Application of Wet Oxidation for the Treatment of Oil Sands Mature Fine Tailings

by

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Abstract

The extraction of bitumen from oil sands in Alberta, Canada, leads to the creation of tailings that are contained in lake-sized ponds under zero discharge policy. Stratification of tailings over time leads to the formation of mature fine tailings (MFT), an oil based emulsion containing residual bitumen and trapping water in between soil particles. Polymer flocculation treatments are effective in dewatering the tailings, however, the consolidated material still contains the residual bitumen which is not environmentally safe. This study investigates the breaking of MFT emulsion from tailing ponds and recovering the trapped water using an advanced oxidation process called Wet Oxidation. Three batch scale experiments were carried out, wet air oxidation (WAO), wet air peroxide oxidation (WAPO) and WAO (extended). The reactor was heated to 200^0C and pressurized at 500 psi (±50 psi). Three process times 5, 15 and 30 min were explored. A fast disintegration of emulsion was observed with rapid release of trapped water and consolidation of solid particles under WAPO. Residual bitumen was collected as froth from the surface by flotation after every cycle of WAO and was calculated in average to be 5% (wt.) per dry weight of MFT during $WAO_{extended}$. Less froth was recovered after WAPO. The released water showed a high transmissivity, increased concentration of dissolved organic carbon (DOC) while inorganic carbon declined with subsequent cycles and was completely removed during $WAO_{extended}$. 80% higher DOC was recorded in recovered water after WAPO compared to WAO. More than 70 – 80% of DOC were low molecular weight carboxylic acids (acetic and formic acids) while the remaining were dissolved natural organic matter (NOMs). Increase in DOC was due to the oxidation of residual bitumen by hydroxyl radicals during oxidation. Mineral composition in the consolidated solids were dominated by quartz, kaolinite and muscovite with a total of 60% clay particles overall. Scavenging effect of hydroxyl radicals towards residual bitumen on particle surfaces were observed under scanning electron microscope with increased surface area of clay particles after oxidation.

Dedication

This research is dedicated to my Parents.

Acknowledgment

In the name of Allah, the most Gracious, the most Merciful.

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Table of Contents

List of Tables

List of Figures

CHAPTER 1: INTRODUCTION

1.1 Overview of Alberta's Oil Sands

During the past few decades Oil Industries have been accelerating the economy of many countries, particularly in Canada. Now a days the production of oil and gas from unconventional sources has become the topic of interest globally and with the advent of new technologies, the trend is increasing significantly and is expected to stay at this rate in the coming years. In Canada, the Oil Sands have become the main area of interest for oil extraction over the years. The Oil sands is a mixture of bitumen, sand and clay, which is very viscous and the heavy oil within needs to be heated in order to flow like a liquid (Masliyah et al., 2004). Presently, Canada holds the status for the third largest oil sand reserves in the world at around 174 billion barrels as shown in figure 1.1. Saudi Arabia (around 264 billion barrels) and Venezuela (approximately 211 billion barrels) are the two top countries in terms of oil reserves (Alberta Energy, 2014; Alberta Oil Sands Industry, 2013).

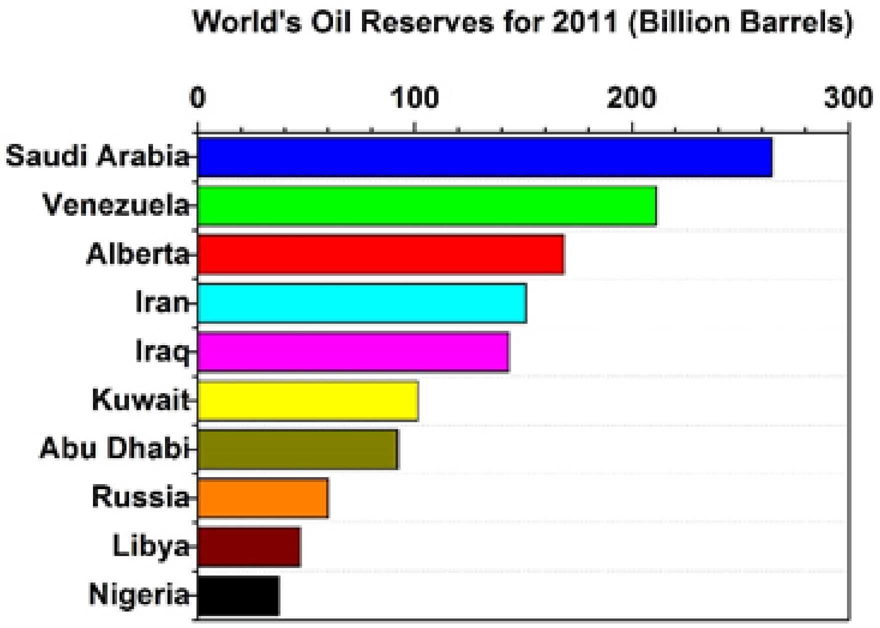


Figure 1.1: Oil Reserves Worldwide as of 2011

Total estimations have revealed that Canada actually holds about 1.7-1.8 trillion barrels of oil reserves in the form of bitumen. With the aid of today's technology, about 174 billion barrels of these reserves can be extracted and used as commercial oil (Alberta's Oil Sands, 2008; Alberta's Oil Sands 2006, 2007; Allen, 2008; Yui, 2008). However, this number could potentially increase with the development of new and advanced technologies (Alberta Oil Sands Industry, 2013). Majority of these oil sands reserves in Canada are found in the Northern Territory of Alberta, in the regions of Athabasca (Specifically Fort McMurray region), Cold Lake and Peace River. Together, these regions cover approximately 141,000 Square kilometers (Alberta Energy, 2014; Johnson and Miyanishi, 2008). Within Alberta, the largest deposit of oil sands are in the Athabasca region as shown in Figure 1.2.

Note: 1 km² = 1 square kilometre = 0.39 square miles

Figure 1.2: Location of Oil Sands Deposits in Alberta with Athabasca covering the largest deposit

(Source: Alberta Government; Reclamation Fact Sheet, 2013)

Oil sand's ores are composed of solid minerals (80-85% by weight), between 10-17% bitumen and the remaining is water (Gray et al., 2009; Srinivasa, 2010; Srinivasa et al., 2012). Bitumen, in its original state in the oil sands is very viscous and is in an unusable state. It needs to be upgraded to synthetic crude oil to be used commercially. Hence, first step needs to be extraction of bitumen from the oil sands.

1.2 Bitumen Extraction from Alberta's Oil Sands

Back in 1920s, Dr. Karl Clark developed the first practical method of bitumen extraction from oil sands while working at the Alberta Research Council (Clark and Pasternack, 1932). His method involved mixing of oil sands in hot water with a slight caustic environment to keep the pH at low alkaline conditions, somewhere between 8.0-8.5. This causes the sand grains to settle at the bottom and the oil, which is in froth form, gradually floats to the surface where it can be easily scraped off. The fine particles, composed mainly of clay, are left behind in the stream and are treated separately (Takamura, 1982).

Commercial oil extraction from oil sands started in 1967 by Great Canadian Oil Company, now called Suncor Energy, in Fort McMurray, Alberta (Johnson and Miyanishi, 2008; Mamer, 2010). There are two methods of oil extraction, namely surface mining and in situ drilling. Surface mining involves shoveling the oil sands into large trucks that carry the mined oil sand ores to the crushers (figure 1.3). These excavated large oil sand ores are crushed into smaller bits by crushers and mixed with alkaline hot water and other chemicals for further bitumen extraction. The oil sand ores, which are now turned into slurry, are then transported through hydro-transport pipelines where they are aerated until they reach the gravity separation vessel. The bitumen starts to separate from the ores during the transport process and floats to the surface in the separation vessel with the aid of air bubbles while the sand, clay and fine solids settle to the bottom before being sent to the tailings ponds (Gray et al., 2009). In situ drilling takes place when oil sands are too deep inside the ground and mining is not economically feasible. This extraction process involves drilling wells from the surface and injecting hot steam to make the oil sand ores less viscous for them to be easily pumped to the surface. Most popular in situ techniques now in use are Steam Assisted Gravity Drainage (SAGD) and cyclic steam stimulation (CSS). Only about 20% of the oil sand reserves are on the surface and can easily be recovered by surface mining while 80% is extracted by in situ drilling.

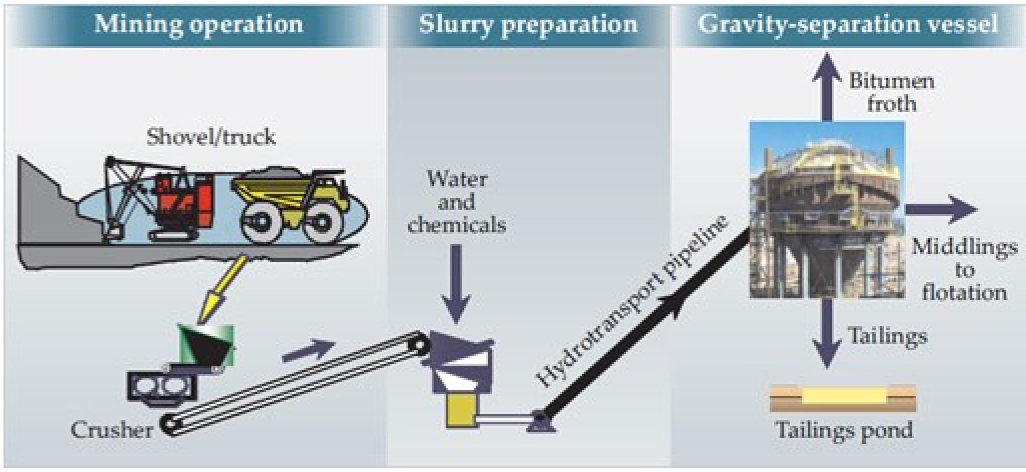


Figure 1.3: Surface mining of Alberta's Oil Sands leading to Bitumen extraction from the oil sand ores (Gray et al., 2009)

It has been estimated that for every barrel of oil produced, industries use around 2-4 barrels of water through surface mining whereas only 0.5 barrels of water is used for in-situ mining (Alberta Government, 2013; Syncrude Canada Limited, 2005). During the in-situ operations, a large amount of water is lost to the formations, on the other hand, water from surface mining is initially recycled. However, the water used in extraction process becomes alkaline, now called processed water, and becomes contaminated with high levels of organic compounds, which were released from the bitumen extraction process, thereby turning the water toxic (MacKinnon and Sethi, 1993). Considered to be unsafe for discharge, this processed water composed of sand, clay and residual bitumen from the oil sands is transferred into a tailings pond (Dominski, 2007).

With the extraction process of bitumen and froth upgrade, all the remaining slurries are contained into the "Oil Sands Tailings ponds" which are composed of a mixture of water, dissolved salts, organics, minerals and unrecovered bitumen. Overtime, these constituents are consolidated in four different layers, namely, oil sands process-affected water (OSPW), fluid or thin fine tailings (FFT or TFT), mature fine tailings (MFT) and sand (Allen, 2008; Mamer, 2010). The coarse sand particles settle quickly under the influence of gravity while MFT, forms a gel like suspension with time that makes settling harder to achieve. MFT is comprised of 30-38% solids (including fine clay particles), 3-4% of bitumen and around 60% water (Allen, 2008; BGC Engineering Inc., 2010; Don Scott et al., 1985). The OSPW is initially recycled in the extraction process but constant recycling of the processed water increases its organic and inorganic content (Giesy et al., 2010), eventually reaching to a point where it is considered hazardous to reuse (Whitby, 2010) and pumped back into the tailings pond, ultimately making the MFT rich in toxic organic and inorganic compounds. The settling of fine clay particles in MFT can take decades (Kasperski, 1992) and complete settlement can even take more than a century (Eckert et al., 1996), therefore, resulting in formation of large tailings pond that keep increasing in size as oil extraction takes place. Houlihan and Haneef (2008) reported that about 750 million cubic meters of MFT already exists in the tailings pond. This number will keep increasing if tailings management is not handled properly.

The aim of this research is to study the applicability of the wet air oxidation process to break the emulsion of the water-clay-bitumen in the mature fine tailings in order to recover the trapped water and residual bitumen, while increasing the consolidation of the fine clay particles. This technology could potentially accelerate the treatment rate and volume of the oil sand's MFT to be treated. Thus, contributing to solve the environmental problem of the Tailings Ponds and the land reclamation using environmental innocuous mineral particles and low carbon recovered water for recycling and/or safe discharge.

CHAPTER 2: LITERATURE REVIEW

2.1 Mature Fine Tailings Problem

It has been reported that oil sand's ores consists of fine clay particles that are trapped around a layer of pore water which is further surrounded by a layer of bitumen extracts (figure 2.1) (Cottrell, 1963; Takamura, 1982).

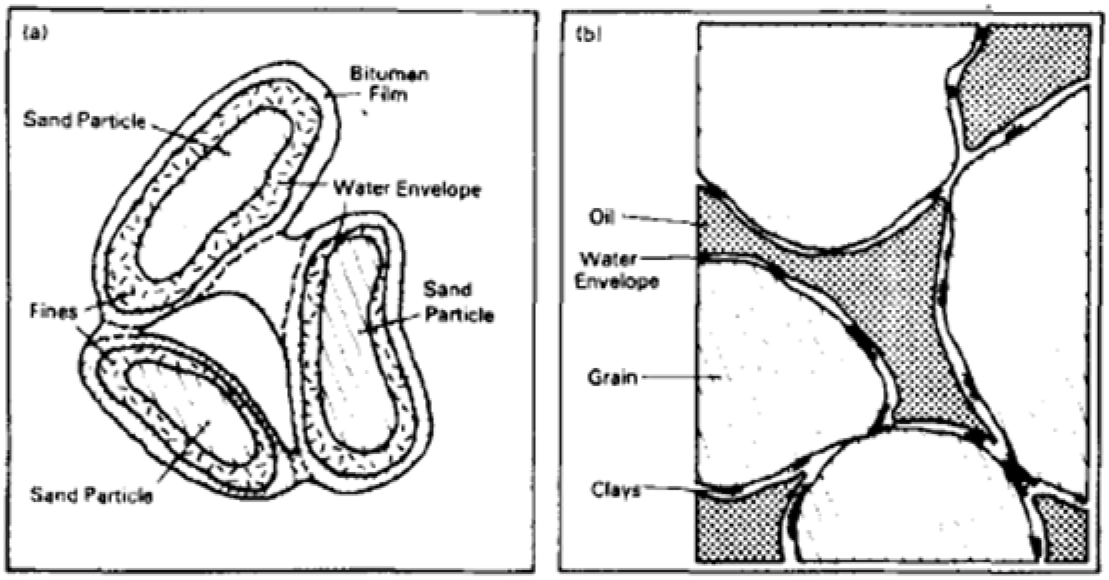


Figure 2.1: Sketch model of structure of oil sands (a) (Cottrell, 1963) and (b) (Mossop, 1980)

Cottrell (1963) was the first person to come up with the idea of this emulsion and was later proved to be right. The outer bitumen layer not only covers the grains but also fills the void space between other grains, which finally forms this aggregate. However, Mossop (1980) later proved a better schematic model of this aggregation. Mossop's model shows that the grains are actually interconnected with each other and do not break that easily. The difference between the two models is that clay minerals are attached to the grains in Mossop's model rather than being suspended in water as illustrated in Cottrell's model. Later Takamura (1982) presented a re-defined model of the oil sands showing the presence of water layer trapped between the grains/clay minerals and bitumen as represented in figure 2.2.

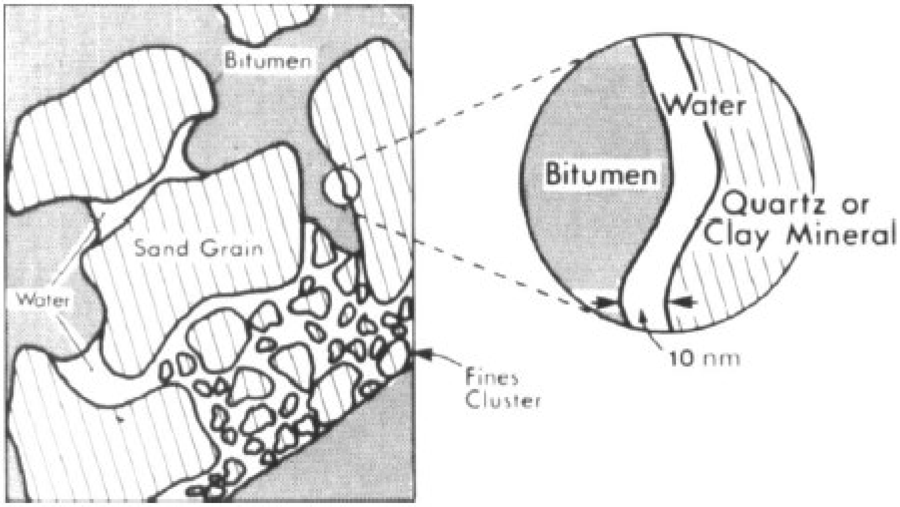


Figure 2.2: Redefined model of Athabasca Oil Sands (Takamura, 1982)

After bitumen extraction, the tailings from underflow of the separation vessel are made up of settled particles with residual bitumen and are contained into the tailings pond. This residual bitumen appears as small bitumen blobs between particles forming an oil based emulsion. Moreover, there is still some water trapped in these emulsions that needs to be recovered. Presence of ultrafine solids in MFT have high tendency of forming gelatinous type formations which result in forming large aggregates together with multivalent cations. It has been illustrated that these aggregates do not settle easily and consist of significant amounts of water (Kotlyar et al., 1995). Due to the hydrophobic properties of bitumen, a network bridge is formed between the particles contaminated with bitumen, which resist the release of the trapped water and forms a stable gel-like formation (figure 2.3) (Angle et al., 1993; Kessick, 1979; Klein et al., 2013). Flint (2005) reported that for every cubic meter of bitumen, up to three cubic meters of water is trapped in the tailings pond. It was also estimated that for every volume unit of bitumen extracted from the oil sands, around 7-8 volume units of wet sand and MFT are formed and are contained in the tailing ponds. This requires approximately 10 volume units of water that is initially recycled to the point where it becomes contaminated with organics, unsafe for reuse and placed back into the ponds. According to WWF-Canada Tailings Report Summary (2010), for every barrel of bitumen extracted from mined ores, 1.5 barrels of MFT are produced and this is expected to reach 2.4 billion cubic meters of

MFT inventory by 2040. In conclusion, increased extraction of bitumen from oil sands results in large quantities of MFT.

The interaction between the water molecules and the clay particles is due to the strong hydrogen bonding between the H atoms of water molecules, the OH groups of oxide minerals and organic matter on soil particles. Presence of cations in clay particles could also contribute to strong hydrogen bonding with water molecules (Schaetzl and Anderson, 2005). The clay particles also comprise of minerals that represent polar sites on the surface that could interact with the positive charges on the residual bitumen. Micelles could also be present in the emulsion that could form a bridge between particles, bitumen and water molecules.

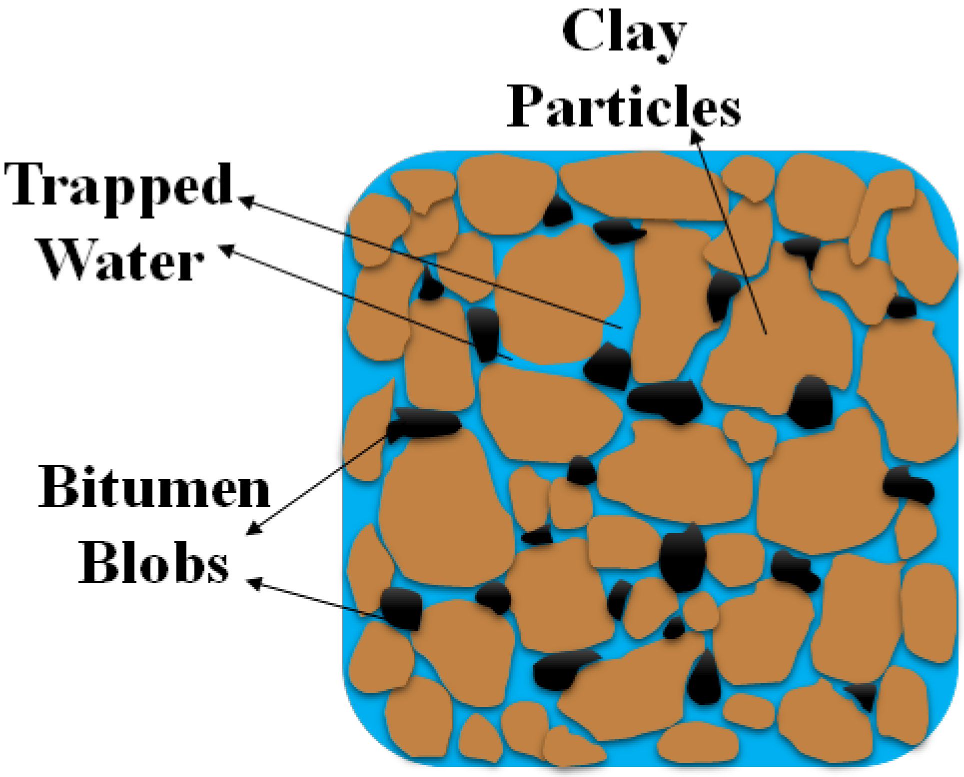


Figure 2.3: Emulsion of water-clay-residual bitumen in Mature Fine Tailings

2.2 Mature Fine Tailings Treatment Technologies

A number of different treatment technologies have been proposed in the past years to tackle the issue of increased MFT. The main objective has always been the enhancement of the settling of clay-sand-silt particles and the recovery of trapped water. Some of the commercially demonstrated and applied technologies are discussed below.

2.2.1 Composite/Consolidated Tailings (CT)

First technology developed for tailings treatment was Composite/Consolidated Tailings (CT), which was pioneered by Caughill et al. (1993) at the University of Alberta. CT technology was used by Suncor during the 1990's. CT involves mixing coarse sand from Densified tailings (resulted from cyclone underflow tailings), Mature Fine tailings (MFT) and the addition of gypsum at a ratio of 4:1 of sand to fines. This mixture results in a non-segregating slurry, which is then deposited in the tailings pond to achieve faster consolidation and water recovery (Beier and Sego, 2008). However, it was later found that CT has a number of limitations, which considering the current rate of extraction of bitumen and formation of MFT, would not be able to reclaim land faster than was previously imagined. Although CT is still practiced by some companies but the technology is continuously being reviewed on account of its drawbacks, such as

- CT is directly connected with the ongoing extraction process. Densified tailings required for CT come directly from the extraction process which means that CT should be carried out somewhere near to the extraction process. This is not ideal in the case of plant maintenance when everything is shut off. This means CT will not take place if extraction process is halted.
- The requirement for all the three ingredients to be in precise quantities. Any disproportion in contents would lead to 'off-spec CT', which would prevent land reclamation.
- CT, once formed, needs to be placed into an existing CT layer in the tailings pond for faster consolidation of the tailings. Failure of such action will result in separation in the pond ending up with MFT again (Mamer, 2010).

2.2.2 Freeze/Thaw Dewatering

Studies on Freeze/thaw dewatering technology have been carried out as a potential outcome of tailings pond management. This technology involves stacking CT or MFT in thin multiple layers close to the winter season in order to freeze the layers which are then allowed to thaw in the following summer. This technique has its limitations in terms of its large dependency on weather conditions, as a large portion of MFT can be frozen in winters of Fort McMurray regions than can be thawed in the summer (Beier et al., 2009). However, positive discoveries have been made regarding water recovery using freeze/thaw. Field-testing of freeze/thaw showed an increase from 30% to 55% sludge solids at the Mildred Lake and Alberta Environment Centre by Johnson et al. (1993). Similar dewatering analysis were observed by Dawson and Sego (1993) and Proskin (1998). Proskin et al. (2010) showed that addition of acid and quicklime before freeze/thaw can increase the hydraulic conductivity of MFT, which results in faster consolidation. Moreover, micro-fabric structures after thawing showed that the pores had changed from edge to face flocculated, compact aggregated fabric, thereby facilitating more release of water.

2.2.3 Flocculation Assisted Drying

Some flocculation technologies have also shown promising results in terms of consolidation and dewatering of tailings. Demoz and Mikula (2012) tested various branched and straight chain flocculants for treating MFT. By using different turbines for mixing, clear water was achieved but without any specifics about the chemistry of the released water or the added cost of their mechanical forces. Alamgir et al. (2012) investigated the addition of a cationic organic-inorganic hybrid polymer, AL-PAM, to diluted 10% MFT, and they proposed a two-step flocculation-assisted filtration. The flocculation of particles was observed, as the turbidity values were sufficiently low after settlement. The sediment was filtered and 85% water was recovered with a filter cake of 23 wt% moisture. Although, the results were positive, no light was shed on bitumen residues in the sediment and whether the recovered water was safe to be discharged or not. The effect of unresolved bitumen on flocculation methods and settling of fines as well as bitumen removal from MFT was also studied by Klein et al. (2013) through solvent washing or flotation. Denver flotation cell showed bitumen removal to be efficient only at certain bitumen content range beyond which the removal was not effective and did not allow flocculation properly. Although, toluene washing had shown better flocculation and consolidation of diluted MFT after bitumen removal but flotation method gave poor results following washing for the resultant MFT.

2.2.4 Tailings Reduction Operation (TRO)

Another commercially operated technology for treating MFT is Tailings Reduction Operation (TRO) also known as MFT drying. TRO involves, removing MFT from tailings pond and adding a polymer flocculent in it as shown in figure 2.4. Polymer flocculent causes the aggregation of clay particles in MFT resulting in water separation. The mixture is then assembled in thin layers and spread in shallow slopes over a sand bank for drying. The dried material is reclaimable either onsite or at a different reclamation site. TRO has shown to achieve much productive results as compared to CT technology (Mamer, 2010). Although a promising technology, TRO is considered to be a lengthy process when evaluated against the high rate of oil sands extraction and formation of tailings pond.

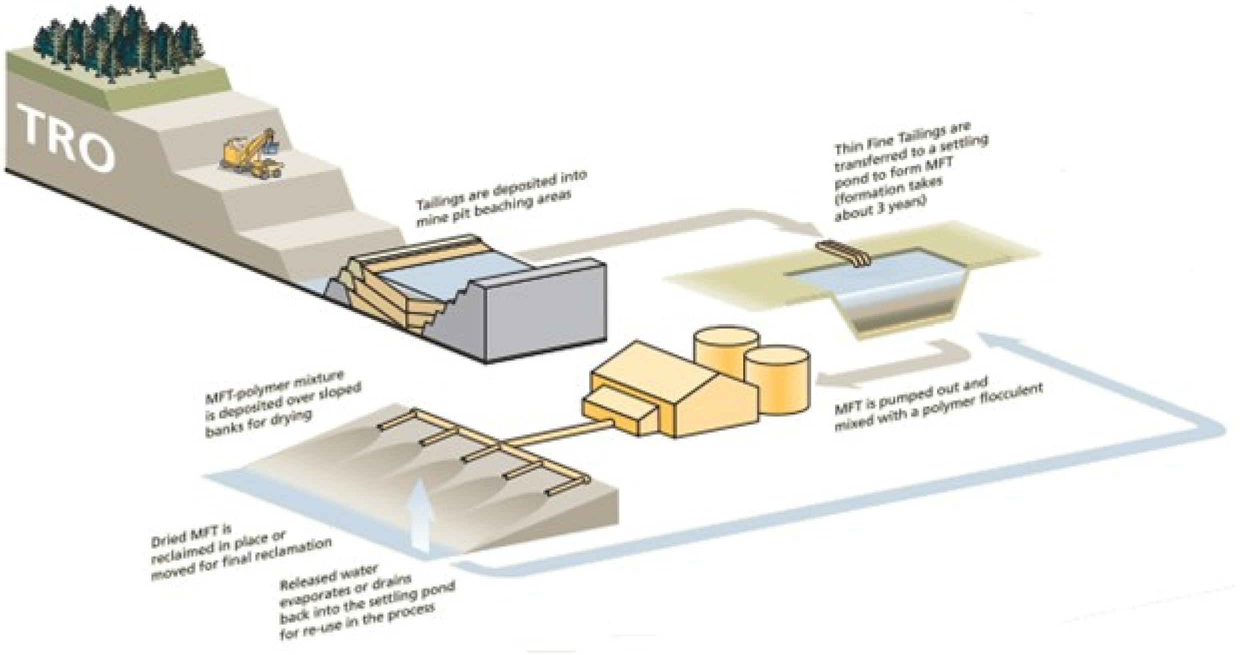


Figure 2.4: Tailings Reduction Operation (TRO) (Mamer, 2010)

Similarly, use of Super Absorbent Polymer (SAP) for rapid dewatering and densifying the MFT has shown to be a promising technique as the dewatered MFT showed high shear strength and solids content. Moreover, used SAP could be regenerated and reused to dewater more MFT (Farkish and Fall, 2013).

