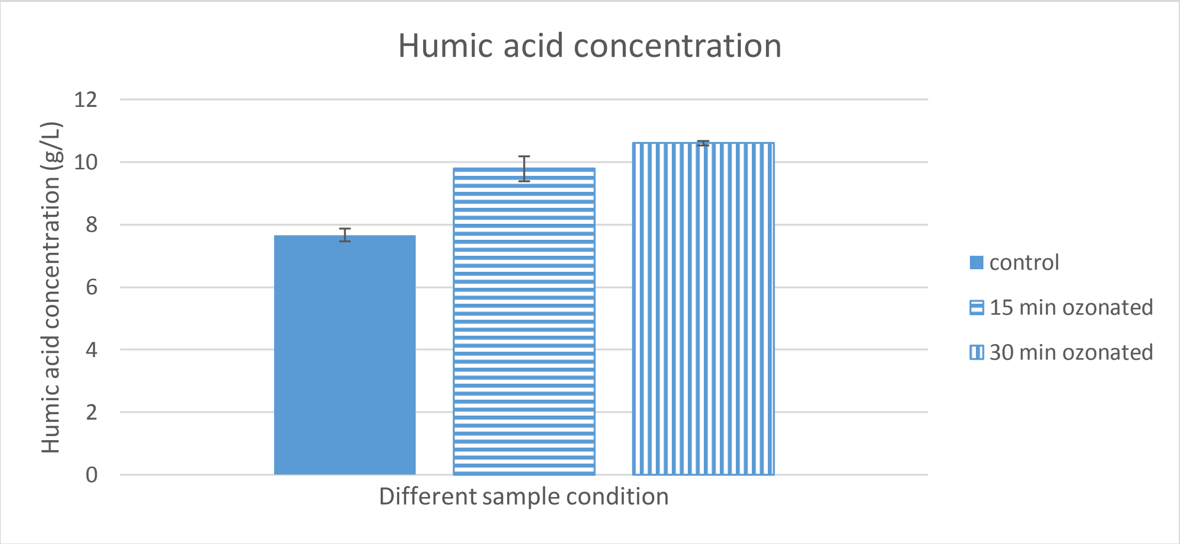


Figure 9: Humic acid concentration in untreated and ozonated MFT sample

Particle settlement in MFT samples during or after ozone treatment might be explained by an increase in surface carboxylate bonds and formation of metal humate complexes as these bonds and complexes can destabilize particle interactions (Reckhow et al. 1986). Figure 9 depicts humic acid concentrations before and after ozone treatment. From the figure 8 concentration of humic acid measured in untreated MFT sample was already as high as close to 8 g/L. Ozonation led to increase humic acid concentration to 10 g/L and 12 g/L in 15 minute and 30 minute ozone treated sample. Organic compounds bound to the clay particle in oil sand, major detected ones are the humic acids and asphatenes (Kessick 1979a; Ignasiak, et al. 1983, 1985; Kotlyar, et al. 1990; Chalaturnyk, et al. 2002).

Though the organic matter coating on MFT particles is partly responsible for holding the particles in suspension, bonding between organic entities on the particle surface might be a probable mechanism introduced by ozone since previous studies showed the dissolution of humate substance from the particle surface by ozonation. Again with only the increment of humic acid might not itself enough to draw the conclusion for this settlement behaviour, ozone has some other controlled mechanisms to enhance fine particle settlement. But this increment of humic acid might be potentially released from the particle surface through oxidation process, may have some conjugation with metal ion to form metal humate complex resulting in the particle aggregation process (Edwards et al. 1993, Jekel 1991, Liu et al. 2009) and could be accounted for MFT settling behaviour.

4.4 Surface Characteristics

4.4.1 Surface conformational changes observed by XPS: Figure 9 represents the surface conformational properties in untreated and ozone treated MFT particle surface. From figure 10 it could be observed that C-C bonding decreased on the particle surface after the ozonation process with the increment of carbonyl bonds, perhaps due to the carboxylic groups. This result agreed with previous studies where ozone treatment was applied in water treatment plants for enhancing the particle settlement. The ozonation process lead to the incorporation of oxygen in between the organic coating of the surface longer molecules to generate more carboxylic bond formation over the surface. (Maier, et al., 1979; Van Breeman, et al., 1979; Edward and Benjamin 1992).

