University of Alberta

Degradation of Naphthenic Acids in Athabasca Oil Sands Process-Affected Water Using Ozone

by

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ABSTRACT

In order to determine the degradation of Naphthenic Acids (NAs) in oil sands process-affected water (OSPW), a series of semi-batch ozonation experiments have been conducted resulting in a maximum reduction of NAs greater than 99%. Compared to the high NAs removal, the reduction of both COD and DOC was much lower under the same conditions. Following ozone treatment of about 80 mg/L, the $cBOD_5$ and $cBOD_5$/COD tripled as compared to original OSPW measurements, suggesting ozone-treated OSPW has a higher biodegradability. The ozone treatment also detoxified the OSPW; with a utilized ozone dose of approximately 100 mg/L, the treated OSPW showed no toxicity using the Mircotox® bioassay. Additionally, the OSPW, treated using a coke/water slurry process, was found to be non-toxic with a utilized ozone dose of about 20 mg/L. The results obtained during this study show the great potential ozone treatment may offer as a possible water treatment application for oil sands water treatment and management.

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LIST OF ABBREVIATIONS AND SYMBOLS

AENV	Alberta Environment
AOP	advanced oxidation process
APCI	atmospheric pressure chemical ionization
bbls/d	barrels per day
BOD	biochemical oxygen demand
CI	chemical ionization
COD	chemical oxygen demand
CSS	cyclic steam stimulation
DCM	dichloromethane
DFO	Department of Fisheries and Oceans-Canada
DSW	dyke seepage water
EC_{20}	20% effective concentration
EI	electron ionization
ERCB	Energy Resources Conservation Board
ESI	electrospray ionization
FAB	fast atom bombardment
FT-IR	Fourier transformed-infrared spectroscopy
GC	gas chromatography
HPLC	high-performance liquid chromatography
IFN	instream flow needs
MF	microfiltration
MS	mass spectrometry
NAs	naphthenic acids
NF	nanofiltration
NTP	normal temperature and pressure
ODF	ozone-demand free

OH ·	hydroxyl radicals
OSPW	oil sands process-affected water
RO	reverse osmosis
SAGD	steam-assisted gravity drainage
TDS	total dissolved solid
THAI	toe-to-heal air injection
TPH	total petroleum hydrocarbon
TS	total solid
UF	ultrafiltration
WIP	west in-pit pond

1. INTRODUCTION

1.1. Background Information

Oil sands deposits in Alberta and Saskatchewan contain more than 170 billion barrels of recoverable oil in the form of bitumen. This ranks Canada second in terms of crude oil reserves, with 15% of world reserves, after Saudi Arabia (Government of Alberta 2008). In contrast to the conventional oil process where oil is found in pools from which it is pumped, the oil sands reserves are held within a matrix of sands and clays (6 to 15 wt % hydrocarbon). In the surface oil sands operations, this sand/clay "ore" is mined and then processed using a hot water extraction method to extract bitumen from oil sands. The extraction process uses large volumes of water, approx. two barrels of water per barrel of bitumen recovered. The large amount of resulting aqueous tailings suspensions are deposited into settling basins, where the process-affected waters are released for recycle back in the process. The demand for steam, utilities and upgrading activities requires the import of fresh water at rates of about three barrels of fresh water per barrel of synthetic oil product (Allen 2008). Surface mine oil sands development in the Athabasca region became commercial in the late 1960's, with more than three billion barrels of oil being produced over the ensuing years. A by-product of this has been the build up of inventory of oil sands process-affected water (OSPW) in the region by current operators. Currently it is estimated that with present usage and technologies, the total volume of fluid tailings contained within settling ponds will exceed 1 billion m^3 by 2015, assuming no new tailing management technologies to be applied (Houlihan et al, 2008). As a result, a great deal of concern regarding the potential effects of seepage from these containment systems has been raised. In an effort to reduce OSPW inventory and mitigate any potential impact on the regional aquatic environment, new water treatment technologies will be required. The goal of these technologies are to support industry needs in the following areas:

- Using OSPW as a replacement for water imported for utilities and upgrading needs;
- Recycling OSPW at higher rates while ensuring the quality still allows the bitumen extraction process without compromising efficiencies;
- Returning OSPW, treated to meet water quality requirements for safe discharge, to the receiving environment with no detrimental effects.

In general, the composition of OSPW has different properties than the surface waters of the region. OSPW contains salts associated with leaching from the oil sands during the extraction process (i.e. NaOH), as well as the addition of ions from process chemicals (i.e. Na^+ and SO_4^{2-} from caustic, acid and gypsum amendments), and upgrading activities (i.e. SO_4^{2-}, NH_4^+). In addition to inorganic ions, OSPW also contains elevated levels of dissolved organics, mainly petroleum acids, known as naphthenic acids (NAs). While metals and un-recovered hydrocarbons are associated with the mineral fraction (clays and sand) of the oil sands tailings, their presence in the water phase as priority metals or PAHs' has been shown to be negligible. Most of the treatment options that have been applied to OSPW have been directed at removing dissolved solids (desalination) and the dissolved organic constituents, namely the NAs. In this study, the focus will be on treatment options directed at the removal of the NAs and assessing how it can facilitate water management in oil sands operations.

NAs, which are natural low molecular weight surfactants released from bitumen during extraction of oil sands ore, as well as ammonia, have been shown to contribute most of the acute toxicity of OSPW. Currently, bitumen extraction is based on a caustic hot water digestion, which results in the NAs being released into the resulting OSPW. The concentrations of NAs in the OSPW are elevated, ranging from 40 to 120 mg/L, depending on ore quality, extraction processes, and the age of OSPW (Quagraine et al. 2005).

NAs are closely related cyclic and alicyclic aliphatic carboxylic acids, with the general chemical formula $C_nH_{2n+z}O_2$, where *n* indicates the carbon number and *Z* is zero or a negative, even integer that specifies the hydrogen deficiency resulting from the ring formation (e.g. Z=0, no rings, Z=-2, 1 ring, Z=-4, 2 rings etc.).

NAs were proven to be the main components responsible for the toxicity of OSPW to aquatic organisms (MacKinnon and Boerge 1986, Holowenko et al. 2002). This is supported by the fact that the acute lethality of OSPW to rainbow trout and water fleas was significantly reduced when the NAs in the OSPW were removed (MacKinnon 1986). Degradation of NAs in OSPW was observed when the NAs native to tailings water were incubated with microorganisms under aerobic, laboratory condition (Scott et al. 2005). While natural biodegradation rates for the concentration of NAs appear to be slow, the reduction of acute toxicity of OSPW is rapid and seems to be associated with the relative decrease of smaller naphthenic acids ($C_{13\text{-}16}$) with lower Z values (Holowenko et al. 2002). NAs with multiple rings appear to have relatively lower acute toxicity and are more resistant to microbial degradation than lower molecular weight NAs with less ring structure (Lo et al. 2006). However, there are concerns regarding the potential for chronic toxicity resulting from the more resistant fraction of NAs. Considering the resistance to natural degradation of the NAs contributing chronic toxicity, and the time required for natural degradation of NAs in OSPW, the treatment of OSPW, specifically the removal of NAs, becomes a critical issue for further water discharge and environmental acceptability.

Peng et al. (2004) applied nano-filtration to water softening and removal of NAs, resulting in a reduction of more than 95% for both hardness and NAs. The sorption of NAs from OSPW was evaluated on a laboratory scale; NAs with carbon numbers ranging from 13 to 17 showed preferential sorption on organic-rich soils (Janfada et al. 2006). Marr et al (1996) showed good NAs removal using commercial activated carbon. Zubot (2009) has described the application of petroleum coke as a treatment option for removal of NAs from OSPW, with extraction efficiencies in the 85 to 95% range. Preliminary studies by Scott et al (2008) have demonstrated that oxidation processes were effective at removing NAs, but efficiencies and rates were not included in that study. The use of carbon as an adsorbent and advanced oxidation for organic matter degradation can both provide treatments targeted at the removal of the NAs from OSPW, without having to handle the salts associated with such waters.

Ozone can effectively oxidize organic pollutants in both municipal and industrial wastewater because of its high oxidation ability (Zhou and Smith 2001; Ikehata 2007). It can potentially be applied to OSPW, in which it will oxidize the NAs, which as stated above, contribute most to its reported toxicity. However, until this work was initialized in 2007, there has not been any reported research related to the application of ozone to the degradation or removal of NAs from OSPW.

1.2. Study Objectives

The reaction of ozone with organic matters in water can be classified into three categories (Beltran 2003):

- oxidation-reduction reactions
- dipolar cyclo-addition reactions
- belectrophilic substitution reactions

In the reactions of ozone (O_3) with organic matter, there is a preference to attack unsaturated organic compounds (e.g. aromatics, olefinic groups) rather than saturated aliphatics. Much of the published research reported on O_3

treatment in aqueous systems has focused on degradation of higher molecular weight natural products such as humic acids (Miao and Tao 2008), fulvic acids (Volk et al. 1997) and other unsaturated organic acids (Gehringer et al. 2006). The use of ozone to degrade organics in OSPW, where the major dissolved organic constituent will be the low molecular weight carboxylic acids (naphthenic acid group), should be a good candidate for treatment. Understanding the effectiveness, rates, dosages and efficiency is required prior to suggesting that the ozone oxidation approach is a potential useful tool for oil sands' application in meeting water treatment needs. The economics of such a treatment will depend on the consumption of O_3 by the constituents of the OSPW, as well as any interferences affecting efficiency.

The objectives of this study include:

1) Assessing the effectiveness of ozone for degrading NAs in OSPW:
    - Examine whether O_3 will remove NAs in OSPW;
    - Determine whether the source of OSPW will affects treatment efficiency; and
    - Determine the degree that O_3 degrades NAs in OSPW.
2) Developing a bench-scale ozonation system to assess and optimize ozone treatment: batch and semi-batch modes;
3) Developing analytical methods to assess the performance of ozonation, including dosage and consumption; and
4) Assessing the impacts of the suspended solids and pH of OSPW on the performance of ozonation.

2. LITERATURE REVIEW

2.1. Oil Sands Industry Overview

There are three major oil sands deposits in northern Alberta, covering over 140,000 km^2, with huge reserves of potentially recoverable oil using either *in-situ* or surface mining methods (Government of Alberta 2009 a). Of the three oil sands areas, the Athabasca region contains the largest bitumen deposit, accounting for more than 80% of the bitumen reserves (See Table 2.1). To date, all surface mining operations are located in the Athabasca region. This is due to the fact that oil sands reserves located within the McMurray Formation region are shallow enough to allow economic recovery using surface mining. As of March 31, 2009, 602 km^2 have been disturbed by commercial mining operations. This includes open pit mines, tailings and overburden deposits, and fluid containment ponds (Government of Alberta 2009 a).

Figure 2.1 Three major oil sands deposits in the northern Alberta: Athabasca, Peace River and Cold Lake (Government of Alberta 2006).

Oil deposits are present as bitumen saturated sands and commonly referred to as oil sands (or ore, when mined), which are mixtures of sands, clay, water and bitumen (averaging about 10 to 12 wt%). The bitumen is a thick, sticky form of crude oil with high viscosity, such that it will not flow unless being heated or diluted with lighter hydrocarbons to overcome its high viscosity.

Compared to conventional oil, oil sands are more costly and energy consumptive to recover and process. After mining the ore, it must be processed to separate the bitumen from the sands, upgraded and then converted into synthetic crude oil. However, with the high global demand for oil and improving extraction techniques, the oil sands industry in Alberta is expanding dramatically. The average bitumen production in Alberta was about 1.3 million barrels per day (bbls/d) in 2007, with the projected production doubling by 2017 (AENV 2008).

Table 2.1 Initial in-place volume of crude bitumen

Oil Sands Area	Barrels ($\times 10^6$ bbls)	Percentage of in-place volumes
Athabasca	1,370	80.9
Cold Lake	195	11.5
Peace River	129	7.6
Total	1,694	100

2.2. Oil sands processes

2.2.1. Mining and Extraction

Depending on the depth of the oil sands deposits, either surface mining or *in-situ* recovery has been used for bitumen recovery. Among the total 170 billion barrels of recoverable reserves, approximately 80% are recoverable through *in-situ* production, with less than 20% recoverable by surface mining.

However, the Canadian Association of Petroleum Production (CAPP) projects bitumen production from mining will be comparable with that from in-situ production over the next decade (CAPP, 2010). In the Athabasca region, surface mining has been used by Suncor Energy Inc., Syncrude Canada Ltd., Albian Sands Energy Inc. and Canadian Natural Resources Ltd. The newly announced Imperial Oil Ltd.'s Kearl project is also a surface mining project. The surface mining techniques are normally applied to the recovery of oil sands ores located near the surface (less than 75 meters). In the surface mining process, the oil sands deposits are mined, moved to a central transfer station using the trucks and shovels, and then sent to the extraction plant by a conveyor belt or by hydro-transport (hydraulic slurry transport). Oil sands ores are then mixed with hot water and a process aid (e.g. caustic soda) to "extract" the bitumen from oil sands. About two tonnes of oil sands ore must be processed to generate a barrel of oil, with roughly 90% of the bitumen being recovered from sands using the hot water extraction method.

Figure 2.2 shows a flowchart of the simplified oil sands processes currently in use - consisting of the four major processes: mining, extraction, utilities and upgrading. Extraction is the process of separating the bitumen from the oil sands ore after they are mined. A hot water extraction process is used for bitumen extraction for the surface mining project. In this process, steam and caustic soda are mixed with oil sands ores to produce slurry that can be pumped through a pipeline to the separation vessels. Hot water is added to reduce the viscosity of the bitumen, and the caustic soda aids the separation process. (Note, when hydro-transport technology is used, extraction takes place during transportation in the pipelines). In the large primary separation vessels, the slurry settles into layers of, from top to bottom, bitumen froth, middlings (comprising bitumen, clay and water) and sands. The bitumen froth is skimmed off of the top and is sent to froth treatment, and the middlings are fed into a secondary separation vessel to undergo more separation to recover the remaining bitumen. The tailings, consisting of sands, clay and water, are pumped through pipelines to tailings ponds. In these ponds, the coarser solids fractions quickly settle out to form beaches and dykes. The fines and water are contained within the pond, where subsequent densification processes lead to the release of process-affected waters as the suspensions de-water.

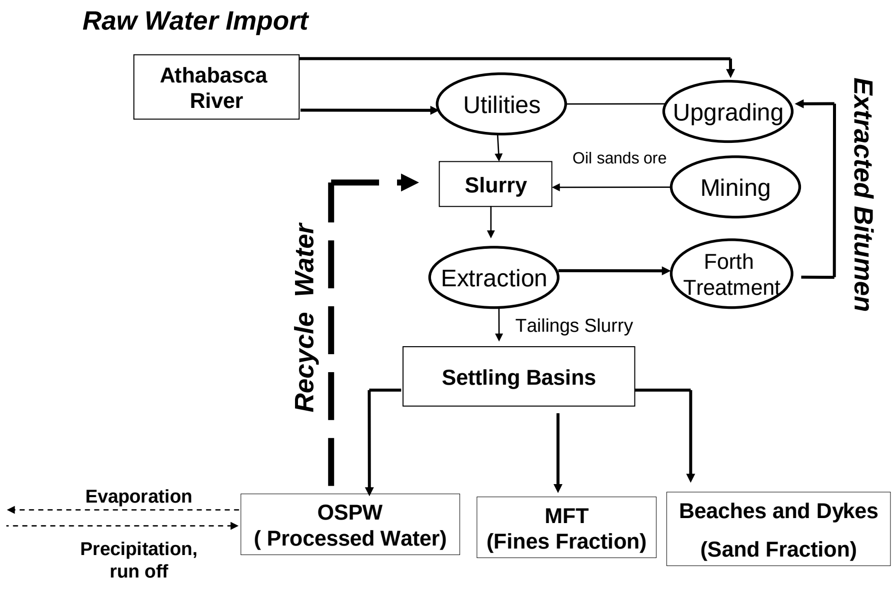


Figure 2.2 Simplified flow diagram for a minable oil sands operation

For oil sands deposits deeper than 75 meters, economics dictates that *in-situ* methods must be employed. In this approach, steam, solvents or thermal energy are applied to make the bitumen more mobile so it is mobilized and pumped to the surface. The cyclic steam stimulation (CSS) and steam-assisted gravity drainage (SAGD) are two commercially used *in-situ* recovery technologies. In CSS, the steam is first injected to the oil formation through a vertical well, the oil formation is soaked and heated for months, and bitumen is pumped until the production slows. Then the new steam cycle is started again. CSS is the main *in-situ* technology used in Cold Lake because it works best in the formations with good horizontal permeability. SAGD is more widely used in the operations in Athabasca region near Fort McMurray. With SAGD, a pair of horizontal wells are drilled into the formation - one on top of the another. The steam is injected to the upper well, heating and softening the oil sands to allow the bitumen to drain to the lower well where it can be recovered to the surface. With regard to *in-situ* oil sands extraction, several other technologies are being developed to inject solvent, carbon dioxide or air into the oil sands formation instead of steam. This will lower the steam requirement and make the recovery processes more economically viable. Such an approach would reduce the large water requirements needed for this operation. For example, in Toe-to-Heal Air Injection (THAI^{TM}), air is injected via a vertical well to the deposit, and heat generated in a controlled combustion process lowers the viscosity of the bitumen.

2.2.2. Bitumen Cleaning: Froth Treatment

The froth treatment facility uses centrifuges or other separating devices to separate bitumen from water, sands and clay in the extraction froth. This froth is produced when bitumen extracted from the oil sands is modified to a froth product by the addition of diluents (naphtha or paraffin). Diluents are added to reduce bitumen’s high viscosity and to speed up the separation of cleaned product prior to being upgraded. The diluents are recovered and bitumen is transported to the storage tank or an upgrading facility. While the clay, water and sands are pumped to tailings ponds.

2.2.3. Upgrading

The process of upgrading involves breaking the long, heavy molecules of bitumen into smaller molecules and removing impurities including sulfur and nitrogen. In this process, water is used to produce the steam that is, in turn, used to produce hydrogen required for hydrocracking and hydro-desulphurization. For oil sands mining operators with on-site upgraders, this water represents a major portion of freshwater that is withdrawn from the Athabasca River.

2.2.4. Utilities

Most of the water required by utilities will also be imported from off-lease sources such as the Athabasca River. Within the utilities, the required fresh water is used for several different processes including: as boiler-feed water for steam generation after deionization, as cooling tower waters, and as gland water for pump sealing. The water quality of the Athabasca River is more acceptable than recycled water from settling basins for plant needs such as; upgrading, consumable/potable water, and water-based fire suppression systems.

2.3. Environmental Challenges –Water Issues

Oil sands mining operators are facing many environmental challenges in terms of water, air, land and wildlife. In respect to water, major issues will be associated with the availability of fresh water, accumulation of oil sands process-affected water and the related environmental impacts.

2.3.1. Availability of fresh water

Reliable fresh water resources are important for the oil sands industry due to the large of amount fresh water consumed throughout the oil sands processes. As discussed above, fresh water is required for, among other things, make-up water for extraction, steam generation, upgrading demands and utilities. In the Athabasca region, the major sources of the fresh water for both surface mining and *in-situ* oil sands operations is the Athabasca River, its tributaries and the ground water from local aquifers. Water will also be added to the site water inventory through the collection of site run-off waters (net precipitation) and connate water associated with the oil sands ore (formation water in pores of ore released during extraction process). The Athabasca River has been used as the primary fresh water supply because of its predictable water quality and quantity and reasonable distances from the operation plants. However, regulatory changes directed towards optimization of the instream flow needs (IFN) to maintain the health of the river will affect the timing of this supply (AENV and DFO 2007).

The Athabasca River is the second largest river in Alberta with a length of 1,400 km and a drainage area of 138,412 km^2 (Science Outreach 2008). The annual river discharge of the Athabasca River averages about 700 m^3/s (during the period from 1957 to 2004) or 23 billion m^3 / year of water flows (Lunn 2008). The total allocation of water to the Oil & Gas industry from the Athabasca River was 2.2% of the natural flow, and the actual water use is much less than the allocation (Lunn 2008). However, the daily discharge of the Athabasca River between 1957 to 2002 averaged about 859 m^3/s in summer (April to November) and 177 m^3/s in winter (December to March) because the Athabasca River is ice-covered for 5 to 6 months per year (Marriott 2004). Compared to the non-seasonal oil sands operations, tremendous seasonal variation in flow rate of the Athabasca River, in addition to the expansion of oil sands development, brings some concerns about the withdrawals during the wintertime. For example, Syncrude Canada Ltd. imports 0.2% of average flow from the Athabasca River but 0.5% of average winter flow (Thompson 2006). The AENV and Department of Fisheries and Oceans Canada (DFO) released Water Management Framework: Instream Flow Needs and Water Management System for the Lower Athabasca River to restrict the industry water withdrawal during low flow periods to ensure the river's ecological health is protected during the oil sands industry development (AENV and DFO 2007). IFN is the amount of water, flow rate, water level or water quality that is required in a river to sustain a healthy aquatic ecosystem. To comply with this framework and its amended version in the near future, contingency storage ponds may be built to manage the timing of water withdrawal and to supply the water needs for oil sands operations when the river flow is low. For the thermal *in-situ* oil sands development, ERCB recently issued a draft of directive to drive the *in-situ* oil sands operations to continuously improve the water conservation, efficiency and production, which regulates the oil sands industry's commitment to the Water for Life: Alberta Strategy for Sustainability (ERCB and AENV 2009).

The oil sands industry has been criticized for the large surface footprint of disturbance associated with the surface mining activities, which include the mine pits, sands and overburden storage deposits, and fluid containment ponds (also called tailings ponds). They are the most visible symbol of the environmental impact of oil sands development that require eventual reclamation (Fordham 2009). According to current licences to operate under the Environmental Protection and Enhancement Act (EPEA), oil sands mining operators do not directly release any water that has been in contact with oil sands ores (i.e. runoff water from exposed ores) or results from the processing (i.e. OSPW) to the environment. The main water losses during the surface mine operations are due to the evaporation, from the water retention ponds or from various process units within the plant operations (See Figure 2.2).

As a result of this "zero" or "delayed" water release practice, the water that has been in contact with ores is stored as released water within the settling basins and "locked water" within the pore volumes of sands and tailings materials. The surface footprint of tailings settling basins reached more than 50 km^2 in 2005 (Government of Alberta 2009 b), while a more than 300 km^2 of other disturbed sites were evident at operating mines in the Fort McMurray region. Currently, it is estimated that the total volume of fluids tailings contained within the settling ponds will exceed 1 billion m^3 by 2015, assuming no new tailing management technologies be applied (Houlihan et al, 2008).