A number of other treatment methods have been tested for tailings treatment with advantages and disadvantages (BGC Engineering Inc., 2010). Although, all the aforementioned technologies have some positives in recovering the pore water from MFT but there are certain drawbacks with each technology such as prolonged treatment, expensive, end product not environmentally safe for reclamation, etc. In addition, the water recovered by some technologies is not necessarily organic free or non-toxic for safe discharge and might require further treatment. Although, polymer flocculation and SAP based rapid dewatering techniques have shown to be most effective in dewatering and consolidation of mature fine tailings but consolidated material still contains the residual bitumen and is not environmentally safe. The reclaimed material needs to be safe enough for land reclamation; but with the presence of residual bitumen in it this may not be achievable. These days, scientists are investigating more towards advanced oxidation processes (AOPs) to solve the issues related to Alberta's Oil Sands tailings as these processes have shown results faster and more effective than traditional treatment methods. AOPs requires environmentally friendly chemicals and they minimize the byproducts generation.

2.3 Wet Air Oxidation (WAO)

Wet Air Oxidation (WAO) is an advanced oxidation process (AOP) first proposed by F. J. Zimmermann (Laughlin et al., 1983; Zimmermann, 1958). A typical wet air oxidation process is represented in figure 2.5. In this oxidation process, toxic organic contaminants can easily be reduced to carbon dioxide and water, or turned to a more biodegradable state that is environmentally safe. WAO comprises of acute conditions with temperatures ranging from 150^{0}C to 320^{0}C and pressures ranging from 0.5-20 MPa at about 15 – 120 min of residence time, in order to keep the waste in aqueous phase (Laughlin et al., 1983; Luan et al., 2012; Luck, 1999; Mishra et al., 1995). Wet air oxidation is carried out using air (containing oxygen) as the oxidant. If pure oxygen is used as the oxidant, the system is termed as Wet Oxidation

(WO). Wastes containing organic contaminants in extremely high concentrations for natural biodegradation or too dilute for incineration can easily be degraded by WAO (Goi et al., 2006).

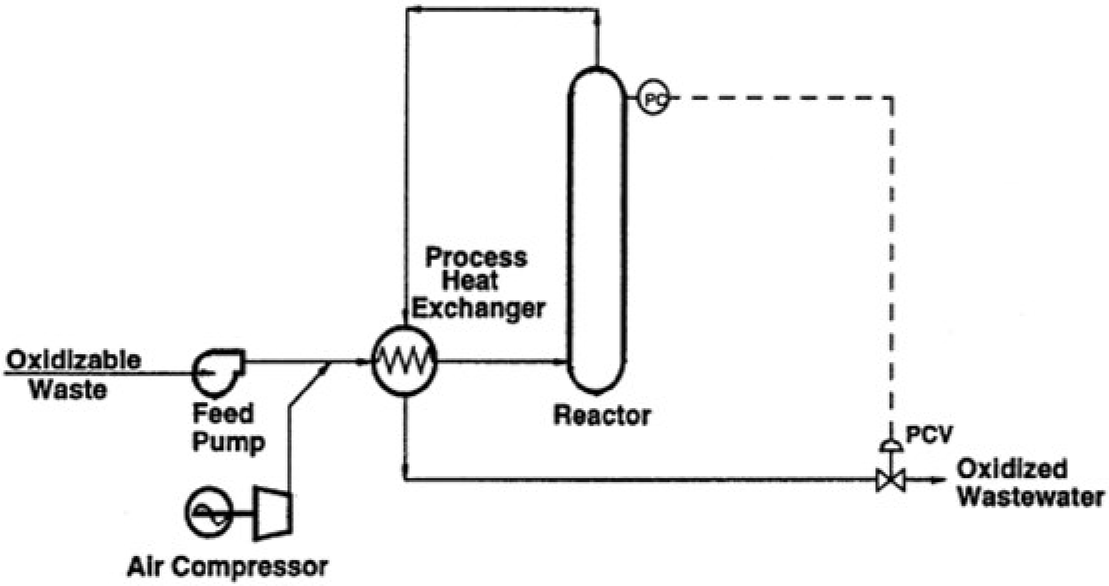


Figure 2.5: General Flow Diagram of Wet Air Oxidation Process (Luck, 1999)

In general, there are two main steps involved in WAO. An initial physical step where oxygen is transferred from gas to liquid phase, and a second chemical step for the reaction between the organic compounds and the dissolved oxygen (Bhargava et al., 2006; Debellefontaine et al., 1996; Debellefontaine and Foussard, 2000). Vaidya and Mahajani (2002) explained the physical step involves the gas and liquid phase mass transfers. Initially, the oxygen is transferred from gas to gas-liquid interface, the saturation phase is instant then the dissolved oxygen moves from gas-liquid interface to the liquid phase.

Wet air oxidation has successfully been used for the treatment of industrial wastes such as industrial wastewaters, sewage sludges (Bhargava et al., 2006; Mishra et al., 1995), landfill leachates, as well as destruction of organic compounds (Avezzu et al., 1992) and oily sludge. However, most of the literature published for WAO is based on treating wastewaters with minimal or without suspended particulates.

Similar to WAO, some scholars have studied wet peroxide oxidation (WPO). WPO is similar to WAO, in that, it uses liquid hydrogen peroxide as the oxidant rather than air or oxygen.

Studies of waste materials that are treated by WAO and having characteristics slightly similar to MFT are discussed in the following sections.

2.3.1 Industrial Applications of Sewage Sludge and Wastewaters

Sludge wastes generated after biological treatment or municipal sewage sludge poses a great deal of problem in terms of disposal. Usually, this type of sludge is discarded either as landfilling or incineration. Both these techniques have their own problems environmentally such as landfilling creates pollution which might make it impossible to reclaim land at any stage and incineration on the other hand is costly and can produce toxic gases. Wet air oxidation has been proven to eliminate the problem of sludge disposal by oxidizing it to a biodegradable state along with water separation and better particle consolidation. In fact, it has been reported that more than 50% of all the WAO plants that are in industrial usage are dealing with sewage sludge treatments (Mishra et al., 1995). Hii et al. (2014) have demonstrated that the mechanism behind sludge oxidation usually follows two pathways, one is the direct pathway to the production of carbon dioxide and water, where all the waste is oxidized. Second is the indirect pathway, where the initial unstable sludge materials are first converted into low molecular weight refractory compounds, such as acetic acid, that are later converted to mineralization. Zimmermann (1958b) carried out sewage sludge treatments at 260^{0}C with 80% COD reduction. First full scale plant treatments of sewage sludge by wet oxidation were conducted by Hurwitz and Dundas (1959) and Perkow et al. (1981) and COD reductions of 82.2% and 75% were reported, respectively. Kalman et al. (1987a) proved that increasing the temperature increased the COD reduction of sludge using WAO. Other lab based studies showed COD decline in sludges within 80-90% (Hurwitz et al., 1965; Ploos Van Amstel and Rietema, 1973). Although Teletzke et al. (1967) reported only 15% COD removal but the total solids were reduced by 7.6% at low temperatures of 149-177^{0}C. Higher temperatures at 300^{0}C were tested by Lendormi et al. (2001) for the treatment of municipal sludge using WAO and higher than 80% COD reduction was achieved at a pilot scale plant. Above 90% of volatile suspended solids (VSS) destruction of sludge was reported (Abe et al., 2011; Strong et al., 2011; Zhu et al., 2004) at temperatures above 210^{0}C whereas only 77% VSS removal was recorded at 150^{0}C by Abe et al. (2013). It was found that destruction of sludge by WAO is enhanced by longer retention time and higher temperatures, which also results in formation of organic acids. High pressure aids in solubility of oxidizing agents, which improves sludge destruction. A retention time of 30min at 240^{0}C temp and 60 bar pressure were reported to be the best optimal conditions for sludge treatment by WAO (Chung et al., 2009).

Industrial wastewaters have also been treated using WAO with promising results. Kalman et al. (1987a) reported a 92 – 96% COD reduction and the resultant effluent had no toxic effect with cyanide removal of 99.9997%. Imamura et al. (1988) and Pujol et al. (1980) established that at around 250^{0}C conditions, almost all contaminants under WAO are converted to mineralization along with some low molecular weight carboxylic acids such as acetic acid. Debellefontaine et al. (1996) studied the oxidation of organic aqueous wastes by WAO and Wet Peroxide Oxidation (WPO). The author reported that lower temperatures using WPO give results similar to WAO with high temperatures. Therefore, hydrogen peroxide produces more hydroxyl radicals that have higher oxidizing ability than air. Zhang et al. (2010) achieved a 56% COD removal at 250^{0}C of organic wastewater with increasing BOD by WAO.

Emulsified wastewaters, containing non-biodegradable substances have been reported to be easily converted into biodegradable by WAO. Tang et al. (2004) reported TOC removals of 79% from emulsified wastewaters at temperatures of 220^{0}C working in a 2L high pressure batch autoclave. At the same temperature, Tang et al. (2003) also reported similar findings of around 86% reduction in COD.

2.3.2 Oily wastewaters and Sludge

Oil refineries produced wastes that are rich in inorganic and organic compounds that are toxic and cannot be discharged to the environment. The organic compounds usually are made up of naphthenic acids and mercaptides (Ellis, 1998). Wet Oxidation (WO) was used by Maitoko et al. (1975) at 200^{0}C in order to reduce the organic and inorganics from wastewaters of refinery. The WO was effective in converting the contaminants to carbon dioxide, water and neutral salts. COD analysis of chemical wastewaters from petrochemical industry containing organic and inorganic compounds subjected to WAO, under testing conditions of 225^0C in the presence of both air and oxygen oxidants, revealed more than 50% removal (Lin and Ho, 1997). Zerva et al. (2003) also studied the wet oxidation of oil wastewater consisting of 11,000 mg L^{-1} of COD and reported temperature to be an important factor in oxidation of such waste. Increasing temperature resulted in increased removal of COD with acetic acid as the residual product. This was termed as the rate limiting reaction as the oxidation rate was decreased due to its resistivity to oxidation at temperatures below 300^0C.

Shale oil productions produce wastewaters that are high in phenols and other organic compounds that are treated by steam stripping. The resulting Stripped Sour Water (SSW) was treated by WO and it was found by Prasad et al. (2003) that <8% TOC reduction was achieved at 175^0C which was increased to 60% when the temperature was raised to 250^0C. Similarly, around 80% of organic reductions were observed by Bi and Han (1990) at 270^0C performing WO on oil shale products. It was suggested that the use of catalyst would result in similar outcomes at lower temperatures. Prasad et al. (2007) reported 70% TOC removal of SSW from oil shale refinery using $Cu\ (NO_3)_2$ under WO. More than 80% removal was achieved with WPO as well.

Large amounts of oily sludge are also generated during oil production, storage, and transportation, which are composed of oil, water and solids. These oily sludges are made up of toxic compounds and cannot be released or disposed in the environment before proper treatment. Jing et al. (2013) investigated the feasibility of WAO for the treatment of oily sludge and proved that WAO was effective in elimination of organic compounds from oily sludge. It was found that increasing temperature results in increased COD removal and a total of 96.15% COD reduction was achieved at 300^0C with acetic acid as the refractory product. Jing et al. (2011) studied the WPO of oilfield sludge and reported residence time and temperature to be the influencing factors in removal of organic compounds. Similar to other studies, increasing temperature resulted in increased COD removal, with a total of 88.68% COD reduction recorded in heating at 340^{0}C for 9mins. More oil sludge studies are presented in section 2.4.2, as distinctions between WAO and CWAO.

2.3.3 Landfill Leachate

Landfill leachates are solid wastes disposed-off as landfill in which organic wastes combine with infiltrating rainwater to become a toxic liquid waste. This leachate usually contains large amounts of organic waste, heavy metals, ammonia-nitrogen and inorganic salts (Li et al., 2010). Various AOPs have been investigated for the treatment of landfill leachates over time, including WAO. Goi et al. (2009) compared the COD and AOX (Adsorbable Organic Halogen) reduction and biodegradability of landfill leachate by WAO using hydrogen peroxide and a Fenton type process. It was observed that WAO endorsed by H_2O_2 was far more efficient in enhancement of biodegradation than the Fenton process while COD reduction was similar in both processes. A study by Karimi et al. (2013) evaluated three treatment strategies for landfill leachates, WAO, WPO and WAO/GAC. Comparing the WPO against WAO, WPO had the highest COD reduction due to the faster formation of oxidizing radicals in the presence of H_2O_2. However, using GAC with WAO, the removal efficiency of COD was increased from 34% with WPO to 48% with WAO/GAC. The author also noticed that at the beginning of the WAO treatment, COD levels were initially increased. This is due to the fact that when large molecular weight organic compounds are degraded they break down into smaller molecules, which causes an increase in the COD levels. But as more retention time is applied the COD values start to decline indicating its removal from the waste.

2.4 Catalytic Wet Air Oxidation (CWAO)

The conditions used in WAO are generally high temperatures and pressures. In order to condense these conditions and achieve similar or better results, catalysts have been introduced. Catalysts increase the rate of reaction and lower the activation energy, thus obtaining results faster even under milder conditions. Different catalysts have been used in order to reduce the required temperature and pressure of WAO, this has led to Catalytic Wet Air Oxidation (CWAO) (Kim and Ihm, 2011) and Catalytic Wet Oxidation (CWO). A lot of studies have been conducted similar to WAO with incorporation of different catalyst to achieve the best results. According to Luck (1996), most commercial CWO processes use either homogeneous catalyst Cu^{2+}, or other supported metal.

2.4.1 Industrial Applications of Sewage Sludge and Wastewaters

Various CWO studies have been conducted on municipal sewage sludge. Harf et al. (1999) showed CWO was effective in treating municipal sludge that was composed of suspended solids. Fractional degradation of organics was reported at mild conditions but the products were capable of biodegradation. Similarly, Harada and Yamasaki (1996) had earlier proved that CWO of sludge ends up with carboxylic acids and aldehydes initially which later turn into carbon dioxide and water. Although the system was termed an efficient process at 280^0C with all organic substance degraded but further improvement was suggested. A two stage treatment process including a non-catalytic and a catalytic wet oxidation was set up to treat sewage sludge by Miyake et al. (2003) yielding positive results. More than 98% of COD removal was achieved. Mori et al. (1998) also achieved similar COD removal by incorporating three different processes in sequence. The sludge was initially treated with ozone, followed by adsorption. Finally, the effluent from adsorption was treated with catalytic oxidation as the last stage using Pt, Ag, Pd, or Au catalysts on various supports. Nitta et al. (1997) used Rh – TiO_2 catalyst to treat sewage with suspended solids by first treating it with non-catalytic wet oxidation followed by CWO. Analysis of final products revealed that the sludge was converted to CO_2, H_2O and N_2. A similar conversion of municipal sewage was observed by Mitsui et al. (1989) working at temperatures between 100 - 370^0C. A Bayer LoProx process was used by Holzer (1994) to treat sewage sludge at 200^0C and 60% - 90% organic carbon conversion to carbon dioxide was reported. Bayer LoProx process involves the use of Fe^{2+} and organic quinone forming substances which produce hydrogen peroxide as intermediate. H_2O_2 and Fe^{2+} together create a strong oxidizing system for degrading organic compounds (Kolaczkowski et al., 1999). Song et al. (1992) found a COD reduction of about 93% in sewage sludge using CWO at 270^0C in 24min.

High strength emulsifying wastewaters from industries containing non-ionic surfactants were investigated for COD and TOC removal by WAO and CWAO (Zhao et al., 2005). $Cu(NO_3)_2$ was found to be fairly efficient at 473 K. WAO resulted in 75% COD and 66% TOC removal which was boosted to 86-89% for COD and 82%

TOC removal with CWAO using Cu/Al_2O_3 and $Mn\text{-}Ce/Al_2O_3$. However, further treatment was suggested as complete oxidation of COD and TOC was not achieved. Sun et al. (2008) used a microwave assisted catalytic wet air oxidation (MW-CWAO) for the treatment of heavily contaminated wastewater from oil refineries. Lower pressure and temperature (150^0C) were used in this study with the aid of GAC (5%) as the potential catalyst. It was noted in 30 min that a significant reduction of COD, up to 90%, was achieved along with improvement in biodegradability. MW irradiations improved reaction rates and gave higher yields with enhanced selectivity. CWAO at temperatures between 160 and 180^0C of emulsified wastewater showed production of fatty acids at an increased rate but oxidation was not observed (Tang et al., 2009). However, at higher temperatures (220^0C), the catalyst Cu^{2+} not only produced fatty acids but also oxidized them at later stages of the reaction process. Acetic acid was considered as the primary intermediate and its oxidation was the rate limiting step in this process. Kim and Ihm (2011) have reviewed the performance of many catalysts including noble metals, oxides and mixed metal oxides for the treatment of various organic and aqueous industrial wastewaters.

2.4.2 Oily Sludge

Recently, a number of articles have been published by Guolin Jing comparing the effectiveness of WAO and CWAO on the treatment of oily sludge using different catalysts. Some of these studies are summarized in table 2.1.

Table 2.1: Oily Sludge Treatment by WAO and CWAO using different Catalyst (Reference)

COD Removal	Catalyst	Reference
WAO = 88.4% CWAO = 92.7%	Na_2CO_3	(Jing GuoLin et al., 2012)
WAO = 88.4% CWAO = 96.8%	Mn^{2+}	(Jing et al., 2012)
WPO = >90% CWO = >80%	$FeCl_3$	(Jing et al., 2012)
WAO = >80% CWAO = 97.8%	Ni^{2+}	(Jing et al., 2013)

When CWAO is compared with WAO (Table 2.1) it is clear that with the aid of catalyst a higher reduction of organic compounds from oily sludge is achieved. However, it appears that when WPO is compared with CWO, better removal is seen when hydrogen peroxide is used in small doses. Similarly, in another study, Jing et al. (2012) studied the removal of organics from oily sludge through CWO and WPO. Initially, WO gave 58.12% reductions of COD, which was later increased to 85.90% with the addition of $NaHCO_3$ catalyst at 330^0C. This clearly shows that addition of catalyst improves oxidation reactions by increasing the production of hydroxyl radicals for oxidation of oily sludge intermediates. Moreover, it was noticed that increasing the concentration of the catalyst increased COD removal. In the later part of the study, WPO was carried out to compare the results with CWO. At the similar temperature of 330^0C, WPO achieved an even higher COD removal of more than 90%, which implies that WPO is a faster oxidation process than WO or CWO. A similar kind of result was observed by Jing et al. (2012) using a soluble metallic salt ($FeCl_3.6H_2O$) as the catalyst.

2.4.3 Landfill Leachate

Researchers have investigated CWAO to treat landfill leachate for degrading organic pollutants within. Li et al. (2004) used Co/Bi catalyst on the degradation of landfill leachate using CWAO. Different parameters were examined for their effects on the removal of TOC and COD. It was found that the reaction temperature and the dosage of catalyst had significant effects on oxidation reactions for degrading the organics and approximately 88% organic acids were detected as intermediates during the reaction. Moreover, Co was not leached out during the degradation process and only trace amounts of Bi were detected which shows that Co/Bi is an effective catalyst in degradation of landfill leachate. In a similar study Garg and Mishra (2010) investigated the CWO of landfill leachate derived from municipal solid waste using different catalysts and/or promoters. The combination of $CuSO_4$ as a catalyst, Na_2SO_3 as a promoter and air proved to be the best in terms of COD removal with up to 90% reduction compared to Fe^{2+} and H_2O_2 mixture. Furthermore, the operating temperature was very moderate, at 150^0C and biodegradability was improved as well. It was noted in WAO cycle without any catalyst that 34% COD reduction was achieved only with the aid of heavy metals already present in the waste material. Therefore, these materials acted as natural catalyst in oxidizing the waste material. Later, Karimi et al. (2012) tested the same combination of Fe^{2+} and H_2O_2 in a different scenario. Initially, a CWPO oxidation was performed on a landfill leachate followed by adsorption using different materials and combinations such as granular activated carbon (GAC), powdered activated carbon (PAC), a combination of PAC and calcium hypochlorite (PAC/Cl_2), and coated iron on granular activated carbon (GAC/Fe). It was found that FeGAC/CWPO gave the best COD removal of 65%. Therefore, although Fe^{2+} and H_2O_2 proved to be less effective in the earlier study but incorporating GAC (coated with iron) treatment after CWPO shows an improvement in COD reduction.

Although all the above literature review of WAO and CWAO had positive results, it should be noted that the waste material to be treated was either wastewater with no solid particles or very minimal solid particulates. Mature fine tailings used in the present study consisted of around 30-40% or more solid particles, 3–4% bitumen and water (~60%). None of the previous studies of WAO or CWAO were carried out on waste material with a higher proportion of solid content.

2.5 Objectives of the Study

The major objective of this study is to investigate the applicability of WAO to break oil-based waste sludge emulsions, such as the Mature Fine Tailings (MFT) from Alberta's Oil Sands tailing ponds. In order to achieve this objective the following specific objectives are discussed:

- Construction of a WAO reactor to be used in different flow regimes
- Separation of artificial clay slurries using WAO
- Treatment of MFT using different temperatures and pressures
- Addition of H_2O_2 to improve the formation of radicals

Some other sub-objectives were also considered as part of the breakage of oil based emulsion, such as,

- Recovering the trapped water from the pores of clay particles after oxidation,
- Recovering the residual bitumen from MFT that holds the emulsion together in a gel like formation,
- Increase the consolidation of solid particles,
- Investigate the oxidation mechanism of WAO and
- Producing an environmentally safe material.

Treatment of MFT using WAO has never been done before; therefore, this study is the first of its kind to study the feasibility of wet air oxidation like process for the treatment of mature fine tailings (MFT) from Alberta's Oil Sand Tailings.

WAO process used in this study involved treating the wastes in a pressurized reactor at temperatures between 150-200°C and pressures between 200-500 psi, pressurized air was used to provide oxygen as the oxidant for the reaction. The main reason behind high pressure is to keep the wastewater in its aqueous state by keeping the applied pressure higher than the vapour pressure of the material (Lin and Ho, 1997). In this process, MFT particles will be oxidized and the sludge will be transformed into a more biodegradable residue by means of a free radical mechanism. The MFT is composed of natural materials/minerals that can act as catalysts, and speed up the oxidation reactions. It is hypothesized that organic compounds will be oxidized and the surface charges of the suspended particles will be removed. H_2O_2 will be used to boost the radical formation and the oxidation mechanism by Wet air Peroxide oxidation (WAPO). The WAO and WAPO process will change the surface chemistry of the MFT particles, breaking the water-clay emulsion and releasing the trapped water. During the process, it is assumed that medium-pressure steam will be generated that potentially could be used for other processes or incorporated within the system to preheat the incoming raw MFT.

The idea is to convert the MFT material into a more biodegradable state with zero toxicity so that trapped water can be extracted and recycled whereas the sediment can be used for land reclamation. A proposed schematic treatment method of Mature Fine Tailings (MFT) is shown in figure 2.6.

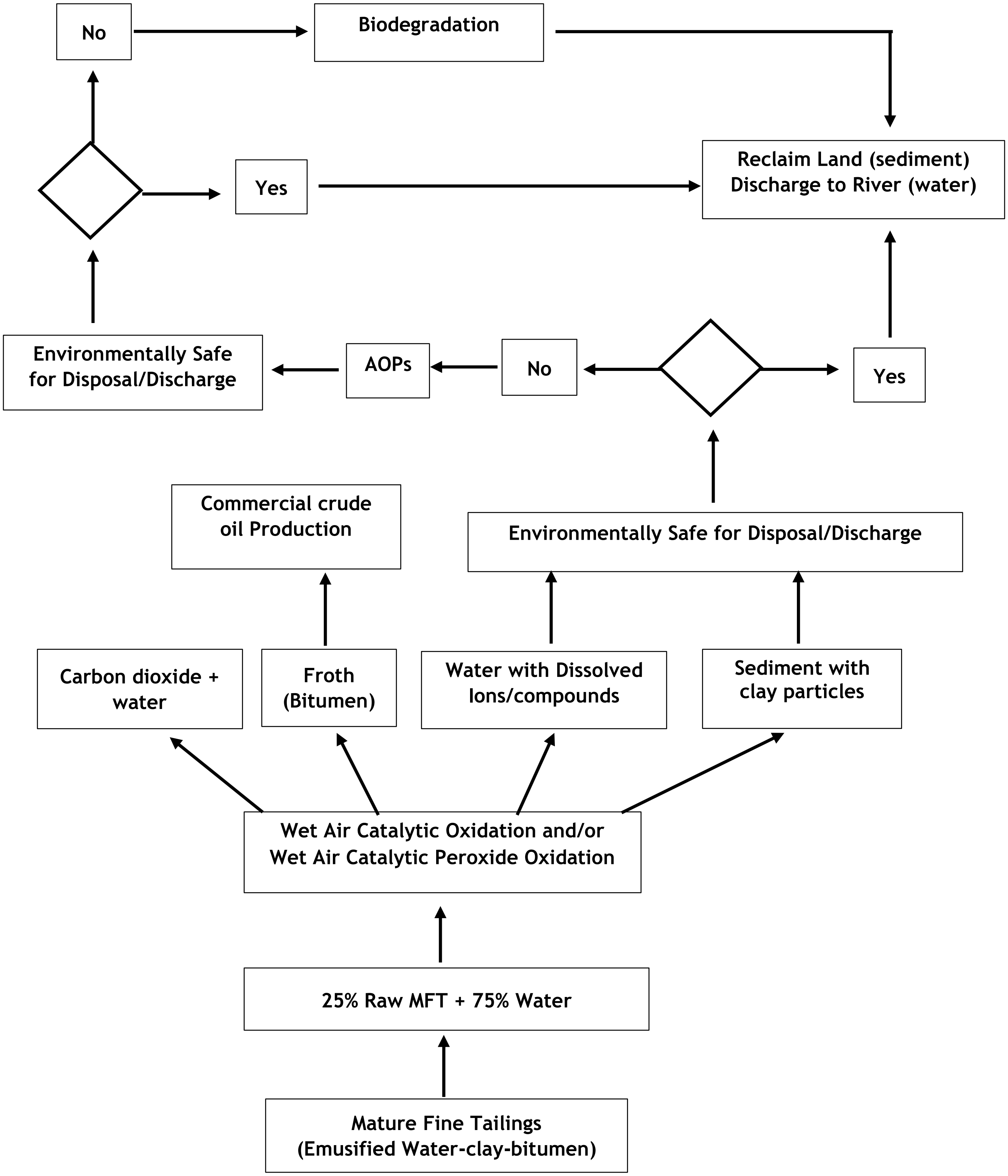


Figure 2.6: Proposed Flow Chart of MFT Treatment using Wet Air Catalytic Oxidation and/or Wet Air Catalytic Peroxide Oxidation

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials and Reagents

Materials and supplies for the WAO system such as pipe lines, valves, fittings, connectors (were SS 316 grade) and gas regulators were obtained from Swagelok (Edmonton Valve & Fitting Inc., Edmonton Canada). The main reactor was a custom made SS-316 cylinder with 230ml of internal volume and 1/8 inch wall thickness. For temperature monitoring, a high accuracy J/K input thermocouple thermometer was used together with a Type-K thermocouple, both from Omega (Stamford, Conn., USA). Pressure was monitored using a customized All-welded system Xsel Pressure Gauge (max pressure 1000 psi), with a diaphragm and a 4-inch cooling element in between for high temperatures (WIKA Instruments Ltd. Edmonton, Canada). Analytical grade chemicals and glassware were purchased from Fisher Scientific (Ottawa, ON, Canada). The heating element was a customized induction coiled system built from a commercial induction cooktop. This induction heating element works through a magnetic field between a ferromagnetic material and copper wires of the heating device. The heating power of induction is instantaneous and temperatures above 100^0C can be achieved in a matter of seconds. Compressed Air (extra dry, O_2 19.5% - 23.5%) was used as oxygen carrier, which is the primary oxidant, and was purchased from Praxiar (Edmonton, AB, Canada). Hydrogen peroxide (50%) which was used as an oxidant booster in order to increase the concentration of hydroxyl radicals, was obtained from Fisher Scientific (Alberta, Canada). Mature Fine Tailings (MFT) were obtained as a composite sample from Syncrude (Fort McMurray, AB, Canada). MFT were stored as received at 4°C in an environmentally controlled temperature laboratory.