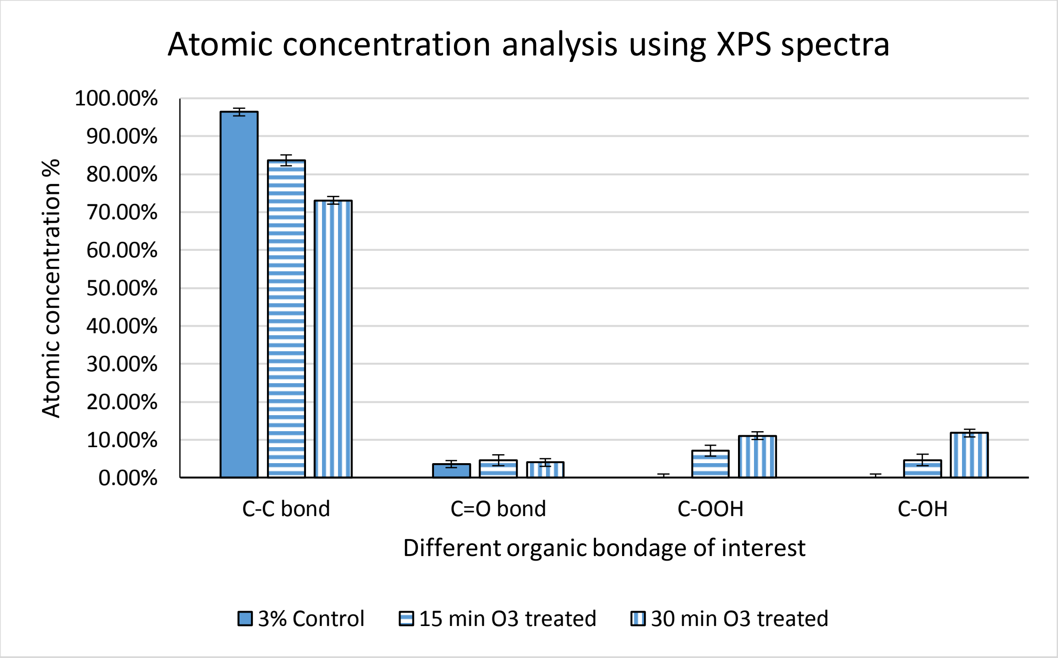


Figure 10: Surface chemical bond analysis by XPS in untreated and ozonated sample

4.4.2 Surface charge change observation by ozonation:

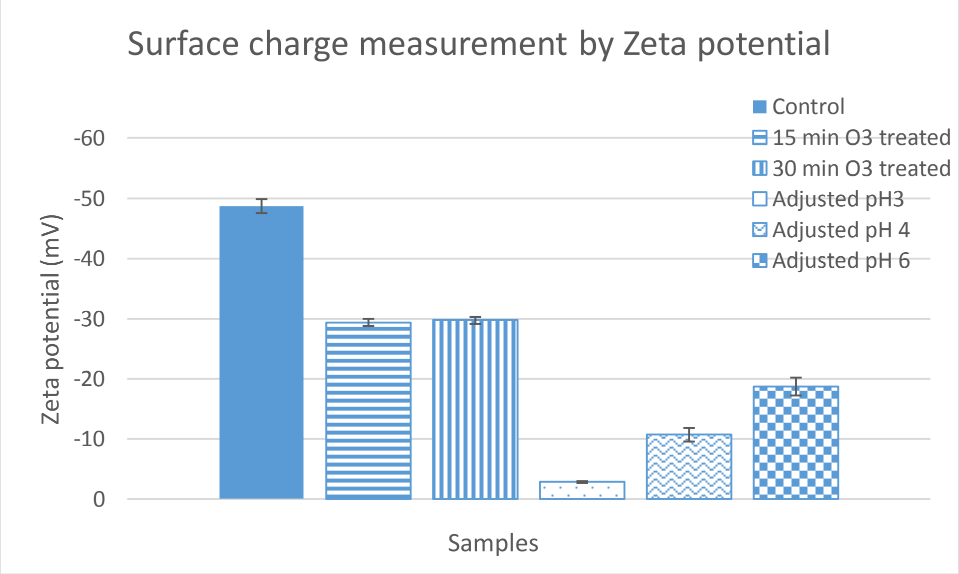


Figure 11: Surface charge measurement in untreated, ozonated and pH adjusted sample