Storing such a large volume of fluids and tailings for indefinite periods poses a liability to the industry. The focus of concern is the potential for uncontrolled release of OSPW (and its elevated constituents of dissolved inorganic and organic constituents from the storage areas) through pathways such as seepage and ground water recharge, which could impact regional surface and ground water in the Athabasca River watershed. Although the fines and sands in tailings ponds are believed to effectively blind off water seepage through the containment structures, some OSPW and its constituents do enter surface and ground waters. The mining operators mitigate the possibility of off-site transport of OSPW with seepage collection systems surrounding the containment ponds. Suncor Energy built the interceptor ditches around the tailings ponds to collect seepage and return it to the tailings ponds (Fordham 2009). Syncrude Canada Ltd. has monitored both the groundwater and the seepage control systems that return sand seepage water back to process water systems. The main tailings pond in Imperial Oil's Kearl project is designed with a series of groundwater wells placed around the perimeter to intercept and collect seepage water, and a series of ground water monitoring wells along the lease boundary to monitor and track off-lease seepage (Imperial Oil 2009). Such efforts are designed to minimize the off-lease transport of OSPW. According to assessments conducted by the Regional Aquatics Monitoring Program (RAMP), a multiparty environmental monitoring program, there has been no significant impact from oil sands development on the Athabasca River (RAMP 2007). However, precautions must be taken to maintain responsible development of oil sands and protection of the Athabasca River's ecological integrity.

2.3.2. Tailings management

As shown in Figure 2.2, the tailings, consisting of coarse sands, fines, clays, water and bitumen residuals, are pumped into a settling basin (either above grade structures with containment dykes or below grade in mined-out pits) to settle and separate (FTFC, 1995). As tailings are delivered to these retention areas, the coarser fractions, sands, will settle out quickly, while it will take much longer periods for the fines enriched suspensions to dewater (Mikula et al, 1996). The coarse sands settle out to form beaches or are used to build dykes, while the released water from the sand or from the fines densification form a clarified water layer which is recycled to the extraction process. The fine sands and clays mixture forms a suspended fluid-like deposition and settles to become less liquid and denser over time, reaching approximately 35% by weight of fine sands and clays. The settled tailings slurry is referred to as mature fine tailings (MFT) and it takes many years for the fines to settle naturally. Therefore, the water trapped in MFT and coarse sands represents significant consumption of water, which can not be recycled in oil sands operations.

The management of MFT is essential to address the concerns associated with the tailings ponds and comply with the related regulations. A great deal of research has been conducted to accelerate the settling rates of fines, which is critical to reduce the MFT inventory and enhance the free-water reuse (FTFC 1995). The most commonly used commercialized technology is called composite tailings (CT), in which the inorganic coagulant such as gypsum, alum and carbon dioxide, are applied to accelerate water release, improve fines captures and reduce dissolved organic matters (MacKinnon et al, 2001; Matthews et al, 2001). However, adding the coagulant leads to elevated ionic content and hardness of water, which could bring the potential problems of scaling and lowering the efficiency of bitumen extraction. Some oil sands operators employ the paste technology to thicken and reduce the volume of tailings by adding polymer flocculants (Haveroen 2005). Other tailings technologies, such as centrifuge MFT technology, accelerate dewatering, and thin lift drying are still in the research and development stage but have been considered as the potential options for tailings management (Fair 2008). The newly issued ERCB Directive 74 sets the performance criteria on the reduction of fluid tailings and the formation of management for a dedicated disposal area (ERCB, 2009). ERCB Directive 74 is “holding the entire oil sands industry to a high standards will benefit everyone and will hopefully improve the public perception of this industry” (Fordham 2009).

2.3.3. OSPW Treatment

The treatment of OSPW must play an important role in optimizing water management in oil sands operations. It has been ranked as a high priority for oil sands development, and water treatment related technology must be considered for application in the oil sands industry (Rogers et al. 2008). Treatment can be focused on both inorganic and organic constituents of OSPW. The product from these treatments may provide additional water for the various applications within different operation processes, leading to the replacement of raw water import, or more efficient recycling of the water. This would result in the lowering of fresh water importation requirement from the Athabasca River and better water usage. In addition, OSPW treatment may result in a reduction in the water inventory stored in tailings ponds, mitigate the liability, eliminate associated environment, health and safety risks, and improve the public image of oil sands industry. Ultimately, the goal would be to produce water quality meeting criteria for its safe return to the aqueous systems of the region.

Water use efficiency has been greatly improved and the current average water use intensity is approximate 2 to 3 m^3 of fresh water imported from the Athabasca River for plant needs per m^3 of synthetic crude produced at oil sands surface mining projects. In Syncrude Canada Ltd’s mining operation, the recycled OSPW accounts for 80 to 85% of total water used in all the operations, and 90% of the water used for the extraction process (MacKinnon 2008). The recycled OSPW drawn from the settling basins can be recycled and reused in the extraction process without treatment. There are other areas where treated OSPW would increase the potential recycle, with treatment targeted to removing properties that limit its application (i.e. turbidity, salinity and scaling-forming constituents). The application of treated OSPW to improve the water use intensity in operational process units, such as pumps, cooling towers and other upgrading units still remain attractive. However, the objective of producing a treated OSPW suitable for return to the area watershed as a water management tool is also an attractive deliverable.

2.4. OSPW water quality

Table 2.2 Inorganic water chemistry of OSPW, the Athabasca River and regional lakes

Variable	**Syncrude MLSB$^{(2003)}$**	**Syncrude demonstration pond$^{(1997)}$**	**Suncor TPW $^{(2002)}$**	**Suncor CT release water $^{(1996\text{-}97)}$**	**Suncor CT Pond seepage (1996-97)**	**Athabasca River $^{(2001)}$**	**Regional lakes $^{(2001)}$**
Total Dissolved Solids (mg/L)	2221	400 to 1792	1887	1551	1164	170	80 to190
Conductivity (µS.cm^{-1})	2400	486 to 2283	1113 to 1160	1700	1130	280	70 to 226
pH	8.2	8.25 to 8.8	8.4	8.1	7.7	8.2	7 to 8.6
Major Ions (mg/L)							
Sodium	659	99 to 608	520	363	254	16	<1 to 10
Calcium	17	15 to 41	25	72	36	30	2 to 25
Magnesium	8	9 to 22	12	15	15	8.5	1 to 8
Chloride	540	40 to 258	80	52	18	6	<1 to 2
Bicarbonate	775	219 to 667	950	470	780	115	9 to 133
Sulphate	218	70 to 513	290	564	50	22	1 to 6
Ammonia	14	0.03 to 0.16	14	0.35	3.4	0.06	<0.05 to 0.57

Note: *MLSB, Mildred Lake Settling Basin; TPW, tailing pond water; TDS, total dissolved solid; COND, conductivity. The unit of COND is $\mu S.cm^{-1}$ and for other variables is mg/L.

Understanding of OSPW water chemistry is important in order for further OSPW treatments to meet the various purposes, and to facilitate the integrity of water management in oil sands operations.

The organics and inorganics existing in OSPW from surface mining are mainly from ore digestion (leaching of ions), process chemicals and tailings processes (recycling from settling basins and engineering tailings options). In the hot water extraction process, ore is digested with water containing process aids such as NaOH, which leads to the release of inorganic ions and dissolved organics in to the OSPW. Additionally, the chemicals added in the tailings engineered process, such as gypsum, also are transferred with recycled water (FTFC, 1995). There have been summaries describing the inorganic and organic chemistries of the OSPW, CT release water and CT pond seepage water, in comparison with those of the Athabasca River and the regional lakes (MacKinnon, 1989; Mikula et al, 1996; MacKinnon et al, 2001; Allen, 2008).

As seen in Table 2.2, the pH values of the OSPW with different resources are approx. pH 8.0, which are close to the pH values of the water from the Athabasca River and regional lakes. The OSPW has moderate hardness (60 to 150 mg/L) and high alkalinity (>500 mg/L) due to the high concentration of bicarbonate. The caustic soda (NaOH) added as an extraction aid and the salt (NaCl) originally from ores contribute to the high concentration of Na^+. High concentrations of Ca^{2+} and SO_4^{2-} are seen when gypsum ($CaSO_4.2H_2O$) is used as a coagulant aid in the engineered tailings processes. The high concentration of ions results in the high conductivity (>1500 µS/cm) of OSPW compared to most of the surface waters of the region. The concentration of ammonia varies greatly in the OSPW with different sources, with high ammonium content seen in the OSPW present in the active settling basins.

Table 2.3 shows a comparison of the organic chemistry of OSPW with that of the Athabasca River and regional lakes. All the variables including: COD, BOD, DOC, phenols, cyanide, TPH and NAs, are much higher in the OSPW than in the Athabasca River. The regional lakes data was too limited to draw any conclusion.

Table 2.3 Organic water chemistry of OSPW, the Athabasca River and regional lakes (Allen 2008)

Variable (mg/L)	Typical SCL OSPW for recycle in 2007	Athabasca River (2001)	Regional lakes (2001)
COD	175 to 225	40	-
BOD	<10	<2	-
DOC	40 to 65	7	14 to 27
Phenols	<0.01	<0.001	0.002 to 0.004
Cyanide	<0.01	0.004	-
TPH	<10	-	-
NAs	50 to 80	<1	1-2

Note: COD, chemical oxygen demand; BOD, biochemical oxygen demand; TPH, total petroleum hydrocarbon; NAs, naphthenic acids.

2.5. Naphthenic Acids

Naphthenic acids (NAs), also known as petroleum acids, are natural constituents of the Athabasca bitumen, released into OSPW during aqueous digestion of the oil sands ore in the extraction process (Cyr and Strausz 1984). NAs release from bitumen during extraction of oil sands ore have been shown to account for most of the DOC and acute toxicity of OSPW (Schramet et al. 1984). The properties of NAs will be discussed in more detail, specifically aspects of their physical and chemical properties, occurrence, toxicity and biodegradation.

2.5.1. Physical and chemical properties of NAs

NAs are closely related cyclic and alicyclic aliphatic carboxylic acids, with general chemical formula $C_nH_{2+z}O_2$, where *n* indicates the carbon number and *Z* is zero or a negative, even integer that specifies the hydrogen deficiency resulting from the ring formation. The Z value is equal to 0 for saturated alicyclic aliphatic carboxylic acids, and while -2 indicates monocyclic naphthenic acids, -4 bicyclic, -6 in tricyclic and so on. It was found that the Z =-4 series predominate in the OSPW (Lai 1995). NAs in the Z=0 family are acyclic, but they are more likely to be branched rather than linear as seen in naturally-occurring fatty acids. Figure 2.4 shows examples of naphthenic acids structures. The naphthenic acid group in OSPW is composed predominately of alkyl-substituted polycyclic carboxylic acids, while the acyclic aliphatic acids account for a minor fraction (<10%). Both commercially-available NAs and NAs freshly released from bitumen during extraction demonstrate higher relative amounts of lower molecular weight and less cyclic character than aged and biodegraded NAs (Scott et al, 2005; Han et al., 2009). During the biodegradation process, the degradation byproducts appear to be hydroxylated NAs, and with natural aging the relative fraction of these hydroxylated constituents increases (Han et al., 2009). It appears that other than the oxidative by-products, the NAs in OSPW predominantly contain only a single carboxyl group, usually on the side chain rather than directly to the cycloaliphatic rings.

NAs are non-volatile and chemically stable natural surfactants. The typical physical and chemical properties of NAs have been summarized (Headley et al. 2004). NAs are viscous liquid with the molecular weight between 140 and 450 amu and the density between 0.97 and 0.99 g/cm^3. However, they are moderately soluble in water, with the controlling factor being pH (Schramm et al. 2003). The dissociation constants (log K_{sp}) of NAs are in the 4.8 to 5.2

range (AENV, 1996). At high pHs, concentrations of NAs were noted to be above 5000 mg/L (Rogers et al., 2002). In the extraction process, caustic soda is added at rates of about 50 to 150 g per tonne of oil sands, which results in pHs in the 8.5 to 10 range, where NAs' solubilities are enhanced to result in NA levels of the OSPW in the 40 to 120 mg/L range (Quagraine et al. 2005). The NAs in the water phase will be present in the ionionized form, sodium carboxyllate (naphthenates) (MacKinnon and Boerger, 1986). The levels of naphthenates in OSPW will vary with ore source, water quality and pH of the extraction process (Schramm et al, 2003). Current OSPW in active settling basins are generally in the 60 to 90 mg/L range.

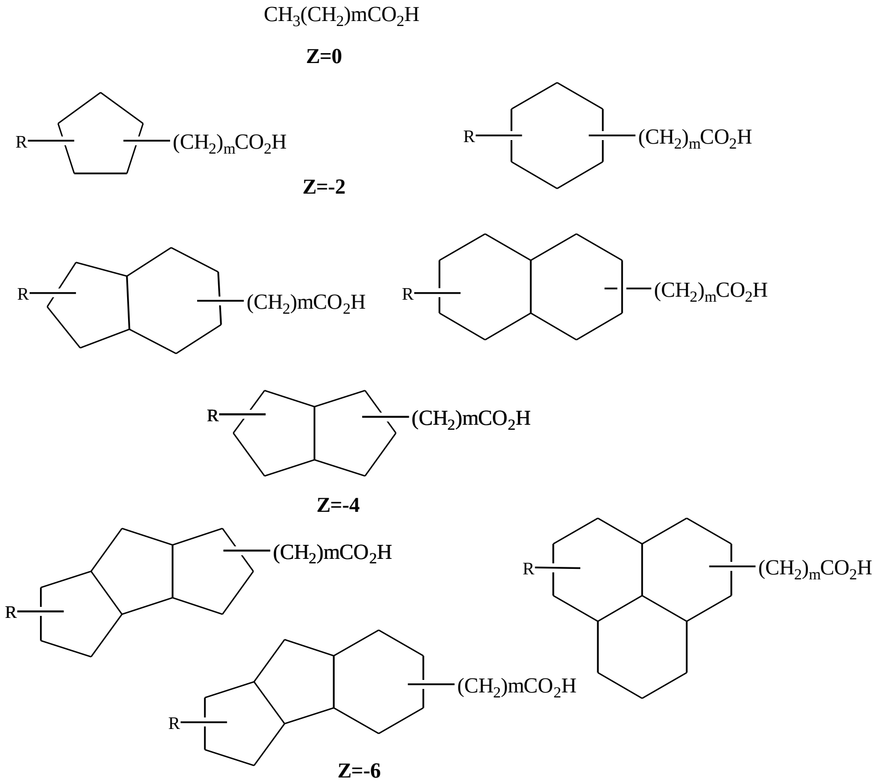


Figure 2.3 Sample naphthenic acid structures, where R is an alkyl chain, Z describes the hydrogen deficiency, and m is the number of CH_2 units (Clemente and Fedorak 2005).

As discussed in the extraction process, bitumen extraction is based on a caustic hot water digestion currently, with the result that NAs are released into the OSPW at concentrations ranging from 40 to 120 mg/L. When isolated from fresh input of OSPW and maintained under aerobic conditions, changes in the concentration and composition of the NAs are seen as bioremediation processes proceed (Han et al., 2009). The NAs concentrations in northern Alberta rivers in the Athabasca oil sands regions near Fort McMurray will contain NAs naturally leached from eroding oil sand deposits, but they will generally be present at very low concentrations (below 0.1 mg/L) because of the high dilution rates and non-optimized pH for solubilization. However, in natural groundwater where there is contact with oil sands within the McMurray Formation, levels of NAs can be found in the 5 to 15 mg/L range (CONRAD 1998).

2.5.2. Analytical techniques

In the OSPW, NAs are a group of organic acids with a small range in molecular weights, and similar chemical and physical properties (high polarity and low volatility) which make NAs difficult to separate and analyze individually (Clemente and Fedorak 2005).

Fourier transformed-infrared spectroscopy (FT-IR) has been widely used to quantitatively measure the total NAs contents in the oil sands materials based on a quantitative method using extracted NAs mixtures (Yen et al. 2004). Briefly, the water samples are acidified and the NAs are quantitatively extracted into HPLC-grade dichloromethane (DCM), which is then evaporated off, leaving the extracted NAs. Prior to collecting FT-IR spectra, the NAs extract is re-constituted with a known mass of DCM. The absorbances at wave-numbers 1743 and 1706 cm^{-1} are the absorbance peaks of the mono-metric and dimeric forms of the carboxylic groups, respectively. The sum of the two absorbances is compared with the standard curve developed using commercially available NAs prepared in DCM. This method measures monomer and dimer absorbance associated with the carbonyl group of carboxylic acids. As a result, it is not specific to individual NAs and has no ability to solve carbon numbers or Z families.

Conventional gas chromatography (GC) and High-performance Liquid Chromatography (HPLC) have also been employed for the separation of NAs, and the derivatization is necessary prior to the chromatographic analysis. For example, Herman et al (1994) used GC with flame ionization detection to analyze the methylated commercial NAs. The NAs methyl esters were eluted as a big hump due to the overlap of the chromatographic retention times of the individual constituents within the NAs' group. The area of the hump was integrated and compared to the area of an internal standard. The HPLC methods with UV detection for analysis of NAs mixtures are similar to the GC methods, but the NAs were esterified with 2-nitrophenylhydrazine in presence of the coupling agent 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide, which was developed by modifying Miwa and his co-workers' HPLC method for measuring fatty acids (Miwa et al. 1985; Miwa 2002). This method has been successfully applied to monitor the biodegradation of NAs in the laboratory cultures and aqueous environmental samples (Clemente et al. 2003; Yen et al. 2004).

The application of Mass spectrometry (MS) methods has been developed for analysis of NAs because of its ability of providing qualitative information, including the average molecular weights distribution (carbon number), degree of hydrogen deficiency (Z-value) and degree of alkylation and branching. This tool allows us to obtain the fingerprints (NAs distribution within extracted samples) and assess variations associated with NAs from different sources and resulting from varying degrees of bioremediation (Headley and Peru 2007).

Different ionization techniques, such as chemical ionization (CI), fast atom bombardment (FAB), atmospheric pressure chemical ionization (APCI), electron ionization (EI) and electrospray ionization (ESI) have been applied to the characterization of NAs mixtures (Fan 1991; St John et al. 1998; Lo et al. 2006; Headley and Peru 2007). Among these ionization techniques, APCI in negative-ion mode can produce very clean spectra with good sensitivity compared to other techniques. ESI, however, is becoming the ionization technique of choice because it is a soft ionization method that produces one major ion from each component and minimizes fragmentation. The negative ionization mode has been the mode of preference, even though both positive and negative ionization have been reported. The application of high-resolution MS has been reported to allow for the characterization of ions of very similar mass but not the same class in complex NAs mixtures due to its high mass accuracy and high resolution (Han et al. 2008). However, the high accurate mass analysis needs longer time to acquire data.

The GC-MS and HPLC-MS have been used successfully for the identification of NAs mixtures with structural information (Holowenko et al. 2002; Clemente et al. 2004). For example, St John et al. (1998) reported the GC-MS analysis results of *tert*-butyldimethylsilyl derivatives of the NAs. By using this method, characteristic ions were yielded and provided the percent composition of the NAs based on Z and carbon numbers. Using GC-MS, Holowenko et al. (2001) demonstrated that the compositions of NAs in the NAs extracts of OSPW from the Mildred Lake Settling Basin are different from those obtained for commercial NAs. The results showed that NAs extracts from OSPW have higher average molecular weight, with greater evidence of NAs with carbon numbers above 20 than those in commercial NAs. The early HPLC-MS methods applied to the NAs analysis were off-line HPLC-MS. Lo et al.(2006) collected the fraction of the NAs using an anion exchange column and then conducted the ESI-MS analysis on the fractions. Application of on-line HPLC-MS for NAs analysis, using a reversed-phase capillary HPLC/QTOF-MS has been developed to characterize the NAs (Gabryelski, et al., 2003; Bataineh et al., 2006). This high resolution method has identified many differences in isomer class profiles compared to an earlier low resolution GC-MS method. The power of HPLC-high resolution MS has enabled the study of the relationship between the molecular structure of NAs and their biodegradability (Han et al. 2008).

2.5.3. Toxicity

Naphthenic acids have been shown to be the main component in OSPW responsible for the toxicity to aquatic organisms. When removed from fresh OSPW, acute toxicity of OSPW to bioassays with fish (LC_{50} of rainbow trout 96-hr static test), zooplankton (LC_{50} of Daphnia magna 48-hr static test), and bacteria (IC_{50} of luminescent_Microtox 15-minute test) was significantly reduced (MacKinnon 1986). However, other toxic components were likely removed, as well as NAs, when the NAs were removed by using the organic solvent extraction method. It should be noted that other than NAs, ammonia, trace metals, phenols and hydrocarbon residuals also contribute to the toxicity of OSPW (Allen 2008). Clemente and Fedorak (2005) summarized the toxicity studies with NAs using different organism including aspen (Kamaluddin and Zwiazek 2002), fish (Young et al. 2007), zooplankton, rat (Rogers et al. 2002) and bacteria (Holowenko et al. 2001). However, it was likely that NAs used in these studies were different due to the complexity and source of tested NAs, so the toxic results are not comparable until these differences in origin are considered. Holowenko et al. (2002) first reported the aquatic toxicity of NAs in OSPW was associated with their compositions by demonstrating the fact that the NAs with higher percent of $>C_{22}$-cluster (the group of acids with greater than 22 carbons) showed lower relative toxicity than the $< C_{22}$-cluster. Their research also indicated that the toxicity of OSPW varies greatly according to its age, source and processes by comparing the toxicity of OSPW sampled from different oil sands operations and different ponds. This argument was used in a ground study looking at the transit of OSPW seepage waters (MacKinnon et al. 2005). Lo et al. (2006)

also reported the fraction of NAs with higher proportion of multi-ring NAs had lower toxicity. Therefore, the toxicity of OSPW is likely associated with the NAs species depending on the structure, molecular weight and carboxylic groups in NAs presenting in OSPW (Allen 2008).