3.2 Experimental Set Up

3.2.1 Sample Preparation

A preliminary investigation of WAO conditions were performed on synthetic slurries of commercial kaoline and bentonite clay and sand to mimic the heterogeneous characteristics of MFT, apart from residual bitumen. Different slurries including Kaolinite clay, kaolinite-sand and Kaolinite-bentonite-sand were studied using 30% (w/w) of each material. Silt was commercially unavailable and was not used in the experiments. Another five slurries were prepared, one was simple clay slurry while different salts namely, Na_3PO_4, NaCl, Na_2SO_4 and $NaHCO_3$, were added in the other slurries. All the slurries were made in duplicates, one at normal pH (pH 6.5-7.5) and the other at alkaline pH (Simple clay slurry pH 10.11, Salt slurries pH 8.5-9.0)) by adding 0.5 M NaOH. Initially, the slurries were mixed and allowed to stand for a specific period of time to assess any separation. Later, the slurries were mixed again and transferred to the WAO reactor to conduct the experiment under specific conditions, as shown in table 3.1. For MFT the emulsion solution was prepared at 25% (v/v) with a total volume of 150ml (75% water). Three experiments were conducted: 1) Wet Air Oxidation (WAO), 2) Wet Air Peroxide Oxidation (WAPO) with the addition of 5ml hydrogen peroxide (50%) and 3) $WAO_{extended}$.

Table 3.1: Experimental conditions for 30% Clay slurry

Experiment	30% Clay in 500ml (v/v)	
Slurry	Kaolin Clay (30%)	
Solvent	Water (70%)	
Volume	500mL	
pH	Normal = 7.19	Alkaline = 10.11
Conditions	Temp = 120 – 150 ^{0}C	Pressure = 280 – 300 psi
Oxidant	Air = 100psi, containing O_2 = 19.5% — 23.5%	
Exp. Time	12 mins	

3.2.2 Experimental Conditions

The Reactor was filled manually and then connected to the system. The reaction was conducted in three cycle runs of 5, 15 and 30 minutes respectively. Every cycle consisted of five steps: 1) air pressurization, 2) heating step, 3) reaction time, 4) cool down, and 5) removal of froth. Air pressurization was done using 100 psi of dry zero air as the oxygen carrier. During the WAO treatment every batch reached a maximum pressure of 500 psi (±50 psi) and a maximum temperature of 220^{0}C (±20^{0}C). The separated residual bitumen, in the form of floating froth, was collected and further weighted. The remaining sample was treated again in the next cycle. In the case of WAPO, the similar protocol was followed with the difference of the addition of 5 ml hydrogen peroxide (50%) at the start of the first cycle as shown in table 3.2. Based on the results and analyzed data, a series of extended cycles with similar conditions were carried out for 30 min by WAO. These extended experiments consisted of 7 cycles for a total reaction time of 210 min.

Table 3.2: Experimental process time for WAO/WAPO run cycles of 25% MFT samples

Time (mins)			**Run Cycles**						
5	5x1	5	**I**						
	5x2	10	I	**II**					
	5x3	15	I	II	**III**				
15	15x1	15	**I**						
	15x2	30	I	**II**					
	15x3	45	I	II	**III**				
30	30x1	30	**I**						
	30x2	60	I	**II**					
	30x3	90	I	II	**III**				
30	30x1	30	**I**						
	30x2	60	I	**II**					
	30x3	90	I	II	**III**				
	30x4	120	I	II	III	**IV**			
	30x5	150	I	II	III	IV	**V**		
	30x6	180	I	II	III	IV	V	**VI**	
	30x7	210	I	II	III	IV	V	VI	**VII**

3.2.3 WAO System arrangement

Different designs were constructed and mapped out in order to test and run the desired process. The first prototype for the reactor design was built as shown in Figure 3.1. This design allowed to transfer the sample into the reactor using vacuum. Once the reactor was filled with the required amount of sample, the vacuum was disconnected and the reactor was sealed using a plug. The reactor was then pressurized with air and the valves were shut to start the heating. After the desired reaction time, the heating was stopped and the reactor was allowed to cool down (≤95^{0}C) to avoid the evaporation of water as much as possible. The treated sample was collected from the same port from where it was initially introduced inside the reactor.

Figure 3.1: 1st Prototype Reactor Design for the oxidation of MFT samples

The initial trials were performed using Kaolin Clay slurries and the consistency was less viscous, thereby allowing it to be easily sucked in using vacuum. However, the MFT samples were not as viscous (figure 3.2) and could not be transferred to the reactor using vacuum. Therefore, a second prototype design was developed as shown in figure 3.3., where the aid of vacuum is not used. Instead, the sample is fed into the reactor manually, sealed and then fitted into the system before filling with air. The initial idea was to build a re-circulation system (figure 3.4), however, due to limitations of not finding a pump that can be incorporated under high temperatures and pressure, re-circulation could not be achieved and batch scale studies was carried out.

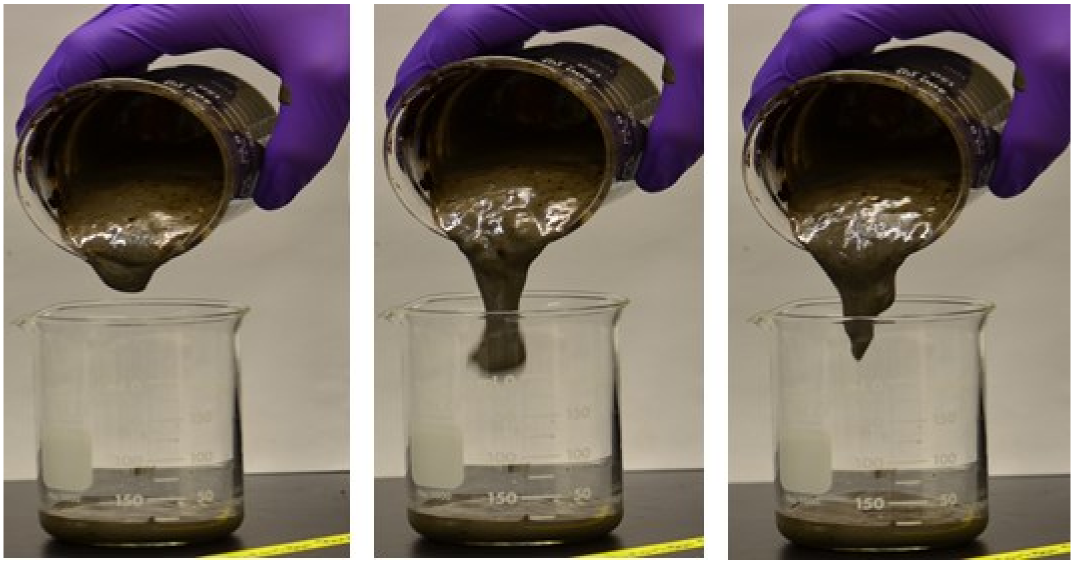


Figure 3.2: Viscous Consistency of Raw Mature Fine Tailings

Figure 3.3: 2nd Prototype Reactor Design for the oxidation of MFT samples

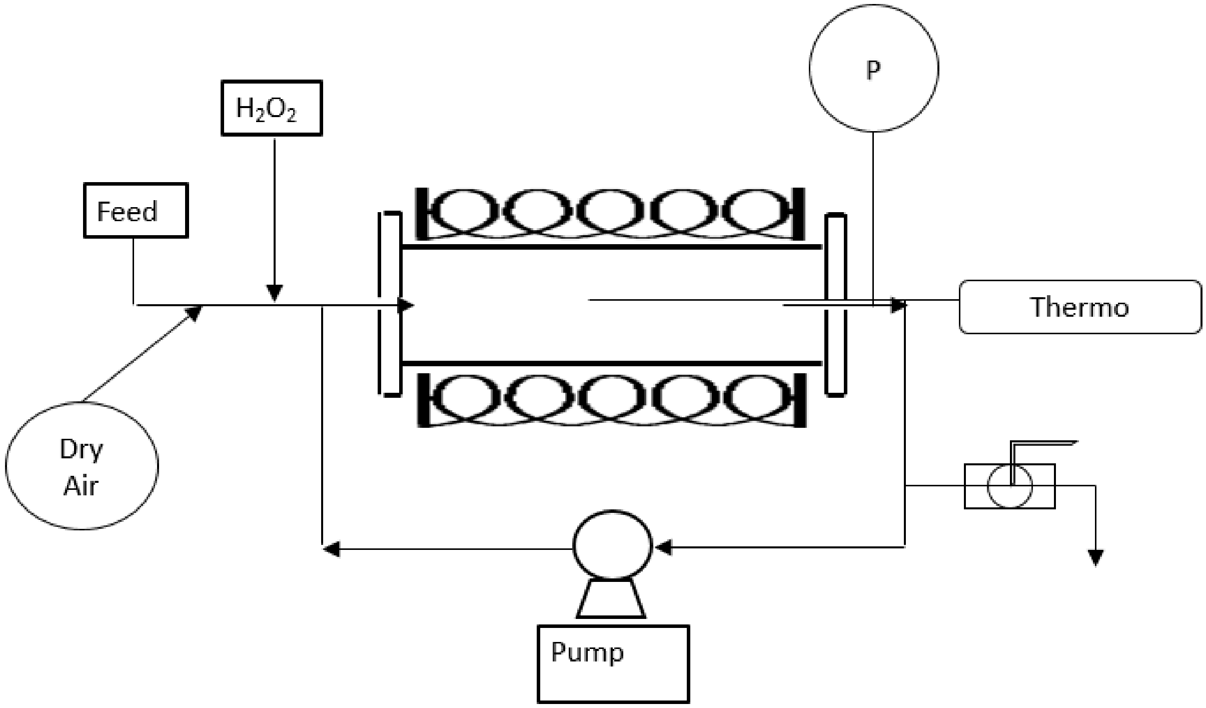


Figure 3.4: Schematic Design for 2nd Prototype of WAO

3.3 Sample characterization

3.3.1 Water Chemistry

For recovered water, Alkalinity, pH, Conductivity, Total Organic Carbon (TOC) and/or Non-Purgeable Organic Carbon (NPOC), Total Inorganic Carbon (TIC), Ion Chromatography (IC) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis were measured.

3.3.1.1 Total Organic Carbon

TOC-$L_{CPH/CPN}$ Analyzer equipped with ASI-L Autosampler, from Shimadzu Corp. (Kyoto, Japan), as shown in figure 3.5, was used.

The treated MFT samples had liquid and solid separation. Some of the treated samples needed centrifugation at 10,000rpm for 2mins in *Sorvall LYNX* 4000 Superspeed Centrifuge (Fisher Scientific, Canada). The supernatant was filtered against 0.45μm filters (PTFE, Fisher chemical, Canada) and diluted 5x with Milli-Q water (18.2 MΩ) for Organic and inorganic Carbon measurement. The total carbon (TC) content could not be measured as some of the inorganic carbon components tend to stick to the furnace and give a false positive result. Therefore, TOC and TIC were measured separately.

Non-Puregable organic Carbon (NPOC) was measured, which represents TOC as other VOCs in the liquid sample are negligible. The calibration standards used for TOC/NPOC measurement was Potassium Hydrogen Phthalate, while that for TIC were sodium hydrogen carbonate and sodium carbonate. A concentration of 400 mgC/L of each standard was prepared according to the TOC-$L_{CPH/CPN}$ Analyzer User Manual (as shown in Appendix A). The instrument was calibrated with blank and standards before analyzing samples. For TIC measurement, the samples were acidified with 85% phosphoric acid and purged with extra pure air. The Carbon dioxide given off is the inorganic carbon and was detected in the non-dispersive infrared detector (NDIR). In the case of TOC/NPOC, the remaining sample after acidification and purging is passed through the furnace heated at 680^0C containing a catalyst and the organic carbon is transformed into carbon dioxide which is then detected. Every sample was injected in triplicates to get an average value for quality assurance.

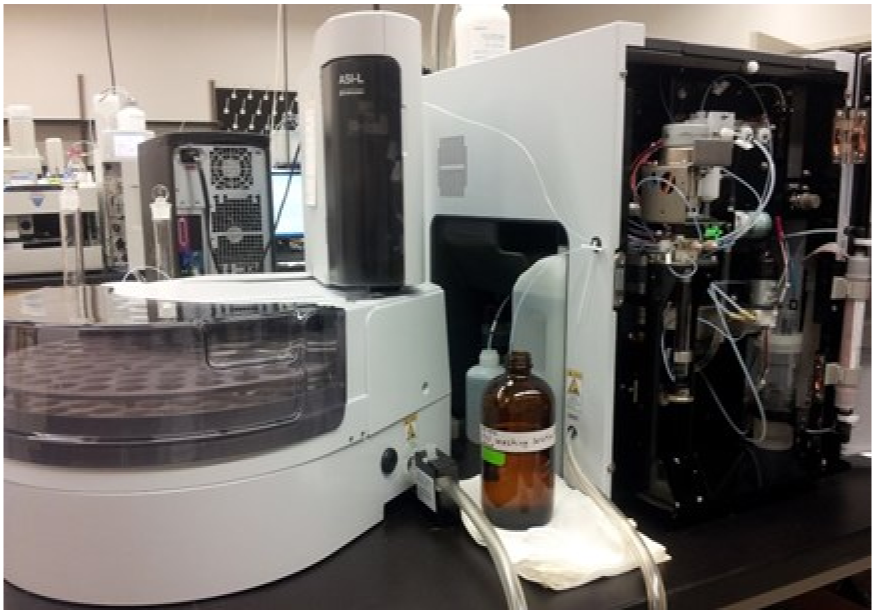


Figure 3.5: TOC-LCPH/CPN Analyzer equipped with ASI-L Auto-sampler used for TOC/NPOC and TIC measurement

3.3.1.2 Alkalinity

Alkalinity was measured in terms of mg/L $CaCO_3$ using a *Mettler Toledo* DL53 autotitrator as shown in Figure 3.6.

Figure 3.6: Mettler Toledo DL53 autotitrator used for alkalinity measurements

The instrument was calibrated using buffer solutions of pH 4.01, 7.00 and 10.00. The titrant used was 0.01992 N H_2SO_4 solution. Standardization of this titrant was conducted using 0.02N Na_2CO_3. 5ml of the extracted water sample was measured in a beaker, diluted to 50ml with Deionized (DI) water and titrated with H_2SO_4 according to standard method. The instrument measures the amount of acid needed to reduce the pH of the sample to 4.5.

3.3.1.3 pH

The pH was recorded using an Accumet® 15 pH meter (Fisher Scientific, Ottawa, ON, Canada). Calibration was done using buffer solutions pH 4.01, 7.00 and 10.00. The Probe was cleaned with DI water and dried using soft tissue between each buffer solution. After calibration, the pH probe was inserted into the sample, stirred to achieve equilibrium and the reading was recorded. After every pH measurement, the probe was inserted back into the storage solution to keep the probe wet while not in use.

3.3.1.4 Conductivity

This parameter was measured using an OrionTM 136S from Thermo-Fisher Scientific (Ottawa, ON, Canada). The extracted water samples were filtered using 0.45μm filters (PTFE, Fisher chemical, Canada). First, the conductivity meter was calibrated using a Traceable® Conductivity Standard (Fisher Scientific, Canada). After cleaning the probe with DI water and wiping it dry, the probe was inserted into the standard solution to observe the conductivity value at the current temperature. The observed current temperature was recorded for adjusting the conductivity value in the meter. A temperature correction factor of 1.912% was used to adjust the conductivity value in the meter as against the displayed temperature. The displayed temperature before measurement for WAO and WAPO (90 min) was 22.8^{0}C whereas it was 23.7^{0}C in WAO$_{extended}$ (210 min). Calculation for adjusting the conductivity value of the standard for the displayed temperature is shown in Appendix - A. After calibration of the meter, the reading of each sample was measured and recorded. The probe was rinsed with DI water between every sample measurement.

3.3.1.5 Ion Chromatography (IC)

Dionex ICS-2100 equipped with an AS-AP auto sampler (figure 3.7) from Thermo Fisher Scientific was used to analyze the common anions and short chain organic acid concentrations in all the samples. The ICS-2100 was equipped with an analytical column Dionex IonPac^{TM} AS18 2x250 mm, 7.5 μm particle diameter (the column was kept at 30^{0}C during the analysis), a guard column Dionex IonPac^{TM} AG18 2x50 mm, a high-capacity electrolytically regenerated suppressor Dionex AERS 500, a carbonate removal device Dionex CRD 200, and an automatic eluent generation cartridge to avoid an inconsistent baseline. Previous to the analysis, samples were filtered using 0.22 μm syringe filters (Millex-GS, Millipore), diluted 10 times using Milli-Q water (18.2MΩ) and placed in 2 mL sample vials, while 10 mL vials were used for standards and blanks. All glassware used for preparation and storage of standards were acid washed prior to usage and storage of samples.

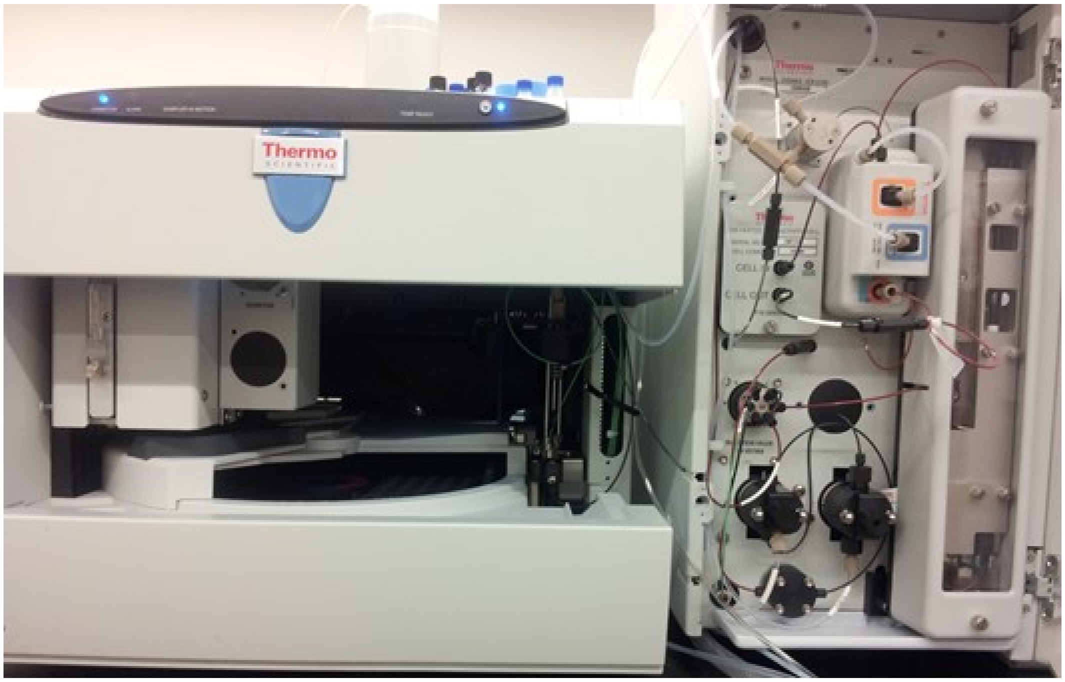


Figure 3.7: Ion Chromatography ICS-2100 equipped with AS-AP auto sampler

3.3.1.5.1 IC Methods

Common anions were analyzed using an isocratic method, 32 mM of KOH. The flow rate was 0.45 ml/min for 15 minutes with a suppressor current of 36 mA. For calibration, seven standard anions, F^-, Cl^-, NO_2^-, SO_4^{2-}, Br^-, NO_3^- and PO_4^{3-}, were prepared in five different concentrations, 20, 10, 5, 1 and 0.1mg/L from a stock solution of 1000mg/L in ultra-pure water (18.2MΩ).

Short chain organic acids were analyzed using a gradient method. The gradient method had a flow rate of 0.45 ml/min with a suppressor current of 34 mA. The concentration of the eluent generator was 1-30 mM from 0-5mins, 30 mM from 5-10mins and 1mM from 10-20mins. For calibration, five different concentrations (10, 5, 1, 0.1, and 0.01 mg/L) were prepared for five standard organic acids (Acetate, formate, maleic, propionate and oxalate).

3.3.1.6 Inductively Coupled Plasma-Mass Spectrometry

An inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer SCIEX ELAN 9000, Waltham, MA) instrument was used for the analysis of cations and trace metal elements. The ICP-MS instrument was equipped with an auto-sampler (Cetac ASX-500; Nebraska, USA). The samples were filtered using 0.22µm pore size syringe filters (PTFE, Fisher chemical, Canada) and diluted 100 times using 1% nitric acid solution (HNO_3; Trace Metal Grade, Fisher Chemical, Canada). Standards for calibration were prepared using multi-element standard, Contract Required Detection Limit Standard, Boron 11 Isotope Standard, Aluminum Standard, Instrument Calibration Standard 3 (SPEX CertiPrep, Metuchen, NJ). 10 mg/L of Mo, P in 1% HNO_3 and 10 mg/L of Si in 1% HNO_3 were prepared internally in the laboratory prior to analysis. A multi-element internal standard 1 (SPEX CertiPrep, Metuchen, NJ) was also added in all samples and standards during preparation. Three types of blanks were prepared, a calibration blank (used during calibration), a check blank (used to monitor contamination) and rinse blank (used between samples and standards to flush the system). A wash solution (0.02% Trition X-100 in 2% HNO_3) was freshly prepared and connected to the auto-sampler for rinsing between samples. The operating conditions of ICP-MS were: vacuum pressure 9.8×10^{-6} torr, neublizer gas flow was 1 L min^{-1}, 1200 Watts ICP RF Power, 8 Volts Lens Voltage, -1800 Volts analog stage voltage and about 1200 Volts pulse stage voltage.

3.3.2 Surface analysis

X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and X-ray Photoelectron Spectrometry (XPS) for surface analysis and hydrometer testing for particle size distribution were carried out.

3.3.2.1 X-Ray Diffraction (XRD)

The Solids/Sediment were analyzed by X-Ray Diffraction (XRD) measurements for mineral compositions. The XRD instrument used for measurement was Rigaku Ultima IV unit (figure 3.8) with a cobalt tube of 38kV and 38mA. Wavelength K average = 1.790260. There are 10 position sample changer. Slit sizes were 2/3, 10mm DHL, open, 13mm. Before the analysis, samples were dried overnight at 110^0C and crushed to fine powder. Samples were analyzed using a top-pack mount at a speed of 2 degrees 2-theta per minute with a step size of 0.02 degrees from 5 to 90 degrees. D/Tex detector was used with Fe filter. Data interpretation was done using JADE 9.1 software and ICDD and ICSD databases.

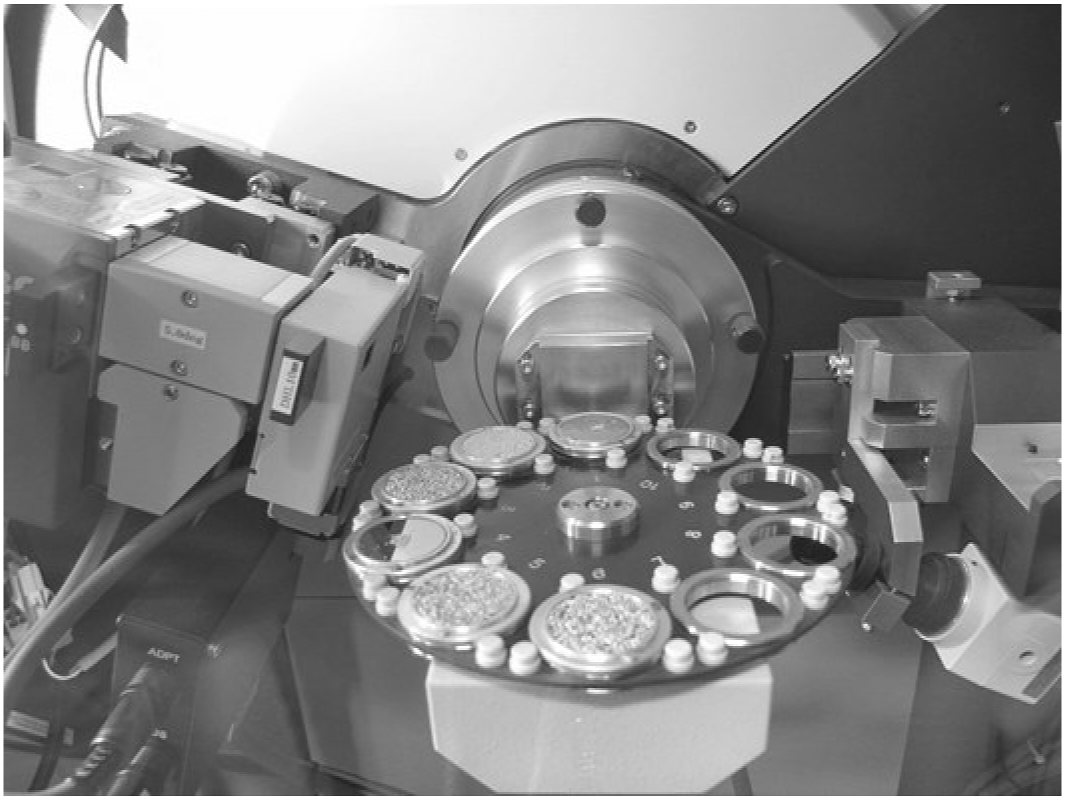


Figure 3.8: Rigaku Ultima IV unit's 10-position sample chamber during sample analysis

3.3.2.2 Scanning Electron Microscope (SEM)

The instrument used was a Zeiss EVO MA 15 LaB6 filament scanning electron microscope as shown in figure 3.9. SEM analysis were conducted outside the department in Earth and Atmosphere Science (EAS) building at the University of Alberta. Similar to XRD, the samples were first crushed into fine powder after overnight drying in an oven. Before, placing the samples in SEM, the powdered samples were stuck on double sided carbon tape and coated with carbon on a specimen stub. Backscattered images obtained using a Si diode detector, whereas, EDS acquired with a peltier-cooled 10 mm^2 Bruker Quantax 200 Silicon drift detector with 123 eV resolution. Secondary electron images were obtained using an *Everhart-Thornley* detector.

