# Use of Ozone for the Remediation and Detoxification of Oil Sands Process-Affected Water

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**Watertech2012**

# Outline

- Background
- Challenges of Oil Sands Tailings Water Treatment
- Constituents of Oil Sands Tailings Water
- Effects of Ozonation on OSPW (WQ, Toxicity, Biodegradability)
- Impacts of Pretreatment Steps on Ozonation Performance
- Synergy of Ozonation and Biological Treatment
- Concluding Remarks

# Water Use and Inventory

- The Province of Alberta contains in-place bitumen reserves estimated to be about 171.8 billion barrels (about 13% of total global oil reserves)
- Between 2 and 4.5 barrels of water are required to produce a barrel of synthetic crude oil
- Oil sands process-affected water (OSPW) is estimated to reach 1 billion $m^3$ in the Athabasca Oil Sands Region by 2025

# Challenges of Oil Sands Tailings Water Treatment

- Changes in policies and regulations
- Balancing the water supply and growing demand
- Possible environmental impacts

# Recycled Water (RCW) Pond

**Syncrude Canada Ltd.**

# Oil Sands Water Sources

| Type of Water Sources | Type of Processes |
|---|---|
| **Tailing Process Water** | ▪ Extraction - function of ore, process conditions, and process aids |
| **Engineered Tailings** | ▪ Composite tailings (CT) - gypsum<br>▪ Thickened Tailings (TT) - anionic polymers<br>▪ Inline Flocculation Tailings (IFT) - anionic and cationic polymers |
| **Surface Runoff/Seepage** | ▪ Basal water - salinity, hardness<br>▪ Surface runoff - contact with exposed oil sands and OSPW<br>▪ Groundwater and seepage with both OSPW and non-OSPW properties |
| **Upgrading Water** | ▪ Upgrading process streams such as cooling tower blow down waters<br>▪ Utilities wastewater and backflushes as well as refinery-type waters |
| **Combined Water** | ▪ Combination of water sources |

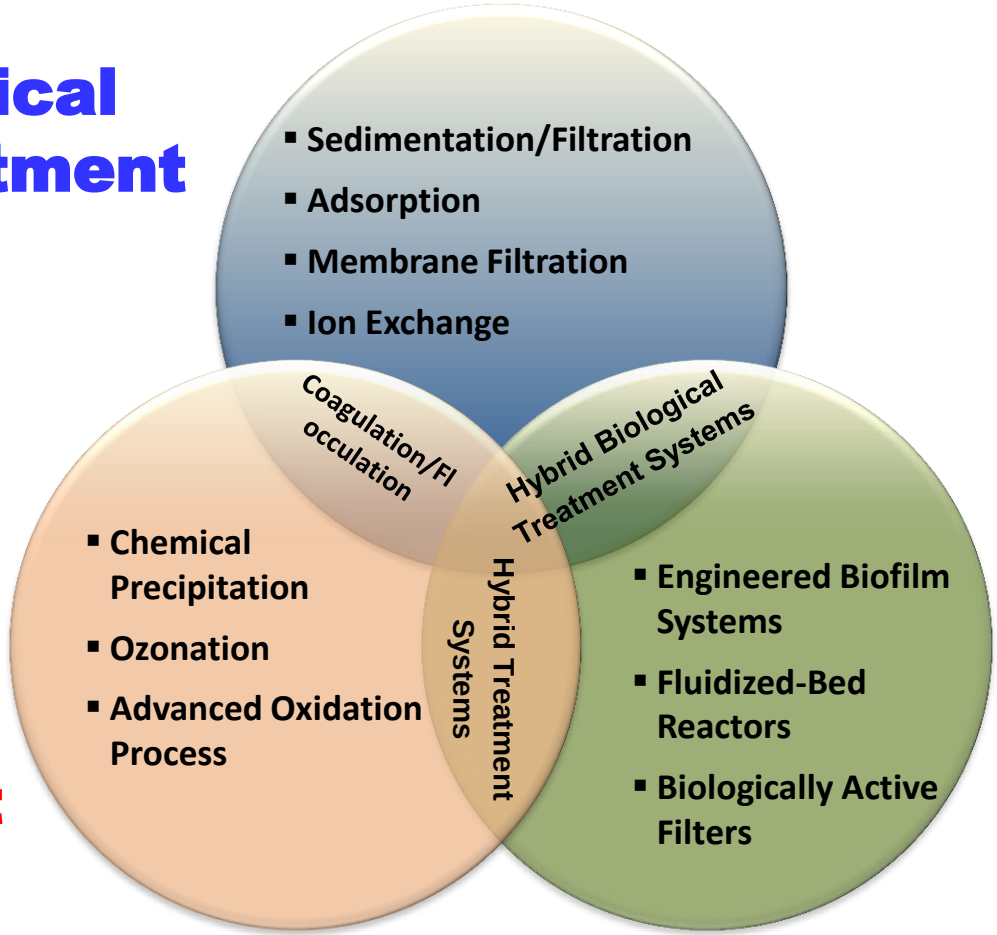
# Typical Constituents of Oil Sands Tailings Water