2.5.4. Biodegradation

NAs, including both commercial NAs and the NAs extracted from OSPW, were found to be more effectively biodegraded when maintained under aerobic conditions, with the process likely proceeding through the functions of aerobical bacteria. A number of microbial studies have demonstrated this. Approximately 50% of commercial NAs and 20% of organic carbon in OSPW extract were shown to mineralize into CO_2 in relatively short time periods (Herman et al. 1994). Clemente et al (2003; Clemente and Fedorak 2004; Abu-Hassan et al. 2005) monitored the fate of commercial NAs (Kodak, Merichem) using GC-MS at different incubation times during the aerobic biodegradation process and found that the fraction with low molecular weight and fewer rings were more liable to degradation. Herman et al. (1994) reported that the carboxylated cycloalkane was less resistant to micro-biodegradation than the methylated carboxylated cycloalkane. In the research of degradability of NAs, the commercially available NAs were commonly used; however, Scott et al (2005) found the NAs in OSPW were less biodegradable in the aerobic condition than the commercial ones. In her study, the micro-degradation of four commercial NAs and two NAs from OSPW were compared. The commercial NAs were completely biodegraded within 14 days, while only about 25% of the NAs from OSPW were biodegraded after 40 to 49 days. The findings indicate that the research on bio-degradation or other treatment options using only commercial NAs should be interpreted with care as their rates and possibly pathways of degradation are likely not representative of the biodegradability of NAs present in OSPW existing in settling basins, tailing storage areas, seepage waters, and aquatic reclamation systems. Han et al. (2008) approached the development of quantitative structure-persistence relationship for both commercial NAs and NAs extracted from OSPW employing the HPLC high resolution MS. The carbon numbers were found to have little effect on NAs' degradation rate while the degree of cyclization played a critical role in the biodegradation of NAs. The dominated highly branched NAs in OSPW lead to their slow biodegradation. This general finding was demonstrated in a constructive wetland mesocosm study that was reported by Toor et al (2009), where definite structural components played a role in the ease of biodegradation.

2.6. OSPW treatment

The OSPW treatment for greater recycle and reuse, or potential release off-lease in the future, is important to water management options at surface mining oil sands operations. Ultimately if applied correctly, proper treatment applications could lead to a minimization of river water (non-OSPW import) withdrawal and optimize the volume of water required to be store in the settling basin inventory. Currently, oil sands mining operators recycle large volumes of OSPW, particularly for extraction processes. For example, the OSPW from settling basins accounts for 80% to 85% of the total water used in operations, with more than 95% of the water used in the extraction process in Syncrude Canada Ltd. coming from recycling of OSPW (MacKinnon 2008). Based on the water quality discussed in Section 2.4, there are issues that must be addressed if recycle and/or reuse rates are to be increased. Aspects of OSPW properties, including suspended solids, dissolved inorganics, hydrocarbons (un-recovered bitumen present as a separate phase), NAs, ammonia and some trace metals may require the use of treatments before OSPW can be recycled and/or reused in other processes at higher rates than currently undertaken. Treatment of OSPW to the quality levels that meet release criteria to the receiving environment will require even greater effort and technology application. Ikehata (2007) summarized the potential application of these wastewater treatment methods to address these issues (see Table 2.4).

However, the extent to which OSPW must be treated depends on the purpose of the treatment and the needs of the ultimate user. According to the targets of OSPW treatment, it can be classified into three different stages. The levels of effort and thus economics increase as more stages are required (Fu 2008).

- First stage: removal or reduction of suspended solids and hydrocarbons. This can be achieved by filtration, centrifugation and physical-chemical treatment (coagulation, flocculation and/or sedimentation);
- Second stage: removal of dissolved organics which are associated with the toxicity of OSPW, namely NAs. The treatment options include carbon adsorption, biological remediation, advanced oxidation and membranes (nanofiltration and reversed osmosis). Some of these options have been shown to work for the dissolved organics removal from OSPW;
- Third stage: deionization of the OPSW selectively, partially or completely. Membrane technologies (nanofiltration for selected treatment; reverse osmosis for more complete removal of ion species) can be applied to reduce dissolved inorganics.

A weak anion exchanger, diethylaminoethyl-cellulose (DEAE-cellulose), was used to rapidly extract NAs from OSPW with the total extraction efficiency of 41.2% (Frank et al. 2006). An efficiency of 85% was reported using solvent-based extraction (Rogers et al. 2002), but it was much more time-intensive compared to the DEAE-cellulose methods. The sorption of naphthenic acids from OSPW on organic rich soils was evaluated in a laboratory scale, and the naphthenic acids with carbon numbers ranging from 13 to 17 showed preferential sorption (Janfada et al. 2006). In addition, the soil with richer organic content tended to cause higher levels of sorption (Peng et al. 2002; Janfada et al. 2006). Zubot et al (2009) described a method to treat OSPW using the petroleum coke produced during the upgrading coking process used at Syncrude's Mildred Lake site and achieved 70 to 90% NAs removal efficiency. In his method, OSPW is used to hydraulically transport petroleum coke, which is a waste from the coke operation. The resulting coke-water slurry, with the coke content of 5 to 30% (wt%), is pumped by pipelines to its disposal site. Contact during transport leads to the adsorption of NAs on the coke. The use of petroleum coke from the coke operation is attractive since no extra coke activation is required, beyond what occurs in the coke burner of the fluid coker, making this method both cost-effective and practical for NAs removal (Zubot, 2009).

Table 2.4 Potential treatment process for OSPW and the targets

Treatment Process	**Metals**	**Hardness**	**Suspended Solids**	**Oil and grease**	**Dissolved Inorganics (salinity)**	**Ammonia, NH_4^+**	**NAs**	**Dissolved Hydrocarbon**
Precipitation	√	√	√					
Coagulation/flocculation			√	√				
Sedimentation/filtration			√	√				
Natural Bioremediation	√		√	√		√	√	√
Advanced oxidation	√			√		√	√	√
Membrane filtration (UF, NF, RO)	√	√	√	√	√	√	√	√
Adsorption	√			√			√	√

Membrane-based treatments are applied for the removal of ionic species from water. The commonly used membrane technologies for wastewater treatment include: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) with a typical operating range from 0.0001 to 2.0 μm (Metcalf & Eddy 2003). Peng et al. (2004) applied the NF to OSPW and demonstrated its applicability for water softening (more than 95% of the hardness), and showed it was also effective for removal of naphthenic acids (>90% removal of NAs). However, fouling and membrane durability are two areas of concern that became evident as factors that limited the robustness of this approach, and hindered the acceptance for a wider application for OSPW. Compared to the synthetic polymer membrane, the ceramic membranes showed better performance in terms of permeability and durability.

As shown in Table 2.4, conventional treatments such as coagulation, flocculation and sedimentation can be applied for the removal of suspended solids and oil and grease; whereas advance oxidation and membranes have the potential to remove the dissolved constituents, both salts (ionic species) and dissolved organics including NAs. The choice of water treatment techniques depends on the water quality requirement of the process the treated OSPW is to be used for, and the regulatory criteria of the water quality that must be met when the treated OSPW is considered for return to environment. The feasibility of a treatment technology will depend not only on its effectiveness at removing the target component, but also on other factors such as the cost (both capital and operating costs), personnel training, by-products of the process, scale-up potential, operability and reliability. The following aspects of water treatment technology selection must be considered:

- potential customer acceptance;
- the operators within operations, if recycled;
- regulatory and stakeholder groups, if released;
- that the produced waters meet the required need.

The integrity, performance and economics of an applied technique must be fully considered before it can be commercially applicable.

2.7. Ozone and Ozone-based advanced oxidation process: Potential Option for OSPW Treatment

2.7.1. Ozone: Background

Ozone is an unstable gas with a molecule of three oxygen atoms. It is a blue gas at room temperature with a distinct odor. Ozone has a vapor density of 2.154 g/L at 0 ℃ and 1atm and solubility of 12.07 mg/L at 20 ℃ in water. The solubility of ozone in water is governed by Henry's Law, and the lower temperature favors the higher solubility (Metcalf & Eddy 2003). Ozone has a half-life of about 20 to 30 minutes in distilled water at 20 ℃, whereas the half-life is shorter in impure and higher salinity solutions (Rice 1986). Ozone is one of the strongest oxidants available for water and wastewater treatment, with an electrochemical potential of 2.07 v. Ozone is also a very active oxidant and reacts with organic compounds, with the pathway being oxidation through either direct ozonation or indirect ozonation. In direct ozonation, the molecular ozone reacts with organic compounds, whereas in indirect ozonation, the highly reactive hyroxl radical (HO ·), first forms through ozone self-decomposition and then reacts with organic matters. The operational conditions under which ozonation occurs, such as pH, temperature, presence of OH ·, dissolved organic matter (type and concentration), transition metals, reduced species (i.e. sulphides), competing non-target oxidizable constituents (NH_4^+, biota) influence the pathway and efficiency under which ozonation will proceed. For example, acidic conditions favor direct ozonation, while the presence of some species such as hydroxides (OH^-) and iron ions (Fe^{3+}, Fe^{2+}) may initiate the indirect ozonation (Glaze 1987; Singer et al. 1992). In addition to being used by itself, ozone can also be used in conjunction with chemicals (e.g. hydrogen peroxide (H_2O_2)) or/and auxiliary energy source (e.g. ultraviolet radiation). The combinations of these technologies, known as advanced oxidation processes (AOPs), allows better generation of the primary oxidant hydroxyl radicals (OH ·) with electrochemical potential of 2.80 v, which is a stronger oxidant than ozone (Ikehata 2007). Examples of ozone-based AOPs include O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV, and the ozonation at high pH (pH>8) is also considered as an AOP because the basic condition favours to generating hydroxyl radicals (Rivas et al. 2003).

Ozone is often produced naturally during lightning and some human activities such as electronic devices and wielding. Commercial ozone generators use the electrical discharge method to produce ozone. In the electrical discharge method, a clean dry oxygen-containing gas passes through an electrical discharge, and high voltage is applied across a discharge gap; collisions occur between electrons and oxygen molecules and ozone gas is generated. Since ozone is quite unstable and can rapidly revert to oxygen after generation, it must be generated on-site.

An ozone system used for water and wastewater treatment usually includes feed-gas supply, ozone generator, ozone contactor and off-gas (un-reacted) ozone destructor. Figure 2.4 shows a typical layout of ozone system. Three kinds of feed gas have been used: pure oxygen, air, and liquid oxygen. The latter is considered as the most cost effective and least complex ozone feed gas system (Rakness 2005). The ozone generator system includes a generator vessel and power supply unit. The ozone contactor is designed to ensure the water/wastewater to be treated is exposed to the required levels of dissolved ozone using special gas/liquid contracting technique. One of the most important considerations regarding the ozone contactor design is the mass transfer rate because ozone in the gas phase is only partially soluble in water. This stage of treatment is critical to optimize the efficiency of a system.

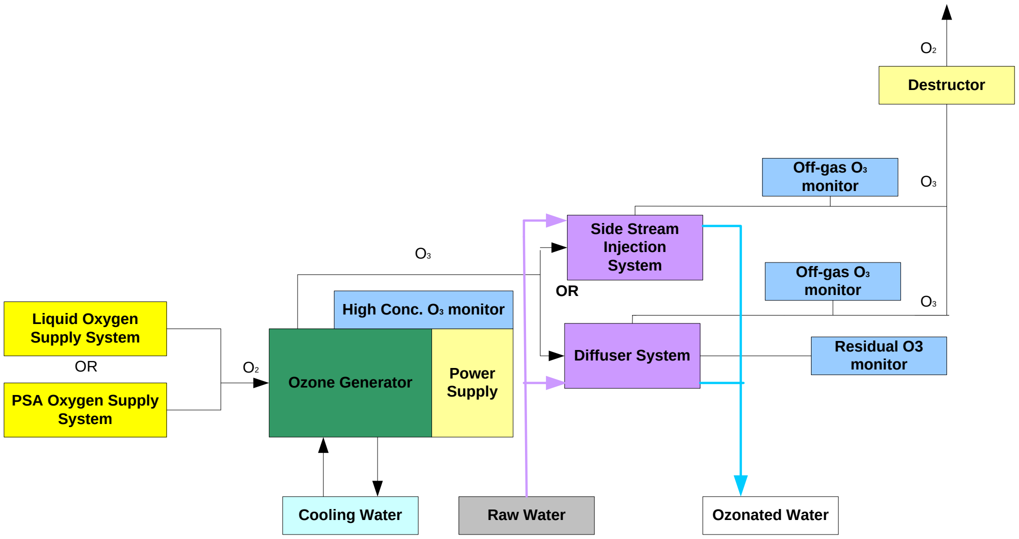


Figure 2.4 Typical layout of an ozone system (Mitsubishi 2008, with permission)

According to the two-film theory of gas-liquid mass transfer, the mass transfer rate can be enhanced by generating finer gas bubbles (increase interfacial surface area), increasing the turbulence (increase mass transfer coefficient) and increasing the ozone concentration in the fed gas. The most common ozone contactor is a bubble-diffuse over-under baffled basin, where baffle walls create an up-and-down water flow pattern (Rakness 2005). In the bubble-diffuser dissolution ozone contactors, ozone is dissolved into water to be treated via a porous stone diffuser that creates small bubbles, and then the ozonated water continuously goes through the contactor for oxidation and disinfection reactions. This kind of ozone contactor combines dissolution and reaction tank. An ozone transfer efficiency of 85% is normally achieved for an air-fed bubble-diffuser contactor that has a diffuse depth of about 20 feet (Rakness 2005).

Another category of ozone contactor is the side-stream ozone dissolution system, in which ozone gas dissolves into a side-stream flow through an injection set-up or other side-stream arrangement. The side-stream flow is subsequently mixed with the main process flow stream, which is directed to a reaction tank or pipeline for oxidation and disinfection reaction. An ozone mass transfer efficiency of more than 90% is normally achieved in side-stream system. Despite its higher operation cost for water pumping, the side-stream injection system is gaining popularity due to its lower maintenance cost. An off-gas ozone destruction unit is required in order to prevent the un-reacted ozone (about 5% to 10% of the delivered O_3) from being discharged in the off-gas. The ozone destructor normally consists of a heating element and catalyst, which is typically manganese dioxide (Rakness 2005).

2.7.2. Water treatment using ozone/ozone-based AOPs

Ozone and AOPs have been used widely in water and wastewater treatment for coagulation (Velasquez and Monje-Ramirez 2006), Fe and Mn removal (Nishimura and Umetsu 2001), color removal (Zhou and Smith 1997; Solmaz et al. 2006), taste and odor control (Hwang et al. 1994), algae removal (Assalin et al. 2007) and disinfection (Machado et al. 2007). Recently, ozone and AOPs have emerged as technologies for removing emerging organic pollutants in water and wastewater. Ikehata and Gamal El-Din (2007) have reviewed the application of ozone and AOPs in the degradations of water soluble pharmaceutics, recalcitrant surfactants and pesticides. Application of ozone and AOPs for degradation of NAs in OSPW is relatively new technology compared to its application in other areas. Scott et al. (2008) conducted the ozonation of OSPW by bubbling the OSPW continuously with ozone gas, but little control over ozone dose This was a preliminary assessment of treatment of OSPW, and degradation potential of OSPW constituents, in particular how the NAs responded to the oxidizing power of O_3, and was not designed to evaluate actual reaction efficiency or optimized dosages. The results showed that the initial acute toxicity of the OSPW was removed by the ozonation, and that the produced water displayed no acute toxicity when assessed by Microtox bioassay after a 50 minute treatment, and the residual NAs were reported as 2 mg/L after 130 min or greater than 95% removal. The GC-MS analysis of the remaining NAs showed that the NAs degradation occurred over the full range of constituents, and indicated a preferential removal of NAs with carbon numbers over 22. This positive finding was insufficient to define a treatment approach to OSPW applications. Information was needed on the dynamics of the ozonation process, including dosages, byproducts and process kinetics. A better understanding of the effectiveness and control factors for application to OSPW is the focus of the present study.

3. EXPERIMENTAL METHODS

3.1. OSPW test waters

The waters used in this study were collected from various sources at Syncrude's Mildred Lake facility, located north of Fort McMurray, Alberta. The main settling basins at Syncrude Canada Ltd. Mildred Lake site are shown in Figure 3.1. They are the main sources of OSPW used in the current study, where MLSB, WIP, SEIP and SWSS stand for Syncrude Canada Ltd.'s Mildred Lake Settling Basin, West In-pit, South East In-pit, and South West Sand Storage, respectively.

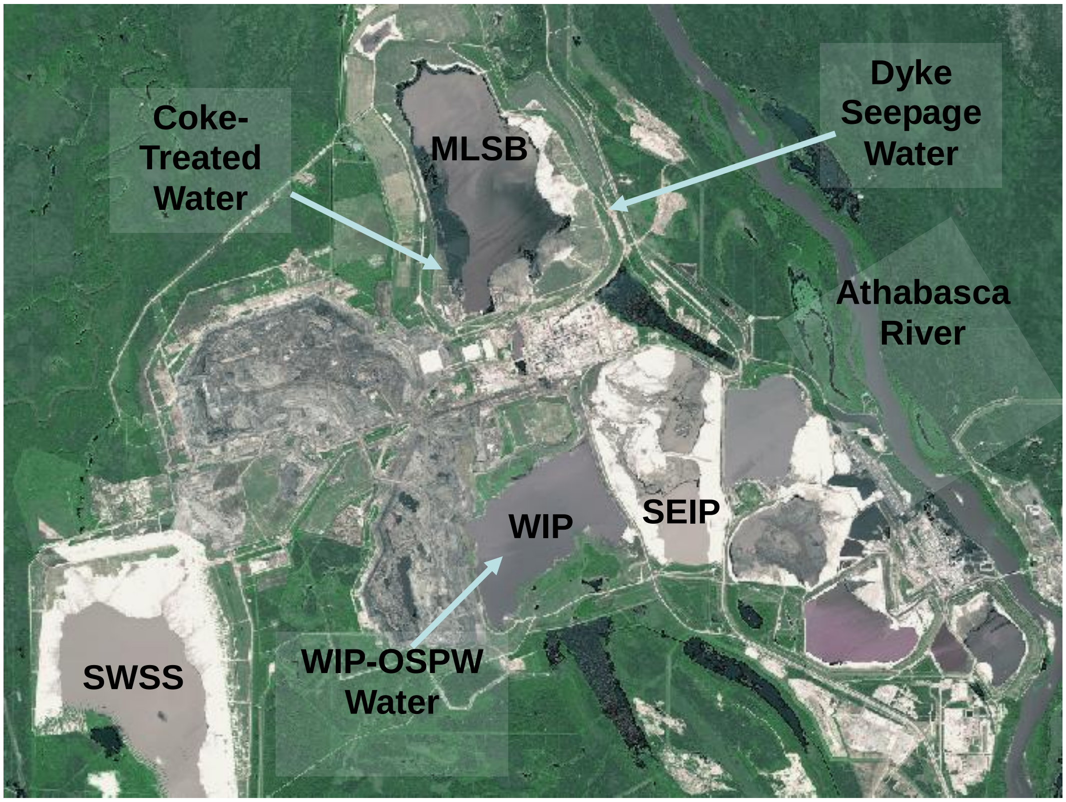


Figure 3.1 Aerial view of Syncrude Canada Ltd.'s Mildred Lake Site, highlighting main settling basins (MacKinnon 2008, with permission).

For the evaluation of the ozonation methods, it was decided to use water representative of process systems, rather than those that might be more likely in a reclamation system where there has been long-term bioremediation prior to treatment. As a result, the water chosen should contain a wider suite of process constituents and should reflect waters that are more difficult to treat. The waters used included:

- WIP-OSPW: Fresh OSPW was taken from an active settling basin, known as the West In-Pit Pond (WIP) which is constantly receiving extraction tails and contains the resulting release water that is recycled back to the plant. The collected WIP-OSPW for batch ozonation treatment was collected in 2004 and filtered using membranes with pore size of 0.45 μm and then was stored at 4 ℃ prior to being treated with ozone. The collected WIP-OSPW for semi-batch ozonation was collected in November 2007 and was stored at 4 ℃ prior to being treated with ozone. This allowed the suspended solids to settle out, so the water for treatment contained less than 10 mg/L suspended solids. Since it was maintained under anoxic conditions, little evidence of bioremediation was seen.
- DSW: Dyke seepage water (DSW) was collected (October, 2007) from an active sand drain at the base of the sand dyke on the east side of Syncrude Canada Ltd.'s main settling basin (Cell 25, drain B2503), the Mildred Lake Settling Basin. The water is representative of the tailings sand pore-water that is slowly released from the sand structures used to contain the above grade settling ponds. The OSPW is released slowly as the phreatic level in the dyke drops as the dyke water slowly seeps out. While this is older, it had been maintained under anoxic conditions in contact with sand so bioremediation was minor and little if any adsorption onto mineral fraction would have occurred.
- Coke water: Excess coke from the coke burner at Syncrude Canada Ltd.'s fluid coker (Plant 8) is mixed with OSPW drawn from the

Recycle Pond and hydraulically transported to its discharge point. A sample of this slurry was collected from the discharge site, stored under quiescent conditions, and the coke water was decanted into containers for subsequent testing.

3.1.1. OSPW: tested using batch ozonation method

Table 3.1 Water samples for the ozone treatments

Treatment Method	**Water Sources**				
	WIP-OSPW		**DSW**	**Coke Water**	
	2004*	2007*	2007*	2007*	2008*
Batch O_3	√		√	√	
Semi-batch O_3		√			√

* Year that the waters were collected.

Table 3.1 summaries the OSPW from different sources tested with both batch ozonation method and semi-batch ozonation method. The three OSPW waters described in Section 3.1 were tested using batch ozonation method. Prior to batch ozonation treatment, all the water samples were filtered using membrane with a pore size of 0.45 μm (Millipore Corporation, Billerica, Massachusetts).

3.1.2. OSPW: tested using semi-batch ozonation method

As shown in the Table 3.1, the OSPW water tested using semi-batch ozonation treatment was collected in December 2007 in the West In-pit Pond by Syncrude Canada Ltd. The semi-batch ozonation was tested with original OSPW, OSPW filtered with Whatman grade 934AH glass fiber filter (Whatman, UK), and OSPW filtered with membrane with a pore size of 0.45 μm (Millipore Corporation, Billerica, Massachusetts).

3.1.3. The coke-treated OSPW for the semi-batch ozonation method

The coke-treated OSPW was provided by Syncrude Canada Ltd. and treated by a water/coke slurry process. The water/coke slurry process uses the following steps: remove coke from a coking operation (without subject to a formal activation process), add OSPW to coke and form a coke/water slurry at an approximate concentration of 22 wt%, mix the coke/water slurry to allow coke to adsorb NAs, and separate the coke from the slurry (Zubot 2009). The coke used to treat OSPW is a by-product produced during thefluid coking process in Syncrude Canada Ltd.'s operation.

Before ozone treatment, coke-treated OSPW was filtered with membrane with a pore size of 0.45 μm (Millipore Corporation, Billerica, Massachusetts).

3.2. Ozonation system

3.2.1. Batch ozonation system

Preparation of Ozone-Demand-Free (ODF) water and ODF glassware:
The ODF water was used for preparing the stock solutions and for cleaning glassware; no O_3 demand occurred during the experiments. Preparation of ODF water involved bubbling ozone gas through water for at least 30 minutes, and then leaving it with the dissolved O_3 solution at room temperature for 3 days. The glassware used for the batch ozonation was ODF glassware, which was prepared by bubbling water with ozone for 30 minutes; soaking glassware in the ozone-saturated water in which further bubbling ozone gas was maintained for another 30 minutes. The O_3 gas sparging ceased and the glassware was allowed to soak in the O_3-enriched water overnight. The preparation of ODF water and ODF glassware used in the semi-batch ozonation system (See 3.2.2) is the same as the ones used in batch ozonation.