Figure 11 shows the zeta potential measurements indicating the surface charge to exhibit the particle stability in untreated and ozonated particle surface. The comparative presentation of zeta potential in manually pH adjusted MFT particle surface. Surface negativity in control or untreated sample was quite high of -48 mV. After the ozonation treatment the surface negativity was supressed to below -30 mV for both 15 and 30 minute. Figure 11 also exhibits surface negativity in pH adjusted MFT particle is much less which is -5mV in pH 3adjusted sample particle and close to -20 mV in pH 6 adjusted MFT particle, which may justify the faster initial settlement of particle in pH adjusted sample than the ozonated one.

4.4.3 SEM images indicating ozone induced particle structural changes:

Images from scanning electron microscopy in figure 12(A,B,C,D) represents that particles surface characterization in untreated, pH adjusted and ozone treated sample for 15 minutes and 30 minutes respectively. From the figure the surface structure in both untreated and pH adjusted MFT fine particle has a finer texture, with surface smoothness. Figures 12C and 12D, have a different surface structure, the particles appear to have rougher surface and bigger particle size. All the samples were collected in the same way and all the pictures are presented in the same resolution.

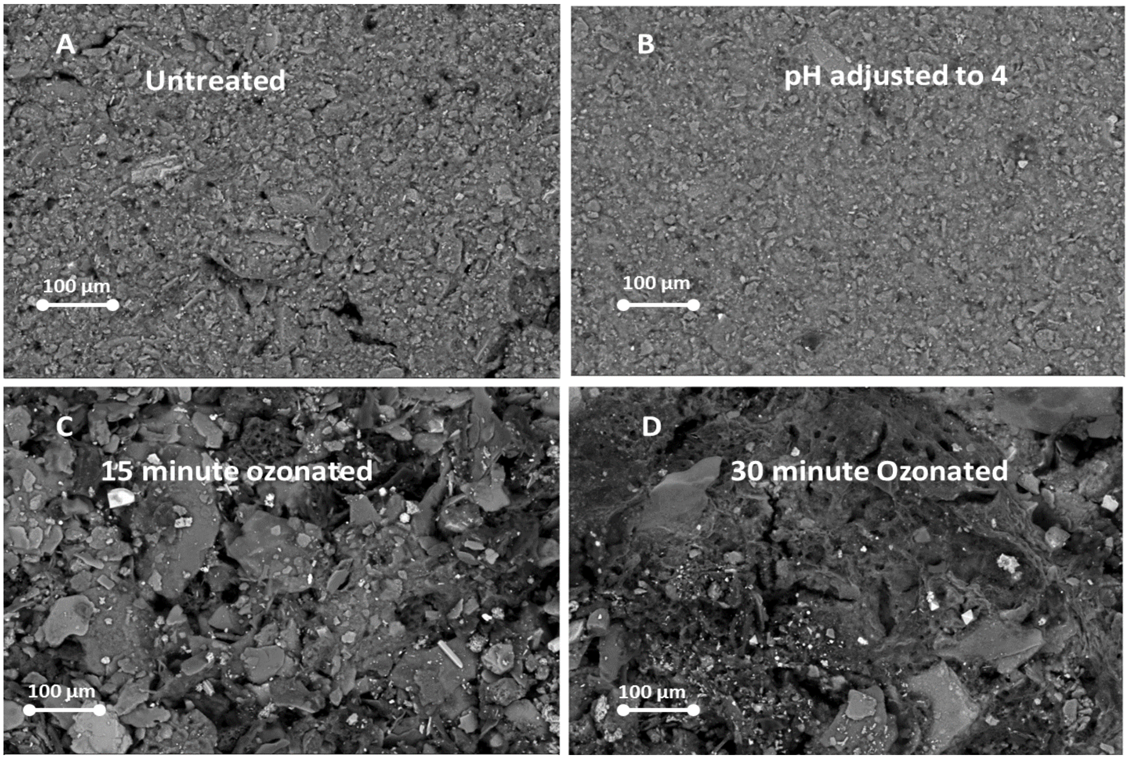


Figure 12: SEM images of 3 wt% MFT particles A. untreated, B. pH adjusted, C. 15 minute ozonated and D. 30 minute ozonated sample

The untreated and pH adjusted samples have almost similar conformation (fine texture without cluster formation) whereas ozonated MFT samples present a rough surface with particles with bigger size and grouped in clusters. Energy-dispersive X-ray spectroscopy (EDX) analysis showed an increment in metal ion mass and carbon content in ozone treated sample particles than in the untreated one; Carbon content increased from 13% in untreated particles, to 23% and 36% for 15 minute and 30 minute ozone treated samples, respectively. EDX analysis of different portions of ozonated samples showed that small particle clusters formed in ozonated sample has a higher carbon concentration.