Figure 3.9: Scanning Electron Microscope used for surface analysis of sediment after WAO/WAPO *(Source: Earth and Atmosphere Science; University of Alberta, 2014)*

3.3.2.3 X-ray Photoelectron Spectrometer (XPS)

X-ray Photoelectron Spectrometer (XPS) measurements were performed on AXIS 165 spectrometer (Kratos Analytical), figure 3.10. Samples in powdered form were used in XPS as well. The base pressure in the analytical chamber was lower than 3 x 10-8 Pa. Monochromatic Al Kα source (hv = 1486.6 eV) was used at a power of 100 W. The analysis spot was 400 x 700 μm. The resolution of the instrument was 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. The survey scans were collected for binding energy spanning from 1100 eV to 0 with analyzer pass energy of 160 eV and a step of 0.4 eV. High-resolution spectra of O1s and C1s peaks were run with pass-energy of 20 eV and step of 0.1 eV, ten scans each. The AXIS electron source was engaged during the measurements to compensate sample charging.

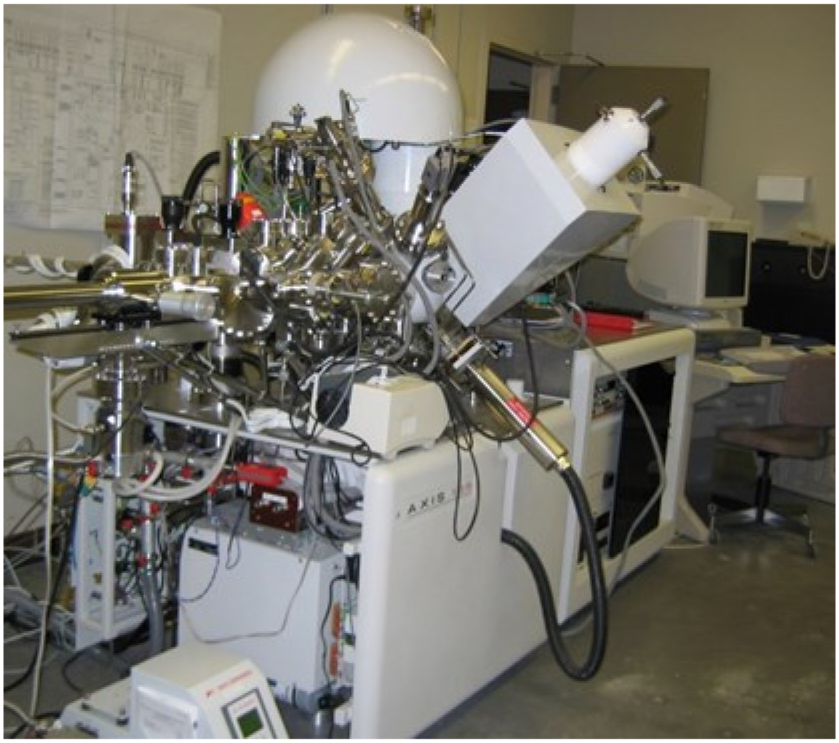


Figure 3.10: Kratos Axis 165 X-ray Photoelectron Spectrometer used for analyzing chemical bonds in the sediment *(Source: Alberta Centre for Surface Engineering and Science, 2014)*

3.3.2.4 Dry Weight and Volatile Organic Carbon

An Isotemp Furnace Oven (Model 550-126; Fisher Scientific, Canada) was used to combust the organic carbon. Dry weight measurement determines the percentage of solids in the sample by evaporating all the water. To determine the percentage of the volatile organic carbon (VOC) in a sample, the sample was dried and placed in a furnace at 900^{0}C for 30 min. The weight lost after combustion is the amount of volatile organic carbon. A portion of the sample was weighed in a crucible and placed in an oven at 110^{0}C overnight for dry weight analysis. Next day, the dried up sample was weighed again to determine the solid content and then placed in a furnace at 900^{0}C for 30mins for volatile organic compound measurement according to Standard Methods.

3.3.2.5 Hydrometer (Particle Distribution)

An ASTM 152H Hydrometer, sedimentation cylinder, thermometer, dispersing agent (sodium metaphosphate), were used for particle distribution analysis. Procedure is according to ASTM standard method for particle size analysis of soils (D422-63).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Preliminary Tests on Synthetic Clay Emulsions

Preliminary tests were performed on 30% synthetic clay slurry using pure Kaolin and bentonite Clay powder at 30% (w/w) in deionized water, to observe the difference in the speed of consolidation of clay particles before and after oxidation. After oxidation at 120^{0}C and 280-300psi, the samples were allowed to stand for the same amount of time and the distance of consolidation of particles was recorded. The samples with salts did not show significant changes in consolidation, however, the 30% clay sample showed positive results with faster separation (Figure 4.1). The normal pH slurry samples were allowed to settle for 24 hours and 16% increase in rate of consolidation of particles was observed. On the other hand, the alkaline samples showed an 18% increase in settling rate of particles in only 4 hours of sedimentation time (figure 4.2).

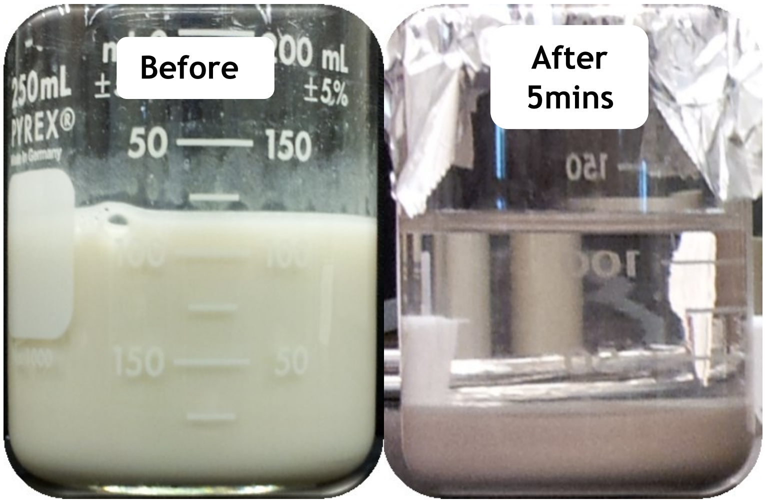


Figure 4.1: Separation of kaoline clay particles before and after oxidation

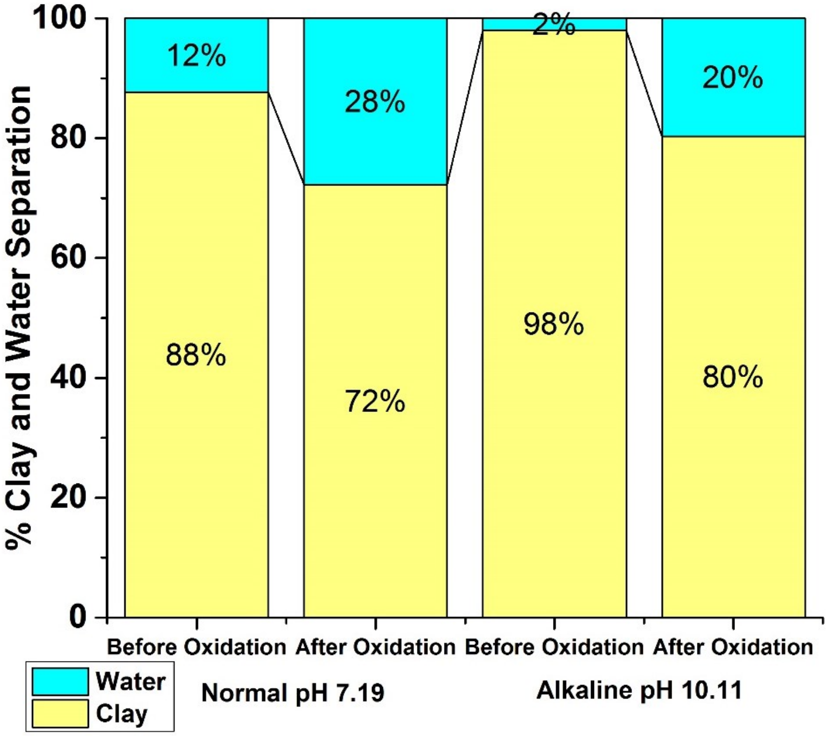


Figure 4.2: Separation of water and clay in 30% Kaolin clay slurry under normal (24hrs sedimentation) and alkaline conditions (4hrs sedimentation) subjected to WAO

It has been reported by Takamura (1982) that the clay minerals in Alberta's Oil sands are dominated by kaolinite. This implies that these minerals make their way to the mature fine tailings through the extraction process. It is clear from figure 4.1, that oxidation at 120^{0}C and 280-300psi using 150psi of air had significant effect on lowering the charge density around the clay particles. The faster sedimentation of particles indicates the oxidation potential of WAO process towards reducing the charge density of the clay particles that keeps them suspended, thereby manipulating the surface chemistry, resulting in faster consolidation. Similar consolidation of particles could be observed during oxidation of MFT as majority of clay minerals in MFT are kaolinite after Quartz. The separation of kaolinite clay particles was substantial and faster after oxidation. As seen in figure 4.2, there is significant improvement in the settling rate of clay particles after oxidation for only 12mins. Both normal and alkaline conditions showed an increased rate of consolidation of particles, as well it shows that clay particles might settle faster in slightly higher alkaline conditions.

4.2 Effect of Temperature and Pressure on Emulsified MFT

Oxidation of 25% (v/v) MFT slurry at similar conditions used for synthetic clay emulsions showed poor results with improper breakage of tight emulsions. Increasing the conditions to 200^{0}C and 500psi showed significant degradation of bitumen froth as observed on the surface (figure 4.3a). In all the cases, intervals of 5, 15 and 30min resulted in desorption of bitumen from the clay particles, bringing it to the surface. Addition of hydrogen peroxide showed more than 50% faster desorption of residual bitumen and sedimentation of particles (figure 4.3b). A sudden increase in internal pressure was observed in samples after addition of hydrogen peroxide.

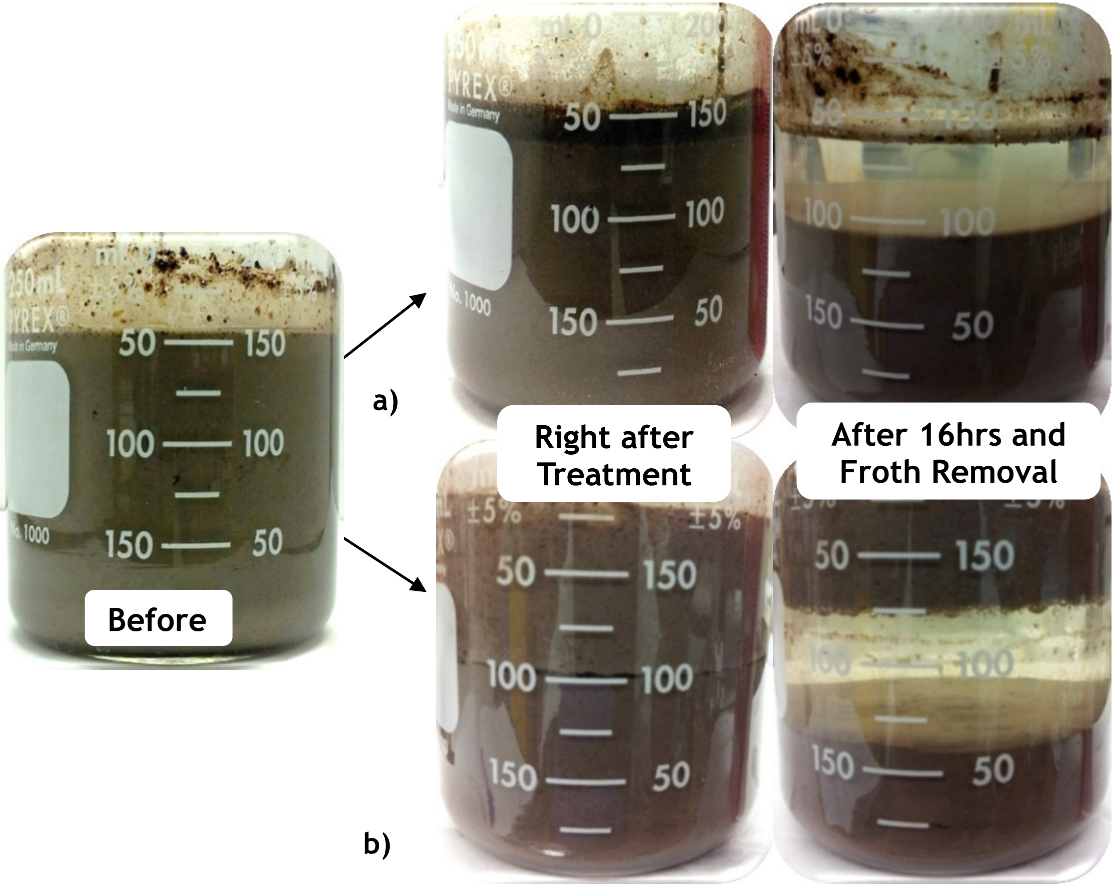


Figure 4.3: Effect of temperature and pressure on emulsified mature fine tailings after oxidation at 200^{0}C and 500psi for 30min residence time using a) WAO for 15mins, b) WAPO for 5mins

Unsatisfactory breakage of 25% MFT slurry was observed under oxidation conditions of 120^{0}C and 280-300psi. However, higher temperature and pressure at 200^{0}C and 450-500psi started to disintegrate the bitumen based emulsion in MFT resulting in the breakage of inter-particle bridge formed between clay particles by residual bitumen blobs. Therefore, once released, the less dense bitumen goes to the top layer as a thick layer of froth. In this oxidation process, temperature and pressure are the most important factors for the oxidation of organic compounds. Higher temperature results in higher rate of formation of free radicals that attack and degrade organic compounds, thereby producing higher COD removal ratios (Jing et al., 2012; Jing et al., 2011; Jing et al., 2012; Jing et al., 2012; Jing et al., 2013; Jing et al., 2013). High temperature and pressure reduces the density of water causing it to move upwards and at the same time it facilitates the sedimentation of solid particles. The upward moving water carries hydroxyl radicals that desorbed, and might later degrade, the bitumen blobs from the particle surface, hence allowing the desorbed bitumen to float as an upper layer and releasing the trapped water between the pores (figure 4.4). Some natural surfactants provide stability of emulsions by forming an interfacial film at the oil-water interface. This stability is reduced and distorted by increasing temperature (Jia, 2010).

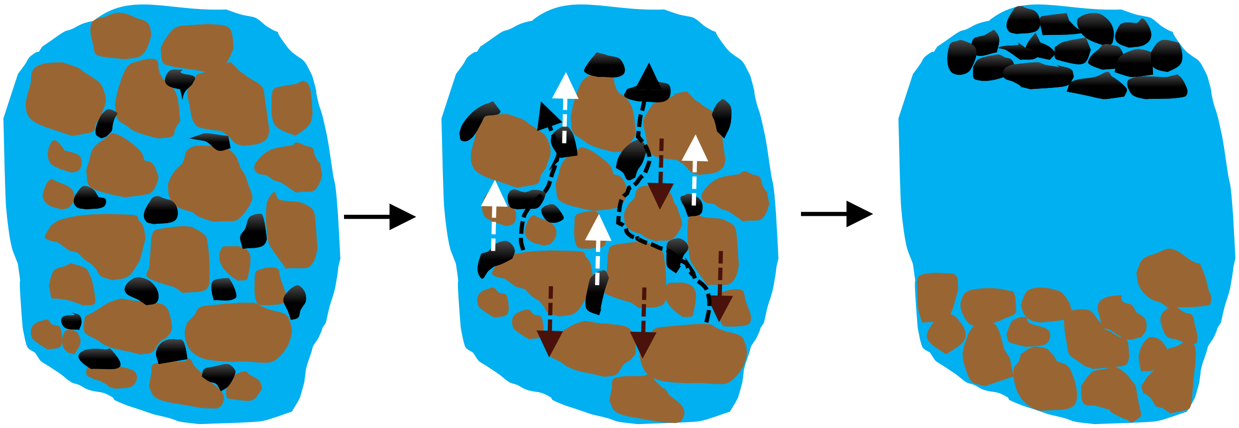


Figure 4.4: Effect of high temperature and pressure on water density

Addition of hydrogen peroxide increase the formation of hydroxyl radicals and induces a rapid degradation of residual bitumen attached to the particles at high temperatures, as seen in figure 4.3b.

This was due to the instantaneous decomposition of hydrogen peroxide at the given high temperature and pressure which results in an excess of free hydroxyl radicals to degrade the organic bitumen (Kolaczkowski et al., 1997; Shibaeva et al., 1969b). The more radicals are formed, the faster will be the rate of degradation of residual bitumen and the sedimentation of particles. Hydrogen peroxide can also decompose into water and oxygen (eq: 1), which could be the reason for the rapid rise in internal pressure upon addition of hydrogen peroxide.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \qquad \text{(eq: 1)}$$

4.3 Effect of Oxidant on Emulsified MFT

Oxidation of MFT using air (containing oxygen) alone and addition of hydrogen peroxide was conducted. Hydrogen peroxide (50%) was spiked (5 mL) to boost the rate of the oxidation process. Figure 4.5 shows the effect of oxidant air on emulsified MFT to have a thick layer of froth on the top whereas the addition of H_2O_2 showed a thick layer of foam with less visible froth on the surface.

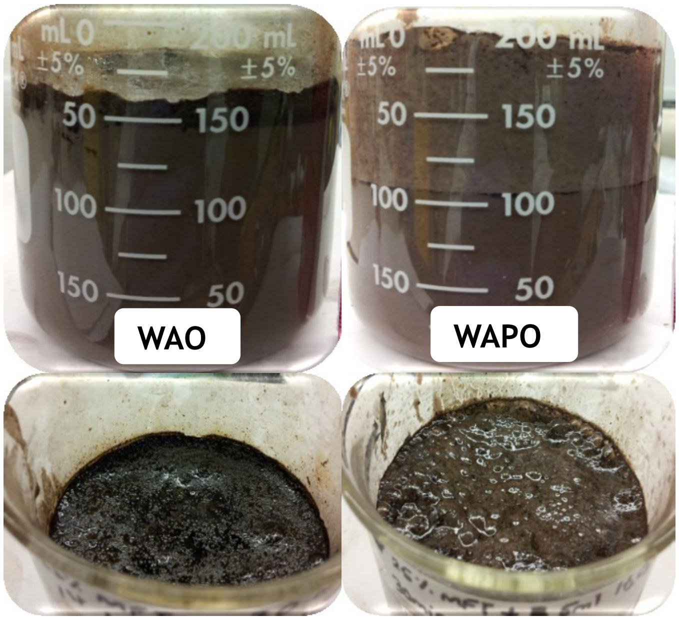


Figure 4.5: Effect of oxidant on emulsified MFT

Compressed air (150 psi) was effective for the disruption of synthetic clay emulsions at 120^{0}C and 280-300 psi. Under similar temperature and pressure, 100 psi and 200 psi air did not break emulsions of 25% (v/v) MFT slurry significantly. On the contrary, the oxidation of MFT with 100psi air at 200^{0}C and 500psi was sufficient to break the bitumen emulsion, bringing the non-soluble froth to the surface. During oxidative degradation of bitumen, mainly by hydroxyl radicals, different degradation byproducts from the bitumen might be formed. The oxidation process could increase their polarity being possible to be dissolved in the water in the form of dissolved organic carbon (DOC). Froth was less visible in samples with added peroxide; this could be due to the fast oxidation of organic bitumen by hydroxyl radicals, which are formed in large amounts. Therefore, most of the released bitumen is oxidized in the water in these samples and only a small amount floats to the surface indicating a higher concentration of DOCs in the released water. Presence of foam is due to the reaction of hydrogen peroxide with naturally available surfactants in MFT and the production of excess oxygen from hydrogen peroxide. These surfactants are present as a result of NaOH introduction during extraction process and can promote desorption of bitumen from the particles with the formation of foamy bubbles (Zhang, 2012).

4.4 Bitumen Recovery

Since the addition of hydrogen peroxide did not produce recoverable froth, bitumen recovery in terms of froth was measured for 5, 15 and 30 min time interval cycles with air as the primary oxidant (figure 4.6). Figure 4.7a shows a gradual increase in froth removal at each interval with exception of 2nd cycle for 5min. After 1st cycle, 5min reaction gives slightly higher froth recovery from MFT. However, from 2nd cycle onwards both 15 and 30min cycles give consistently higher percentage removal than 5min. Almost 93% froth is removed after 5 cycles of 30min intervals whereas approximately 92% was removed during 5min intervals. Figure 4.7b shows after 180mins of oxidation in 30min time intervals, most of the insoluble froth was extracted out of the emulsified MFT.

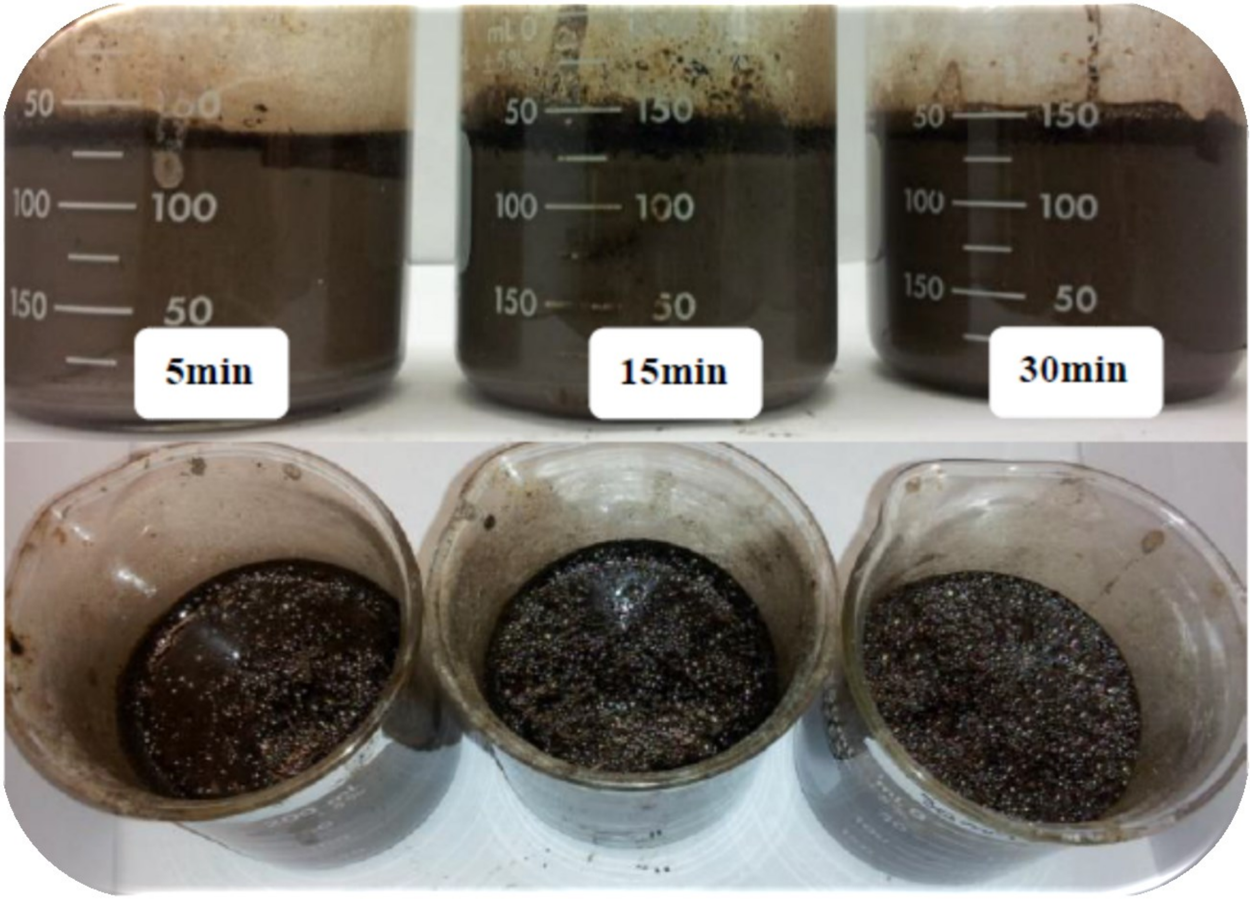


Figure 4.6: Bitumen recovery after WAO with 100psi air for 5, 15 and 30min retention times

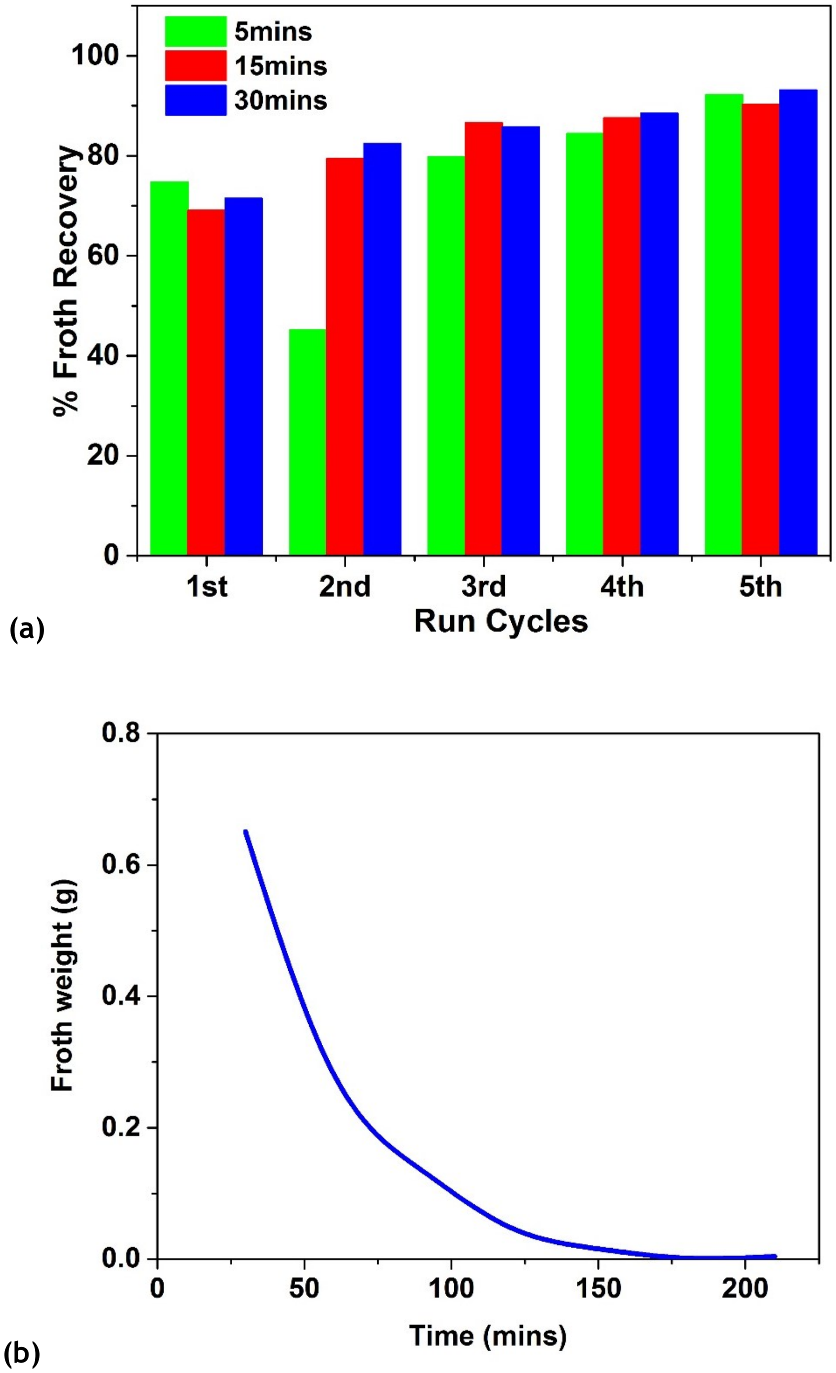


Figure 4.7: Recovery of bitumen from emulsified MFT as, (a) percentage froth recovery after each time interval cycle, and (b) froth weight recovered with oxidation time for 210mins

Figure 4.7a reflects the amount of froth removed from a 25% MFT sample using air (oxygen). As the oxidation process degrades the bitumen attached to soil particles, it is detached by means of imbalance in the charges created by hydroxyl radicals. The detached part of bitumen being less dense than water moves towards the surface along with the released water. It appears that apart from the 2nd cycle, froth removal produced by 5min cycles is quite close to 15 and 30 min cycles. This is visually represented in figure 4.6, where recovered froth on the surface seems quite similar after all retention times. Five cycles of 5min oxidation removed an equivalent of approximately 92% froth from the sample compared to around 93% by 30min cycles (figure 4.7a) indicating that WAO can breakdown the emulsion and recover significant amount of bitumen froth from MFT. It also shows the oxidative power of WAO process within 5mins. WAO has been proven to be a feasible process to break down bio-resistant organics in wastewater and eliminate toxicity (Mantzavinos et al., 1997; Mantzavinos et al., 1997; Mishra et al., 1995; Randall and Knopp, 1980; Zhao et al., 2005). In this study, the control sample had about 17.88% of volatile organic hydrocarbons of the dry weight of MFT. Declining curve in figure 4.7b indicates desorption and release of bitumen froth from the emulsified MFT with oxidation time. It was found that after 210mins of oxidation, the recovered bitumen from 25% MFT slurry was estimated to be approximately 5% (wt.) without adding H_2O_2. A 30 min oxidation with no air or H_2O_2 produced around 1.5% wt. (of dry wt. MFT) less froth than with air as the oxidant. This means that WAO conditions can produce radicals without the supply of compressed air or hydrogen peroxide through the decomposition of water as well as presence of oxygen from atmospheric air already present in the reactor. Although, at a very slow rate it indicates that longer process time is required to achieve oxidation.