In the batch ozonation system, the stock ozone solutions were prepared by bubbling ozone through ozone-demand-free (ODF) water for 30 minutes in an ice bath throughout the procedure. The ozone concentration in the stock solutions was determined by measuring UV adsorption at 260 nm. The stock solutions with ozone concentration of 0, 10, 20 or 40 mg/L were prepared and poured into a 1 L Pyrex Brand bottle (batch reactor) which was filled with 500 mL water samples to be treated. A phosphate buffer was used for pH control. The buffer was prepared dry (0.1922 g $NaH_2PO_4 \cdot H_2O$ + 5.0960 g $Na_2HPO_4 \cdot 7H_2O$) and then added into the reactor with the test water, where it was allowed to dissolve into the water sample (500 mL) before the ozone stock solution (500 mL) was added. Therefore, the final ozone doses for the water samples were 0, 5, 10 and 20 mg/L, respectively, due to dilution by adding ozone stocks, and the final concentration of phosphate buffer was 0.020 mol of P/L with the pH value of 8. The solutions were mixed gently overnight at room temperature and then stored at 4 ℃.

3.2.2. Semi-batch ozonation system

Figure 3.3 shows the schematic of the semi-batch ozonation system that allows for treatment of OSPW using ozone in a continuous flow mode. An ozone generator (GSO-40, WEDECO, Herford, Germany) was utilized to produce ozone gas using extra dry, high purity oxygen. The ozone contactor where the O_3 reaction occurs was constructed of a Pyrex Brand bottle with a capacity of 2000 mL. Ozone gas was introduced from the bottom through a glass diffuser. The ozone concentrations (g/m^3) in feeding gas were monitored by a high concentration ozone monitor (HC500 Ozone monitor, WEDECO, USA). The ozone concentrations in the off gas were monitored with an ozone monitor or by trapping ozone using KI wash bottles. The ozone residual in the reactor was measured using the Indigo method (APHA AWWA WEF 1992). The gas flow rate was measured by a wet test meter, which is a device to measure gas flow by counting the revolutions of a shaft upon which water-sealed, gas-carrying cups of fixed capacity are mounted. The ozone dose consumed for water treatment in this system can be calculated by subtracting both the waste ozone dose and the residual ozone dose from the applied ozone dose (See Equation 3.1 to 3.3). After treatment with ozone, the OSPW was purged by a purified nitrogen gas for *5* minutes (the pressure of outlet gauge of pure nitrogen cylinder kept at 68.9 kPa) to strip the ozone residual off the reactor.

All the solutions used in the treatments, including sulphuric acid, KI, standard sodium thiosulfate titrant, were prepared with ODF water. The tubing used for this system are either stainless or TFE tubing.

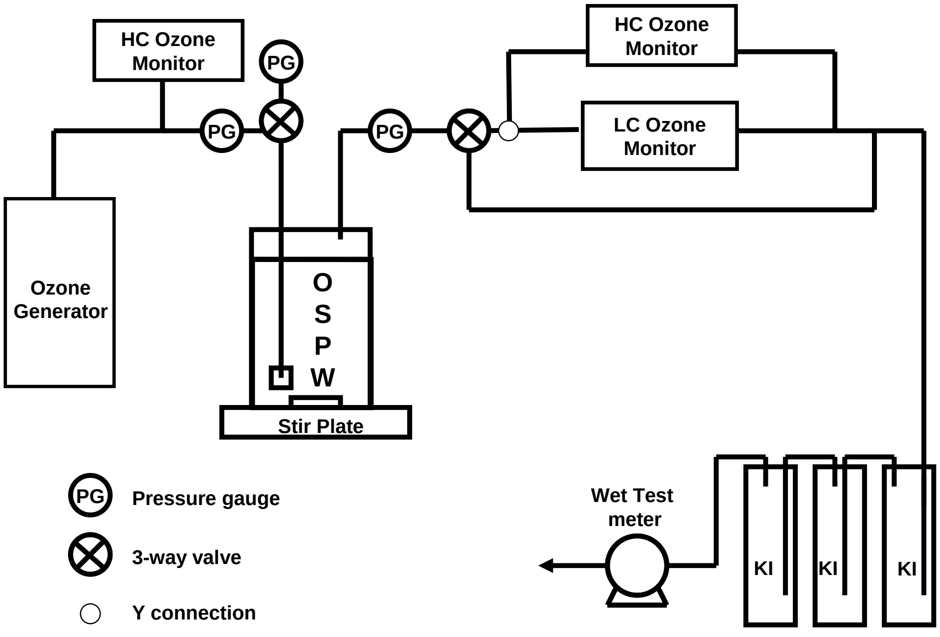


Figure 3.2 The schematic of semi-batch ozonation system

3.2.2.1.Calibration of ozone monitor

Ozone monitors can be calibrated using the KI titration method (Rakness 2005). This method is suitable for ozone concentration in the range of 0 to 200 mg/L at normal temperature and pressure (NTP) in the process gas.

Ozone gas generated from the ozone generator was directly connected to three KI wash bottles in series, which were filled with 200 mL KI solution (20 wt%) each. The gas flow was measured by a wet test meter. The concentration of ozone in the feeding gas can be calculated using the following equation:

$$Ozone\ dose\,(mg/L) = \frac{N \times V \times 24}{V_{wet\ meter}} \quad \ldots\ldots\ldots\ldots\ldots \text{(3-1)}$$

Where: N = normality of $Na_2S_2O_3$,

V = mL $Na_2S_2O_3$, and

$V_{\text{wet meter}}$ = L feeding gas

The calibration curve is shown in Figure 7.1 in the Appendix.

3.2.2.2. Applied ozone dose

The applied ozone dose is the amount of ozone fed to the ozonation system. It can be calculated using the following equation:

$$Applied\ \ Ozone\,(mg/L) = \frac{a \times C_{ozone\ monitor}}{V_{reactor}} \ldots\ldots\ldots \text{(3-2)}$$

Where: a = the factor converting ozone concentration (wt %) to ozone concentration (mg/L). The value of “a” can be calculated by calibrating the ozone monitor, and “a” is equal to 0.0753 (See Figure 7.1 in the Appendix).

$C_{\text{ozone monitor}}$ = the reading from ozone monitor, and

V_{reactor} = L, the volume of reactor

3.2.2.3. Wasted ozone dose

The wasted ozone dose is the amount of ozone in the off gas, which has not reacted and passed through the reactor. It can be calculated using the following equation:

$$Wasted\ Ozone\ dose\,(mg/L) = \frac{N \times V \times 24}{V_{wet\,meter}} \quad \ldots\ldots\ldots\ldots\ldots (3\text{-}3)$$

Where: N = normality of $Na_2S_2O_3$,

V = mL $Na_2S_2O_3$, and

$V_{\text{wet meter}}$ = L feeding gas

3.2.2.4. Ozone residuals in the reactor

The ozone residuals in the reactor (Fig 3.3) were measured using the Indigo method. A sample of the ozonated water (1 mL) was taken from the reactor vessel, right after the flow of the ozone gas to the reactor ceased. The water was mixed with 19 mL of ODF water and then the absorbance at 600 nm was measured.

3.2.2.5. Stripping ozone residuals

The ozone residuals, which are the un-reacted O_3 present in the test sample once O_3 delivery has stopped, can be quenched using either Indigo method or sodium thiosulfate. However, the Indigo reagent and sodium thiosulfate could interfere with subsequent $cBOD_5$ measurements, so a gas stripping method was employed where the water in the reactor after ozonation was purged with pure nitrogen to strip the ozone. The preliminary tests demonstrated that the ozone residual was below 0.05 mg/L in the OSPW after 5 minutes of stripping with pure nitrogen (the pressure of outlet gauge of pure nitrogen cylinder was kept at 68.9 kPa (10 psi.)).

3.2.2.6.Ozone use efficiency

Ozone use efficiency is used to assess the amount of ozone used for the NAs degradation, and it was calculated using the following equation:

$$Ozone\,use\ efficiency\ \ (\%) = \frac{Applied\ \ ozone - Wasted\ ozone}{Applied\ \ ozone} \times 100\%$$

……………………………………………….…………… (3-4)

3.3. Chemical Oxygen Demand (COD)

3.3.1. COD measurement: High COD samples.

This method was applied to the samples with a COD greater than 50 mg/L. Materials and Chemicals: The stock standards of potassium hydrogen phthalate (KHP) (1000 mg O_2/L) was prepared by dissolving KHP, (850.9 mg of anhydrous KHP was dried at 120 ℃ for 2h or 105 ℃ over night) in 1 L of DI water. About 3 to 4 drops phosphoric acid was added to make the solution more stable. A standard curve with the KHP was prepared using a range of COD water samples (dilute 0, 10, 25, 100, 125, 150 and 200 mL of the KHP stock solution with 100 mL of DI water). The COD digestion solution was prepared by diluting 10.216 g potassium dichromate (dried at 103 ℃ over night), 167 mL concentrated sulfuric acid and 33.3 g mercuric sulfate ($HgSO_4$) into 1 L DI water. The Sulfuric Acids Reagent was prepared by mixing 10.12 g Ag_2SO_4 with 1 L concentrated sulfuric acid.

Procedure: The COD measurement was conducted as per the procedure described below: mix 2.00 mL digestion solution, 3.5 mL sulfuric acid reagent with 2.0 mL aliquot of sample in the COD test vials, then incubate the mixtures in a digester (Bioscience Institute, Pennsylvania) which was preheated at 140 ℃, reflux for 2 h at 140 ℃, read the absorbance at 600 nm after the samples were cool down.

3.3.2. COD measurement: low COD samples

This method was used for the water samples with a COD in the range of 0 to 80 mg/L (McGill University 2000).

Materials and Chemicals: The sulfuric acid reagent and the KHP standards used in this method are same as those used in the method for the high COD samples (See 3.2.3.1.). The COD digestion solution was prepared by diluting 1.0216 g potassium dichromate (dried at 103 ℃ over night), 167 mL concentrated sulfuric acid and 33.3 g mercuric sulfate ($HgSO_4$) into 1 L DI water.

Procedure: The COD measurement was conducted as per the procedure described below: mix 1.2 mL digestion solution, 2.8 mL sulfuric acid reagent with 2.0 mL aliquot of sample (exact volume) in the COD test vials, then incubate the mixtures in a digester (Bioscience Institute, Pennsylvania), which was preheated at 150 ℃, reflux for 2 h at 150 ℃. The absorbance at 420 nm was measured after the samples were cooled to room temperature.

3.4. 5-day Carbonaceous Biological Oxygen Demand ($cBOD_5$)

3.4.1. Materials and reagents

Seeds: The seeds for $cBOD_5$ testing were cultured by the following procedure: aerate 500 mL primary effluent from Gold Bar Wastewater Treatment Plant (Edmonton, Alberta) and feed bacteria in the effluent with 5 g glucose each day for the first 5 days, then add 20 mL water samples to be tested and 5 g glucose alternatively, test the seeds after 20 days using Glucose-glutamic acid solution (the Standard check solution) and stop feeding 2 days before the $cBOD_5$ testing.

Dilution Buffer: Dilute 20 mL phosphate buffer solution, 20 mL magnesium sulphate solution, 20 mL calcium chloride solution and 20 mL ferric chloride solution in 20 L DI water and saturated with dissolved oxygen (20 ℃, aerated with organic free air over night). Stop bubbling the diluted buffer two hours before testing and tap the bottle to rid it of small air bubbles in the diluted buffer. The phosphate buffer solution was prepared by dissolving 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4.7H_2O$ and 1.7 g NH_4Cl in 1 L DI water. The magnesium sulphate solution is made by dissolving 22.5 g $MgSO_4.7H_2O$ in 1 L DI water. The calcium chloride solution is prepared by dissolving 27.5 g $CaCl_2$ in 1 L DI water, and the ferric chloride solution is made by dissolving 0.25 g $FeCl_3.6H_2O$ in 1 L DI water.

Nitrification inhibitor: Nitrification Inhibitor Formula 2533 (Hach, Germany) was chosen and used at a dose of 0.16 g per 300 mL sample.

Glucose-glutamic acid solution (Standard check solution): The glucose-glutamic acid stock solution was used as the standard checking solution and prepared by dissolving 1500 mg Glucose and 1500 mg glutamic acid, which were dried at 103 ℃ for 1 h, in 1 L DI water. For 150 mg/L glucose and 150 mg/L glutamic acid solution, the theoretical BOD_5 is 306.9 mg O_2/L. Note: it is important to prepare the standard checking solution fresh immediately before use.

3.4.2. cBOD$_5$ procedure

Sample: Pipet appropriate amount (depending on the dilution) of sample, add 2 mL of seeds to each of the bottles, mixing gently and fill the 300 mL incubation bottles (with stoppers and Wheaton sealer caps) with dilution buffer to the bottle neck, measure DO with a YSI 50 DO meter, top up with dilution buffer, close stopper, water seal, and cap the bottles and incubate samples in an air incubator (20 ±1 ℃) in darkness. Read DO at day 0 and day 5.

Water check: Fill incubation bottles with dilution buffer but without seeds and follow the same procedure as the one for samples. Read DO at day 0 and day 5.

Standards: Pipet 6 mL glucose-glutamic acid standard solution, add 2 mL seeds, mix gently, fill with dilution buffer to bottle neck and measure DO and incubate the standards as outlined in the procedure for samples.

Seed control: Pipet 2 mL seeds, fill the dilution buffer to the incubation bottles to bottle neck, measure DO, incubate the seed control samples in an air incubator (20 ±1 ℃) in darkness. Read DO at day 0 and day 5.

3.5. Dissolved Organic Carbon (DOC)

The DOC was tested by Maxxam Analytics (Calgary) using the Combustion-Infrared Method (APHA AWWA WEF 1992). Prior to analysis all water samples were filtered with membrane with a pore size of 0.45 μm (Millipore Corporation, Billerica, Massachusetts). Concentrations were reported as mgC/L.

3.6. Acute Toxicity: Luminescent bacterial bioassay

This bioassay was used since it was fast and used small samples (< 20mL) that are suited to the scale of the current experiment design. Earlier work has shown a strong correlation between standard rainbow trout static bioassay results (96-hr LC_{50}) and bioluminescence bioassays (15-minute EC_{50}) for OSPW (MacKinnon et al, 1982, 1986).

Material: Microtox® reagent (lyophilized the clonated bacterial isolated *Vibrio fischeri*), Microtox® Reconstitution Solution, Microtox® Diluent and Microtox® Osmotic Adjustment Solution and glass cuvettes (12×75 mm) were purchased from AZUR Environmental (Carlsbad, U.S.A.). The toxicity of water samples were tested using Microtox® Model 500 Analyzer (AZUR Environmental, Carlsbad, U.S.A.), which serves both as an incubator and luminometer. The wells arranged in six rows of five wells each were maintained at 15℃, and a separated Reagent Well was kept at 5 ℃ for stocking culture tube of luminous bacteria. The analyzer is interfaced with a computer installed *MicrotoxOmni* software package for data collection and analysis. All the samples were filtered with membrane with a pore size of 0.45 μm (Millipore Corporation, Billerica, Massachusetts) before the toxicity bioassay.

Procedure: Set the Microtox® Model 500 Analyzer in Acute Mode and the 81.9% test procedure. Put cuvettes in wells A1, A2, B1, B2 and Reagent Well; Add 300 μL and 1000 μL Microtox® Diluent to cuvettes in the Reagent Well and wells in A1 row, respectively. Add 1000 μL sample and 100 μL Microtox® Osmatic Adjustment Solution to each cuvette in A2 row, mix the solution with the pipettor; wait for 5 minutes; reconstitute a vial of Microtox® reagent with the 300 μL Microtox® Diluent sitting in the Reagent Well, add 100 μL reconstituted Reagent to cuvettes in the wells of B1 and B2 and wait for 15 minutes; Place cuvettes in B1 and B2 to Read Well and read the I_0, and then transfer 900 µL solutions from the cuvettes from A row to the cuvettes in B row, mix contents and read light intensity 5 minutes after the addition of reconstituted reagent. The toxicity test of phenol standards (around 10 mg/L) was also conducted to assess the procedure, and EC_{50} in the range of 13 to 26 was obtained with 5 minutes of incubation.

The ratio of light lost to light remaining (Γ) was calculated using following equation:

$$\Gamma = \frac{C_r \times I_0 - I_{t=5}}{I_{t=5}} \quad \text{…………… ……………} \; (3\text{-}5)$$

Where C_r is the correction factor (the fraction of light remaining in the blank samples after t minutes of incubation arranged between 0.8 to 0.9),
I_0 and I_5 are the light intensities at the time 0 and 5 minutes.

A linear relationship can be obtained in the log-log plot of Γ against sample concentrations. Usually the 50% effective concentration (EC_{50}) was defined as the concentration where the Gamma value was equal to 1. In this work, the EC_{20} was used because of the relatively low toxicity of OSPW.

3.7. NAs concentrations in water samples: quantitation using Fourier transform infrared spectroscopy (FT-IR)

This method has been widely applied to OSPW samples (Clemente and Fedorak, 2005; Han et al, 2009). It is based on the measurement of the carboxyl group in dichloromethane extractables. It is not intended to provide qualitative information on the NAs, but is applied to follow concentrations of the total NAs in both feed and ozone-treated waters. No interference with the method for the samples included in this study was identified.

3.7.1. Liquid-liquid extraction of NAs

The NAs in OPSW were extracted using the liquid-liquid extraction methods according to the following protocol: Weigh approx. 40 mg water sample, adjust the pH values below pH 2.0 by adding 3 to 4 drops of 50% (v/v) H_2SO_4, extract the water samples with HPLC grade dichloromethane (Fisher Optima grade) twice, combine the extracts and concentrate to dryness using organic-free air flow.

3.7.2. FT-IR

The FT-IR testing for the measurements of NAs was conducted using a Nicolet 8700 FT-IR Spectrometer (Thermo Electron Corporation, Waltham, U.S.) at the Syncrude Canada Ltd.'s Research Centre (Edmonton, Canada). Briefly, the extracted NAs from water samples were reconstituted with dichloromethane, and the total absorption at 1703 and 1740 cm^{-1} measured by FT-IR (Nicolet 8700 FT-IR spectrometer, the Thermo Electro Corporation) was compared with the standard curve, which showed the relationship between the concentration of commercial Naphthenic Acids, Kodak^{TM} acids, and their total absorption of these acids at 1703 and 1740 cm^{-1}.

4. RESULTS AND DISCUSSION

4.1. Ozonation of OSPW

There are several OSPW storage ponds operated by Syncrude Canada Ltd. at its Lease 17/22 site, including Mildred Lake Settling Basin (MLSB), West In-pit (WIP), Southwest Sand Storage Basin (SWSS), as well as a South East In-pit (SEIP) and South West In-pit (SWIP). After the extraction process, tailings slurries are pumped into the various retention areas where water is released, and this clarified OSPW is recycled back to operations. As part of its tailings management program, operators such as Syncrude Canada Ltd. have developed a seepage collection system to collect and return any OSPW seepage waters from these structures. This seepage water is pumped back to the seepage water ponds in order to mitigate impacts to the surrounding aquatic systems. In the current study, this water is referred to as dyke seepage water (DSW) and has properties (salinity, NAs, NH_4) comparable to those within the settling basins (Han et al. 2009).

The characteristics of OSPW vary greatly due to the different ores, extraction processes, ages and other issues. WIP is an active settling basin and is “fresh”; DSW is aged anaerobically, and sand filtered, coke-treated OSPW is “fresh” OSPW that has been in contact with approx. 22 wt% hot petroleum coke.

Table 4.1 shows some of the characteristics of the OSPW with different resources used in batch ozonation. The pH values of all the water samples was about 8, but the COD and NAs contents varied greatly. The OSPW used in the semi-batch ozonation was taken from WIP and is considered as fresh OSPW when compared to the OSPW which have been stored in MLSB for more than 10 years (and referred as aged OSPW). The characteristics of the OSPW used in semi-batch ozonation were measured, and the results, including pH, conductivity, NAs, COD, DOC and $cBOD_5$, are showed in Table 4.2. All the values were in the normal range compared to the routine testing results from Syncrude Research and Development Centre in Edmonton, Canada (MacKinnon 2008).

Table 4.1 The characteristics of the OSPW for batch ozonation

Water	pH	COD	NAs
		mg/L	mg/L
WIP-OSPW	8.3	230	63
DSW	8.03	254	84
Coke-treated OSPW	8.37	64	10

Table 4. 2 The characteristics of the OSPW for semi-batch ozonation

pH	Conductivity	NAs	COD	DOC	cBOD$_5$	EC$_{20}$
	µS/cm	mg/L	mg/L	mg/L	mg/L	%
8.66	3150	75	250	52	8	24

The most commonly used bench-scale ozonation methods include both batch ozonation and semi-batch ozonation (APHA AWWA WEF 1992). In the batch ozonation method, the ozone stock solution is used to add ozone to the water samples, while in the semi-batch system gaseous ozone is continuously added to water samples. These bench-scale ozone tests are widely used to understand the site-specific water quality effects on the ozone demand and ozone decay. They are, therefore, important for the engineering design of the scaled-up ozonation system.

4.1.1. Batch ozonation

Batch reactor is one of the principle types of reactors used for the treatment of wastewater. In a batch reactor, the flow of water to be treated enters, is treated and discharged, and then the next cycle repeats. Therefore, during one cycle of the reaction, no other flow enters or leaves the reactor. The liquid in batch reactor are mixed completely (Metcalf & Eddy 2003). Batch ozonation was first conducted to assess the performance of ozone on the degradation of NAs since batch ozonation process does not need complicated equipments and the experimental parameters are easily to be controlled.