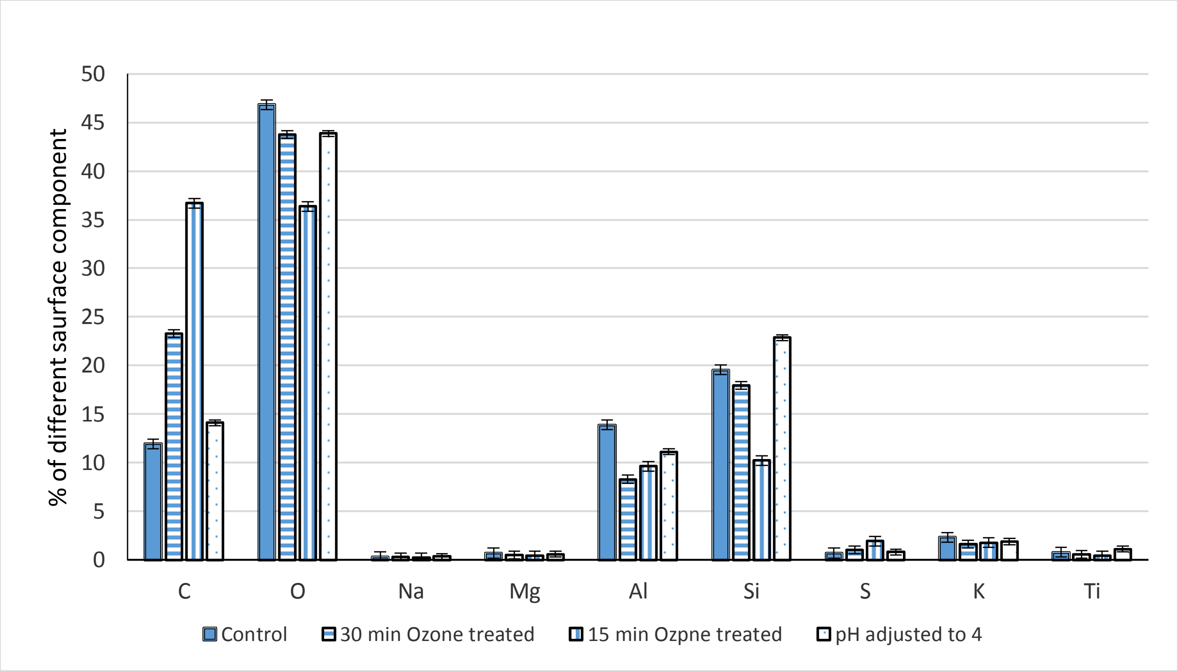


Figure 13: EDX analysis for the control, ozone treated and pH adjusted MFT particle

In our study it is unlikely that the much energy provided by ozone in MFT particles is not high enough to lead to the particle crystallization. The roughness observed by the SEM image in ozonated MFT particles may be induced by ozone treatment, where the surface organic coating got oxidized, new carboxylic bonds were formed and organometallic complex formed. Previous studies on the ozone assisted particle destabilization in water treatment plant (Gerval and Bablon, 1983; Gurol and Pidatella, 1983; Shepherd and Long, 1987) also reported different conformational and structure changes of the particles, e.g., bigger particle formation, organometallic bond formation, carboxylic bond introduction, etc. though mostly indicating the formation of flocs since their research referred here were applying ozonation for the improvement of particle settlement mostly by flocculation, coagulation.