4.4.1 Froth Solubility

The recovered froth was tested for solubility in different solvents including water, methanol and dichloromethane (DCM) (figure 4.8).

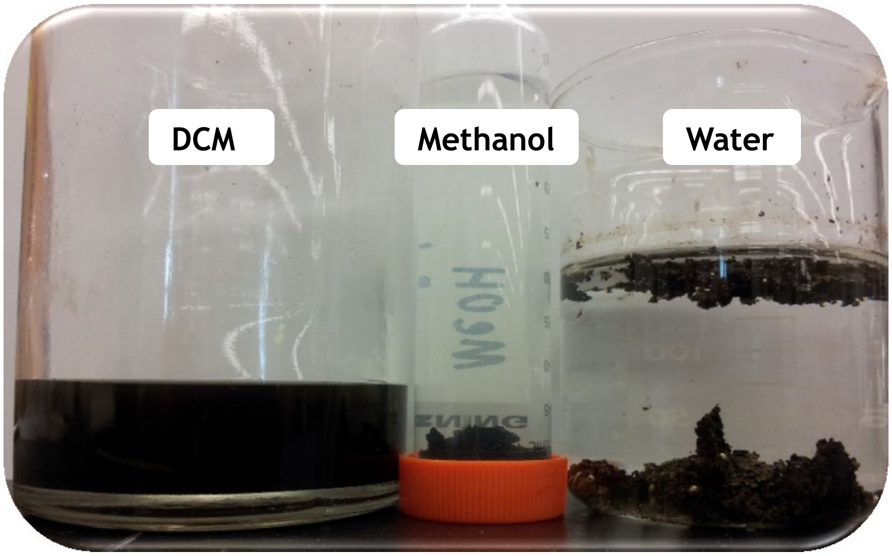


Figure 4.8: Solubility analysis for the recovered froth in different solvents

The froth was completely soluble in DCM proving that the extracted bitumen material is nonpolar, composed of hydrocarbons/organics and had odor similar to gasoline. DCM is an organic solvent that dissolves only nonpolar substances and is not miscible with water.

4.5 Water Recovery

Separation of water from particles in figure 4.9a shows more than 50% recovered sample as water after oxidation with air and hydrogen peroxide for 30, 60 and 90mins. A layer of foam was also produced above the released water after oxidation with hydrogen peroxide. On the contrary, only 48% recovered sample was water after oxidation with air for 210 mins (figure 4.9b).

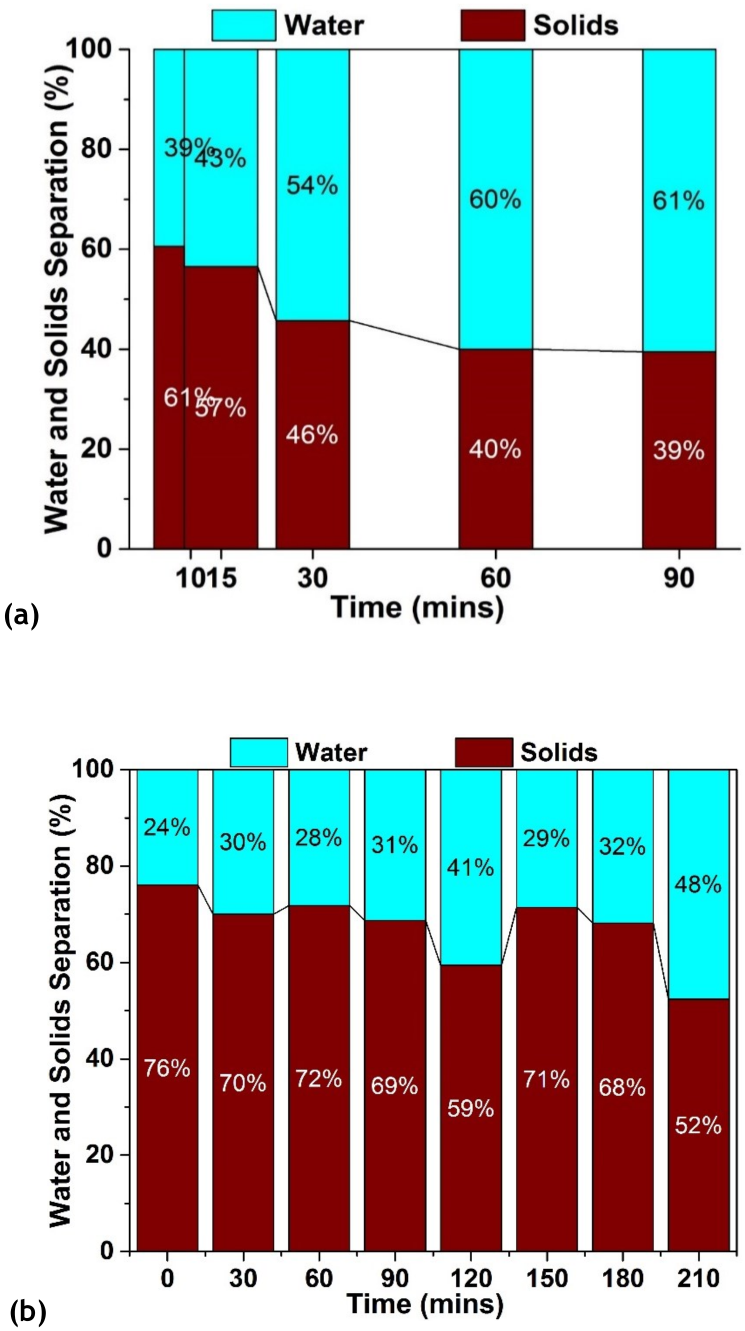


Figure 4.9: Effect on separation of water and particles a) water and particle separation after WAPO at 200^{0}C and 500 psi for 90mins, b) water and particle separation after WAO$_{extended}$ at 200^{0}C and 500 psi for 210mins

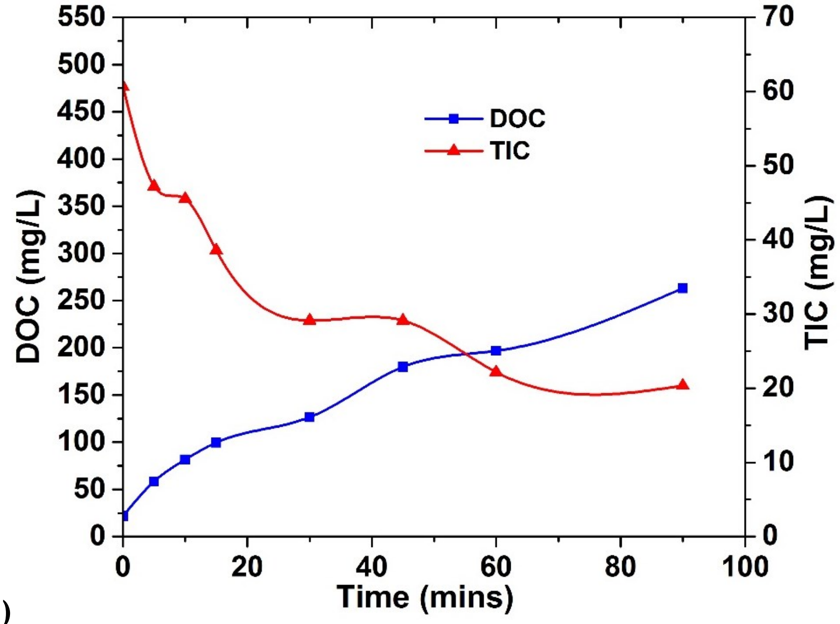
The WAO alone showed a fast disintegration of the emulsion and a rapid release of water. With the addition of peroxide, the particle consolidation and the amount of water release was increased by more than 50%. Although, resulting in less froth production, but rapid release of trapped water and in higher amounts was more evident in samples when H_2O_2 was added. During first 10mins, the emulsion might not be completely distorted so less water is recovered but as oxidation time increases, hydroxyl radicals attack more clogged bitumen blobs and break free the clay particles and the trapped water from within the pores. As mentioned previously, at high temperatures and pressure, water density is reduced and moves upward even from within the pores of the particles, thus extracting all the trapped water. The more hydroxyl radicals are formed at high temperature, the faster the rate of degradation of residual bitumen from the particle surfaces, thereby resulting in rapid separation. The heavy particles, now free from bitumen fall under the influence of gravity while less dense water moves towards the surface along with recovered bitumen as froth. The release of water using air solely seems slower as only 48% recovered sample was water, after 210 mins of oxidation. This means that there were less radicals produced by oxygen from air or at a much slower rate which resulted in slower release of trapped water from the particles. Figure 4.9 (a & b) shows the percentage of water and sediment recovered in terms of height. It is clear that as the oxidation time increases, the percentage of water increases in the sample while that for solid particles decreases. This is due to oxidation as the bitumen had been extracted out of the solid particles along with pore water reducing its volume and only clay and sand particles are left behind. Although care was taken during sampling, however, because the reaction conditions are at such high temperature and when the effluent is collected for analysis, there are possibilities that some portion of the extracted water would have turned to steam and lost on opening the valve. As the released gas was not analyzed in this study, it was possible to encounter some errors in terms of recovered water.

4.6 Recovered Water Chemistry

WAO resulted in breaking the emulsion, dissolving ions and bitumen into the water. The released water showed a high transmissivity. Analysis was conducted on the recovered water to study its chemistry.

4.6.1 Dissolved Organic and Total Inorganic Carbon (DOC & TIC)

The extracted water was analyzed in TOC analyzer for dissolved organic carbon (DOC) and total inorganic carbon (TIC). DOC increased gradually to more than 250 mg/L after 90mins of oxidation with air (figure 4.10a). However, a rapid increase with 80% higher DOC was observed in the extracted water with the addition of H_2O_2 after 90 min oxidation (figure 4.10b) which was close to DOC recorded after 180mins during $WAO_{extended}$ (figure 4.10c). 66.4% reduction in total inorganic carbon (TIC) was obtained during 90mins of oxidation with air (figure 4.10a). The reduction was enhanced to 92.6% in the presence of hydrogen peroxide (figure 4.10b). 210 mins of oxidation with air showed TIC to be almost completely eliminated with approximately 99% removal (figure 4.10c).



(a)

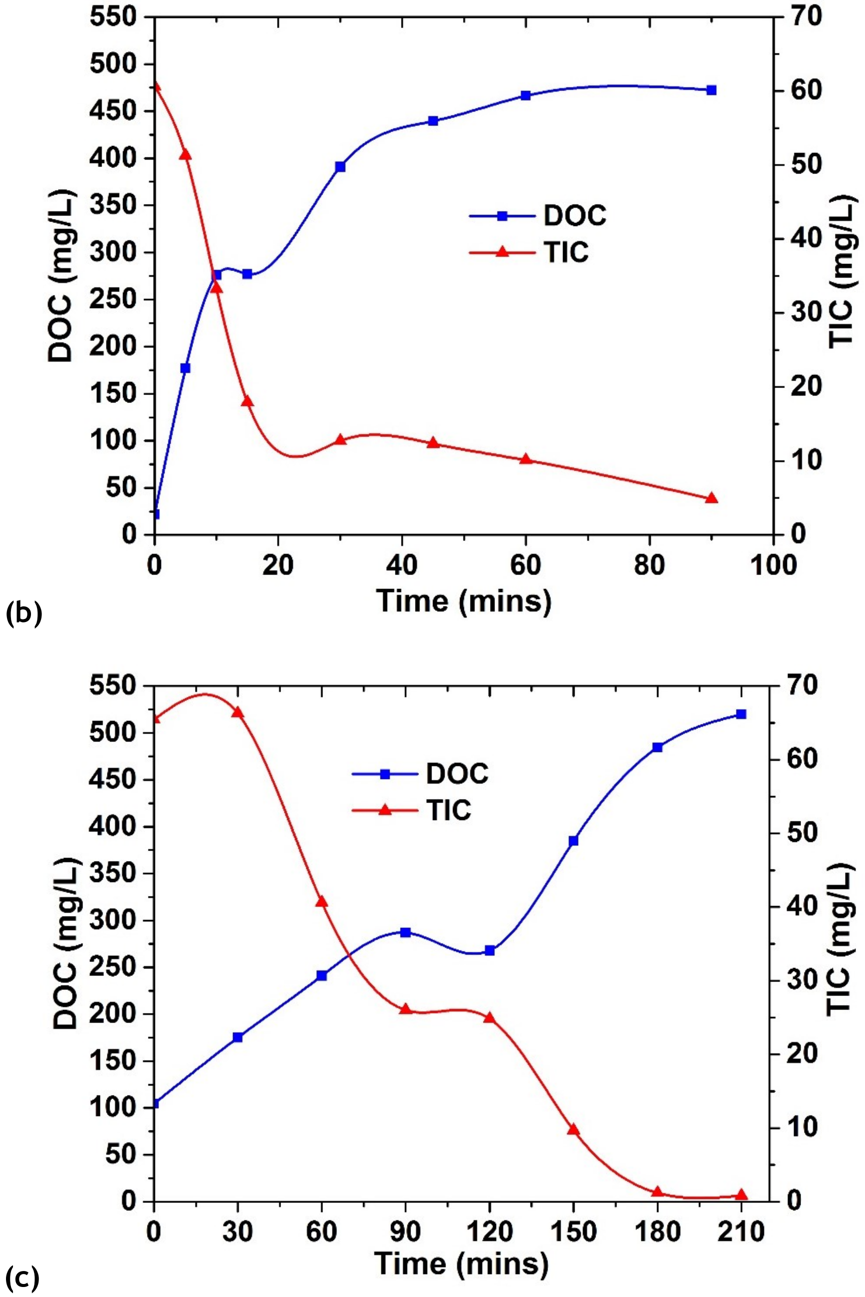


Figure 4.10: Concentration of dissolved organic carbon (DOC) and total inorganic carbon (TIC) in extracted water after oxidation at 200^{0}C and 500 psi with a) WAO for 90mins, b) WAPO for 90mins and c) WAO$_{extended}$ for 210mins

After oxidation, the treated sample had remarkable separation of froth, liquid and sediment. Water analysis showed increasing concentrations of DOC with residence time whereas the inorganic carbon decreased (figure 4.10). Increasing DOC implies the degradation of organic bitumen blobs due to oxidation. 80% higher DOC in figure 4.10b is due to the addition of peroxide which enhances the oxidation reaction faster. Organic bitumen is nonpolar, once degraded and detached from solid particles, most of it floats to the surface as froth. Some portion of the bitumen gets degraded to the point where it gets dissolved in water, hence, the increase in DOC concentration. Hydrogen peroxide provides hydroxyl radicals in excess that keep degrading the bitumen into dissolved form, therefore less froth is recovered and higher DOC is observed. Although figure 4.10a & c show different initial concentration of DOC in water but after 90mins of oxidation, the concentration of DOC was approximately similar in both trials which shows that the amount of bitumen in MFT does not affect the oxidation mechanism and the rate of oxidation proceeds in correlation to the temperature, pressure and oxidant provided. Concentrations of dissolved organic carbon increases in water as the oxidation/residence time and temperature is increased (Genc et al., 2002; Khan et al., 1999). This is due to the release and breakdown of organic bitumen in water. However, after dissolution of organic bitumen, the increased temperature (180 - 220ºC) results in increased removal of TOC (Tang et al., 2003).

It can be observed in figure 4.10c that after 180 mins of oxidation, the gradual increase in DOC concentration is leveling off. This indicates that all the organic bitumen blobs forming the emulsion, have been detached and degraded from the particles either as froth (which is recovered from the top, figure 4.7b) or dissolved in water as DOC and this DOC is now being further oxidized and reaching its limit. It is implied that further oxidation would reduce DOC concentration in water. The concentration of DOC at 180mins of retention time with air was similar to the concentration of DOC at 90mins with the addition of H_2O_2. This shows that oxidation time could be reduced with the aid of H_2O_2 as faster oxidation could be achieved in less residence time. However, it was evident from figure 4.5, that presence of H_2O_2 might also degrade most of the residual bitumen rapidly reducing bitumen recovery as froth.

On the other hand, the total inorganic carbon (TIC) concentration decreases progressively as the retention time increases. The inorganic carbon is a combination of carbonates, bicarbonates, carbonic acid and carbon dioxide. Oxidation of inorganic carbon at high temp and pressure reduced carbonates to end products of carbon dioxide and water. Approximately 26% faster reduction in TIC was achieved during 90mins of WAPO which shows the oxidation power of hydroxyl radicals. Similar to organic carbon, rapid oxidation of TIC could also be achieved in less time which was evident from figure 4.10b & c where 180mins of oxidation with air provided >90% TIC reduction which was achieved in 90mins with WAPO. Theoretically, the inorganic carbon is an indication of buffer capacity of the treated sample (Stumm and Morgan, 1970), therefore, reduction in TIC would indicate the decline in buffer capacity.

4.6.1.1 Oxidation Mechanism

The MFT in its original state is composed of long chains of high molecular weight organic compounds forming the bitumen. The degradation of organic compounds takes place on the basis of free radical mechanism (Bhargava et al., 2006; Li et al., 1991; Tufano, 1993). The initiation of radical formation has been proposed to take place through various reactions, including bimolecular and unimolecular reactions as shown

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \qquad \text{(eq: 2)}$$

$$O_2 \rightarrow O^{\bullet} + O^{\bullet} \qquad \text{(eq: 3)}$$

$$H_2O \rightarrow OH^{\bullet} + H^{\bullet} \qquad \text{(eq: 4)}$$

$$RH \rightarrow R^{\bullet} + H^{\bullet} \qquad \text{(eq: 5)}$$

It has been found that the activation energies of the unimolecular reactions (eq: 3 – 5) are much higher than the activation energy of the bimolecular reaction (eq: 2), which suggests that (eq: 2) is most likely to be the initiation reaction for radical formation with higher rate constant. According to this reaction, when the molecular oxygen absorbs energy from heat, it attacks the weakest C – H bond to give two radicals, an organic radical ($R^{\bullet}$) and a hydroperoxyl radicals ($HO_2^{\bullet}$). Authors in the past have suggested this theory (Emanuel et al., 1980; Mantzavinos et al., 1996; Rivas et al., 1998; Rivas et al., 1999).

Emanuel et al. (1980) also suggested that if the organic compound is present in large quantities, a trimolecular reaction can take place for radical initiation reactions as shown in (eq: 6).

$$RH + O_2 + RH \rightarrow 2R^\bullet + H_2O_2 \qquad \text{(eq: 6)}$$

Once the organic radical ($R^\bullet$) and a hydroperoxyl radicals ($HO_2^\bullet$) are formed in (eq: 2), a chain of propagation reactions proceeds as follows:

Scheme 1		**Scheme 2**	
$R^\bullet + O_2 \rightleftarrows ROO^\bullet$	(eq: 7)	$RH + HO_2^\bullet \rightarrow H_2O_2 + R^\bullet$	(eq: 10)
$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$	(eq: 8)	$H_2O_2 \rightarrow 2OH^\bullet$	(eq: 11)
$ROOH \rightarrow RO^\bullet + OH^\bullet$	(eq: 9)	$H_2O_2 + R^\bullet \rightarrow ROH + OH^\bullet$	(eq: 12)

In (eq: 10), as soon as hydrogen peroxide is formed as the product, it decomposes into two hydroxyl radicals ($OH^\bullet$) instantaneously due to the conditions provided in this study (200^0C, 400-500psi). Rapid decomposition of hydrogen peroxide under 448K and 3 MPa, close to the conditions used in this study, have been reported (Kolaczkowski et al., 1997; Shibaeva et al., 1969b). It is also possible for hydrogen peroxide to react with an organic radical to give an alcohol compound and hydroxyl radical. However, due to faster reaction rate for (eq: 11), this reaction is more likely to take place rather than (eq: 12). Both scheme 1 and 2 result in the production of hydroxyl radicals.

In comparison to the organic radical and hyroperoxyl radical, the hydroxyl radical is a very powerful and dominant chemical oxidant that can react with organic compounds almost instantly when formed (Munter, 2001). Moreover, the rate constant for $^\bullet OH$ radical is much faster than the organic radical ($R^\bullet$) and the electron affinity is large as well. Therefore, once the hydroxyl radical is formed, it attacks almost all organic compounds rapidly. It was also suggested that the common reaction between hydroxyl radical and organic compounds is through abstraction of hydrogen atom (eq: 13) from the organic molecule resulting in another organic radical which follows (eq: 7) and the cycle continuous (Li et al., 1991; Munter, 2001; Rivas et al., 1999).

$$RH + OH^\bullet \rightarrow R^\bullet + H_2O \qquad \text{(eq: 13)}$$

(eq: 13) has a low activation energy which suggests that the rate of reaction must be rapid (Khar'kova et al., 1989), degrading the organic compounds in the sample. Alkoxyl radicals formed in (eq: 9) can combine with organic compounds to give alcohols and organic radicals. These alcohols act as intermediates which are eventually degraded to low molecular weight organic compounds such as acetic acid.

Hydroxyl radicals play an important role in the reduction of inorganic carbon to end products. Formation of carbonate radicals results in the degradation of bicarbonate and carbonate ions (eq: 14 & 15). The carbonate radical further reacts with hydroxyl radical to release the end products (eq: 16) (Mak et al., 1997).

$$OH^{\bullet} + HCO_3^{-} \rightarrow {}^{\bullet}CO_3^{-} + H_2O \qquad \text{(eq: 14)}$$

$$OH^{\bullet} + CO3^{2-} \rightarrow {}^{\bullet}CO_3^{-} + OH^{-} \qquad \text{(eq: 15)}$$

$$OH^{\bullet} + {}^{\bullet}CO_3^{-} \rightarrow \text{Products} \qquad \text{(eq: 16)}$$

After the required oxidation of organic compounds is accomplished, the termination steps for the decomposition of radicals takes place towards the formation of end products (Bhargava et al., 2006; Mantzavinos et al., 1996).

$$R^{\bullet} + R^{\bullet} \rightarrow R - R \qquad \text{(eq: 17)}$$

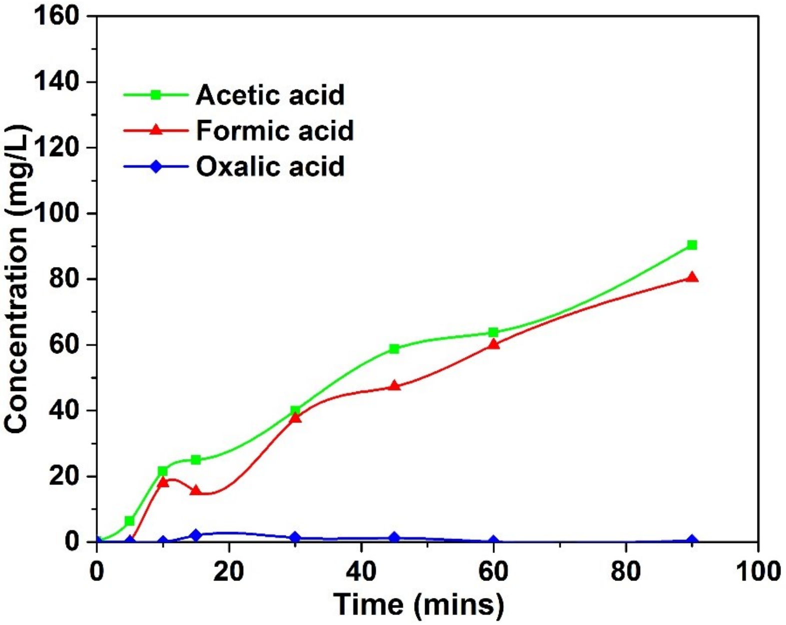
$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad \text{(eq: 18)}$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \qquad \text{(eq: 19)}$$

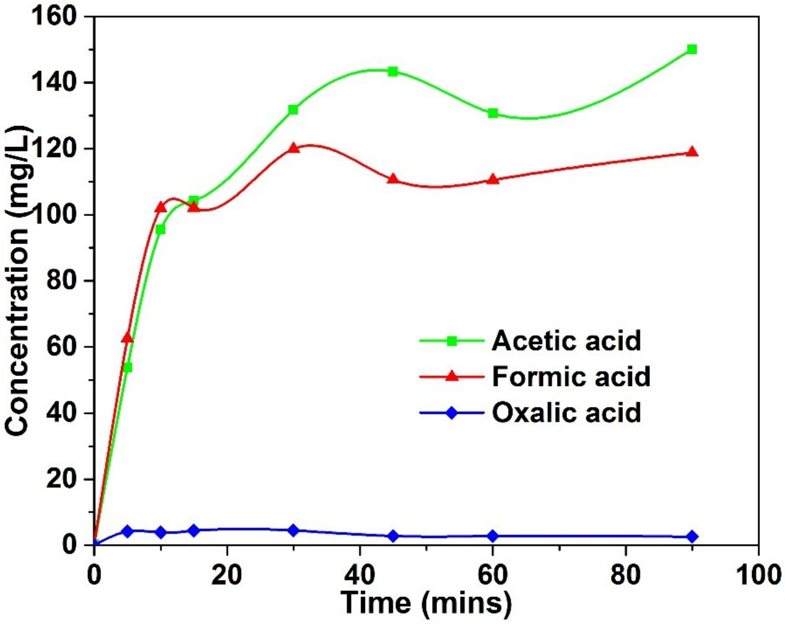
4.6.2 Dissolved Organic Acids

Presence of dissolved organic acids in recovered water after WAO were analyzed by ion chromatography and showed three organic acids including acetic, formic and oxalic acids. During 90mins of oxidation with WAO, increasing concentrations of acetic and formic acid were recorded along with oxidation time, however, oxalic acid concentrations were quite low (figure 4.11a). Addition of hydrogen peroxide showed similar trend with 66% (acetic acid) and 48% (formic acid) higher concentrations (figure 4.11b).