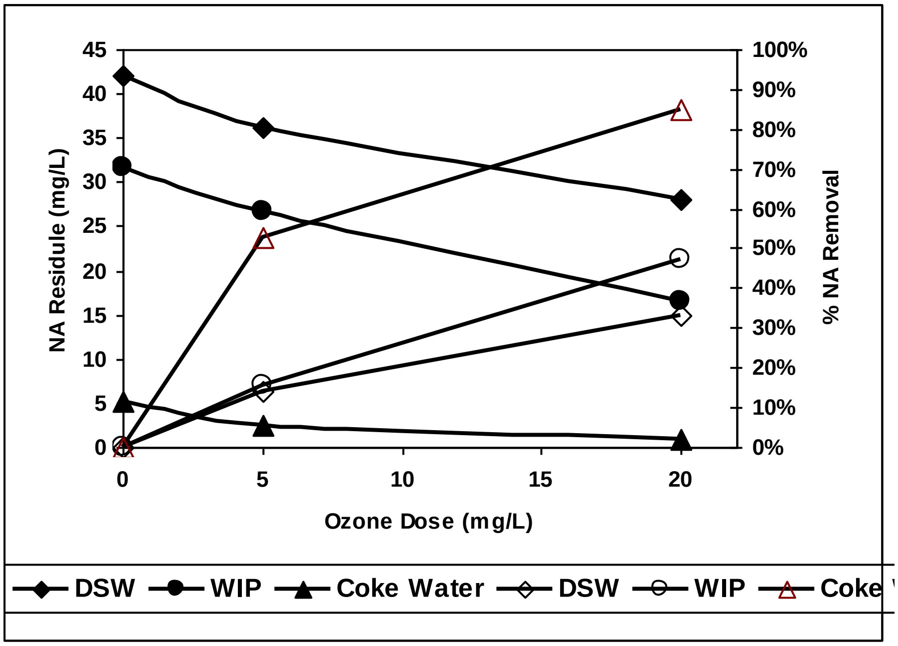


Figure 4.1 The NAs degradation vs. ozone dose using the batch ozonation method. (The solid markers present the NAs residual and the hollow markers present the %NAs removal; The NAs concentrations in the waters have been diluted to 50% due to addition of ozone stock solutions. For example, the NAs content in DSW with the ozone dose of zero was 84 mg/L, but the tested concentration was 42 mg/L because of the dilution.)

Figure 4.1 shows the NAs degradation trends when the OSPW from different sources is applied to different ozone doses. The NAs contents in different OSPW water samples decreased with increased ozone doses. With the ozone dose of 20 mg/L, the NAs concentration in DDW dropped from the 42 to 28 mg/L, representing 33% of NAs reduction. The removal of 47% of NAs in WIP-OSPW was obtained for WIP-OSPW, dropping from 31.6 to 16.6 mg/L. The most promising NAs degradation efficiency (>85% removal) was achieved when the test OSPW water was the coke-treated water. At ozone dosages of 20 mg/L ozone, the NAs concentration in the coke-treated OSPW went down to 0.8 mg/L, corresponding to about 15% of the initial NAs concentration of 5.3 mg/L. The ozonation of different OSPW using the batch ozonation method indicates that ozone can effectively degrade the NAs in OSPW water samples. However, less than 50% reductions of NAs were achieved for the OSPW with high NAs, including DDW and WIP-OSPW, with the ozone dose of 20 mg/L.

The stoichiometrics of the complete oxidation of NAs using ozone can be showed in the following equation:

$$C_nH_{2n+Z}O_2 + (3n + Z/2 - 2)/3O_3 \rightarrow n\,CO_2 + (n + Z/2)H_2O \ldots\ldots(\text{ 4-1 })$$

According to the GC analysis conducted by (Clementre and Fedorak 2005), the dominant NAs in the extract from OSPW are those with carbon numbers of 13 to 15 and Z numbers of -4 to -8, and the corresponding molecular mass of the predominant NAs range from 200 to 240 amu. For the most dominant NAs (n=14, Z=-6) in this analysis instance, the molecular mass is 220 amu and the amount of ozone for the complete oxidation of 220 mg dominant NAs is around 592 mg, which was calculated based on the equation 4-1. Figure 4.2 shows the estimated ozone required for completed oxidation of the dominant NAs found in OSPW. Therefore, in order to completely oxidize the NAs with a similar molecular mass and structure, the ozone dose for complete ozonation of NAs of 42 mg/L (DSW), 31.5 mg/L (WIP), and 5 mg/L (coke water) would be 113 mg/L, 85 mg/L and 13 mg/L, respectively (without considering the ozone self-decomposition). However, the ozone dose of 20 mg/L, which corresponded to 40 mg/L ozone stock, was close to the highest ozone dose that can be applied to the OSPW water samples due to the solubility limit of ozone in the water and the dilution during the batch ozonation process. The solubility of ozone in water is 0.64 (v/v) at 0 ℃

and 1 atm (Rakness 2005), and the highest ozone concentration in ozone stock solutions are in the range from 30 to 40 mg/L with an ice bath (APHA AWWA WEF 1992). In addition, self-decomposition of ozone will occur in the batch ozonation system, which also constrained the effective ozone dose used for NAs degradation in OSPW water samples. Thus, the ozone dose in the batch ozonation experiments is not enough to handle the OSPW with high NAs content. Therefore, semi-batch ozonation was selected as an alternative ozonation system. It is capable of handling the oxidation of higher NAs concentrations in tested waters since it can provide continuous ozone gas. Such a semi-batch system can effectively deliver higher ozone doses than would be capable with the batch method.

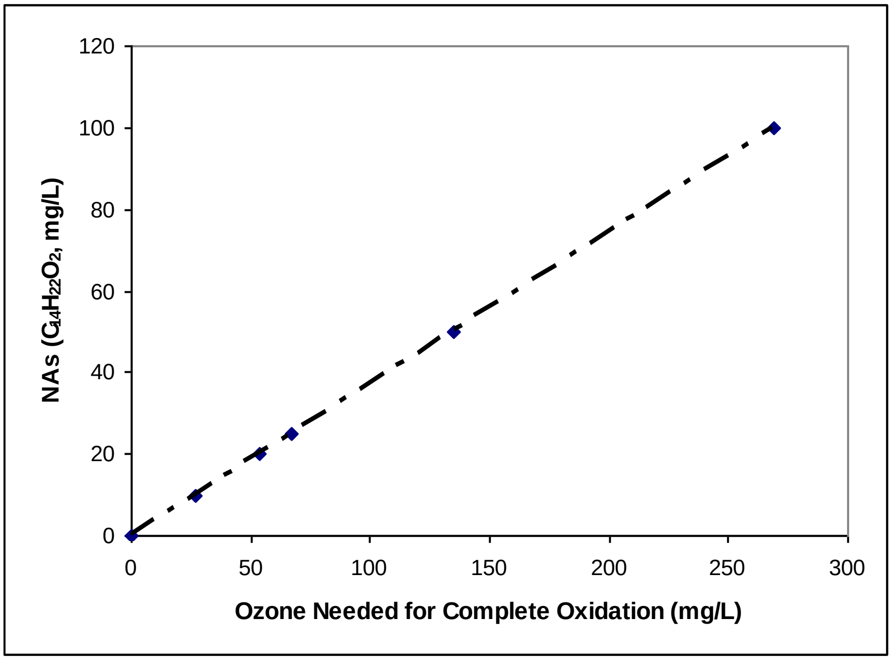


Figure 4.2 Ozone needed for complete oxidation of the dominant NAs in the OSPW extracted.

4.1.2. Semi-batch ozonation

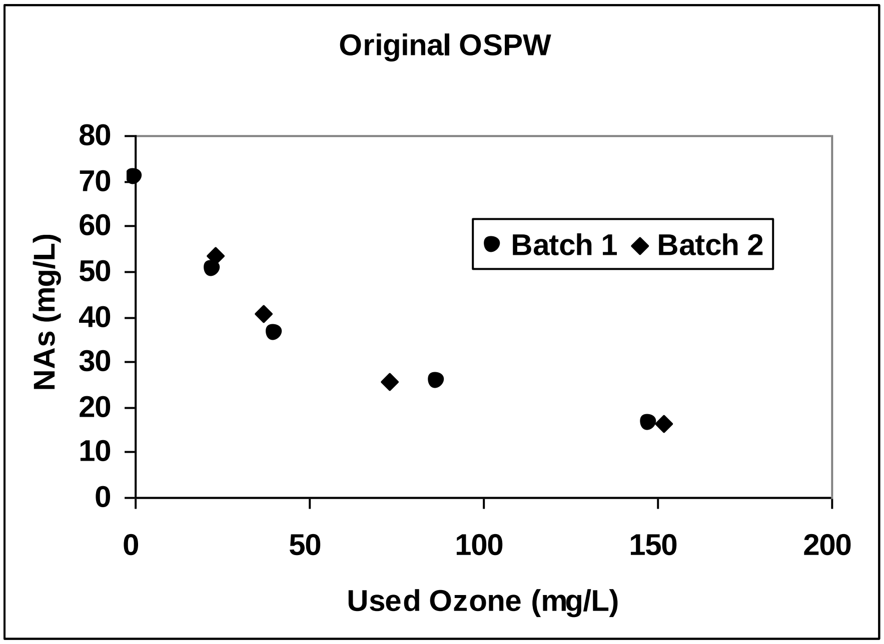
The results from the batch ozonation of OSPW water samples showed ozone can degrade NAs, however, the application of ozone for the degradation of NAs at higher concentration levels still needs to be developed. Because ozone supply in the semi-batch system is continuous, a semi-batch ozonation system was constructed to investigate the potential of ozone for degradation of NAs at elevated levels in OSPW.

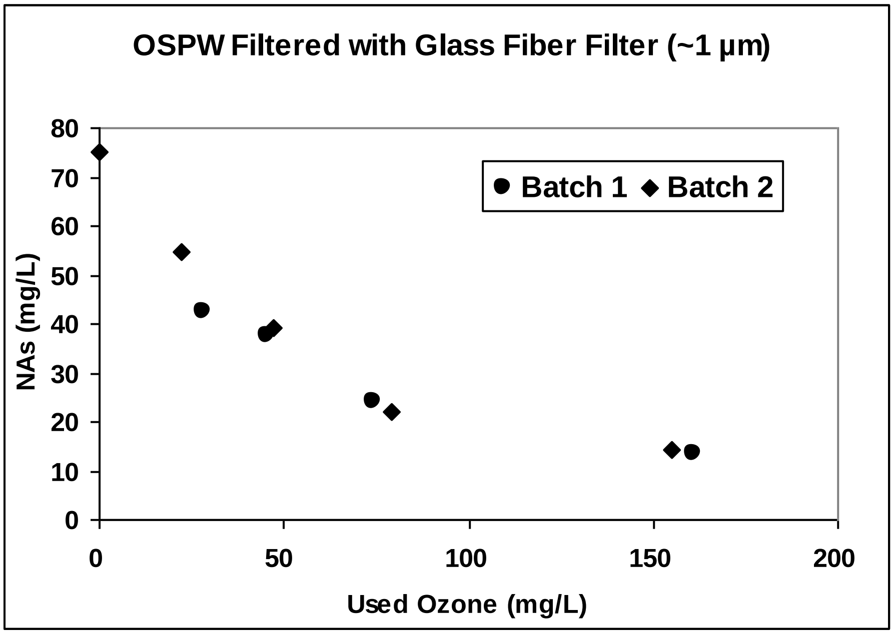
The schematic of semi-batch ozonation system was shown in Figure 3.2. Similar to the commercial ozone treatment system, the semi-batch ozonation system consists of four major parts, the feeding gas, ozone generator, contactor and ozone destructor (Rakness 2005). Using this method, the amount of ozone in the feeding gas, off gas and ozone residues in the reactor could be quantitatively controlled.

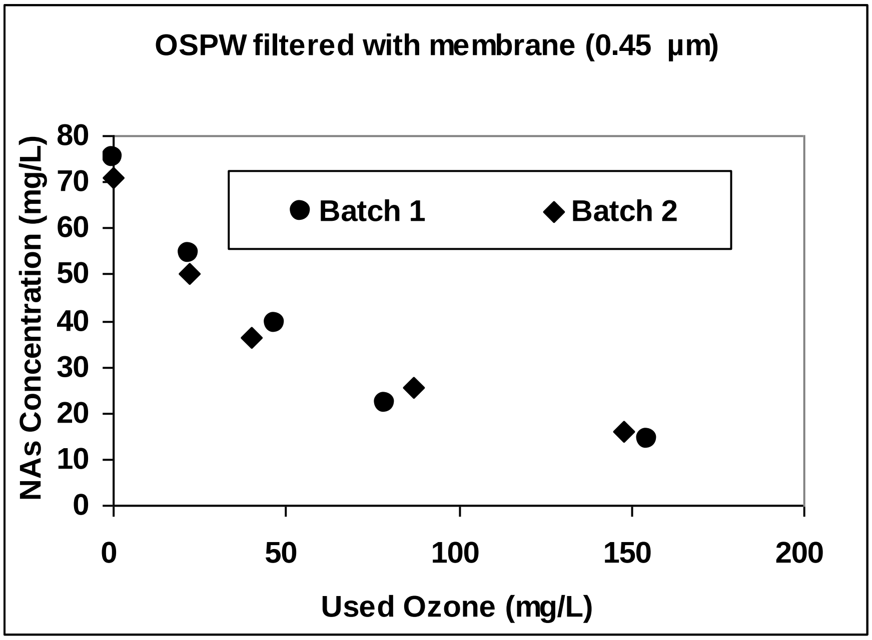
4.1.2.1. Reproducibility of ozone decomposition of NAs in OSPW: Efficiency of semi-batch ozonation system

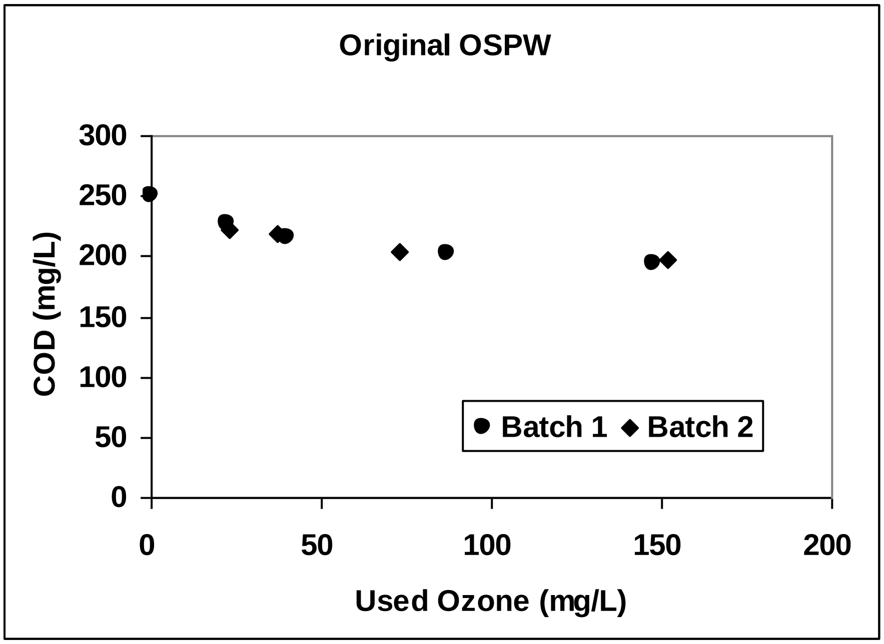
The reproducibility of the semi-batch ozonation system was tested by comparing the NAs and COD removals from OSPW over a range of ozone doses. The Figure 4.3 shows the comparable NAs and COD reductions have been obtained by using similar ozone doses. This indicated the semi-batch ozonation system is a feasible approach for assessing the ozonation of OSPW and be able to monitor and control the ozone dosages. However, t-test and ANOVA can not be applied to compare whether the deduction results are statistically different between two batches because the ozone doses applied in batch 1 and batch 2 could not be controlled.

In many research publications related to water/wastewater treatment using ozone, ozone doses were reported as the time of ozonation. It is acceptable to use ozonation time to represent ozone doses in the preliminary experiments; however, it is difficult to know the exact ozone used for the ozonation. This also makes experimental replication difficult and potentially less valuable for the further engineering design that will be required for scaling up the system.


Original OSPW
NAs (mg/L)
80
70
60
50
40
30
20
10
0
0
50
100
150
200
Used Ozone (mg/L)
● Batch 1 ◆ Batch 2


OSPW Filtered with Glass Fiber Filter (~1 µm)
NAs (mg/L)
80
70
60
50
40
30
20
10
0
0
50
100
150
200
Used Ozone (mg/L)
● Batch 1 ◆ Batch 2


OSPW filtered with membrane (0.45 µm)
NAs Concentration (mg/L)
80
70
60
50
40
30
20
10
0
0
50
100
150
200
Used Ozone (mg/L)
● Batch 1
◆ Batch 2


Original OSPW
COD (mg/L)
300
250
200
150
100
50
0
0
50
100
150
200
Used Ozone (mg/L)
● Batch 1
◆ Batch 2

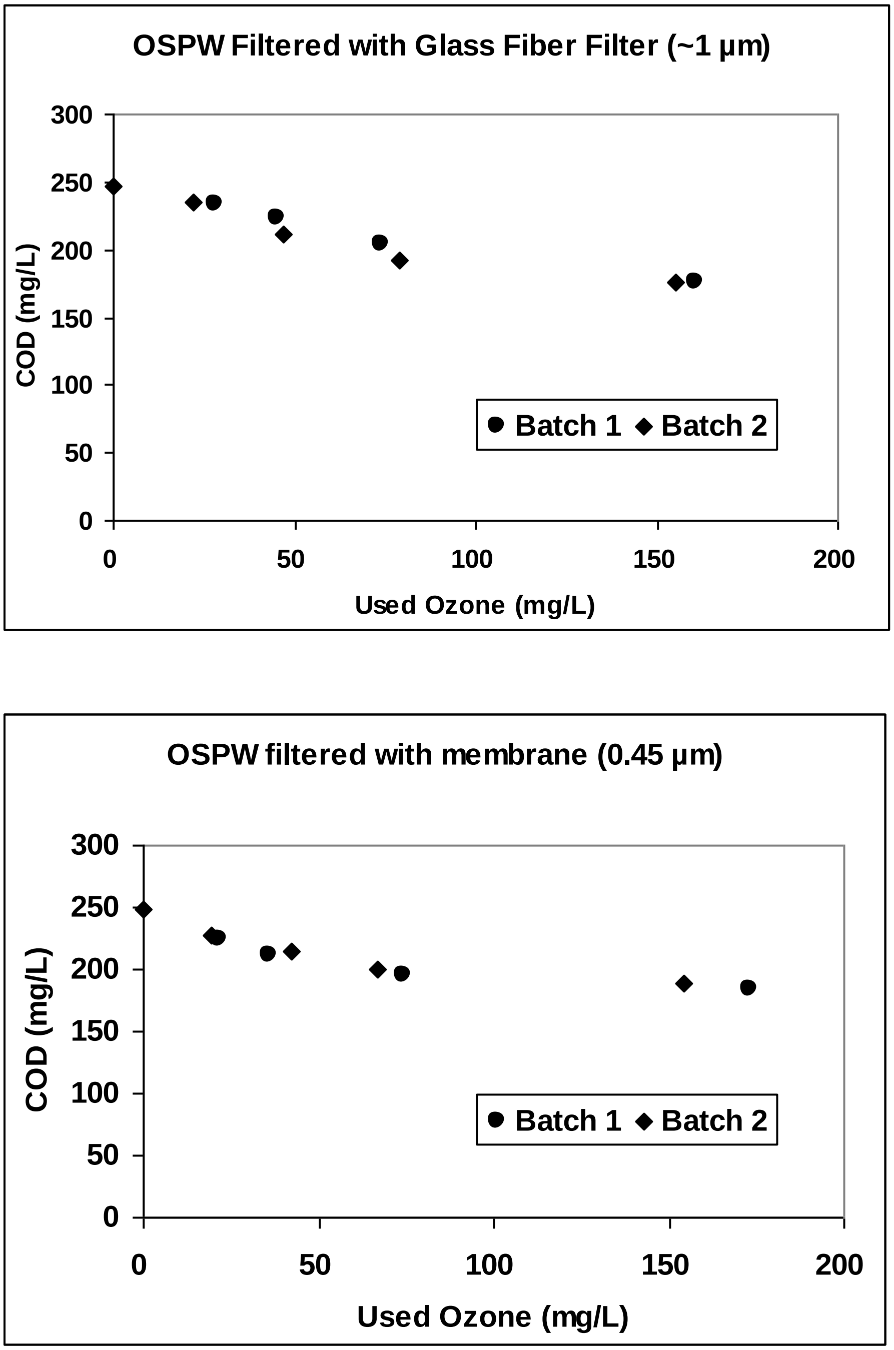


Figure 4.3 The comparison of NAs and COD levels as a function of used ozone. (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

The ozone use efficiency using the semi-batch ozonation system was calculated using equation 3.4, and the average of the ozone use efficiency for the 45 semi-batch ozonation experiments on OSPW was 16.8% (See Appendix 7.4.2), which is very low compared to the common ozone use efficiency of 85% in the drinking water treatment industry (Rakness 2005). There are a lot of factors affecting ozone use efficiency, such as water quality, geometry and size of the reactor, the mass transfer and hydrodynamics. The objective of the current study was not the optimization of these factors, but rather to examine the applicability of ozonation for NAs degradation from OSPW and degree of NAs removal.

4.1.2.2. Ozone dose

The used ozone dose shown in figures (Figure 4.3 to 4.21) in this section includes both the ozone consumed in the reaction with constitutes in the OSPW and in the process of self-decomposition. It is calculated by subtracting both the waste ozone dose (monitored by KI bottles) and the residual ozone dose (measured using Indigo method) from the Applied Ozone dose (obtained by the reading of the HC500 ozone monitor for the feeding gas). The NAs, COD, DOC, $cBOD_5$ residuals and toxicity (EC_{20}) of the original OSPW and ozone-treated OSPW samples have been measured to assess the performance of ozone treatment.

4.1.2.3.NAs residuals

The measurement of NAs in the test waters prior to (initial) and after (residual) ozonation in the reactor vessel was conducted using FI-IR, which has been described in the section of 3.7.2. Figure 4.4 shows the relationship between the used ozone dose and the residual naphthenic acids. The naphthenic acid residuals decreased rapidly and almost linearly as the used ozone dose increased from 0 to 79 mg/L. With the used ozone dose of 79 mg/L, 70% of the initial naphthenic acids in the OSWP were removed, dropping from 75 mg/L to 22 mg/L. Therefore, almost 0.66 mg/L of NAs was removed per mg/L of Used Ozone. However, the NAs removed per mg/L used ozone decreased after the used ozone dose exceeded 80 mg/L, reaching around 0.09 mg NAs/mg Used Ozone. The reduction of 94% was achieved with the used ozone dose of 280 mg/L, with the NAs residual of 4.7 mg/L. The lower NAs residual around 1 mg/L (close to the detection limit of the FT-IR methods for naphthenic acids) was achieved when a higher ozone dose was applied. Based on the data above, ozone has shown a promising effect on the degradation of naphthenic acids in OSPW from Athabasca oil sands industry. Since the inflection of delta used ozone dose (mg/L) per NAs removal (mg/L) took place with the used ozone dose of 80 mg/L, the optimized used ozone dose for the removal of NAs in OSPW from WIP was in the range of 80 mg/L for this semi-batch ozonation system.