One more probable reason might be the sequential settlement of particles as per size in settling after the treatment with ozone. (Rueter, et al., 1995). For ozonated sample the particle went through the conformational changes, as the particle organic coating might get dissociated through oxidation processes, particles of different size were exposed to the system and settled according to the size. Whereas for pH adjusted sample, particles were settled by losing the surface negativity. So when sample was collected from the same depth of settled sludge (bottom half of the settled sludge), in ozonated sample particles collected might have the larger ones in that position, where as in control and pH adjusted sample sludge settlement might not sequential. Moreover the settled sludge in all the samples may not represent the homogenized particle settlement, hence in ozonated sample the larger particles might be sampled for SEM analysis, which should be confirmed in future analysis. Here the SEM pictures presenting the increment of particle size is not explainable with the fundamental properties and common mechanisms, so the exact mechanism associated with the structural changes of the particles presented by the images are to be explained, so further investigation is required.

4.5 Biomass Assay by Plate Counting

Though it was expected that after ozonation some microorganism might be detected by plate counting, but this method was not sensitive enough to detect the microbial community after ozonation. In control (untreated sample) culturable microorganism counted was $5X10^3$ CFU/mL and after ozonation, no culturable bacteria were observed by plate counting. Further advanced microbiological technique such as QPCR, DGGE can be applied.

4.5.1 Long term observation of settlement after ozonation: Ozonated sample were kept for six months to observe any further settlement of MFT. A minor change observed, that can be due to natural settlement enhanced by ozonation or might be the result of microbial activity inside. Further analysis can be conducted.

4.5.2 Results for scaling up the sample volume: After scaling up the sample volume to 1 liter preparing the same 3wt% MFT ozone with same applied dose and flow rate with 2L/min was applied for 15 minutes and 30 minutes. For 15 minute the settling rate was not satisfactory but for 30 minute the settling rate was really fast life the previous result. Analyzing the pH at 15 minutes and 30 minutes ozonated 1 liter sample pH 7±0.2 and pH 5.8-6 was observed. So here again it can be concluded that to break the card house structure of fine particle in MFT the pH should be lowered below 6 (Chalaturnyk et al., 2002)

Chapter 5

Conclusion and Recommendation

5.1 General Summary

The major objective of the present study was to elucidate the settlement mechanism of MFT particle by ozone treatment. The conformational distortion of particles, changes in water chemistry and during the oxidation process are fundamental in order to understand the settlement mechanism. The most probably settlement mechanism start with the formation of radical species from the decomposition of ozone, afterwards organic compounds and NOM are degraded by these radicals producing oxidation intermediates and/or carboxylic acids. Once the particles lost the coating provided by the organic compounds and/or NOM they loss the cohesion precipitate to form a consolidated dense mud. Samples with pH adjusted and without ozone treatment showed an alternative mechanism. This mechanism could be described purely with the changes in the surface charges. Once the pH drops from 8 to 6 the negatively charged particles no longer can be suspended and will precipitate forming the same consolidated mud. Furthermore, the ozone treatment introduced the change in particle conformation that allowed the particle to settle not only with the suppression of surface negativity but also the cluster formation in between or forming complex with other metal ions.

5.1.1 One of the suggested possible pathways of oxidation in proposed treatment process that may lead to the pH drop in the system: Reason behind the pH drop, formation of basic organic acids after the oxidation process was assumed, which can contribute the quick drop of pH in the system. Ozone can lead to the formation of small organic acid from the larger organic compounds (Martin, et al. 2013). This assumption was proved in the study. Even from the XPS result in the previous experiment we observed the introduction of carboxylic bonds after the treatment process which lead to conclude the possibility of formation the organic acids from the larger organic compounds, since a decrease in C-C bond was observed as well. Carboxylic group has got high affinity for the metallic ion to have the association that helps in particle settlement process. SEM images represent the change in particle structure in the ozonated sample where as in untreated (control) or pH adjusted sample particles seem finer. Oxalic acid consists of two carboxylic groups and a common bi-product of oxidation path way of longer organic compound to the short form by ozone. The probable pathway can be as followed:

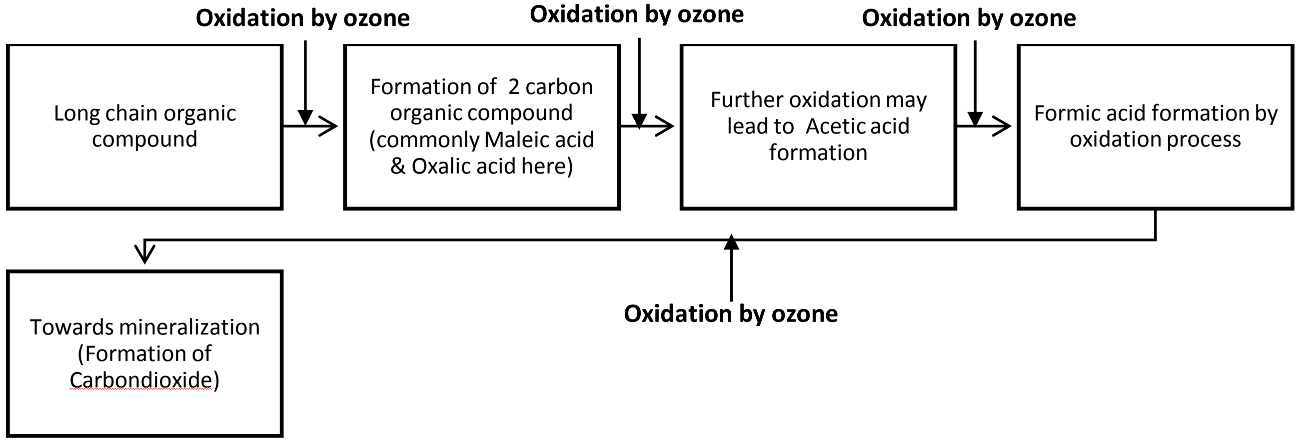


Figure 14: Schematic presentation of one of the probable oxidation pathways of larger organic compound to simple organic acid by ozonation in proposed mechanism

Ultimately all the oxidation process tends to the mineralization. However, the trend of increment in the intermediates indicates that the system won’t reach total mineralization in less than 30 minutes of reaction. By another hand, if the applied ozone is increase the system might reach total mineralization. The most prominent degradation by-product was oxalic acid, and since its trend was found to increase, this as well could confirm that the oxidation process have not reach its maximum point, after which the oxalic acid concentration will start to decrease.

Surface analysis showed that oxidation process as well can alter the surface properties of the MFT particles, may be by introducing alteration and distortion of particle surface organic coating to help them settle. The brown colour of the released water in ozonated MFT sample may be due to the presence of high concentration of humic acid or some metal complex with oxalate formed. Overall this study has demonstrated that the ozone treatment enhance the dewatering of the MFT accelerating the natural consolidation time.

5.2 Conclusion

The following conclusions can be made from the overall mechanistic study carried out in the project:

I. Quick and successful particle settlement in MFT is possible by introducing ozone as a treatment method, moreover from the comparative analysis with the ozonated and pH adjusted MFT sample, it can be concluded that pH playing an important role in particle destabilization and thus enhancing the dewatering process.

II. Increase in ionic strength after ozone treatment is mostly due to the pH drop, though oxidation process by ozone can play some role in metal ion oxidation to accelerate the settlement process.

III. Ozonation increase the total dissolved solid content, conductivity as well lowering the turbidity and alkalinity allowing the favourable condition for MFT fine particle settlement thus help in releasing trapped water with even a minimum ozone treatment of 15 minutes with a specific applied treatment condition.

IV. Reason behind the drop of pH through the system is mostly due to the formation of small organic acids due to the oxidation process. Here the detected ones are the acetic acid, formic acid and oxalic acid that can lower the pH condition to introduce the change in water chemistry for particle settlement process.

V. Humic acid concentration got increased after the ozonation, that may indicate to the formation of metal-humate complex that contribute in destabilization of particle

VI. Surface property analysis concluded the ozonation process to introduce the conformational change over the particle surface that can overcome the particle stability by destabilizing the electrophoretic mobility among them.

VII. Particle surface negativity is supressed by ozone treatment, but in pH adjusted sample addition of concentrated acid led to the fast and more suppression comparing to the ozonated MFT particle. That is why particle settlement was faster in pH adjusted MFT sample.

VIII. SEM images refer to the change in particle structure of MFT particles than in pH adjusted ones.

IX. By scaling up the sample size it was observed that longer ozonation time is required for larger sample size (by volume) to lower the pH at least below 6 to initiate the settlement process (though no other investigation was conducted for scale up sample volume)

X. From basic plate counting no culturable bacteria was detected after ozone treatment. Though with advanced microbiological techniques existence of methanogens can be examined.