WAO$_{extended}$ also showed increasing concentrations of acetic and formic acids with residence time (figure 4.11c). Oxalic acid was not present at t=0 but was later found to be decreasing with oxidation time.



(a)



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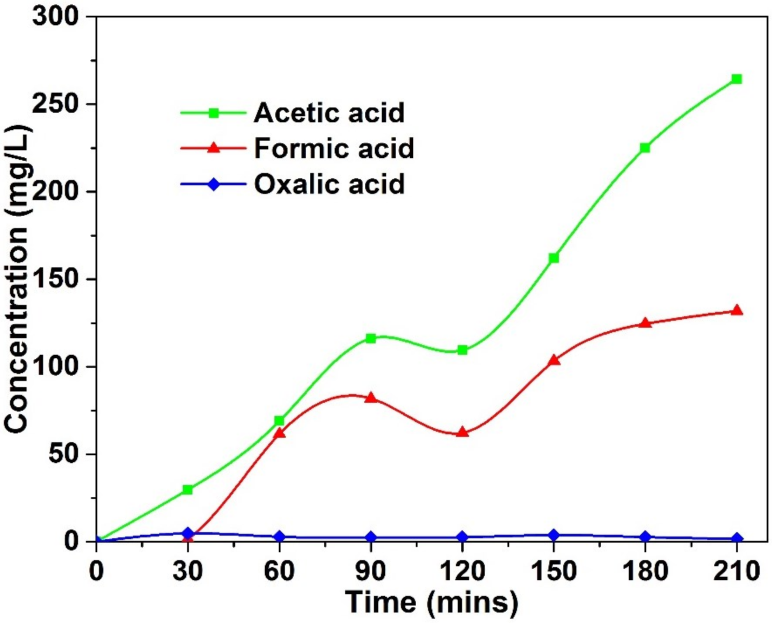


(c)

Figure 4.11: Concentration of dissolved organic acids in the recovered water after oxidation at 200^{0}C and 500psi with a) WAO for 90mins, b) WAPO for 90mins and c) WAO$_{extended}$ for 210 mins

Chromatographic analysis revealed presence of acetic and formic acid, which indicated that oxidation mechanism is rapid at the operated conditions and leads to low molecular weight carboxylic acids without the formation of any intermediates (with the exception of oxalic acid, which was detected at very low concentrations) during the oxidation pathway. The increasing concentration of these acids with residence time indicates the detachment and degradation of organic bitumen attached to the clay particles with oxidation time. The higher the temperature of oxidation, the more organic acids will be formed (Barlindhaug and Odegaard, 1996; Chung et al., 2009; Neyens and Baeyens, 2003). Acetic acid is the last stage of degradation before carbon dioxide and water. 66% and 48% higher concentrations of acetic and formic acids after WAPO proved that oxidation mechanism was enhanced and much faster in degrading the bitumen to dissolved form. Increasing the oxidation time with air from 90mins to 210mins increased the concentrations of acetic (192.6%) and formic acids (64.1%). The reason why acetic acid concentration was increasing at a faster rate than formic acid with increasing retention time could be due to the operating conditions. The pathway that leads to formation of formic acid might be slower than the pathway leading up to acetic acid. Acetic acid is quite resistant to degradation at temperatures below 300^0C during oxidation by WAO/WO/CWO and results in the last stages of oxidation (Debellefontaine et al., 1996; Laughlin et al., 1983; Luck, 1999; Mishra et al., 1995; Pujol et al., 1980; Randall and Knopp, 1980). Although, the presence of some catalytic properties in the MFT itself should be able to degrade the acetic acid to carbon dioxide and water without increasing the temperature to a very acute condition, but it seems, the naturally present catalyst in MFT are not strong enough to have any particular effect on the degradation of acetic acid and would need enhancement by adding potential catalysts manually. Incorporation of a homogeneous $CuSO_4$ results in effective WAO as it degrades acetic and formic acids as well (Shende and Mahajani, 1997).

Theoretically, the degradation pathway for organic compounds involves oxalic acid and maleic acid as well. However, in this study, there was no maleic acid detected in the treated effluent through ion chromatography while only minute quantities of oxalic acid were recorded with gradual reduction. A possible explanation for such results could be that the organic compounds are ring compounds attached to long chains of carbon atoms. A double bond is weaker than single bond, hence if a maleic acid (comprising of a double bond) was formed during some stage of oxidation pathway, it was broken down instantly due to the oxidation conditions provided. The reason behind having so small concentrations of oxalic acid could be that the oxidation conditions, along with the naturally occurring mineral catalysts in the MFT sample, were strong enough to oxidize the organic compounds faster through the degradation pathway towards mineralization, therefore, low concentrations of oxalic acids were formed and detected during oxidation and were found to be decreasing as oxidation proceeded (Shende and Mahajani, 1994). Formic acid has been detected as a major intermediate during the oxidation of oxalic acid (Shende and Levec, 1999).

Another possible explanation for no maleic acid or any other intermediate compound could be that after oxidation, the organic compounds are only degraded in their long carbon chains and not the ring itself. Therefore, the rings being nonpolar and insoluble are still intact but the chains are being degraded by oxidation into acetic acid and formic acid and low concentrations of oxalic acids. Consequently, the nonpolar rings float to the surface as froth and the degraded chains get dissolved in the water in the form of acetic acid and formic acid (figure 4.12). This leads to accumulation of acetic acid and formic acid in the extracted water as the last stage of oxidation for the allotted residence time. Less visible froth with the addition of H_2O_2 indicates the oxidation power of hydroxyl radicals to degrade the ring compounds as well at a rapid pace resulting in only low molecular weight carboxylic acids.

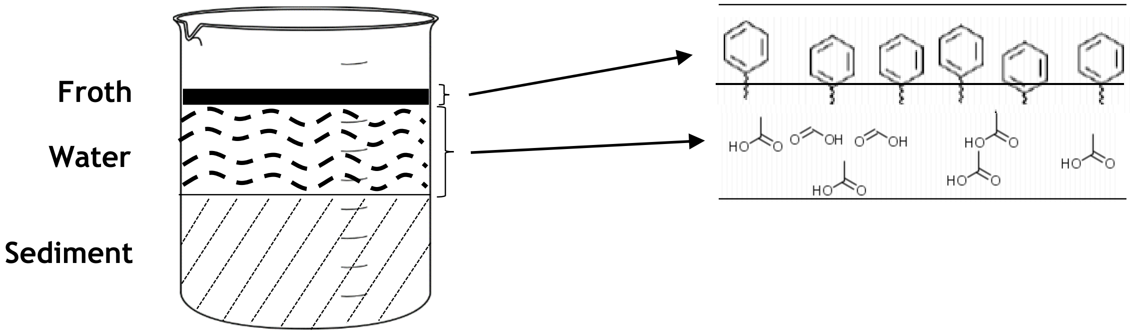


Figure 4.12: Enhancement of possible separation layers of treated MFT samples into froth, water and sediment with froth layer showing nonpolar organic rings and water layer showing dissolved acetic and formic acids

4.6.3 Dissolved Natural Organic Matter (NOM)

Comparison between total DOC and total carboxylic acids was conducted and the difference was estimated to be roughly around 35% after WAO for 90mins, 42.5% after addition of hydrogen peroxide and 23% after 210mins of oxidation with air (figure 4.13).

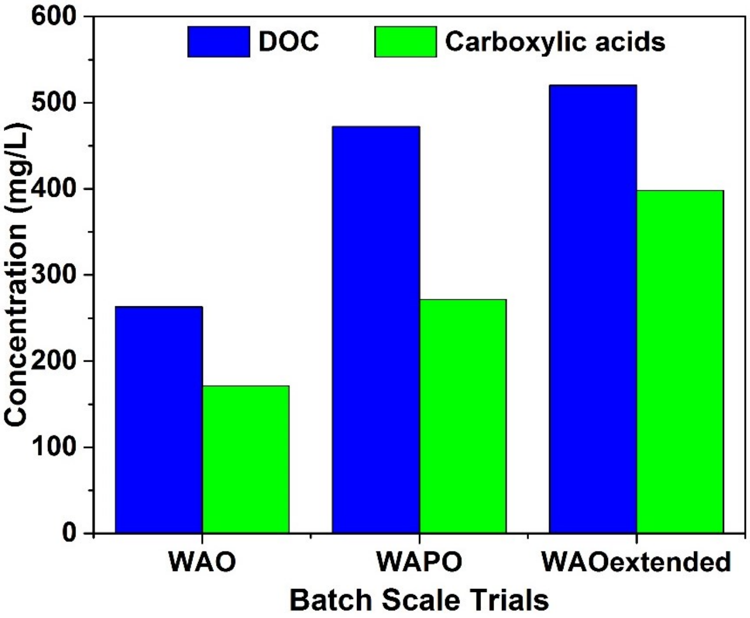
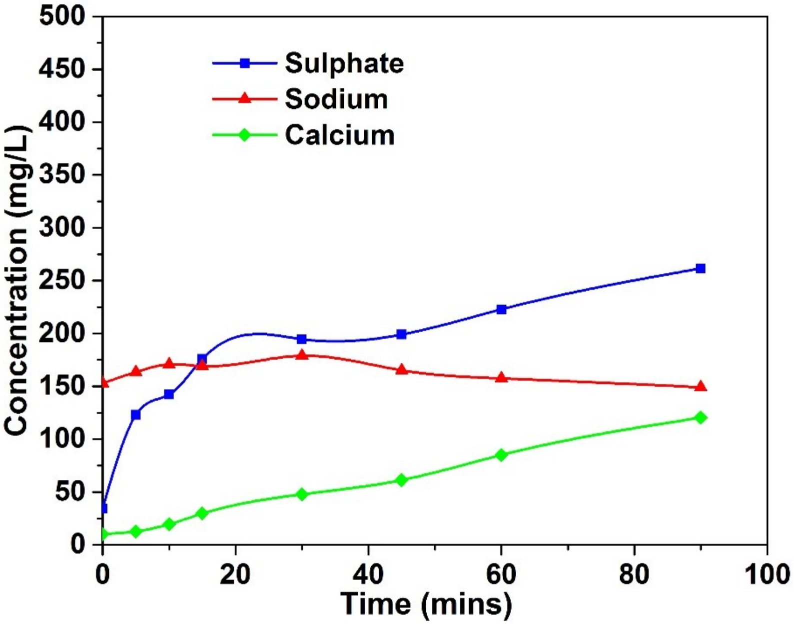


Figure 4.13: Comparison of Dissolved organic carbon and organic acids during different batch scale trials of WAO

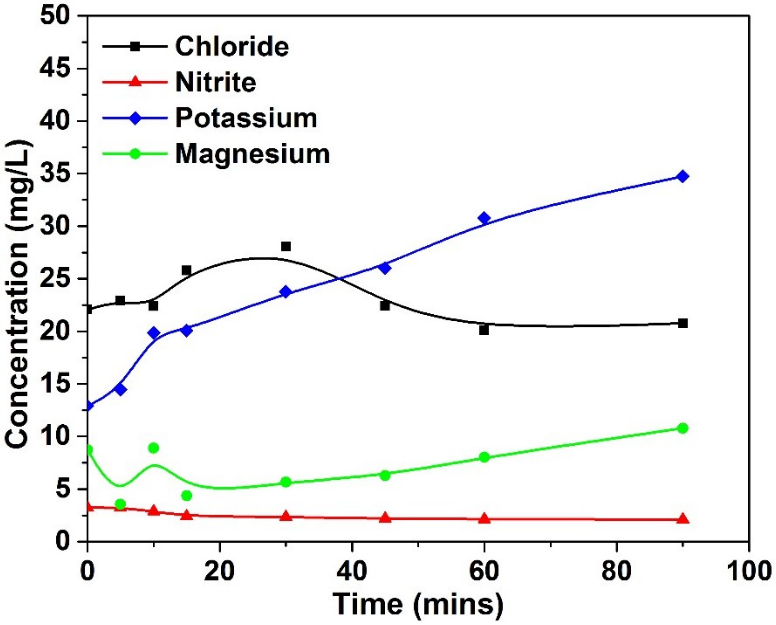
Increasing concentrations of DOC in water was due to the degradation and dissolution of residual bitumen, however, further analysis showed that majority of the DOC were low molecular weight carboxylic acids. The remaining proportion of dissolved compounds should be natural organic matter (NOM). All soils comprise of natural organic matter containing humic and fulvic substances. These NOMs are part of oil sand ores and are not easily separated from the soil particles after the extraction process (Darcovich et al., 1989) and could well be still present in MFT sticking to the clay particles. They are present as insoluble organic matter (IOM) (insoluble in organic solvents) and are associated with inorganic minerals in the oil sands (Majid et al., 1991). Majid and Sparks (1992) reported this organic matter to be the reason of incompressibility of oil sands tailings. After oxidation with WAO, these organic material get detached from the minerals, dissolved in water and were detected as low molecular weight end products with yellowish brown color of the recovered water. The proportion and intensity of color was much higher with the addition of hydrogen peroxide which could indicate either the NOM were detached and dissolved in water faster by the excess of hydroxyl radicals or the organic bitumen was degraded at a faster rate than dissolution of NOMs. Comparing the two WAO batch scales (90 and 210 mins), the proportion of NOM was reduced as the oxidation time increased indicating the conversion of majority of DOC to low molecular weight carboxylic acid, such as acetic acid.

4.6.4 Dissolved Ions

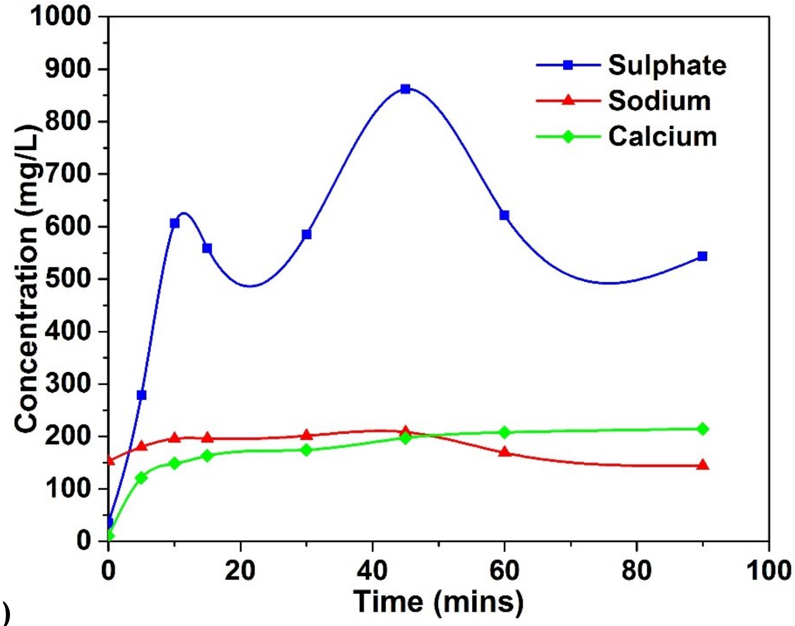
Ionic analysis conducted on the recovered water showed high concentrations of sulphate and calcium ions with increase of oxidation time for 90 mins of WAO. Addition of hydrogen peroxide further increased the concentrations of sulphate (100%) and calcium (>75%) during 90mins, whereas, sodium increased briefly in both trials and then declined (figure 4.14a & c). Compared to WAO (90 min), the concentration of sulphate increased by 126% when oxidation time was increased during $WAO_{extended}$ (210 min). Even higher increments are shown for calcium ions after 210mins while sodium was reduced by 30% (figure 4.14e). Chloride ion concentrations were reduced by 5.8% during WAO (90mins) and 51.1% (210 mins) after $WAO_{extended}$. A higher reduction of 43.7% (90mins) was observed during WAPO. Nitrite was found in low concentrations and was reduced by 34.6% (WAO) and 89.8% (WAPO). Both potassium and magnesium ions were increased during WAO and WAPO. Magnesium ions increased until 30mins of oxidation with the aid of H_2O_2 and declined thereafter (figure 4.14b & d). $WAO_{extended}$ showed higher reduction at 51% for chloride and 100% for nitrite, whereas, increasing concentrations of potassium and magnesium ions were recorded (figure 4.14f). Magnesium was fairly stable until 120 min and then increased linearly till 210 mins.


Sulphate
Sodium
Calcium
Concentration (mg/L)
0
50
100
150
200
250
300
350
400
450
500
Time (mins)
0
20
40
60
80
100

(a)

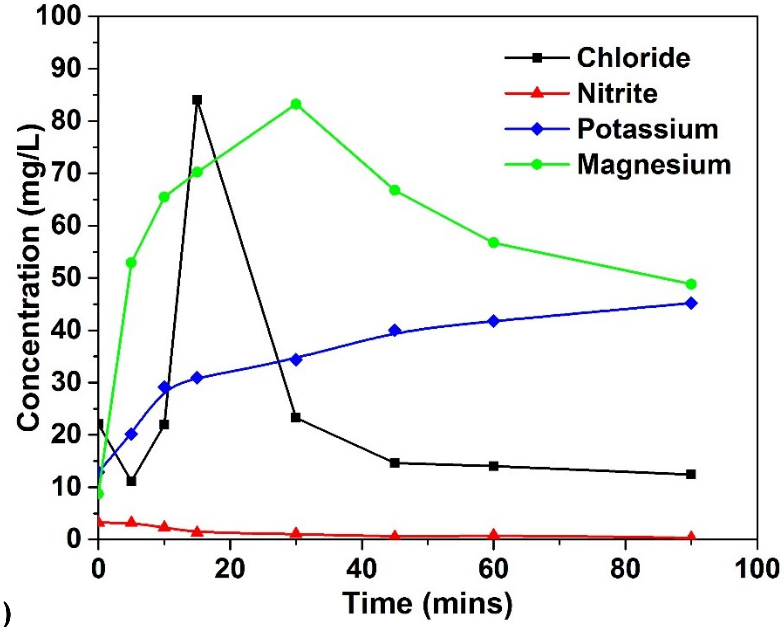

Chloride
Nitrite
Potassium
Magnesium
Concentration (mg/L)
0
5
10
15
20
25
30
35
40
45
50
Time (mins)
0
20
40
60
80
100

(b)



Concentration (mg/L)
Time (mins)
Sulphate
Sodium
Calcium
0
100
200
300
400
500
600
700
800
900
1000
0
20
40
60
80
100

(c)



Concentration (mg/L)
Time (mins)
Chloride
Nitrite
Potassium
Magnesium
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100

(d)

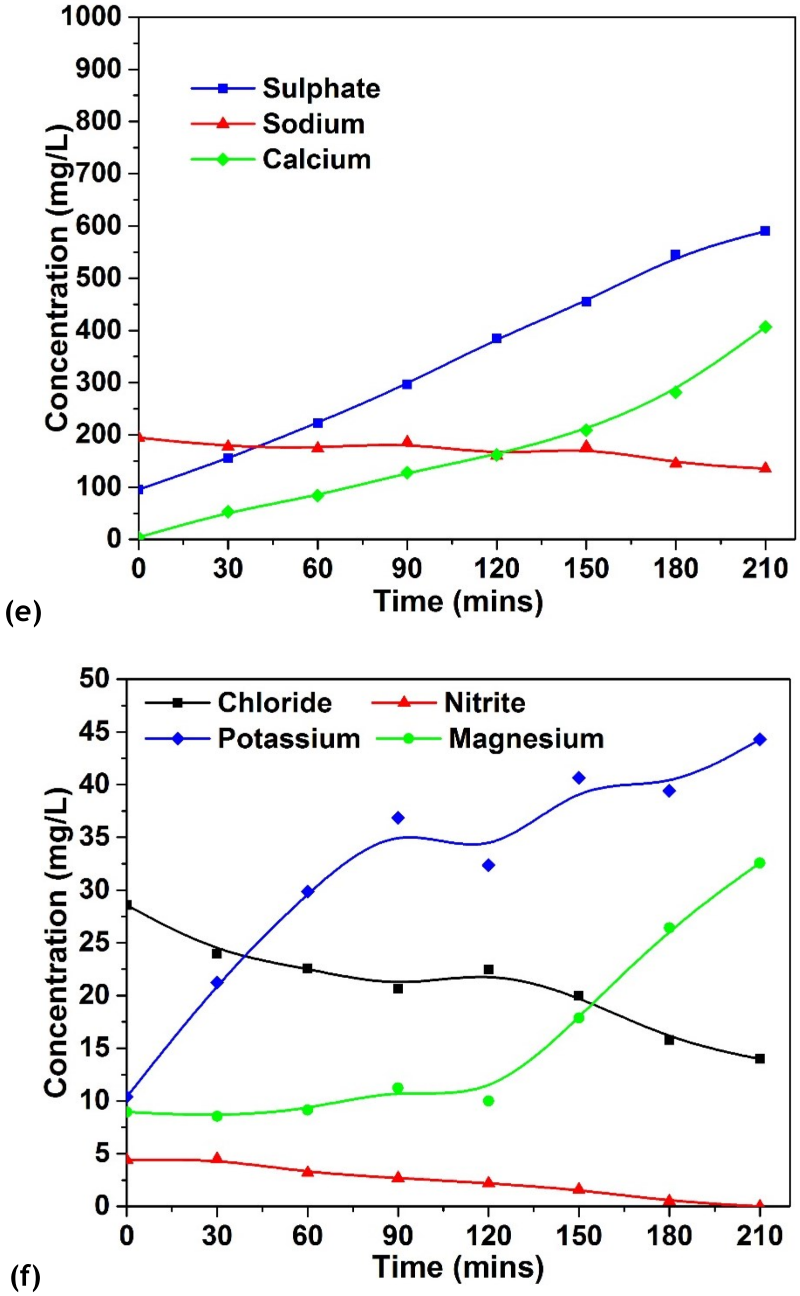


Figure 4.14: Concentrations of dissolved anions and cations after oxidation with, a) and b) WAO for 90mins, c) and d) WAPO for 90mins, e) and f) $WAO_{extended}$ for 210 mins

As the oil based emulsion in MFT broke down, increasing concentrations of sulphate and calcium ions were released in the recovered water as the retention time increased. Faster disintegration of emulsion was noticed with the addition of H_2O_2 as higher concentrations of sulphate and calcium ions compared to WAO were detected. During tailings treatment, calcium sulphate is added to enhance its hardness and salinity (Marr et al., 1996). Therefore, the increase in calcium and sulphate indicates the release of these ions initially trapped in the emulsion from the tailings treatment. Concentration of sodium and chloride ions appeared to be declining due to oxidation, indicating reduction in salinity. Presence of sodium is from the Clark hot water extraction process where NaOH is added during froth recovery. Calcium, magnesium and ferrous sulphate were also reported by Clark and Pasternack (1932) in bituminous sands from Northern Alberta. Bitumen is composed of hydrocarbons containing sulphur compounds and other inorganic ions such as chloride, nitrite, magnesium, calcium, etc (Allen, 2008; Jia, 2010; Mahdavi et al., 2012). Therefore, presence of these ions in the extracted water after oxidation are indication of organics degradation.

Low concentrations of nitrite were observed in recovered water after first few cycles of WAO but were completely removed after 210 min (100%) of $WAO_{extended}$. Addition of H_2O_2 provided >90% removal of nitrite ions in 90 min which indicated that faster precipitation of nitrite ions can be achieved with the aid of H_2O_2. Magnesium and potassium ions were also detected by ICP-MS. Surprisingly, concentration of potassium ions was more after conventional WAO while magnesium was observed to be higher than potassium when H_2O_2 was added. Increase in magnesium ions by H_2O_2 addition was due to the rapid release of ions from the breakage of the emulsion but sedimentation is observed later as the concentration declines. Concentration of potassium and magnesium ions were below 50 mg/L after $WAO_{extended}$ and WAPO which are not alarmingly high and can be precipitated easily. Clay minerals are composed of anions, cations and trace metals. Oxidation of these minerals caused the release of these potassium and magnesium ions into the exracted water. Less than 1mg/L concentrations of other cations and few trace metals were also detected in the extracted water (see table B1, B2 and B3 in Appendix B)

4.6.4.1 Conductivity of recovered water

Conductivity of the extracted water increased with increase in oxidation time. 63.7% (WAO) and 141.8% (WAPO) increase in conductivity was observed from the control samples after 90 min of oxidation (figure 4.15a). Increased oxidation time (WAO$_{\text{extended}}$) almost doubled the conductivity of the recovered water to 126.6% (figure 4.15b).