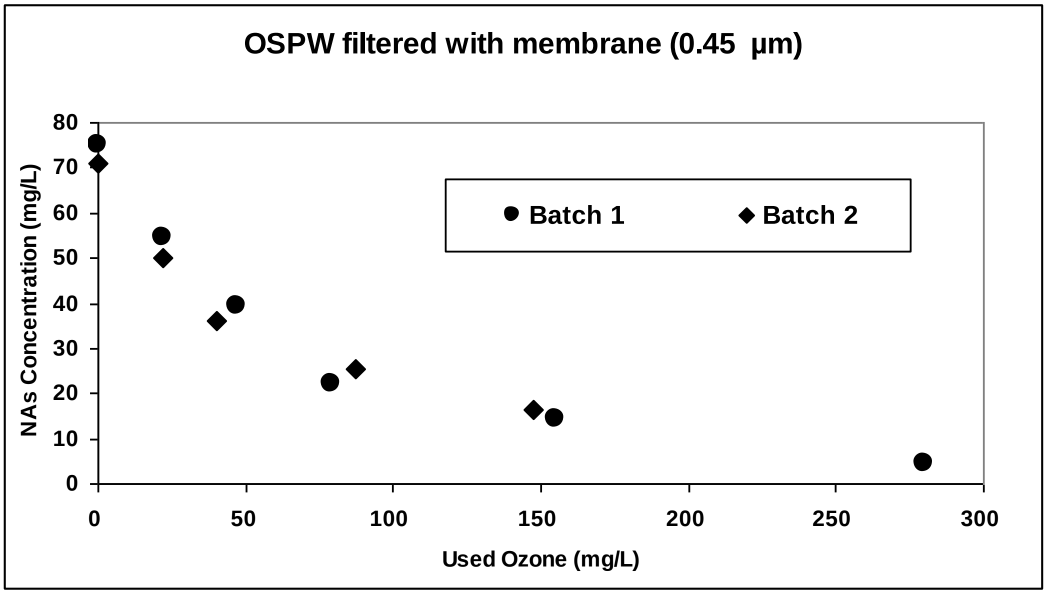


Figure 4.4 The effect of used ozone dose on the NAs degradation. (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix.)

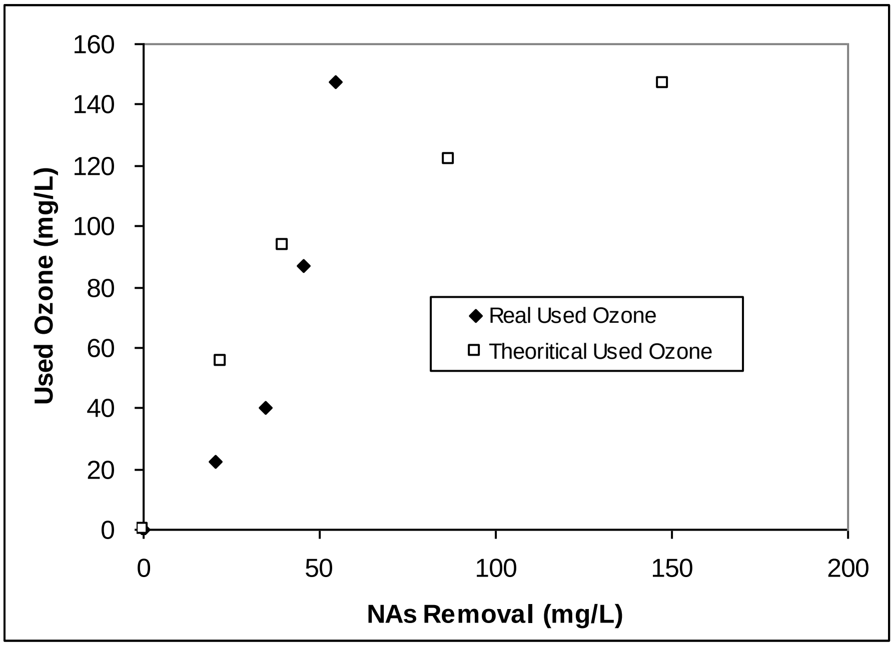


Figure 4.5 The comparison of real and theoretical NAs removal. (The experimental condition is identical to that in Figure 4.4).

Figure 4.5 shows both the real and theoretical used ozone for NAs removal. The theoretical used ozone is the used ozone dose that is required to completely oxidize NAs. The deviation of real NAs removal could mean a number of things: (1) There are some components in OSPW which consume ozone other than the NAs; (2) A complete stoichiometric balance as in the pathway of decomposition may be partial rather than complete; (3) There are some NAs exiting in the OSPW which are tougher to be oxided than the dominant species; and (4) the efficiency of contractor need to be improved.

Recent research (Martin 2010) reported that the major by-products of NAs are oxidized NAs, i.e., hydroxyl- or keto-NAs. However, the NAs presented in Figure 4.5 were measured by FT-IR, which responses to the carboxyl groups in NAs. Therefore, FT-IR cannot differentiate the NAs and oxidized NAs, and the NAs concentrations showed in Figure 4.5 include both NAs and oxided NAs.

4.1.2.4.COD & DOC

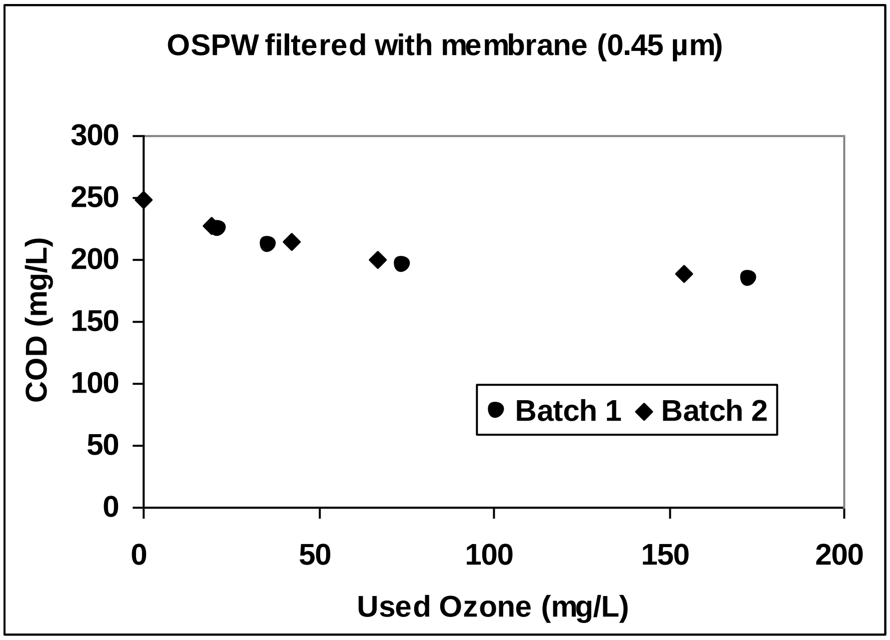


Figure 4.6 The effect of the used ozone dose on COD deduction. (The experimental conditions are shown in Table 7.2 and Table 7.4 of the Appendix)

Figure 4.6 shows the effect of the used ozone dose on the COD residuals. The COD decreases gradually, dropping from the original COD of 247 mg/L to 176 mg/L with the applied ozone doses of 155 mg/L, reaching a COD reduction of 29%, which is much lower than the naphthenic acids reduction (81%) with the same used ozone. The low COD reduction may be explained by the assumption that the large organic molecules break into smaller organic molecules, which also contribute COD. However, the mechanism of the naphthenic acids degradation pathways is still unclear, and further experiments are needed to prove this assumption.

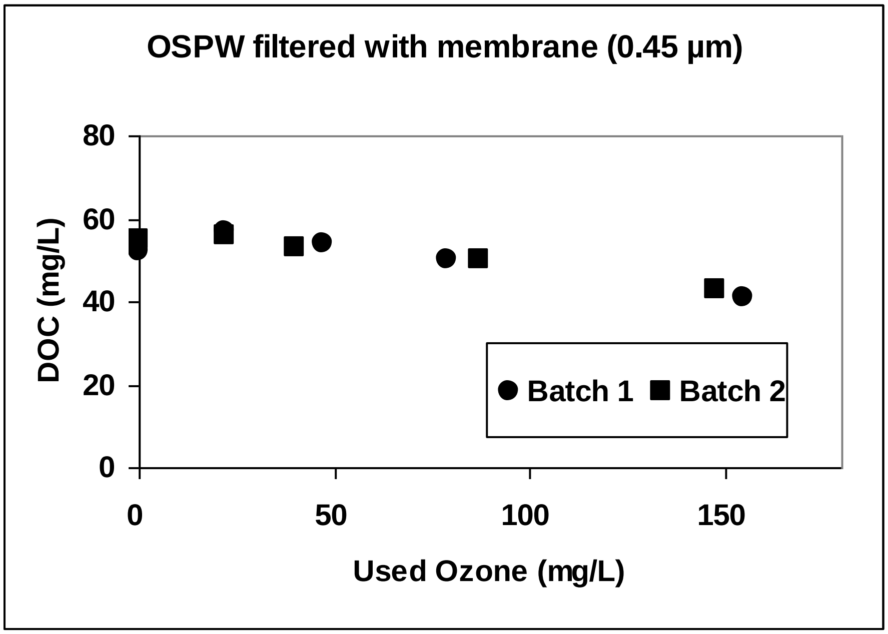


Figure 4.7 The effect of used ozone does on DOC reduction. (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

The relationship between the DOC residual and the applied ozone dose is shown in Figure 4.7. The DOC residual increased from 52 mg/L to 57 mg/L with the applied ozone dose of 22 mg/L and then dropped to 43 mg/L with the applied ozone dose of 155 mg/L, 83% of original DOC.
Comparing the deductions of both naphthenic acids and DOC, it is easy to find that the naphthenic acids reduction (81%) is much higher than the DOC reduction (21%) after the OSPW was treated with the used ozone of 155 mg/L. This indicates that NAs have been broken down into some organic molecules which do not have carboxyl groups. It may suggest that ozonation is proceeding through de-carboxylation rather than complete dissolved organic matter (DOM) re-mineralization. However, further identification of the intermediate ozonation productions is needed to understand the pathway of the ozonation of NAs in OSPW.

It should be noted that a higher DOC value (56 mg/L) was observed with the used ozone dose of 22, compared to the DOC value in the untreated samples. This increase is due to an inefficient combustion of organics in the samples when they were tested. In order to achieve an efficient combustion, Gamal El-Din’s group (2010) developed a new methodology for TOC and DOC testing employing a higher temperature of 850 ℃ for complete combustion (compared to 680 ℃ currently used by most of the commercial analytical labs), a high temperature titanium dioxide based platinum catalyst (to replace a platinum catalyst), a higher acid concentration and longer purging time (60-90 seconds).

4.1.2.5. $cBOD_5$ & $cBOD_5$/COD ratio

The “fresh” OSPW present in settling basins (eg. WIP) and seepage waters (eg. DSW) have low $cBOD_5$, less than 10 mg/L. The low $cBOD_5$ shows the low bio-degradability potential of OSPW. Figure 4.8 shows $cBOD_5$ of OSPW treated with various ozone doses. For the membrane-filtered OSPW, with the increasing ozone doses the $cBOD_5$ increased from the original value of 4 mg/L to 25 mg/L. This occurred as the measured used ozone dose was 79 mg/L. As the used ozone dose increased further during the semi-batch runs, the $cBOD_5$ was higher and then stayed at this elevated level.

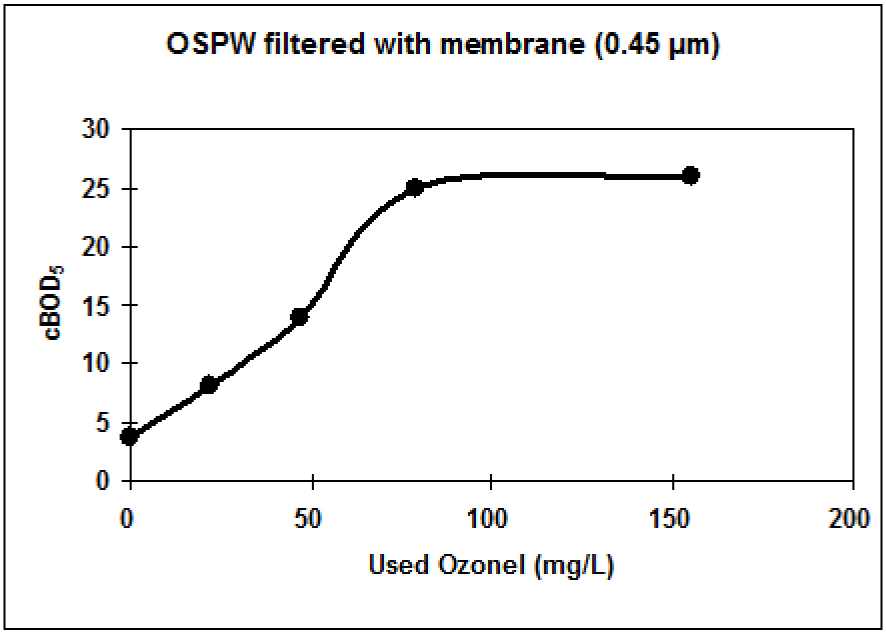


Figure 4.8 The relationship between cBOD$_5$ and used ozone dose. (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

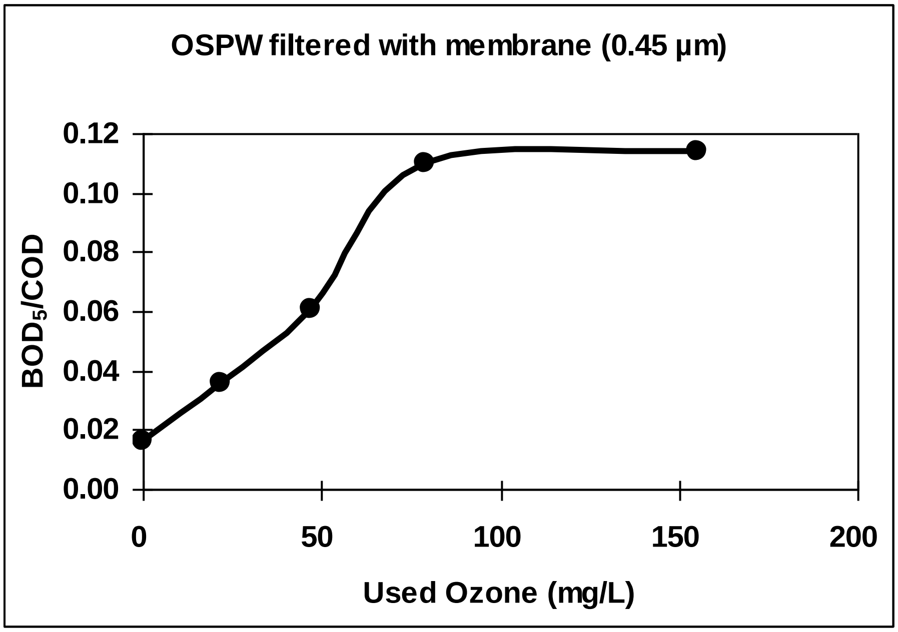


Figure 4.9 The cBOD$_5$/COD vs. used ozone (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

The higher $cBOD_5$ values indicate that the ozone-treated OSPW waters are becoming more biodegradable with the ozonation process. This change is positive since it would suggest that the produced waters would be more amenable to bio-treatment processes afterwards. The $cBOD_5$/COD ratios for OSPW treated with different used ozone doses are showed in Figure 4.7. Similar to the trend shown in Figure 4.8, the $cBOD_5$/COD ratios increase as the used ozone doses increased, reaching the maximum of 0.11 with the used ozone of 155 mg/L (See Figure 4.9).

4.1.2.6. Toxicity

The Bioluminescent Bacterial (Microtox®) Acute Toxicity Test was used for the acute toxicity test of water samples because of its speed, simplicity, sensitivity and convenience. In earlier studies, a good correlation between this bacterial acute bioassay (EC_{50}) and rainbow trout acute bioassay (LC_{50}) results for OSPW were reported (MacKinnon et al, 1981, 1986). Figure 4.10 shows the Microtox Acute Toxicity, representing as EC_{20}, for the OSPW water samples treated with ozone. The EC_{50} values for the untreated waters indicate low acute toxicity (>91%) that likely resulted from the storage time between the collection of the fresh OSPW and that which was used in the semi-batch experiments. In addition, the EC_{50} values of the entire ozone-treated OSPW water sample were greater than 91%, which indicates low acute toxicity. As a result for this study, an EC_{20}, instead of EC_{50}, is used to represent toxicity. The EC_{20} defines the highest tested concentration not causing a reduction in natural bioluminescence of as much as 20% in the luminescent bacteria population relative to a non-test reference sample. As a result, the higher EC_{20} indicates lower toxicity.

As seen in Figure 4.10, the toxicity of untreated OSPW was 23% (EC_{20}=23% vol/vol). The toxicity decreased (higher EC_{20} values) with the increasing ozone dosage, reaching above >91% with a used ozone dose of 79 mg/L. This indicates the ozone-treated OSPW was non-toxic with respect to the applied bioassay after having been stored for an extended period and treated with a dose above 79 mg/L. Based on the results from the Microtoxic Acute Toxicity bio-assay, ozonation is an effective technique to detoxify the stored OSPW in the Athabasca oil sands industry. Recalling the cBOD$_5$ values of ozone treated OSPW, ozonation has demonstrated a process which facilitates the followed bio-treatments since it increases the biodegradability and lowers the toxicity of the ozone-treated WIP-OSPW.

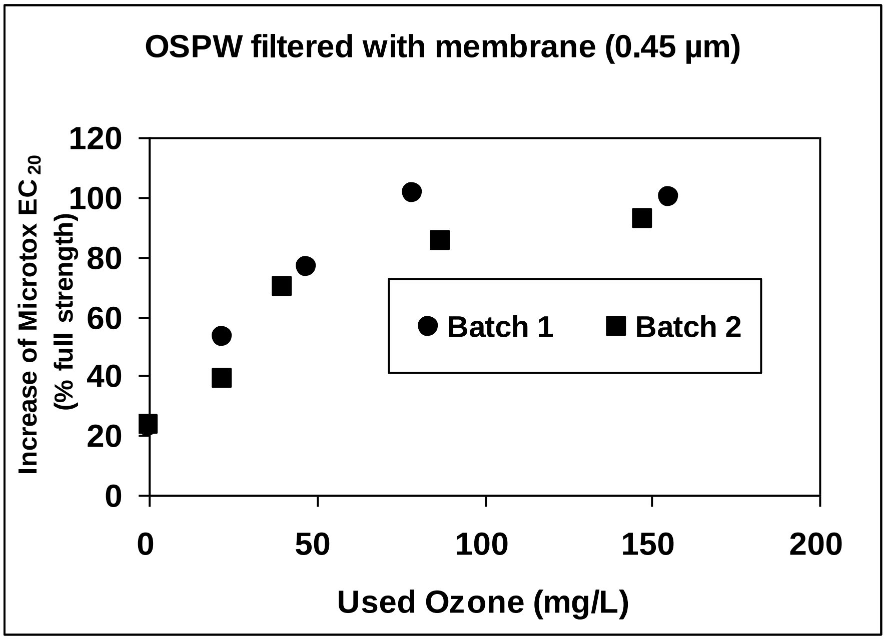


Figure 4.10 EC$_{20}$ vs. used ozone dose for OSPW (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

It should be noted that the toxicity of OSPW tested using the Microtox bioassay is an assessment of toxicity of OSPW to the bioluminescent bacteria. It can not be simply used to predict the toxicity of OSPW to higher organisms such as fish and invertebrates or other aquatic organisms.

4.1.3. Effect of filtration on the ozonation performance

The characteristics of OSPW vary according to different ore and extraction processes. The OSPW used for this work looked more turbid than the OSPW from other batches. The total solid (TS) content (dissolved plus particulate) was found to be 2380 mg/L, of which the suspended fraction was about 350 mg/L. Such high suspended solid loads may impact ozonation effectiveness. Therefore, a study of the effect of filtration on the ozonation performance was conducted. The OSPW water samples were filtered either by glass fiber filters or membrane filters with the pore size of 0.45 µm. The Whatman grade 934AH glass fiber filter was chosen because it has been used for the measurement of total dissolved solid (TDS) in the standard method.

Ozonation in the semi-batch unit was applied to the OSPW with total suspended solids of 350 mg/L (original OSPW) and the OSPW in which suspended solids were partially removed (OSPW after filteration with glass fiber filter at effective pore size of about 1 µm; and after membrane filtration at effective pore size of less than 0.45 µm). In Figures 4.11 to 4.15, the resulting relationship between used ozone dose and the resulting NAs residuals, COD deduction, cBOD$_5$ values, cCBOD$_5$/COD ratios, EC$_{20}$ values for the unfiltered and filtered (either glass fiber filters or membrane filters) OSPW are shown. No significant differences were observed from the OSPW water sample with or without different filtration treatments.