XI. Keeping the ozonated sample for a longer period of time (7 months) further settlement of particles was not that significant, but a minor change was observed (further investigation required).

5.3 Recommendation / Future Work Plan

The following recommendations are proposed to further study this dewatering oxidative process:

I. Investigation over toxicity measurement might be conducted in future.

II. Cost cycle analysis should be conducted.

III. Conduct different pre-treatments in order to lower the alkalinity, since high alkalinity of MFT is a significant draw back for particle settlement, and removing the alkalinity even with the lower ozone dose particles settlement in MFT is possible.

IV. Couple the ozonation with a post treatment of the water for reusing in bitumen extraction process. Since caustic is added for the extraction process, correction for pH can be manageable issues afterward and with the increment of pH lots of metallic ions that can interrupt the extraction process will be precipitated with increment of pH after caustic addition.

V. Investigate in advanced microbiological level can be conducted as well to understand the presence of methanogens even after ozonation that can contribute in further settlement process by producing bubbles of methane and carbon dioxide gas.

VI. Study the minimum ozone dose needed for MFT consolidation.

VII. Different ozone dose may be applied with different application time to study the difference in efficiency.

VIII. Study the combination effect of ozone with hydrogen peroxide to increase the efficiency.

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Appendix

Raw Data

- **Initial Settling Curve:**

Interface position calculated over time:

	Control	15 min O3 treated	30 min O3 treated	pH 3	pH 4	pH 6
0	1	1	1	1	1	1
20	1	0.995833333	1	0.99	0.96	0.98
40	1	0.9875	0.991666667	0.96	0.94	0.96
60	1	0.983333333	0.970833333	0.91	0.86	0.95
80	1	0.970833333	0.9625	0.88	0.72	0.92
100	1	0.95	0.925	0.75	0.7	0.8
120	1	0.929166667	0.879166667	0.65	0.64	0.75
160	1	0.804166667	0.845833333	0.57	0.56	0.67
180	1	0.72	0.7	0.52	0.53	0.59
200	1	0.65	0.62	0.51	0.52	0.52

Interface position = N/n (N= total volume ; n= mud line or solid interface position)

- **Water Chemistry:**

IC/ ICP-MS Result:

Sample	**Cl**	**SO4**	**Na**	**K**	**Ca**	**Mg**	**Al**	**Fe**	**Mn**
Control	24.00	30.00	60.00	3.50	<LOD	<LOD	17.76	3.50	0.03
15 min ozonated	27.00	85.00	70.00	6.00	35.00	12.00	2.73	62.00	2.7
30 min ozonated	24.00	150.00	70.00	7.00	55.00	20.00	3.75	150.00	8.70
pH 3	56.00	7.00	70.00	9.00	78.00	25.00	2.65	180.00	14.20
pH 4	35.00	7.00	70.00	18.00	64.00	20.00	1.11	70.00	5.10
pH 6	20.00	14.00	70.00	55.00	20.00	7.00	0.17	<LOD	0.77

Alkalinity Results Using HACH Kit:

Sample		Alklinity (mg/L CaCO3)	Av. Alkalinity	SD
Control	1	73	72	1.732051
	2	73		
	3	70		
15 min O3 treated	1	39	38.5	0.5
	2	38		
	3	38.5		
30 min O3 treated	1	17	18	1.732051
	2	20		
	3	17		
pH 3 Adj	1	15.7	15.66666667	0.351188
	2	15.3		
	3	16		
pH 4 Adj	1	18.1	18.3	0.2
	2	18.5		
	3	18.3		
pH 6 adj	1	50	49.7	0.264575
	2	49.5		
	3	49.6		

Conductivity Result:

Temp	Sample	Conductivity(us/cm)	Average	SD
25 C	Control1	250	261.3333	34.42867
25 C	Control2	234		
25 C	Control3	300		
25 C	15 min Ozonated1	650	640.6667	10.06645
25 C	15 min Ozonated2	630		
25 C	15 min Ozonated3	642		
25 C	30 min ozonated 1	832	830.3333	2.081666
25 C	30 min ozonated 2	828		
25 C	30 min ozonated3	831		
25 C	pH adjusted to 3-1	1943	1942.667	4.50925
25 C	pH adjusted to 3-2	1938		
25 C	pH adjusted to 3-3	1947		
25 C	pH adjusted to 4-1	1014	1015.667	2.081666
25 C	pH adjusted to 4-2	1015		
25 C	pH adjusted to 4-3	1018		
25 C	pH adjusted to 6-1	732	732	2
25 C	pH adjusted to 6-2	734		
25 C	pH adjusted to 6-3	730		