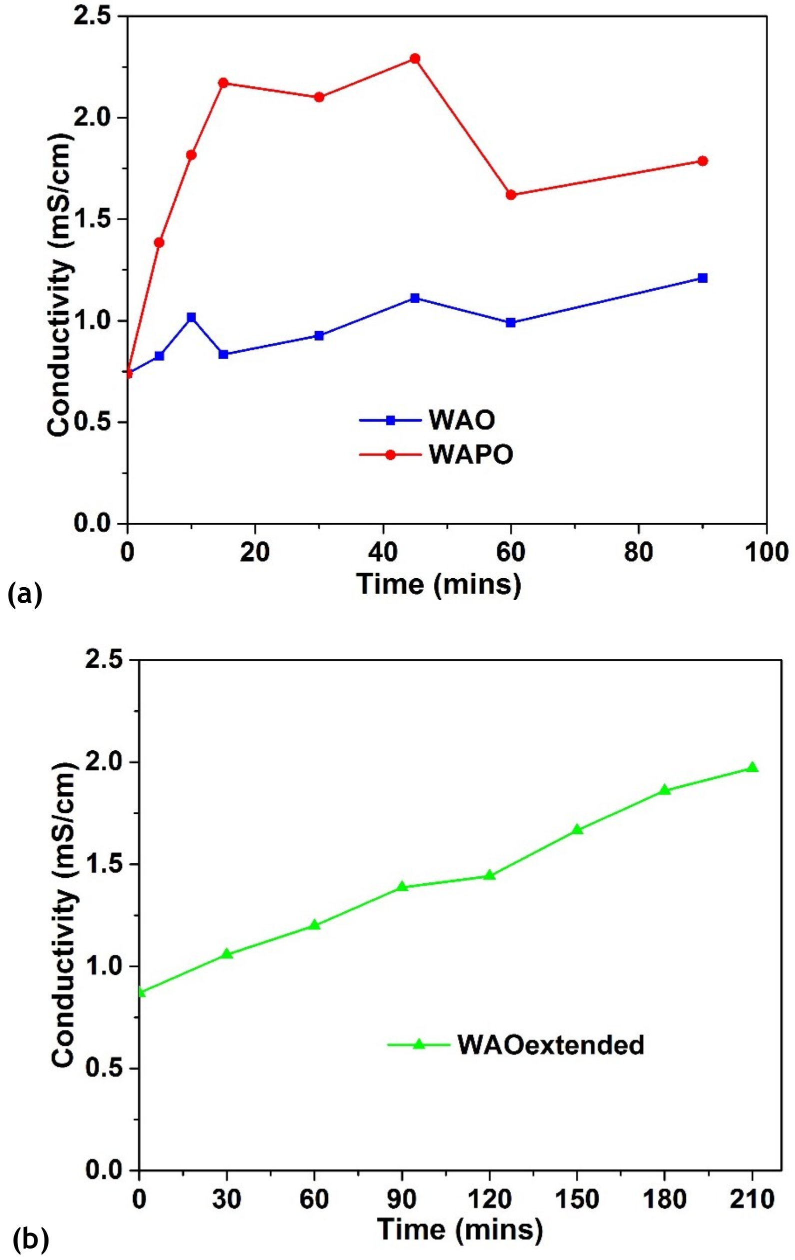
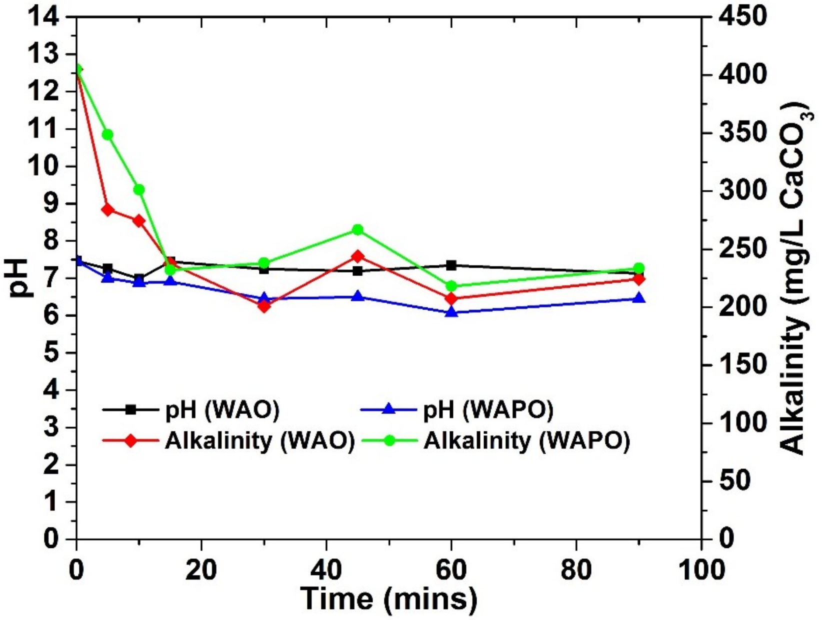


Figure 4.15: Conductivity of recovered water after a) WAO and WAPO for 90mins and b) WAO$_{\text{extended}}$ for 210 min

Conductivity is the ability of water to conduct electric current. The more ions present in the water, the higher the conductivity. This indicates the ionic strength of the extracted water to be high which indirectly shows the compression of the double layer of particles. The more charged ions in solution, the lower the double layer. It is observed that significant increases in sulphate, calcium and gradual increases in low concentrations of potassium and magnesium ions caused an increase in conductivity of the extracted water.

4.6.5 Effects on pH and Alkalinity

pH and alkalinity measurements were recorded before and after each cycle of oxidation. Changes in pH after oxidation were not significant. The pH dropped by only 4.4% after 90 min of WAO while 13.5% reduction was recorded with H_2O_2 addition (figure 4.16a). $WAO_{extended}$ resulted in 27.2% pH reduction (figure 4.16b). Alkalinity values were also reduced after WAO (90 & 210 min) and WAPO (90 min) to a certain degree.



(a)

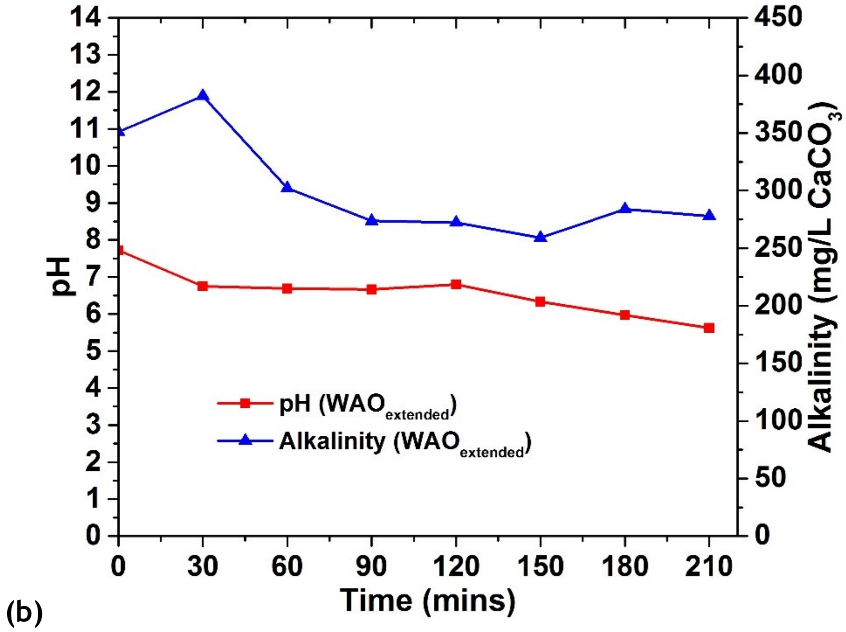


Figure 4.16: pH of 25% MFT samples after treatment and alkalinity measurements of recovered water after a) WAO and WAPO and b) $WAO_{extended}$

The pH of the sample before oxidation is close to neutral at around 7.70. Figure 4.16a shows that there is not much difference in pH change as the oxidation time increases showing high buffer capacity in the MFT samples. pH during WAPO is slightly lower compared to WAO which implies that oxidation with the addition of H_2O_2 aids in overcoming the buffer capacity to some extent. During $WAO_{extended}$, pH is reduced further after 120 mins of oxidation. The slow decrease in pH was recorded due to the formation of carboxylic acids as WAO end products. Moreover, the dissociation of water into hydrogen (H^+) and hydroxyl (OH^-) ions at high temperatures might result in the conversion of the OH^- into $OH^•$, leaving behind the protons and causing a decrease in pH towards the acidic side.

Alkalinity measurements were conducted to prove the diminishing of buffer capacity by oxidation. 90 min trial showed a significant reduction in alkalinity values initially from around 400 mg/L reduced to about 250 mg/L $CaCO_3$ within 15 mins after which the reduction slowed down. It is clear from figure 4.10c, that inorganic carbon was almost zero after 210 mins of oxidation during $WAO_{extended}$, indicating that buffer capacity should have been diminished. Since most of the carbonates and bicarbonates are being degraded by hydroxyl radicals, the buffer capacity is being reduced indicated by decrease in alkalinity.

Bhargava et al. (2006) explained the effects of pH on free radical intermediates and the reactions involved. Temperature, pH conditions and organic compounds in the sample undergoing oxidation govern the reactions involving free radicals, what kind of free radicals and their stability. Several free-radical reactions were postulated by the authors depending on the chemical state of the sample. It has been reported that alkaline conditions negatively affect the oxidizing ability of free-radical intermediates. In this study, the pH of the sample shifts from close to neutral side towards slightly acidic side, therefore, it is safe to say that the oxidizing strength of the free-radicals are not altered.

4.7 Proposed Kinetics for Wet Air Oxidation

It is hypothesized in this study that as oxygen diffuses into the liquid phase, it enters the emulsified MFT breaking the layer of bitumen and water and releasing the trapped fine clay particles. Due to continuous oxidation, the bitumen further breaks into smaller organic compounds until low molecular weight carboxylic acids are formed.

It has been reported previously in a number of studies that WAO reactions are based on the formation of free radical mechanism (Collado et al., 2010; Li et al., 1991; Mishra et al., 1995; Padoley et al., 2012; Tufano, 1993). Similarly, it is assumed that the oxidation process by WAO, in the present study, takes place by means of a free radical mechanism. The mechanism for WAO applied here can be expressed in a combination of series and parallel reactions as shown in figure 4.17.

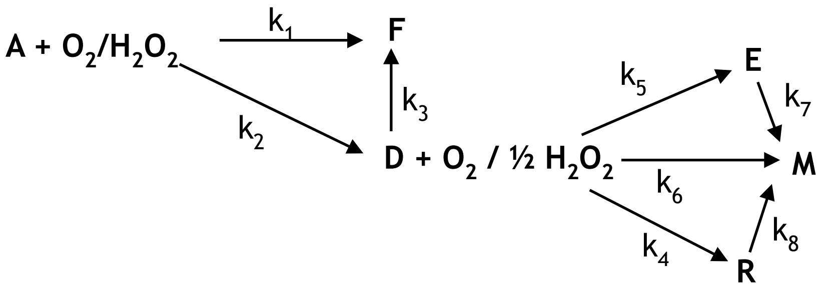


Figure 4.17: Generalized Proposed Kinetic model of WAO/WAPO

Initially, the MFT (A), containing the emulsion of oil-water-clay, is oxidized quickly through two parallel reactions. The first reaction ends in formation of froth (F), which is bitumen and nonpolar. It is insoluble and floats to the surface of the reactor. The froth, which is composed of hydrocarbon/crude oil, can be collected from the surface and used on a commercial scale downstream. The second reaction ends up in degradable compounds (D) after partial oxidation. These degradable compounds are soluble in water and get dissolved within. The degradable compounds (D) are further oxidized into three parallel reactions and a small amount of froth is again formed. One reaction ends in partially oxidized refractory products (R). These refractory products are low molecular weight carboxylic acids, specifically organic acids, which might not be able to fully oxidize under current operating conditions. The second reaction gives end products (E) which are probably natural organic matter (NOM). These are the difference of TOC and organic acids. The final reaction ends in complete oxidation of (D) leading to mineralization (M) with carbon dioxide and water. A similar type of mechanism was also reported by Bernal et al. (1999) for wet air oxidation of oil/greases wastes from ships. The reaction for the degradable compounds is a repeated process with froth forming in each cycle until all bitumen has been extracted, eventually leading to the formation of either end products (E), refractory products (R) or mineralization (M). The End products (E) can be further oxidized to mineralization, while, some refractory products are very resistant and would either take a long time to mineralize or higher temperatures. Therefore, because this last reaction takes a long time to take place, it is identified as the rate limiting step.

4.8 Particle Sedimentation

4.8.1 Organic Carbon in Particles

Hydrocarbon (HC) percentage in the consolidated solids/particles after $WAO_{extended}$ were evaluated by ignition at 900^0C. HC fractions interconnected with particles were observed to decrease with oxidation time (figure 4.18). Less than 30% hydrocarbons are left in the consolidated particles after 210 mins.

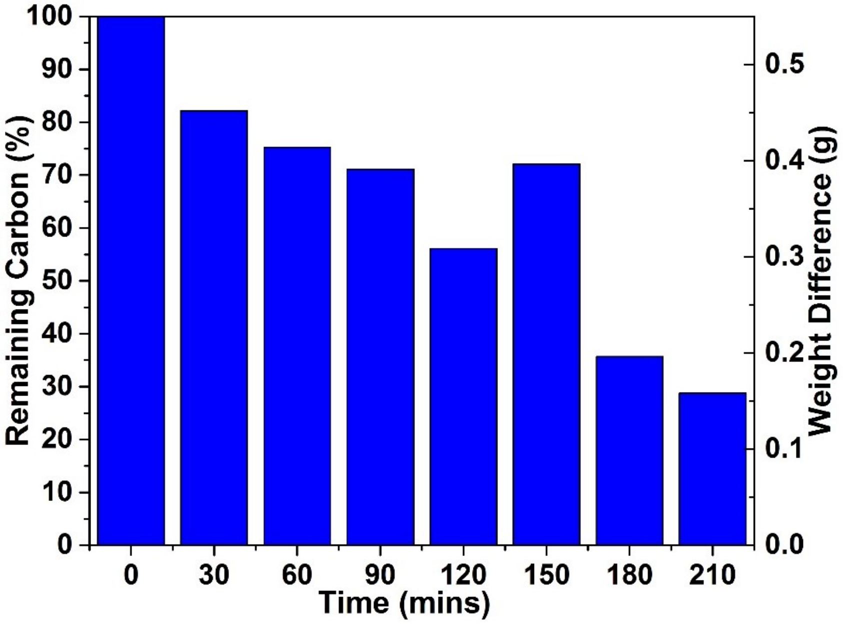


Figure 4.18: Percentage of Hydrocarbons remaining in the consolidated particles after WAOextended

Clay particles from oil sands tailings have hydrophobic surfaces that allow them the ability to form inter-particle bridging pattern with each other through residual bitumen causing a gel like formation that resists consolidation. These hydrophobic surfaces of clay particles are composed of humic substances (Majid et al., 1990; Majid and Ripmeester, 1990). Reduction in hydrocarbons from the particles means that residual bitumen bridging these particles together had been either extracted out as froth or dissolved in water as DOC by oxidation. This proves that the hydrophobic surface chemistry of these clay particles seem to have changed due to oxidation making them free of not only residual bitumen but NOMs as well, thereby allowing their sedimentation.

4.8.2 Mineral Composition after WAO

Particle size distribution showed majority of solids to be clay and silt particles (figure 4.19). Consolidated particles after treatment with the addition of peroxide gave sharper and/or reduced intensity peaks as compared to WAO under X-ray diffraction analysis (figure 4.20). High peaks were identified as Quartz, with smaller peaks belonging to kaolinite, muscovite and halite.

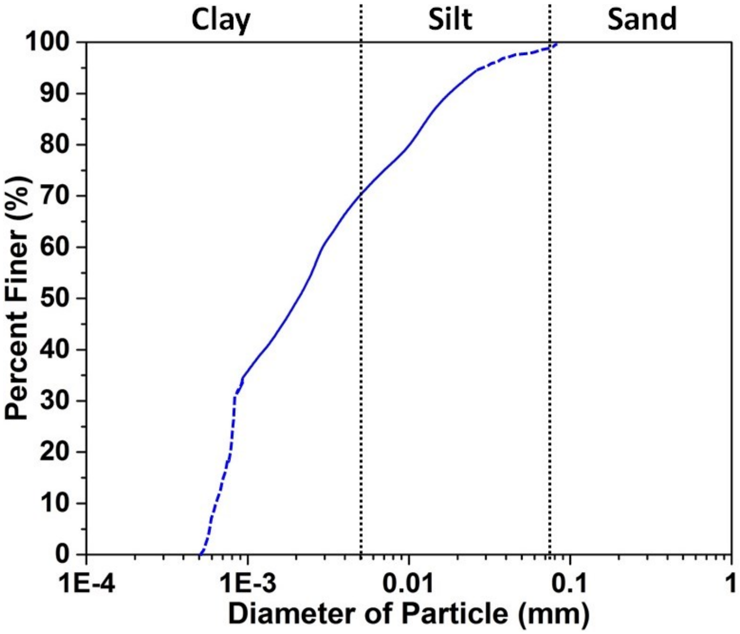


Figure 4.19: Hydrometer analysis for particle size distribution between clay, silt and sand

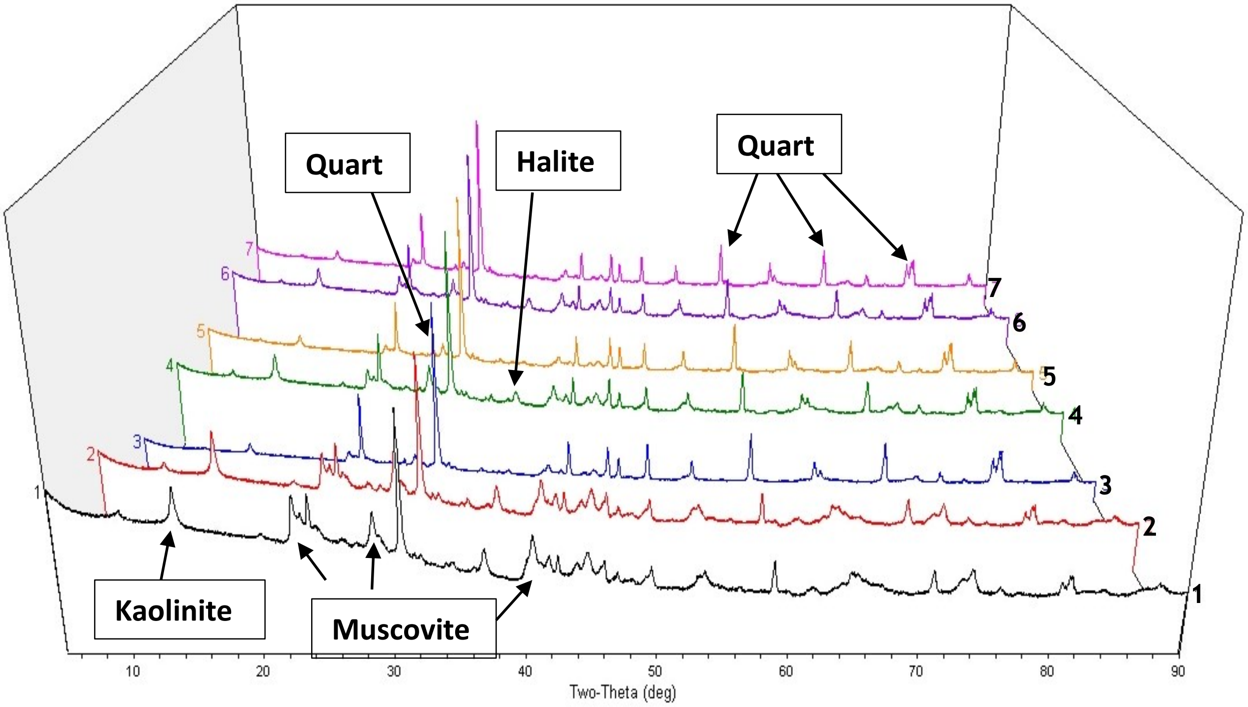


Figure 4.20: XRD analysis of Control (1), 5min WAO (2), 5min WAPO (3), 15min WAO (4), 15min WAPO (5), 30min WAO (6) and 30min WAPO (7), consolidated sediment after overnight drying at 110^{0}C

Too much hydrogen peroxide can cause a negative effect and lead to its inefficient consumption in the oxidation mechanism process by reacting with hydroxyl radicals and decreasing their accessibility to react with organic compounds (eq: 20). Moreover, excess hydrogen peroxide can also remove oxygen molecules from reaction medium resulting in less oxidant being available to initiate the degradation mechanism of organic compounds (eq: 21).

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad \text{(eq: 20)}$$

$$H_2O_2 + O_2 \rightarrow 2HO_2^{\bullet} \qquad \text{(eq: 21)}$$

Addition or presence of a suitable catalyst can overcome the inefficient use of hydrogen peroxide by reacting with the additional H_2O_2 and forming hydroxyl radicals (eq: 22) (Rivas et al., 1999).

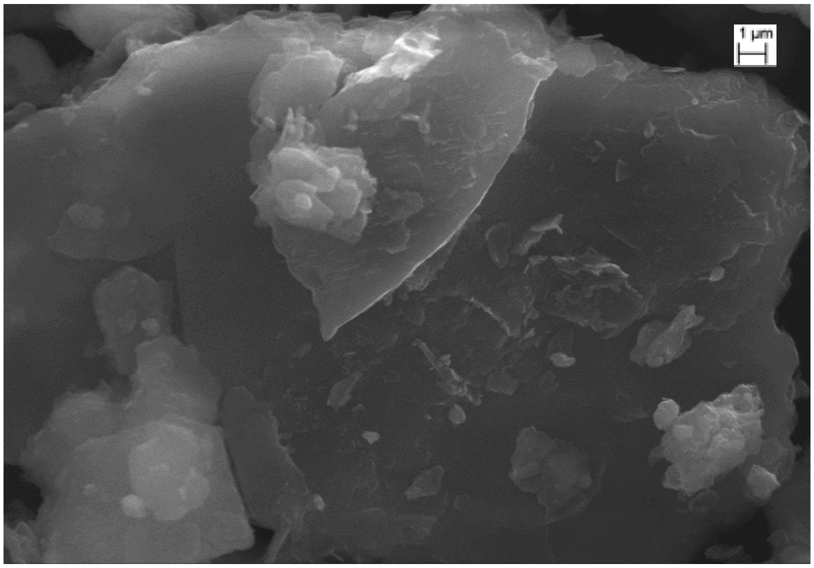
$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^{-} + OH^{\bullet} \qquad \text{(eq: 22)}$$

Presence of clay minerals could act as potential catalyst to reduce the negative use of hydrogen peroxide. Moreover, low concentrations of manganese were also detected which could also behave like catalysts (Jing et al., 2012).

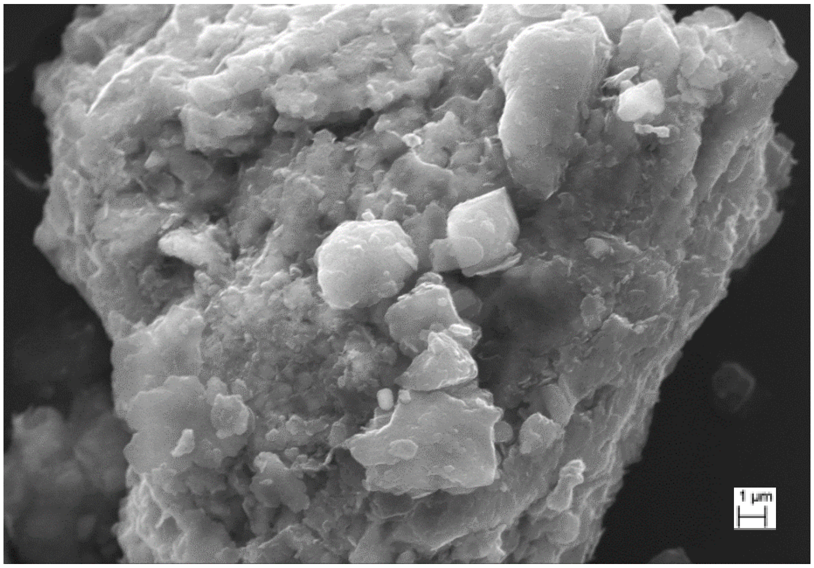
Majority of the clay in Athabasca oil sand is composed of Kaolinite 40 – 70% by weight, illite, also known as hydrous mica and muscovite (Chalaturnyk et al., 2002). MFT was reported to compose of 4% sand, 78% silt and 19% clay in which quartz dominated at 33.6% followed by kaolinite at 31.3% and 21.8% muscovite (Farkish and Fall, 2013). Proskin et al. (2010) had reported 85% kaolinite and 15% muscovite compositions in MFT. In this study, hydrometer analysis revealed around 70% clay, 29% silt and 1% sand particles. X-ray diffraction analysis showed that majority of the clay particles detected in the consolidated solids after WAO and WAPO were kaolinite and muscovite with small amounts of inorganic salts. Quartz was recorded as the major mineral present in the sediments after treatment (See Table B-4 in Appendix B). It is clear that the peaks of samples with the addition of peroxide are much sharper when compared to samples oxidized by air as well as control, which indicates the liberation of clay minerals from the emulsion and their faster sedimentation. The more clay particles released from the bitumen based emulsion, the sharper the peak gets. Moreover, some peaks were reduced in intensity with the addition of peroxide indicating the degradation of particles as well.

4.8.3 Surface Analysis of Particles

Surface analysis was conducted on the consolidated particles using scanning electron microscopy. Changes in surface area after WAO and WAPO were quite visible under 1µm. The control sample shows smooth particle surfaces as compared to uneven, rough surface of particles in the oxidized samples (figure 4.21).



(a)



(b)

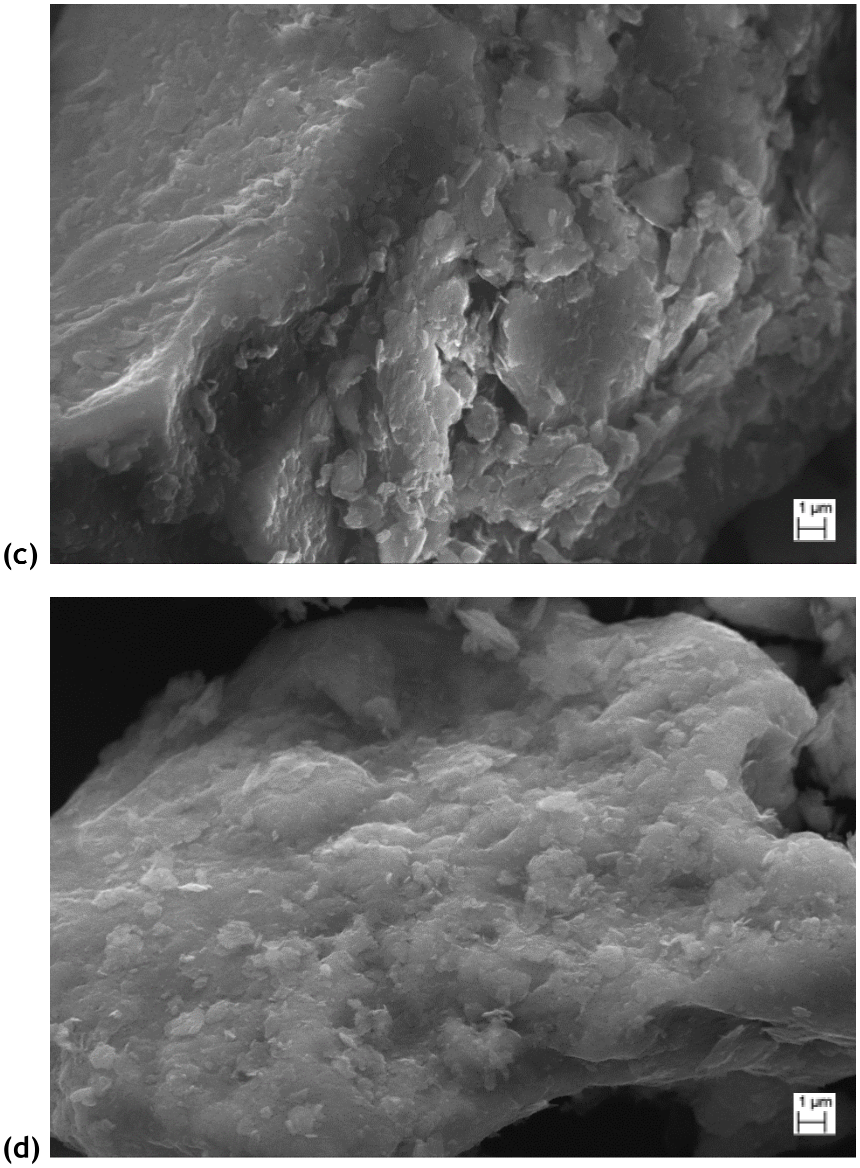


Figure 4.21: Scanning Electron Microscopic Images showing difference in surface area to volume ratio after oxidation of particles for a) Control, b) 30min WAO, c) 5min WAPO and d) 210min $\text{WAO}_{\text{extended}}$

As hydroxyl radicals are formed during oxidation, they constantly desorb the residual bitumen from the clay particles. The scavenging effect of these radicals on the surfaces of clay particles results in increased surface area. The more hydroxyl radicals are formed, the faster the rate of detachment of residual bitumen from the clay particles. Figure 4.21c shows surface area to be increased within 5mins of oxidation with WAPO compared to 30 and 210mins of longer oxidation by WAO (figure 4.21b & d). Clearly

WAPO had high concentrations of hydroxyl radicals from the beginning through the decomposition of H_2O_2, therefore, the rate of residual bitumen detachment by the radicals was quite rapid resulting in an increased surface area of the consolidated particles. The more the surface area is exposed, the more there is a possibility of improvement in the natural catalytic properties of the minerals present in the clay particles which could further enhance the oxidation mechanism.