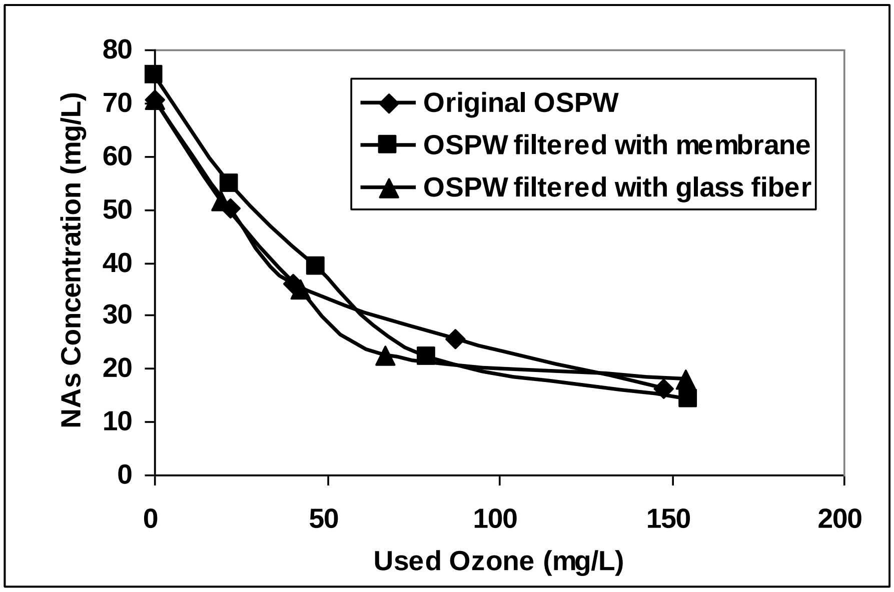


Figure 4.11 The relationship between NAs degradation and used ozone dose for OSPW waters with different filtration treatment. (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

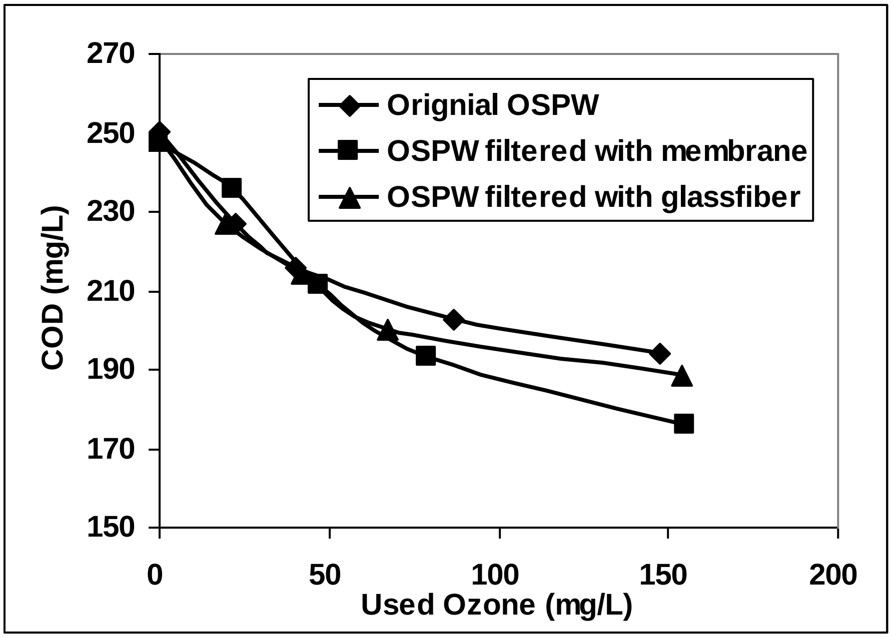


Figure 4.12 The relationship between COD degradation and used ozone dose for OSPW waters with suspended solids and after different filtration treatment**.** (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

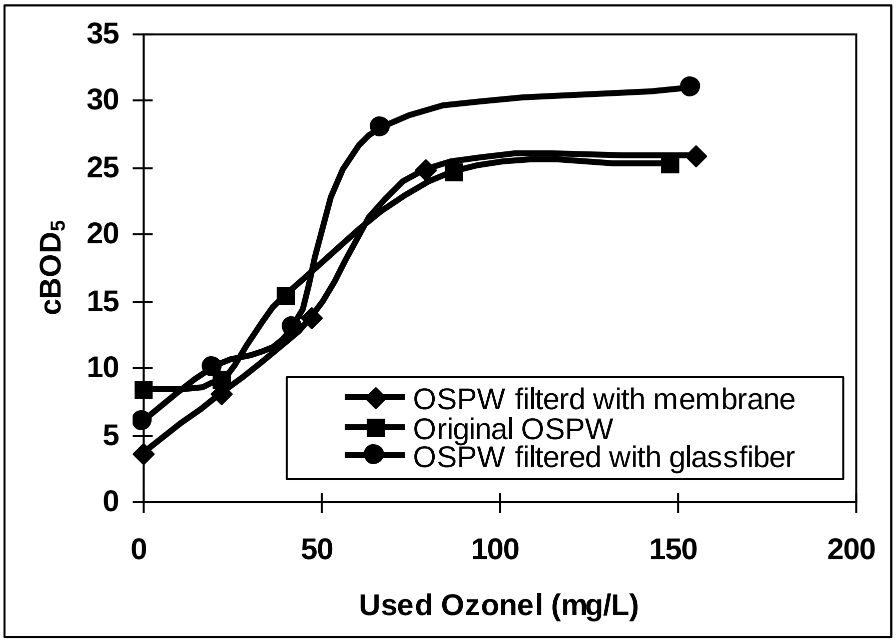


Figure 4.13 cBOD$_5$ vs. used ozone dose for OSPW waters with suspended solids and after different filtration treatment. (* The experimental conditions are shown in Table 7.2 and Table 7.4 in the Appendix)

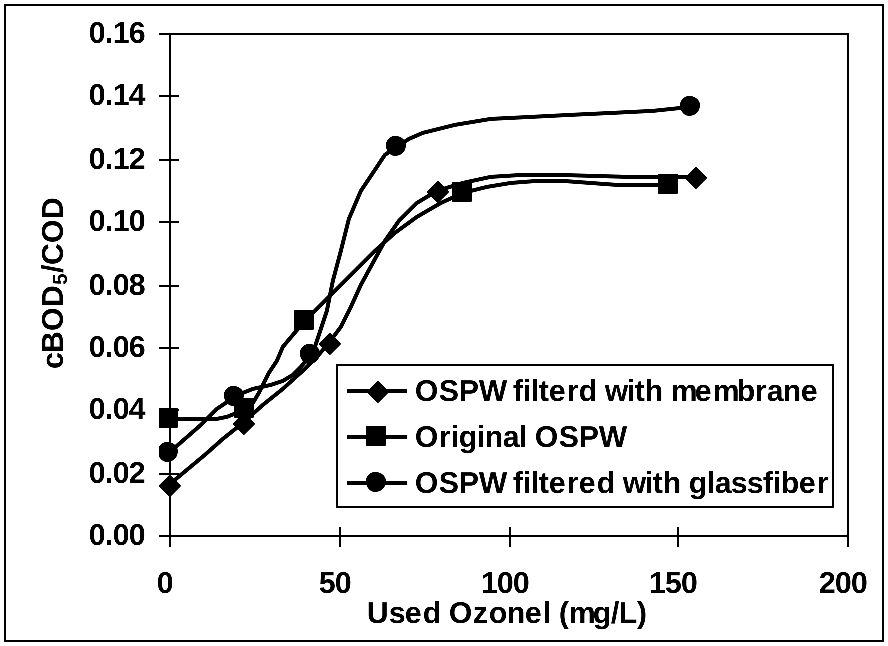


Figure 4.14 cBOD$_5$/COD ratio *vs.* used ozone dose for OSPW waters with suspended solids and after different filtration treatment**.** (* The experimental conditions are shown in the Table 7.2 and Table 7.4 in the Appendix)

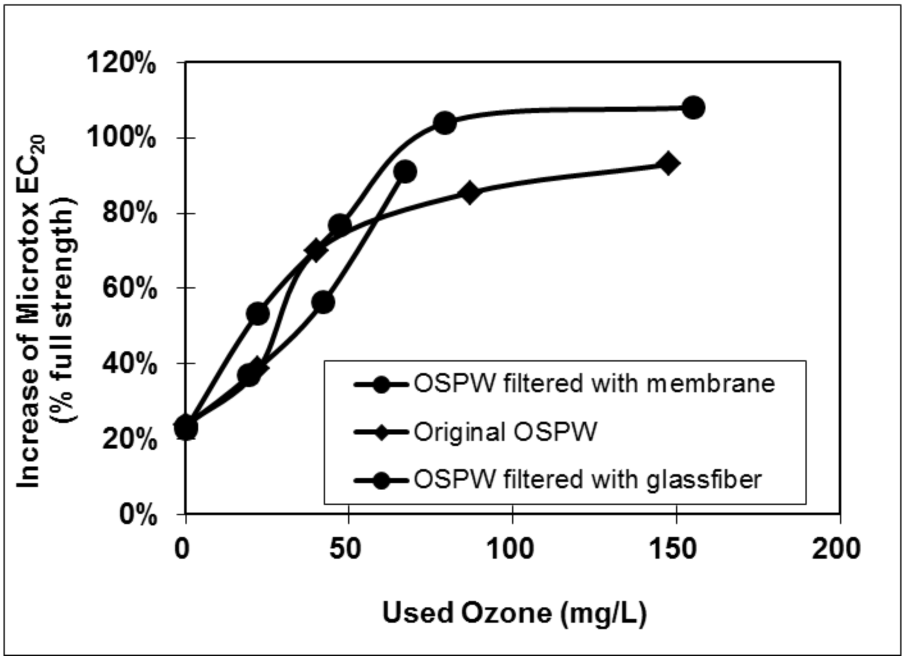


Figure 4.15 EC_{20} *vs.* used ozone dose for OSPW waters with suspended solids and after different filtration treatment. (*The experimental conditions are shown the Table 7.2 and Table 7.4 in the Appendix)

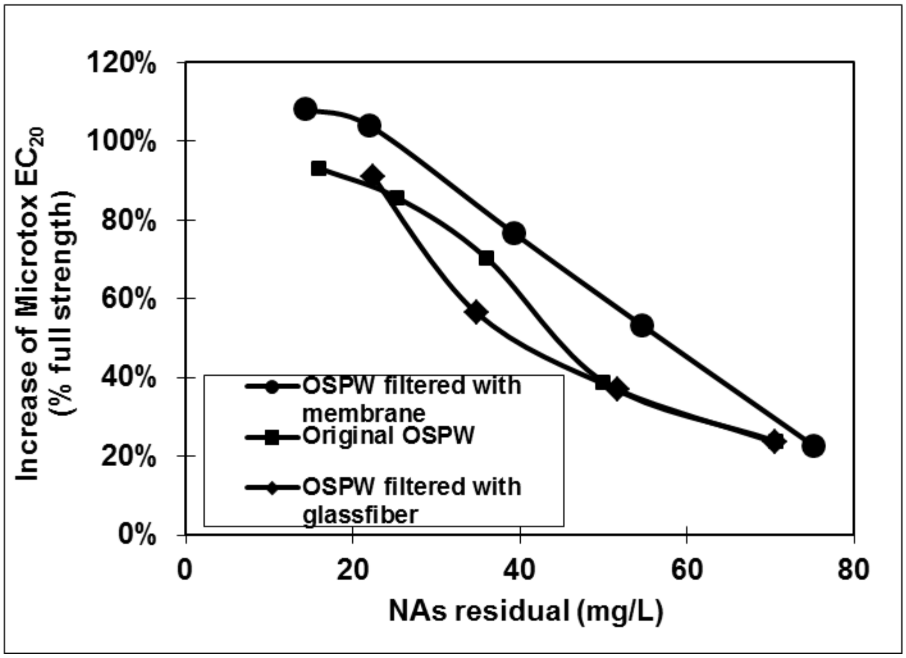


Figure 4.16 EC_{20} vs. NAs for OSPW waters with suspended solids and after different filtration treatment. (*The experimental conditions are shown in the Table 7.2 and Table 7.4 in the Appendix)

Figure 4.16 shows the toxic response, as measured by EC_{20}, of produced waters with higher NAs residuals was greater. The role of suspended solids on ozone efficiency and properties of produced waters seems minor. It has been shown in earlier studies that NAs is the major resource contributing to the toxicity of OSPW (MacKinnon and Boerger, 1986, AE, 1996, Clemente and Fedorak, 2005). Research also has found that the toxicity demonstrated by OSPW is related not only to the content of NAs, but to the species of NAs present, i.e., the molecular weight, structure and number of rings (Holowenko, et al, 2001; Scott et al, 2007; Han et al, 2009).

Figure 4.16 also shows that the EC_{20} values of the various OSPW waters were above 90%, which indicate low toxicity measured by Microtox bioassay, when the NAs concentrations in OSPW were approx. 20 mg/L. However, extra caution should be taken to explain these toxicity results because of the complex nature of NAs and OSPW. First, the results from Microtox bioassay cannot be simply used to predict the toxicity of OSPW to higher organisms such as fish and invertebrates or other aquatic organisms. Second, the NAs presented in Figure 4.16, which were measured by FT-IR, include the concentrations of both NAs and oxidized NAs. The oxidized NAs were reported as major ozonation by-products of OSPW, but the toxicity associated with those oxidized NAs is not clear (Martin 2010). Thirdly, the ozonation process will not help to remove ions such as $Mg^{2+,}$ Ca^{2+} in OSPW, and the ions with elevated concentration may have acute or cumulative impacts on aquatic ecosystems.

4.1.4. Effect of pH on the ozonation performance

The pH of water plays an important role in the ozonation process. Under acidic conditions, the direct reaction where ozone reacts with reactants in the molecular form is favored. Under basic conditions, the indirect reaction where hydroxyl radicals are generated and react with reactants, seems to be the main reaction pathway. In Figure 4.17 and 4.18, the effects of pH of the membrane-filtered OSPW on the degradation of NAs and COD are shown, respectively. No significant differences of NAs residuals were found among the water samples with different initial pH values; however, the order of COD reductions were observed as pH 8.5>pH 6.5>pH10.0. Recalling the alkalinity of OSPW is usually in the range of 500-600 mg/L, and carbonate, which is a hydroxyl radical scavenger, will be the dominated ions at pH 10.0. Because of the presence of carbonate, the concentration of hydroxyl radical at pH 10.0 could be lower than when pH is at 6.0, resulting in a lower COD reduction.

The pH values of OSPW prior to and after ozonation did not show a significant difference (±0.5 pH).

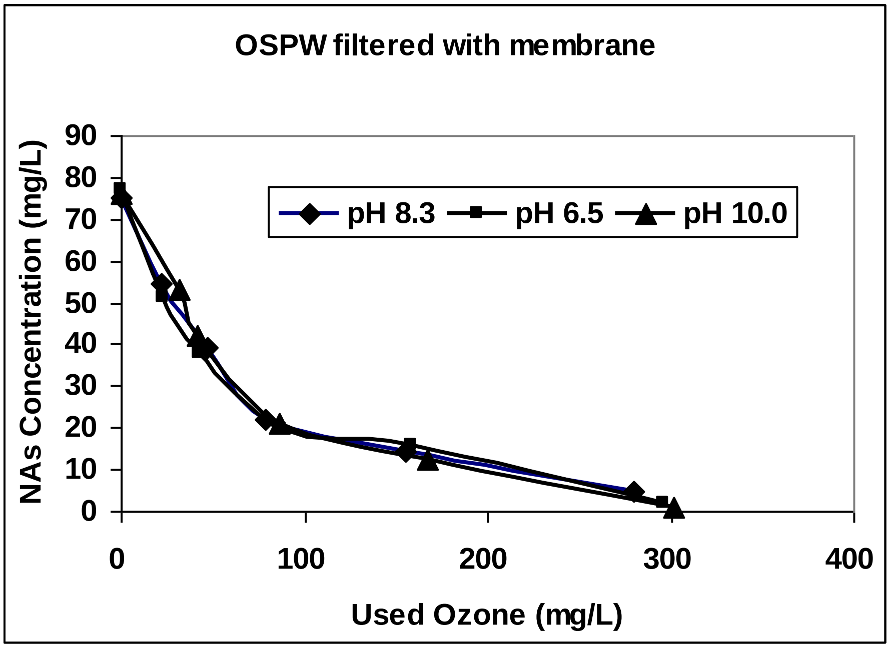


Figure 4.17 The effect of used ozone dose on the NAs degradation under different initial pH values. (* The experimental conditions are shown in the Table 7.2 and Table 7.4 in the Appendix)

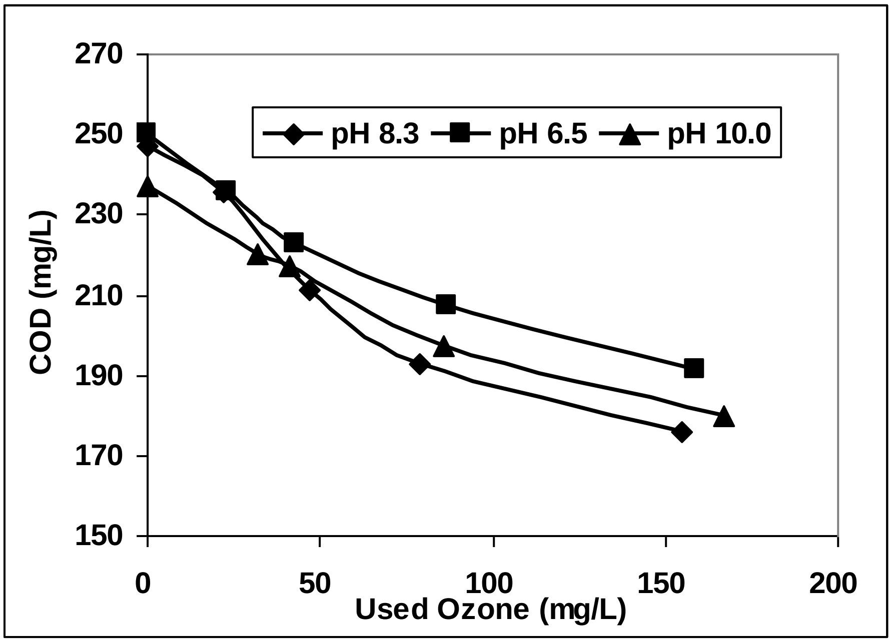


Figure 4.18 The relationship of COD deduction vs. used ozone dose for the OSPW with different initial pH values**.** (* The experimental conditions are shown in the Table 7.2 and Table 7.4 in the Appendix)

4.2. Ozonation of coke-treated OSPW

The coked-treated OSPW water samples were collected from Syncrude's coke slurry system that is used to transport hot petroleum coke to deposition sites. In Table 4.3 the basic water characteristics are presented. Compared to the non-coke contacted WIP-OSPW, the coke-treated OSPW has similar pH value, and slightly lower conductivity, but much lower NAs, COD, DOC values and higher $cBOD_5$ value. The coke-treated waters also demonstrate less toxicity. The differences are due to the removal of NAs and other hydrocarbons by adsorption using coke (Zubot, 2009).

Table 4.3 The characteristics of the OSPW and coke-treated OSPW

	pH	Conductivity	NAs	COD	DOC	cBOD$_5$	EC$_{20}$
		µS/cm	mg/L	mg/L	mgC/L	mg/L	vol %
OSPW	8.7	3150	75	250	52	8	24
Coke-treated OSPW	8.3	2400	5.7	44	15	18	>91

The relationship between the NAs residuals and used ozone dose for coke-treated OSPW is shown in Figure 4.20. The coke-treated OSPW contained 5.7 mg/L NAs, which represented 9% of the NAs in the OSPW (63 mg/L) before the coke treatment. The NAs residuals drop to 1.3 mg/L by applying a used ozone dose of 15 mg/L, and reached 1 mg/L with used ozone doses above 60 mg/L.

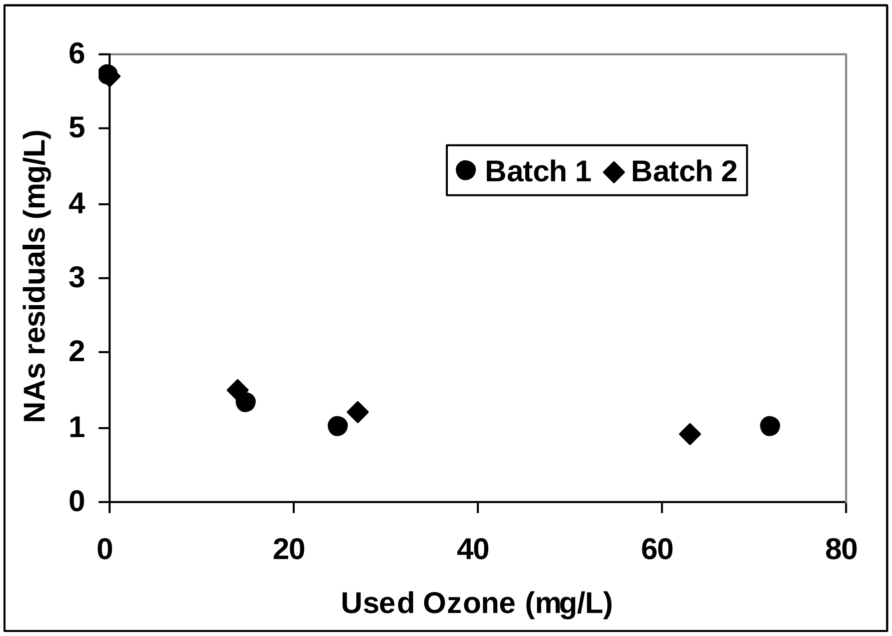


Figure 4.19 NAs residuals vs. used ozone dose for coke-treated OSPW.
(* The experimental conditions are shown in the Table 7.3 and Table 7.5 in the Appendix)

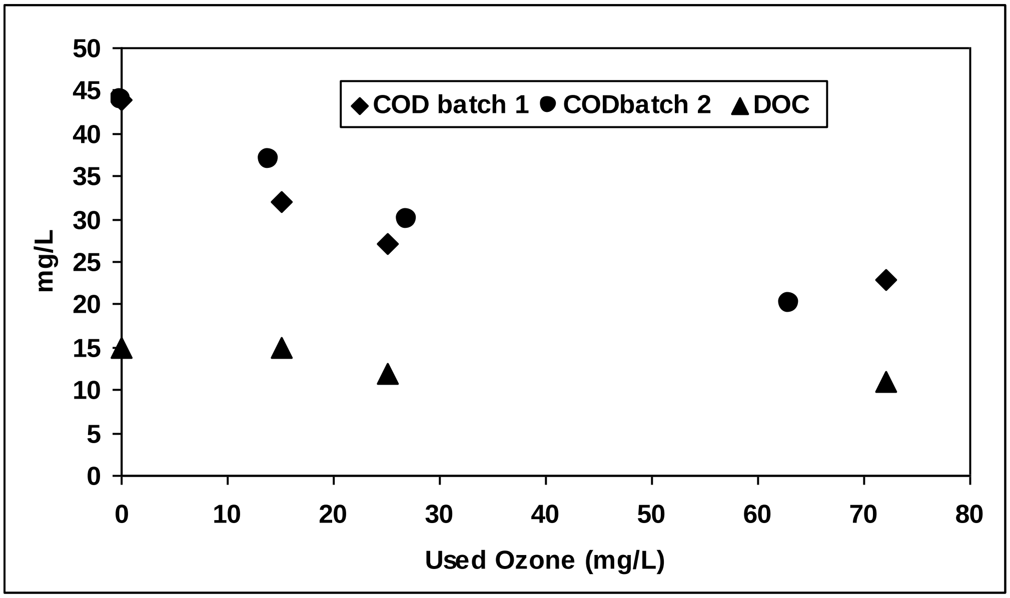


Figure 4.20 COD and DOC residuals vs. used ozone dose for coke-treated OSPW. (* The experimental conditions are shown in the Table 7.3 and Table 7.5 in the Appendix)

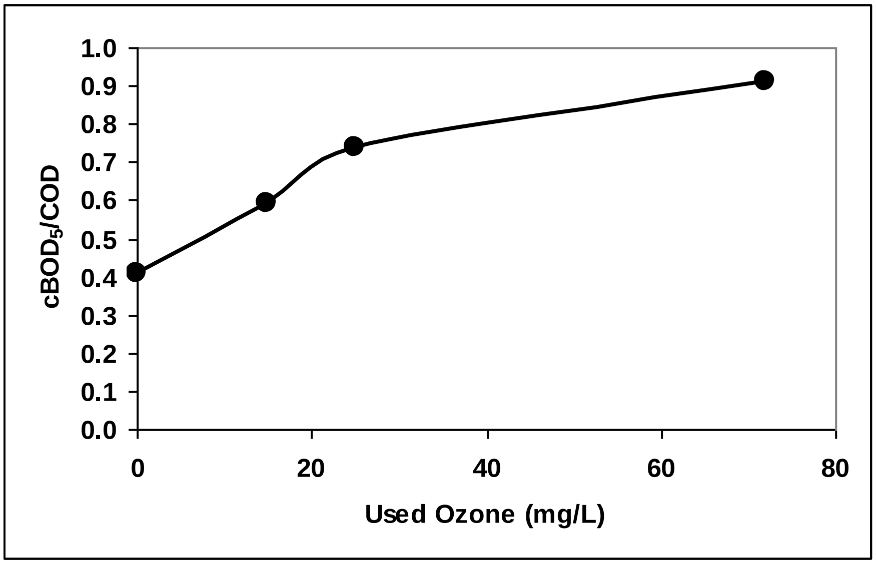


Figure 4.21 $cBOD_5$/COD ratio vs. used ozone dose for coke-treated OSPW. (* The experimental conditions are shown in the Table 7.3 and Table 7.5 in the Appendix)

The COD and DOC residuals in the ozone treated coke-OSPW are shown in Figure 4.20. Both COD and DOC decreased when the used ozone dose was increased. The degradations of COD and DOC were 47% and 27%, respectively

Figure 4.21 shows the relationship between the $cBOD_5$/COD ratios vs. used ozone dose. The $cBOD_5$/COD ratios increased from the initial 1.2 to 1.9 with 72 mg/L of used ozone. Compared to the results shown in Figure 4.9 and Figure 4.14, the initial $cBOD_5$/COD ratios of coke-treated water is comparable with ratios of OSPW treated with 155 mg/L used ozone. The higher $cBOD_5$ and lower COD values of coke-treated OSPW resulted in a high $cBOD_5$/COD ratio, indicating that coke-treated OSPW and ozonated coke-treated OSPW have higher biodegradability than the OSPW.