TOC and IC Results:

Sample		**TOC(mg/L)**	**Avg TOC(mg/L)**	**SD**	**IC(mg/L)**	**Avg IC (mg/L)**	**SD**
Control	1	5.402	5.081	0.333096082	2.9641	2.6007	0.474415
	2	4.737			2.064		
	3	5.104			2.774		
15 m O3	1	48.68	51.00333333	2.210346881	0.4831	0.499966667	0.043242
	2	53.08			0.5491		
	3	51.25			0.4677		
30 m O3	1	77.18	75.98	2.893095228	0.2055	0.2704	0.10683
	2	78.08			0.3937		
	3	72.68			0.212		

Zeta Potential Measurement:

Sample	**Zeta potential(mV)**	**Average**	**SD**
Control 1	-48	-48.6667	1.154701
2	-50		
3	-48		
15 min O3 treated 1	-29	-29.3667	0.550757
2	-30		
3	-29.1		
30 min O3 treated 1	-30	-29.7	0.608276
2	-30.1		
3	-29		
pH 3(1)	-2.8	-2.83333	0.152753
2	-3		
3	-2.7		
pH 4(1)	-10	-10.6667	1.154701
2	-12		
3	-10		
pH 6(1)	-19	-18.6667	1.527525
2	-20		
3	-17		

Total Organic Acid Concentration Measurement Using FT-IR

(WITH Naphthenic acid Background):

FTIR Extraction Result

Organic Acid (mg/L)				SD
Control	1	18.63	19.58194	0.928839
	2	20.48581		
	3	19.63		
15 min ozonated	1	30.9	28.97667	2.009983
	2	29.14		
	3	26.89		
30 min ozonated	1	35.94	36.21333	0.447698
	2	36.73		
	3	35.97		

Organic Acid Detection and Quantification by HPLC:

Organic Acid Detection and Quantification by HPLC :

Sample	**Oxalate (mg/L)**	**Avg**	**SD**	**Acetate (mg/L)**	**av.**	**SD**	**Formate (mg/L)**	**Avg.**	**SD**
Control 1	< LOD	Na	NA	< LOD	NA	NA	< LOD	NA	NA
2	< LOD			< LOD			< LOD		
3	< LOD			< LOD			< LOD		
15 min O3 treated 1	**269.45**	**265.65**	**4.50**	**14.5**	**13**	**1.410673598**	31.8	31.33333	0.450925
2	**266.82**			**11.7**			31.3		
3	**260.68**			**12.8**			30.9		
30 min O3 treated 1	**553.75**	**549.76**	**23.94**	**21.3**	**20.8**	**0.435889894**	40.3	40.46667	0.152753
2	**524.08**			**20.5**			40.5		
3	**571.45**			**20.6**			40.6		

Humic Acid Measurement:

Humic Acid Concentration Measurement:

Sample	Conc. In mg/L	Conc (g/L)	Average	SD
Control 1	7730	7.73	7.656666667	0.219393102
2	7830	7.83		
3	7410	7.41		
15 min O3 1	9695	9.695	9.786666667	0.390651166
2	10215	10.215		
3	9450	9.45		
30 min O3 1	10585	10.585	10.60666667	0.070059499
2	10550	10.55		
3	10685	10.685		

Contribution of Measured Oxalic Acid in Total AEFs Concentration (by FTIR)

Sample	Organic acid in mg/L(FT-IR)	Avg	SD
Control 1	18.63	19.58194	0.928839
2	20.48581		
3	19.63		
15 min O3 treated 1	30.9	28.97667	2.009983
2	29.14		
3	26.89		
30 min O3 treated 1	35.94	36.21333	0.447698
2	36.73		
3	35.97		
500 mg/L oxalic acid 1	8.18	8.553333	0.402658
2	8.5		
3	8.98		
250 mg/L oxalic acid 1	7.45	7.433333	0.015275
2	7.43		
3	7.42		