4.8.4 Chemical Bonding on Particles

Further evidence of changes in surface chemistry were supported by XPS analysis. The control sample shows mostly saturated hydrocarbon bonds with C-C and C-H (figure 4.22). The intensity of these bonds increases after 30mins with the appearance of C=O bond. After 90mins, higher intensity of C-C and C-H bond is recorded again and ester bond is detected. Finally after 210mins, reduced intensity is seen for C-C and C-H bond while a slight increment of ester bond.

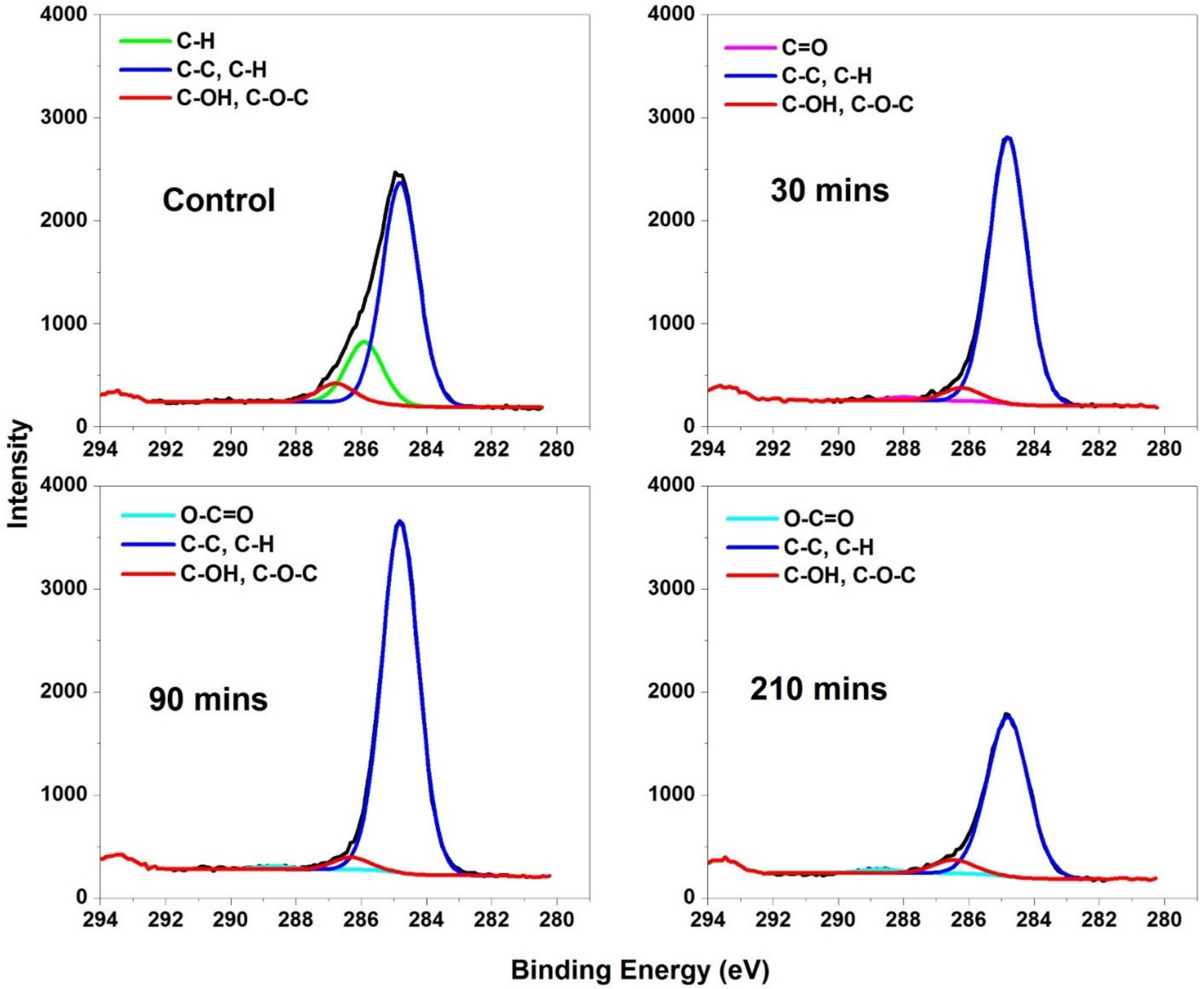
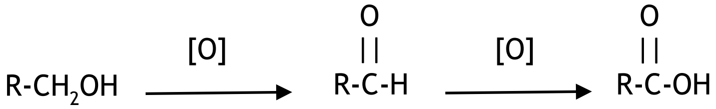


Figure 4.22: X-ray Photoelectron Spectrometer analysis of consolidated sediment after WAOextended displaying chemical bonding of carbon bonds

The C-C and C-H bonds are from bitumen froth made of alkanes. The C-OH (alcohols), C-O-C (ethers) bonds are water soluble but are initially trapped within the emulsion. As the oxidation takes place, the emulsion breaks, surface area is increased and exposes more alkanes out on the surface, therefore, an increase in intensity of the C-C, C-H peaks was observed after 30mins. A small amount of C=O bond (carbonyl) was observed as well in the 30min sample which were unsaturated hydrocarbons caused by oxidation. This could be the formation of carboxylic acids. It was assumed that initially, the trapped alcohols were converted to aldehydes by oxidation and reaction proceeded in further oxidation of aldehydes to carboxylic acids. This was due to the easier oxidation mechanism of aldehydes to carboxylic acid compared to alcohols to aldehydes, therefore, the reaction didn't stop at aldehyde formation but proceeded to the formation of carboxylic acids (Solomons and Fryhle, 2003). The overall reaction is shown in (eq: 23)

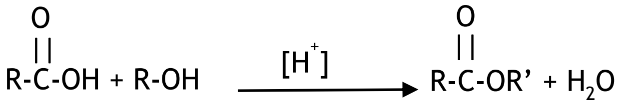


$$R\text{-}CH_2OH \xrightarrow{[O]} R\text{-}\overset{\overset{O}{||}}{C}\text{-}H \xrightarrow{[O]} R\text{-}\overset{\overset{O}{||}}{C}\text{-}OH$$

(eq: 23)

The 90 min sample showed a small appearance of O-C=O functional group (esters) with the intensity of alkanes increasing more compared to the control and 30 min sample, while the alcohols and ethers stayed constant. The formation of esters could be the carboxylate salts of carboxylic acids as it was observed previously that some cations had started to precipitate in the water. Thus, the carboxylic acids were converted to their respective carboxylate salts by oxidation.

Another possible reaction could be the acid-catalyzed esterification called the Fisher esterification (Chakraborti et al., 2009; Chen and Munot, 2005; Ishihara et al., 2005; Ishihara et al., 2002; Komura et al., 2008; Solomons and Fryhle, 2003; Srinivas et al., 2003). The free protons in the medium can catalyze the reaction of carboxylic acids with alcohols to form esters. A possible reaction is shown in (eq: 24)



$$R\text{-}\overset{\overset{O}{||}}{C}\text{-}OH + R\text{-}OH \xrightarrow{[H^+]} R\text{-}\overset{\overset{O}{||}}{C}\text{-}OR' + H_2O$$

(eq: 24)

Finally, after 210mins of oxidation, the intensity of alkanes has reduced down to below 2000 compared to about 3500 in the 90min sample indicating the oxidation of saturated hydrocarbons and their removal from particle surface. Moreover, the intensity of esters has increased in 210min sample compared to the 90min. This implies that more carboxylate salts and/or esters are being formed as oxidation proceeds converting the carboxylic acids into its respective salts as ions precipitate.

CHAPTER 5: CONCLUSION AND FUTURE WORK

Conclusion

In this project, unconventional oil based emulsions, such as mature fine tailings from Syncrude's oil sand tailings were treated using wet air oxidation. In this process, high temperature and pressure are used to generate free radicals for a rapid desorption of a non-polar substance from a particle surface. WAO conditions were initially tested using synthetic clay (Kaolin) emulsions prepared in the laboratory. Three batch scale studies were carried out on MFT emulsions including, WAO for 90mins, WAO with the addition of hydrogen peroxide for 90mins and WAO for 210 mins. A schematic figure for the complete WAO process conducted in this study is shown in figure 5.1.

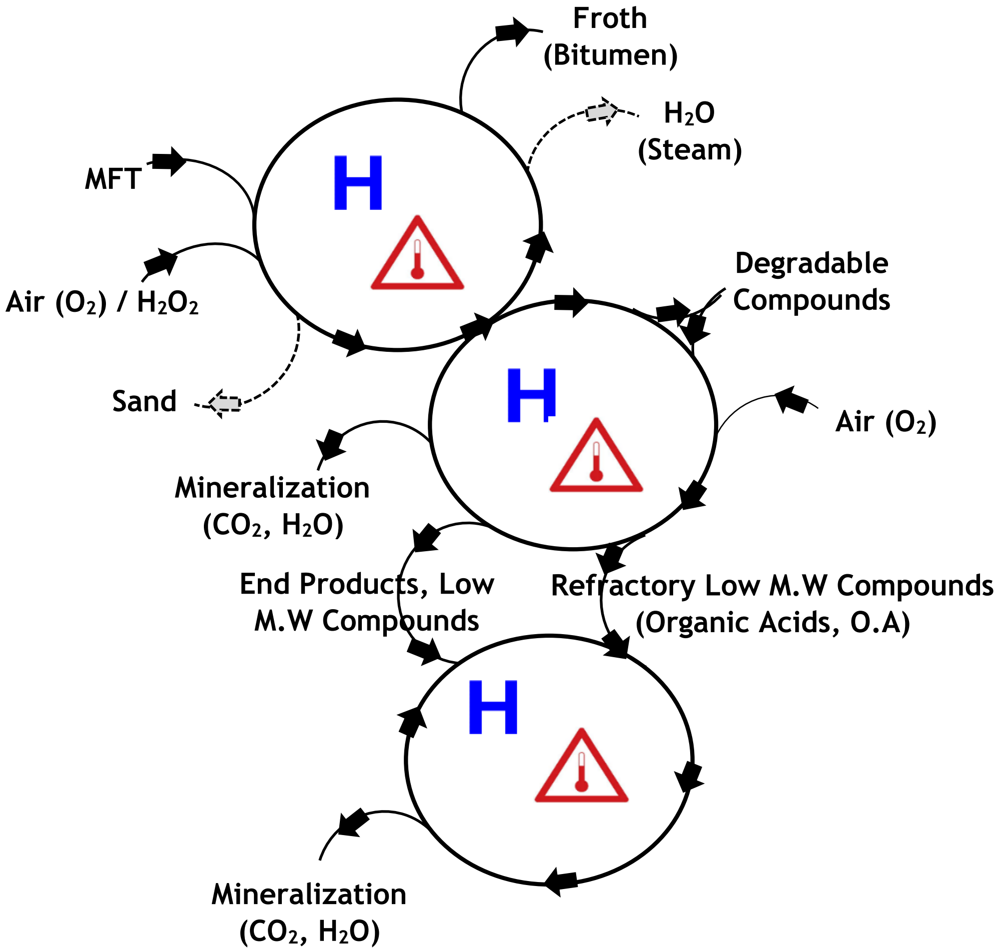


Figure 5.1: Schematic Pathway for WAO/WAPO Process

The following conclusions can be drawn from this study;

- 120^{0}C and 280-300 psi experimental conditions proved to be effective in breaking the synthetic clay emulsions. However, these conditions were not quite useful in the MFT emulsions.
- 200^{0}C and 500 psi internal pressure were sufficient to break the emulsion in MFT and separate bitumen, water and particles.
- Formation of hydroxyl radicals during oxidation resulted in detachment of residual bitumen from solid particles.
- Degradation of residual bitumen by hydroxyl radicals resulted in high DOC in recovered water.
- Addition of Hydrogen peroxide provided faster separation of particles and water, although most of the bitumen was degraded due to fast oxidation reactions by access of hydroxyl radicals. Further study needs to be done on addition of peroxide at a specific time.
- 5min residence time seemed a good option to recover froth compared with 30mins in order to reduce process time as there was not much difference between 5 and 30 min froth recovery. 5% (wt.) of froth was recovered by WAO in 210 mins.
- Recovered froth was assessed to be upgradable for commercial use.
- DOC increased with oxidation time due to degradation of organics while inorganic carbon was completely oxidized.
- Low molecular weight carboxylic acids were detected in the recovered water such as acetic and formic acid.
- More than 70-80% of the DOC was composed of low molecular weight carboxylic acids, which were environmentally safe and easily biodegradable. Although, the presence of some catalytic properties in the MFT itself should be able to degrade the acetic acid to carbon dioxide and water without increasing the temperature to a very harsh condition, but it seemed, the naturally present catalyst in MFT are not strong enough to have any particular effect on the degradation of acetic acid and would need enhancement by adding more effective catalysts manually. Remaining DOC was composed of NOMs from soil such as humic and/or fulvic substances.

- Recovered water can either be further treated to degrade the remaining DOC or can be allowed natural biodegradation as it contains mostly low molecular weight carboxylic acids and NOMs.
- Increased concentrations of sulphate and calcium were detected in the extracted water, which proved the degradation of organic bitumen. High sulphate in recovered water can be precipitated and recovered as elemental sulphur. Faster release of dissolved anions and cations can be accomplished with the aid of hydrogen peroxide to reduce process time.
- Consolidated particles showed reduced amount of bitumen, calcium and sulphate ions.
- SEM analysis showed surface area of particles to increase after oxidation which indicates the oxidation potential of hydroxyl radicals
- Carboxylate salts were detected through XPS analysis in the consolidated particles indicating their precipitation.
- The consolidated solids can be used in construction of roads or for land reclamation as the residual bitumen has been extracted out and is environmentally safe material.

Future Work

From the outcome of the results of WAO on MFT, following interesting objectives are suggested for future work;

- Development of a continuous WAO system that can be incorporated at the site of the tailings generation, therefore, to treat the tailings as they are produced, ultimately avoiding the formation of tailings pond.
- Studying the catalytic properties of the naturally present clay minerals found in the tailings
- Investigating the specific oxidation conditions of WAO (Temperature, Pressure, oxidation time) that results in the best and fastest water recovery from the tailings.
- Studying the feasibility of reusing the steam that is generated during WAO.
- Studying the treatment of fluids and wastes that are generated during hydraulic fracking of shale oil/gas extraction, using WAO and/or WAPO.

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APPENDICES

Appendix A: Sample Calculations

Organic Carbon Standard

According to the manual, dissolving 2.125g of Potassium Hydrogen Phthalate (KHP) in 1 liter of Milli-Q water (18.2 MΩ) will give a concentration of 1000 mgC/L of KHP Standard. Only 250 ml of the KHP standard was prepared. Therefore,

2.125 g KHP → 1000 mL

<u>0.53125 g</u> KHP → 250 mL

A concentration of 400 mgC/L of KHP standard is required for analysis. 25 mL volume is required for TOC vials, therefore, 50 mL of 400 mgC/L of KHP was prepared as follows

$M_1 \times V_1 = M_2 \times V_2$

1000 mgC/L x V1 = 400 mgC/L x 50 mL

$V_1 = \frac{400\frac{mgC}{L}.\ 50mL}{1000\ mgC/L}$ = 20 mL of 1000 mgC/L is dissolved in 30 mL of Milli-Q water (18.2 MΩ).

Inorganic Carbon Standard

According to the manual, dissolving 3.497 g of Sodium Hydrogen Carbonate (Na2HCO3) and 4.412 g of Sodium Carbonate (NaCO3) in 1 liter of Milli-Q water (18.2 MΩ) will give a concentration of 1000 mgC/L for TIC Standard. Only 250 ml of this standard was prepared. Therefore,

3.497 g Na_2HCO_3 → 1000 mL

<u>0.87425 g</u> Na_2HCO_3 → 250 mL

4.412 g $NaCO_3$ → 1000 mL

<u>1.103 g</u> $NaCO_3$ → 250 mL

A concentration of 400 mgC/L of TIC standard is required for analysis. 25 mL volume is required for the vials, therefore, 50 mL of 400 mgC/L of KHP was prepared as follows

$M_1 \times V_1 = M_2 \times V_2$

1000 mgC/L x V1 = 400 mgC/L x 50 mL

V1 = $\frac{400\frac{mgC}{L}\,.\,50mL}{1000\,mgC/L}$ = 20 mL of 1000 mgC/L is dissolved in 30 mL of Milli-Q water (18.2 MΩ).

Alkalinity Measurement

Alkalinity in mg/L $CaCO_3$ = $\frac{Nt\,.\,Vt\,.\,50000}{Vs}$

Where,

N_t = Normality of titrant used = 0.01992 N

V_t = Volume of titrant used

V_s = Volume of sample used = 5 mL

Example: V_t for 120min sample in trial two (210mins) was 1.367 mL. Therefore,

Alkalinity in mg/L $CaCO_3$ = $\frac{0.01992\,.\,1.367\,.\,50000}{5}$ = **272.3064** mg/L of $CaCO_3$

Alkalinity of every sample was calculated as shown above.

Conductivity Standard Calibration:

The conductivity value of the standard was adjusted according to the displayed temperature as follows: Adjustment factor of 1.912% for trial two samples (210mins). Recorded temperature was 23.7^{0}C for standard solution of 1000 μS/cm

- 25 – 23.7 = 1.3
- 1.3 x 0.01912 = 0.024856
- 0.024856 x 1000 = 24.856
- 1000 - 24.856 = **975.144**

Dry Weight and Volatile Hydrocarbon Calculation of Sediments

Sample calculation of 30 mL of 25% MFT

A = Weight of empty crucible = 32.1463 g

B = Weight of 25% MFT (30ml) + Crucible = 63.5978 g (Before Drying)

C = Weight of 25% MFT (30ml) + Crucible = 36.7004 g (After Drying at 110 ^{0}C)

D = Wet Weight of 25% MFT = B – A = 31.4515 g

E = Dry Weight of 25% MFT = C – A = 4.5541 g

Water Weight in 25% MFT = D – E = 26.8974 g

Weight % of Solids = $\frac{E}{D}\, x$ 100 = 14.48 %

F = Weight of 25% MFT (30ml) + Crucible = 35.8806 g (After Combustion at 900 ^{0}C)

G = Fixed Weight = F – A = 3.7343 g

H = Volatile Hydrocarbon Weight = E – G = 0.8198 g

Weight % of Volatile Hydrocarbons = $\frac{C-F}{C-A}\, x$ 100 = 18.00 %

Froth weight after 210mins WAO

150 mL of 25% MFT Sample was oxidized by WACO and a total of 1.1354 g of froth was collected after 210mins of oxidation.

30ml of 25% MFT contains = 4.75g dry wt. MFT

150ml of 25% MFT will contain = 23.75g dry wt. MFT

$$\frac{\mathbf{1.1354}\boldsymbol{g\ Froth}}{\mathbf{23.75}\boldsymbol{g\ dry}\ \mathbf{25\%}\ \boldsymbol{MFT}}\ \boldsymbol{x}\ \mathbf{100\%} = \mathbf{4.78\%} \sim \mathbf{5.00\%}$$

Appendix B: Raw Data

Table B1: Cations and Trace Metal Composition (mg/L) in Recovered Water after WAO for 90 min

Element	Control	5min	10min	15min	30min	45min	60min	90min
B	0.881	3.075	3.282	3.545	3.977	4.120	4.018	3.996
Al	0.241	0.155	0.000	0.000	0.000	0.000	0.000	0.000
Si	3.654	12.674	14.690	17.221	30.738	32.660	34.566	42.337
V	0.036	0.173	0.056	0.082	0.103	0.034	0.051	0.017
Cr	0.002	0.002	0.000	0.000	0.004	0.013	0.006	0.001
Mn	0.033	0.05	0.478	0.158	0.189	1.117	0.657	1.952
Fe	0.069	0.040	0.016	0.137	0.101	0.575	0.158	0.300
Ni 58	0.000	0.002	0.006	0.021	0.009	0.008	0.008	0.010
Co	0.000	0.000	0.011	0.007	0.000	0.001	0.000	0.001
Ni 60	0.000	0.004	0.012	0.023	0.009	0.010	0008	0.012
Zn 64	0.035	0.013	0.031	0.031	0.039	0.032	0.045	0.020
Zn 66	0.035	0.011	0.028	0.034	0.038	0.030	0.052	0.016
As	0.004	0.008	0.004	0.002	0.004	0.004	0.006	0.006
Rb 85	0.019	0.027	0.044	0.037	0.045	0.060	0.050	0.077
Sr 86	0.420	0.385	0.907	0.547	0.734	1.166	0.945	1.527
Rb 87	0.019	0.024	0.044	0.036	0.040	0.061	0.049	0.090
Sr 88	0.350	0.330	0.785	0.470	0.646	1.012	0.8203	1.240
Mo 95	0.190	0.260	0.189	0.247	0.257	0.117	0.150	0.084
Mo 96	0.197	0.260	0.191	0.245	0.256	0.116	0.147	0.086
Ba	0.107	0.077	0.166	0.056	0.113	0.180	0.150	0.239

Table B2: Cations and Trace Metal Composition in Recovered Water after WAPO for 90 min

Element	Control	5min	10min	15min	30min	45min	60min	90min
B	0.881	2.121	3.729	3.974	3.974	5.397	3.380	4.065
Al	0.241	0.000	0.000	0.000	0.056	0.000	0.000	0.000
Si	3.654	7.425	13.009	11.704	31.584	33.265	50.674	49.247
V	0.036	0.0156	0.000	0.000	0.003	0.001	0.000	0.001
Cr	0.002	0.013	0.005	0.004	0.014	0.001	0.012	0.006
Mn	0.033	2.712	4.221	4.114	8.503	9.944	9.203	8.789
Fe	0.069	0.442	0.626	0.461	0.560	0.840	0.906	0.664
Ni 58	0.000	0.060	0.044	0.075	0.177	0.045	0.073	0.041
Co	0.000	0.029	0.013	0.025	0.058	0.016	0.035	0.019
Ni 60	0.000	0.065	0.042	0.080	0.190	0.054	0.083	0.055
Zn 64	0.035	0.022	0.037	0.048	0.070	0.044	0.048	0.032
Zn 66	0.035	0.018	0.029	0.031	0.058	0.031	0.042	0.023
As	0.004	0.000	0.000	0.002	0.001	0.003	0.002	0.002
Rb 85	0.019	0.076	0.094	0.095	0.098	0.110	0.113	0.118
Sr 86	0.420	1.306	1.729	1.632	1.743	2.633	1.578	1.774
Rb 87	0.019	0.079	0.097	0.098	0.097	0.133	0.129	0.114
Sr 88	0.350	1.130	1.466	1.401	1.666	2.143	1.357	1.585
Mo 95	0.190	0.022	0.044	0.024	0.019	0.019	0.012	0.015
Mo 96	0.197	0.024	0.044	0.025	0.020	0.020	0.012	0.015
Ba	0.107	0.133	0.120	0.115	0.176	0.179	0.220	0.248

Table B3: Cations and Trace Metal Composition (mg/L) in Recovered Water after WAO for 210 min

Element	Control	30min	60min	90min	120min	150min	180min	210min
B	1.330	3.864	4.427	4.824	4.728	5.528	4.900	4.789
Al	0.017	0.000	0.000	0.000	0.000	0.000	0.000	0.169
Si	4.034	33.948	38.781	34.574	41.997	49.354	57.350	76.981
V	0.002	0.061	0.034	0.019	0.010	0.016	0.000	0.000
Cr	0.007	0.007	0.007	0.005	0.007	0.080	0.001	0.004
Mn	0.043	0.796	1.528	2.414	2.137	4.119	10.037	13.410
Fe	0.113	0.160	0.325	0.354	6.074	2.622	0.762	1.849
Ni 58	0.005	0.011	0.009	0.009	0.003	0.019	0.040	0.069
Co	0.001	0.001	0.001	0.001	0.000	0.003	0.012	0.028
Ni 60	0.002	0.010	0.012	0.017	0.006	0.022	0.052	0.075
Zn 64	0.013	0.029	0.027	0.025	0.021	0.032	0.038	0.057
Zn 66	0.015	0.029	0.030	0.018	0.020	0.031	0.027	0.051
As	0.004	0.006	0.006	0.004	0.007	0.006	0.004	0.004
Rb 85	0.016	0.043	0.060	0.064	0.068	0.085	0.083	0.101
Sr 86	0.413	1.005	1.271	1.609	1.762	2.055	2.452	2.710
Rb 87	0.015	0.044	0.066	0.069	0.071	0.093	0.094	0.123
Sr 88	0.350	0.876	1.026	1.368	1.484	1.714	2.044	2.318
Mo 95	0.274	0.220	0.133	0.097	0.084	0.062	0.022	0.010
Mo 96	0.286	0.223	0.132	0.101	0.086	0.065	0.021	0.009
Ba	0.099	0.124	0.242	0.272	0.249	0.295	0.227	0.247

Table B4: Mineral Composition of Consolidated Sediment after WAO and WAPO

Control	5min I WAO	15min I WAO	30min I WAO	5min I WAPO	15min I WAPO	30min I WAPO	Control	90 min WAO	210 min WAO
Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2	Quartz - SiO_2
	Magnesite - $Mg(CO_3)$	Magnesite - $Mg(CO_3)$	Magnesite - $Mg(CO_3)$		Magnesite - $Mg(CO_3)$		Magnesite - $Mg(CO_3)$		
Halite - NaCl	Halite - NaCl	Halite - NaCl	Halite - NaCl	Halite - NaCl	Halite - NaCl		Halite - NaCl	Halite - NaCl	
		Calcite - $CaCO_3$	Calcite - $CaCO_3$		Calcite - $CaCO_3$		Calcite - $CaCO_3$		
Kaolinite - $Al_4(OH)_8(Si_4O_{10})$	Kaolinite - $Al_4(OH)_8(Si_4O_{10})$	Kaolinite - $Al_4(OH)_8(Si_4O_{10})$	Kaolinite - $Al_2(Si_2O_5(OH)_4)$	Kaolinite - $Al_4(OH)_8(Si_4O_{10})$	Kaolinite - $Al_4(OH)_8(Si_4O_{10})$	Kaolinite - $Al_4(OH)_8(Si_4O_{10})$	Kaolinite - $Al_2(Si_2O_5(OH)_4)$	Kaolinite - $Al_4(OH)_8(Si_4O_{10})$	Kaolinite - $Al_2Si_2O_5(OH)_4$
Muscovite - $(K_{0.93}Na_{0.052})(Al_{1.718}Fe_{0.149}Mg_{0.099}Ti_{0.02}Mn_{0.02})(Si_{3.055}Al_{0.945})$	Muscovite-2M1 - $KAl_2(Si_3Al)O_{10}(OH,F)_2$	Muscovite-2M1 - $KAl_2(Si_3Al)O_{10}(OH,F)_2$	Muscovite-2M1 - $KAl_2(Si,Al)_4O_{10}(OH)_2$	Muscovite - $(K_{0.93}Na_{0.052})(Al_{1.718}Fe_{0.149}Mg_{0.099}Ti_{0.02}Mn_{0.02})(Si_{3.055}Al_{0.945})$	Muscovite - $(K_{0.93}Na_{0.052})(Al_{1.718}Fe_{0.149}Mg_{0.099}Ti_{0.02}Mn_{0.02})(Si_{3.055}Al_{0.945})$	Muscovite - $(K_{0.93}Na_{0.052})(Al_{1.718}Fe_{0.149}Mg_{0.099}Ti_{0.02}Mn_{0.02})(Si_{3.055}Al_{0.945})$	Muscovite-2M1 - $KAl_2(Si,Al)_4O_{10}(OH)_2$	Muscovite - $KAl_2(AlSi_3O_{10})(OH)_2$	Muscovite-2M1 - $KAl_2(Si,Al)_4O_{10}(OH)_2$
								Anhydrite - $CaSO_4$	Rutile - TiO_2