All the EC_{20} values of coke-treated OSPW and coke-treated OSPW with the treatment of ozonation are above 100%, indicating that these water samples have low toxicity.

5. CONCLUSIONS AND PATH FORWARD

The results of degradation of NAs in OSPW using ozone indicated that ozonation is a promising water treatment technology for the removal of naphthenic acids from both OSPW and coke-treated OSPW. A maximum reduction in NAs of more than 99% has been achieved. When compared to the high NAs removal, the reduction of both COD and DOC were much lower at similar utilized ozone doses under the same conditions. This shows that during the ozonation process, the NAs from the OSPW were not completely mineralized, but their character as carboxylic acids was removed. The degradation products appeared to include smaller organic molecules, which still contribute to both COD and DOC in treated OSPW, but these hydroxylated or simple aliphatic hydrocarbons are not measured by the FT-IR method that respond to the carboxyl functional group. The ozone treatment with a utilized ozone dose of about 80 mg/L, the $cBOD_5$ and $cBOD_5/COD$ tripled compared to their original measurements in OSPW. While some re-mineralization of NAs is occurring during the ozonation, the current results suggest that, compared to OSPW that has not been ozonated, the remnants and by-products of the oxidation of the NAs will result in OSPW with a suite of dissolved organics with higher biodegradability after ozone treatment.

The ozone treatment also detoxified the OSPW. With the utilized ozone dose of about 80 mg/L, the ozone-treated OSPW showed no toxicity using Mircotox® bioassay ($EC_{20} > 91\%$). Therefore, ozonation offers great potential as a water treatment application for water management in the oil sands industry. Moreover, ozone also can be applied with other OSPW treatment methods since it provides a method targeted only at the oxidizable constituents of OSPW, and can be complementary in making water treatment more effective and less costly. For example, OSPW can be partially ozonated before the bio-remediation process because the ozonated OSPW has been demonstrated to be more biodegradable and less toxic. In this work, the coked-treated OSPW (i.e., OSPW was treated with a coke/water slurry process) was found to be non-toxic with the utilized ozone dose of less than 20 mg/L. Thus, a water treatment strategy may include multiple treatment processes, where the treatment train may contain physical/chemical processes (eg. coke/slurry adsorption, membrane treatment), biological treatment processes (bioreactors) in conjunction with ozonation as a pre- or post- treatment to improve overall efficiency and the ability to meet water quality criteria. Ozonation has a great potential to be commercially attractive for water treatment and management for reuse in the oil sands industry because of its low cost, flexibility, and high effectiveness at removing constituents of concern from OSPW as part of reclamation options.

Further research will focus on the following issues:

1. Enhance the ozone use efficiency

   The semi-batch demonstrates promise as a bench-scale ozone treatment method, and the applied ozone, wasted ozone and ozone residuals in the reactor can be quantitatively monitored, measured and controlled. However, the average of the ozone use efficiency of this semi-batch ozonation system was found to be 16.5%, which indicates that most of the ozone feeding into the OSPW ozonation system was exhausted with the off-gas. Therefore, this semi-batch ozonation should be optimized to increase the ozone use efficiency by optimizing the reactor geometry and contactor efficiency by using injectors to enhance the mass transfer.

2. Apply ozone-based AOPs to OSPW treatment

   As discussed in Section 2.7.2, hydroxyl radicals are produced in AOPs, providing stronger oxidants than ozone. Therefore, the ozone-based AOPs including O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV could be a more effective method for the degradation of NAs. Moreover, the AOPs may achieve comparable ozone performance more cost effectively.

3. Mechanism study

   Understanding the mechanism of NAs degradation pathways and characterization of by-products are important to demonstrate ozonation processes and to achieve the higher ozone performance for the degradation of NAs. It is likely this understanding will be required to obtain the regulatory acceptance for returning ozonated-OSPW to the environment.

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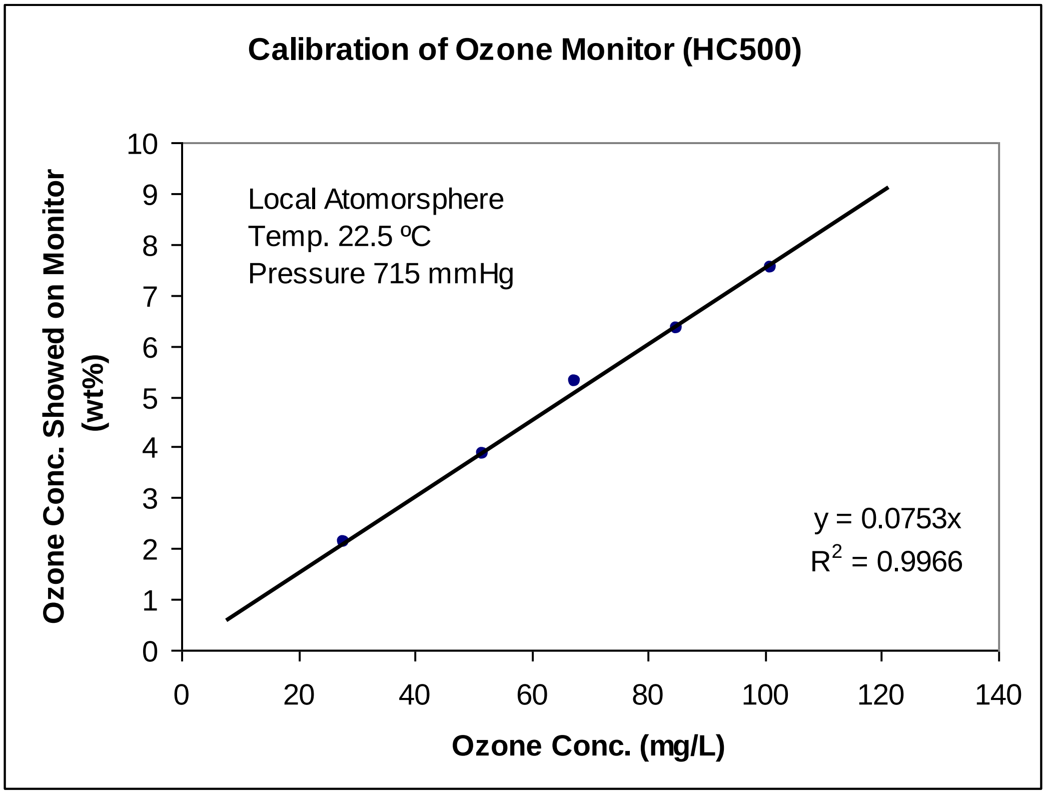
7. APPENDIX

7.1. Calibration of ozone monitor (HC500)



7.2. OSPW samples used in semi-batch ozonation

Sample ID	Water source	Filtered	pH before treatment
HF_EXP6_1	OSPW	No	8.66
HF_EXP6_2	OSPW	No	8.66
HF_EXP6_3	OSPW	No	8.66
HF_EXP6_4	OSPW	No	8.66
HF_EXP6_5	OSPW	No	8.66
HF_EXP6_6	OSPW	No	8.66
HF_EXP6_7	OSPW	No	8.66
HF_EXP6_8	OSPW	No	8.66
HF_EXP6_9	OSPW	No	8.66
HF_EXP6_10	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_11	OSPW	Yes ,0.45 µm membrane	8.66
HF_EXP6_12	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_13	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_14	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_15	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_16	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_17	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_18	OSPW	Yes, 0.45 µm membrane	8.66
HF_EXP6_19	OSPW	Yes, glass fiber	8.66
HF_EXP6_20	OSPW	Yes, glass fiber	8.66
HF_EXP6_21	OSPW	Yes, glass fiber	8.66
HF_EXP6_22	OSPW	Yes, glass fiber	8.66
HF_EXP6_23	OSPW	Yes, glass fiber	8.66
HF_EXP6_24	OSPW	Yes, glass fiber	8.66
HF_EXP6_25	OSPW	Yes, glass fiber	8.66

Sample ID	Water source	Filtered	pH before treatment
HF_EXP6_26	OSPW	Yes, glass fiber	8.66
HF_EXP6_27	OSPW	Yes, glass fiber	8.66
HF_EXP6_28	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_29	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_30	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_31	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_32	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_33	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_34	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_35	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_36	OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_37	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_38	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_39	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_40	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_41	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_42	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_43	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_44	OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_45	OSPW	Yes, 0.45 µm membrane	10

7.3. Sample ID of coke-treated OSPW

Sample ID	Water source	Filtered	pH before treatment
HF_EXP6_46	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_47	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_48	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_49	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_50	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_51	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_52	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_53	coke-treated OSPW	Yes, 0.45 µm membrane	8.3
HF_EXP6_54	coke-treated OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_55	coke-treated OSPW	Yes, 0.45 µm membrane	6.5
HF_EXP6_56	coke-treated OSPW	Yes, 0.45 µm membrane	10
HF_EXP6_57	coke-treated OSPW	Yes, 0.45 µm membrane	10

7.4. Semi-batch ozonation

7.4.1. The semi-batch ozonation experimental conditions for OSPW

Sample ID	**Exposure time** (min)	**Applied ozone dose** (mg/L)	**Wasted ozone dose** (mg/L)	**Residual** (mg/L)	**Used ozone dose** (mg/L)	**Volume of water** L	**pH before treatment**
HF_EXP6_1	15	915	753	15	148	2	8.66
HF_EXP6_2	10	559	462	10	87	2	8.66
HF_EXP6_3	5	279	235	5	40	2	8.66
HF_EXP6_4	2.5	133	110	2	22	2	8.66
HF_EXP6_5	0	0	0	0	0	2	8.66
HF_EXP6_6	15	908	739	16	152	2	8.66
HF_EXP6_7	10	547	463	11	73	2	8.66
HF_EXP6_8	5	278	239	3	37	2	8.66
HF_EXP6_9	2.5	134	110	2	23	2	8.66
HF_EXP6_10	15	904	735	14	155	2	8.66
HF_EXP6_11	10	582	493	10	79	2	8.66
HF_EXP6_12	5	285	236	2	47	2	8.66
HF_EXP6_13	2.5	126	101	2	22	2	
HF_EXP6_14	0	0	0	0	0	2	8.66
HF_EXP6_15	15	916	742	12	161	2	8.66
HF_EXP6_16	10	575	491	10	74	2	8.66
HF_EXP6_17	5	279	230	3	45	2	8.66
HF_EXP6_18	2.5	139	109	2	28	2	8.66
HF_EXP6_19	15	896	730	12	154	2	8.66
HF_EXP6_20	10	590	513	9	67	2	8.66
HF_EXP6_21	5	292	247	4	42	2	8.66
HF_EXP6_22	2.5	138	117	3	19	2	8.66
HF_EXP6_23	0	0	0	0	0	2	8.66
HF_EXP6_24	15	905	719	12	173	2	8.66
HF_EXP6_25	10	601	517	9	74	2	8.66
HF_EXP6_26	5	265	224	5	36	2	8.66
HF_EXP6_27	2.5	145	120	4	22	2	8.66

Sample ID	**Exposure time** (min)	**Applied ozone dose** (mg/L)	**Wasted ozone dose** (mg/L)	**Residual** (mg/L)	**Used ozone dose** (mg/L)	**Volume of water** L	**pH before treatment**
HF_EXP6_28	15	903	733	14	159	2	6.5
HF_EXP6_29	10	656	557	12	87	2	6.5
HF_EXP6_30	5	313	263	7	43	2	6.5
HF_EXP6_31	2.5	151	121	7	23	2	6.5
HF_EXP6_32	0	0	0	0	0	2	6.5
HF_EXP6_33	15	881	713	15	152	2	6.5
HF_EXP6_34	10	652	563	8	81	2	6.5
HF_EXP6_35	5	305	260	6	39	2	6.5
HF_EXP6_36	2.5	140	113	6	21	2	6.5
HF_EXP6_37	15	930	761	2	167	2	10
HF_EXP6_38	10	610	523	2	86	2	10
HF_EXP6_39	5	258	216	1	41	2	10
HF_EXP6_40	2.5	144	111	1	32	2	10
HF_EXP6_41	0	0	0	0	0	2	10
HF_EXP6_42	15	937	772	3	163	2	10
HF_EXP6_43	10	596	512	3	81	2	10
HF_EXP6_44	5	255	212	1	42	2	10
HF_EXP6_45	2.5	142	113	1	28	2	10

7.4.2. The ozone use efficiency

Sample ID	**Exposure time** (min)	**Applied ozone dose** (mg/L)	**Wasted ozone dose** (mg/L)	**Used ozone dose** (mg/L)	**Ozone use efficiency *** %
HF_EXP6_1	15	915	753	148	16%
HF_EXP6_2	10	559	462	87	16%
HF_EXP6_3	5	279	235	40	14%
HF_EXP6_4	2.5	133	110	22	17%
HF_EXP6_5	0	0	0	0	
HF_EXP6_6	15	908	739	152	17%
HF_EXP6_7	10	547	463	73	13%
HF_EXP6_8	5	278	239	37	13%
HF_EXP6_9	2.5	134	110	23	17%
HF_EXP6_10	15	904	735	155	17%
HF_EXP6_11	10	582	493	79	14%
HF_EXP6_12	5	285	236	47	16%
HF_EXP6_13	2.5	126	101	22	17%
HF_EXP6_14	0	0	0	0	
HF_EXP6_15	15	916	742	161	18%
HF_EXP6_16	10	575	491	74	13%
HF_EXP6_17	5	279	230	45	16%
HF_EXP6_18	2.5	139	109	28	20%
HF_EXP6_19	15	896	730	154	17%
HF_EXP6_20	10	590	513	67	11%
HF_EXP6_21	5	292	247	42	14%
HF_EXP6_22	2.5	138	117	19	14%
HF_EXP6_23	0	0	0	0	
HF_EXP6_24	15	905	719	173	19%
HF_EXP6_25	10	601	517	74	12%
HF_EXP6_26	5	265	224	36	14%
HF_EXP6_27	2.5	145	120	22	15%
HF_EXP6_28	15	903	733	159	18%
HF_EXP6_29	10	656	557	87	13%
HF_EXP6_30	5	313	263	43	14%

Sample ID	**Exposure time** (min)	**Applied ozone dose** (mg/L)	**Wasted ozone dose** (mg/L)	**Used ozone dose** (mg/L)	**Ozone use efficiency *** %
HF_EXP6_31	2.5	151	121	23	15%
HF_EXP6_32	0	0	0	0	
HF_EXP6_33	15	881	713	152	17%
HF_EXP6_34	10	652	563	81	12%
HF_EXP6_35	5	305	260	39	13%
HF_EXP6_36	2.5	140	113	21	15%
HF_EXP6_37	15	930	761	167	18%
HF_EXP6_38	10	610	523	86	14%
HF_EXP6_39	5	258	216	41	16%
HF_EXP6_40	2.5	144	111	32	22%
HF_EXP6_41	0	0	0	0	
HF_EXP6_42	15	937	772	163	17%
HF_EXP6_43	10	596	512	81	14%
HF_EXP6_44	5	255	212	42	16%
HF_EXP6_45	2.5	142	113	28	20%

7.5. The semi-batch ozonation experimental conditions for coke-treated OSPW

Sample ID	Exposure time	Applied ozone dose	Wasted ozone dose	pH before treatment	Residual	Used ozone dose	Volume of water
	min	mg/L	mg/L		mg/L	mg/L	L
HF_EXP6_46	10	622	541	8.3	9	72	2
HF_EXP6_47	5	290	256	8.3	9	25	2
HF_EXP6_48	2.5	145	126	8.3	4	15	2
HF_EXP6_49	0	0	0	8.3	0	0	2
HF_EXP6_50	10	620	548	8.3	9	63	2
HF_EXP6_51	5	281	246	8.3	9	27	2
HF_EXP6_52	2.5	147	128	8.3	4	14	2
HF_EXP6_53	0	0	0	8.3	0	0	2
HF_EXP6_54	5	287	253	6.5	10	24	2
HF_EXP6_55	0	0	0	6.5	0	0	2
HF_EXP6_56	5	285	262	10	3	19	2
HF_EXP6_57	0	0	0	10	0	0	2

7.6. COD, DOC, $cBOD_5$ and toxicity measurements of ozonated-OSPW

Sample ID	Used Ozone mg/L	COD mg/L	$cBOD_5$ mg/L	$cBOD_5$/ COD	COD/ $cBOD_5$	EC_{20}	DOC mg/L	NAs mg/L
HF_EXP6_1	148	194	25.33	0.11	9.0	92.93%		16
HF_EXP6_2	87	203	24.73	0.11	9.2	85.43%		26
HF_EXP6_3	40	216	15.44	0.07	14.7	70%		36
HF_EXP6_4	22	227	9.11	0.04	24.9	38.58%		50
HF_EXP6_5	0	250	8.36	0.04	27.2	23.71%		71
HF_EXP6_6	152	197						16
HF_EXP6_7	73	204						26
HF_EXP6_8	37	219						41
HF_EXP6_9	23	221						53
HF_EXP6_10	155	176	25.9	0.11	8.8	108.10%	41	14
HF_EXP6_11	79	193	24.9	0.11	9.1	103.90%	50	22
HF_EXP6_12	47	211	13.83	0.06	16.4	76.68%	54	39
HF_EXP6_13	22	236	8.11	0.04	28.0	53.29%	57	55
HF_EXP6_14	0	247	3.66	0.02	62.0	22.66%	52	75
HF_EXP6_15	161	176						13
HF_EXP6_16	74	204						24
HF_EXP6_17	45	223						38
HF_EXP6_18	28	233						42
HF_EXP6_19	154	189	31	0.14	7.3			18
HF_EXP6_20	67	200	28	0.12	8.1	90.94%		22
HF_EXP6_21	42	214	13	0.06	17.5	56.33%		35
HF_EXP6_22	19	227	10	0.04	22.7	36.85%		52
HF_EXP6_23	0	249	6	0.03	37.8	23.54%		70
HF_EXP6_24	173	184						12
HF_EXP6_25	74	196						17

Sample ID	Used Ozone mg/L	COD mg/L	cBOD$_5$ mg/L	cBOD$_5$/ COD	COD/ cBOD$_5$	EC$_{20}$	DOC mg/L	NAs mg/L
HF_EXP6_26	36	211						36
HF_EXP6_27	22	224						49
HF_EXP6_28	159	191	28	0.12	8.1			16
HF_EXP6_29	87	207	28	0.12	8.1	88.83%		19
HF_EXP6_30	43	223	19	0.08	11.9	63.65%		38
HF_EXP6_31	23	236	12	0.05	18.9	54.93%		51
HF_EXP6_32	0	250	4	0.02	56.8	23.46%		77
HF_EXP6_33	152	196						20
HF_EXP6_34	81	206						27
HF_EXP6_35	39	231						45
HF_EXP6_36	21	239						56
HP_EXP6_37	167	180	19	0.08	11.9			13
HP_EXP6_38	86	197	17	0.07	13.4			21
HP_EXP6_39	41	217	17	0.06	16.7	46.77%		42
HP_EXP6_40	32	220	11	0.05	20.6	37.05%		53
HP_EXP6_41	0	237	7	0.03	32.4	24.30%		76
HP_EXP6_42	163	176						17
HP_EXP6_43	81	194						20
HP_EXP6_44	42	209						32
HP_EXP6_45	28	219						51

7.7. COD, DOC, $cBOD_5$ and toxicity measurements of ozonated coke-treated OSPW

Sample ID	Used Ozone	COD	$cBOD_5$	$cBOD_5$/ COD	EC_{20}	DOC	NAs
	mg/L	mg/L	mg/L			mg/L	mg/L
HF_EXP6_46	72	23	21	0.9	>100%	11	1
HF_EXP6_47	25	27	20	0.7	>100%	12	1
HF_EXP6_48	15	32	19	0.6	>100%	15	1.3
HF_EXP6_49	0	44	18	0.4	>100%	15	5.7
HF_EXP6_50	63	20					0.9
HF_EXP6_51	27	30					1.2
HF_EXP6_52	14	37					1.5
HF_EXP6_53	0	44	18	0.4		15	5.7
HF_EXP6_54	24	37	19	0.5	>100%	16	0.9
HF_EXP6_55	0	64	18	0.3	>100%	22	5.2
HF_EXP6_56	19	39	19	0.5	>100%	10	1.5
HF_EXP6_57	0	81	18	0.2	>100%	15	5.9