| Parameters | Fresh OSPW | Aged OSPW |
|---|---|---|
| pH (unit) | 8.1 | 8.13 |
| Total Dissolved Solids (mg/L) | 2200 | 2863 |
| Total Suspended Solids (mg/L) | 1100 | 200 |
| Conductivity (µS/cm) | 3290 | 4280 |
| COD (mg/L) | 184 | 150 |
| BOD (mg/L) | 3.4 | 16.6 |
| Bicarbonate (mg/L) | 803 | 1040 |
| Chloride (mg/L) | 490 | 925 |
| Ammonia (mg N/L) | 15 | 4.4 |
| Total Nitrogen (mg N/L) | 12.1 | 6.1 |
| Total Phosphorus (mg P/L) | < 0.02 | 0.005 |
| Total Acid Extractable Organics | 75 | 50 |
| Naphthenic Acids | 25 | 15 |

**Source**: Syncrude Canada Ltd.

# Water Treatment Options

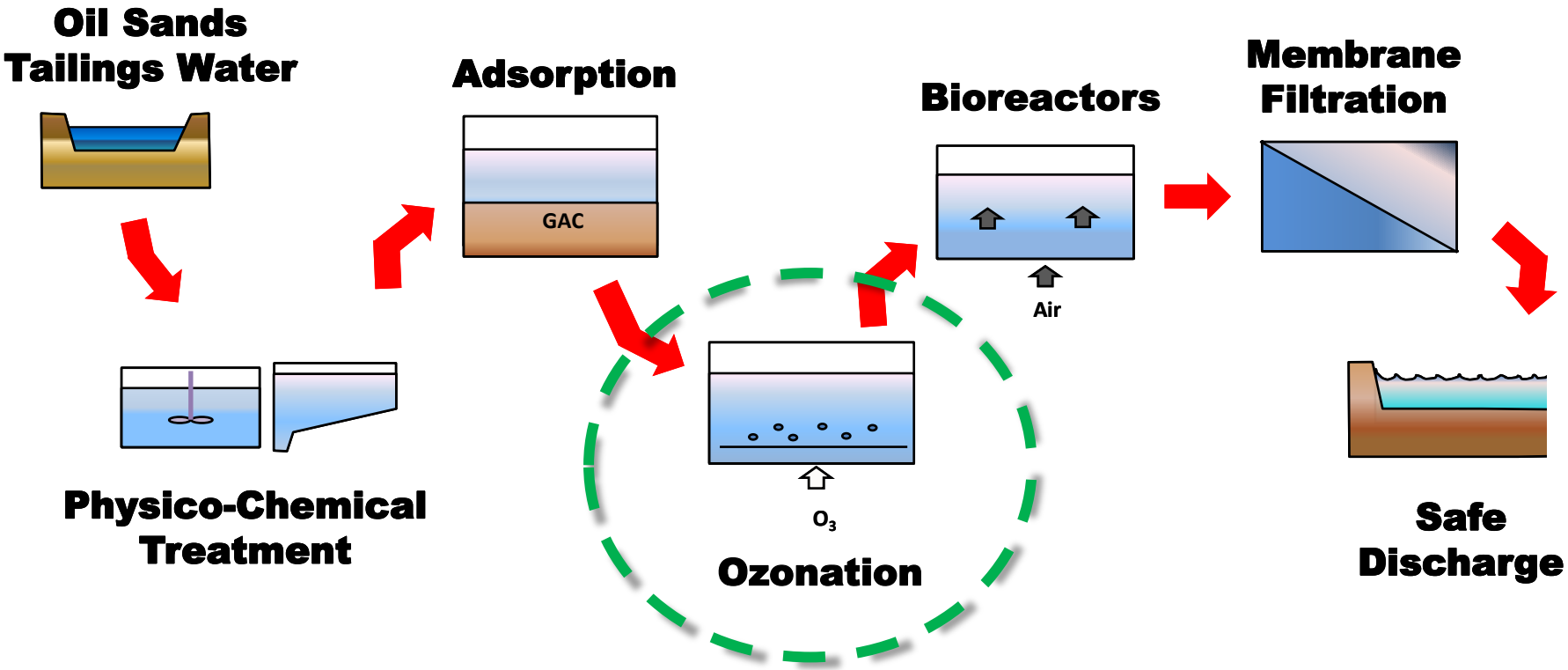
**Physical Treatment**




**Chemical Treatment**

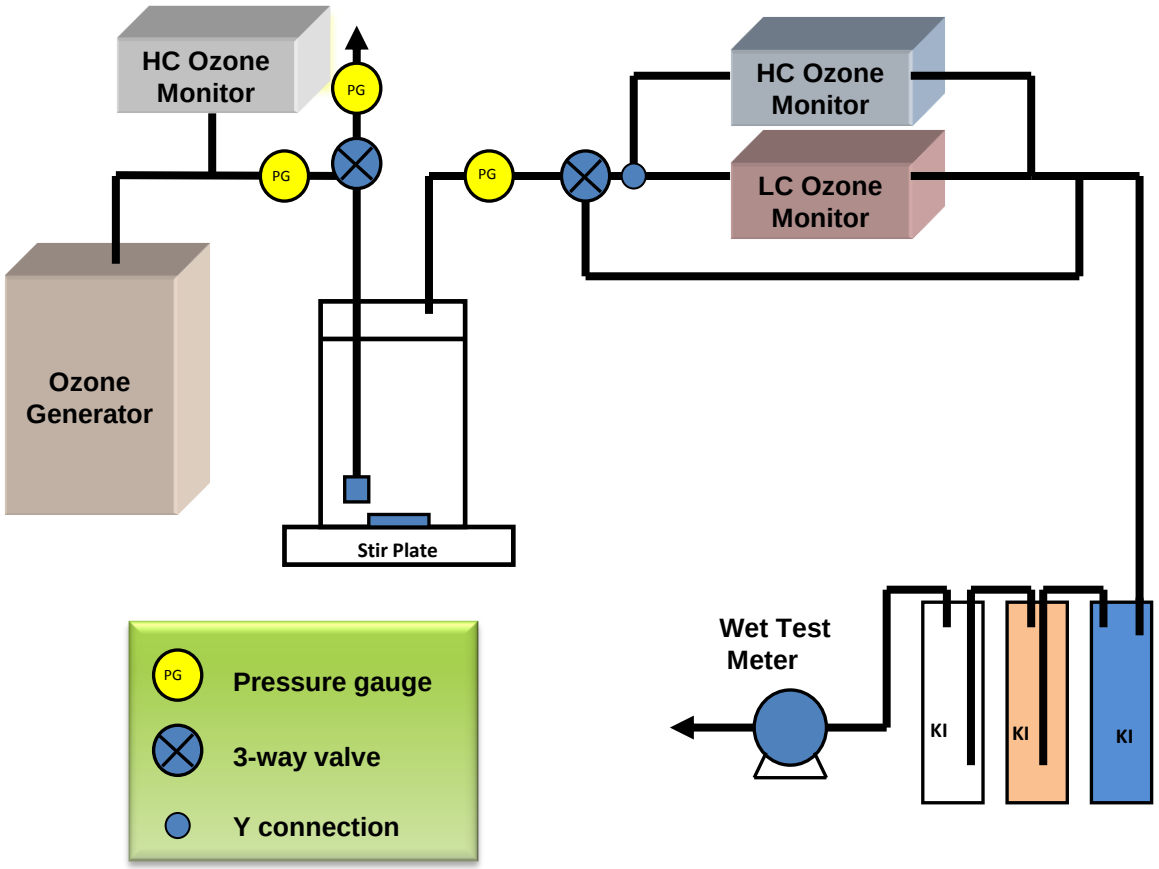
**Biological Treatment**

# Hypothetical Treatment Train



# Effects of Ozonation on OSPW Characteristics

# Ozonation in Semi-Batch Rectors




*Source: Gamal El-Din et al. 2011. Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. Sci. Total Environ., 409(23), 5119-5125.*

# Applied and Utilized Ozone Doses

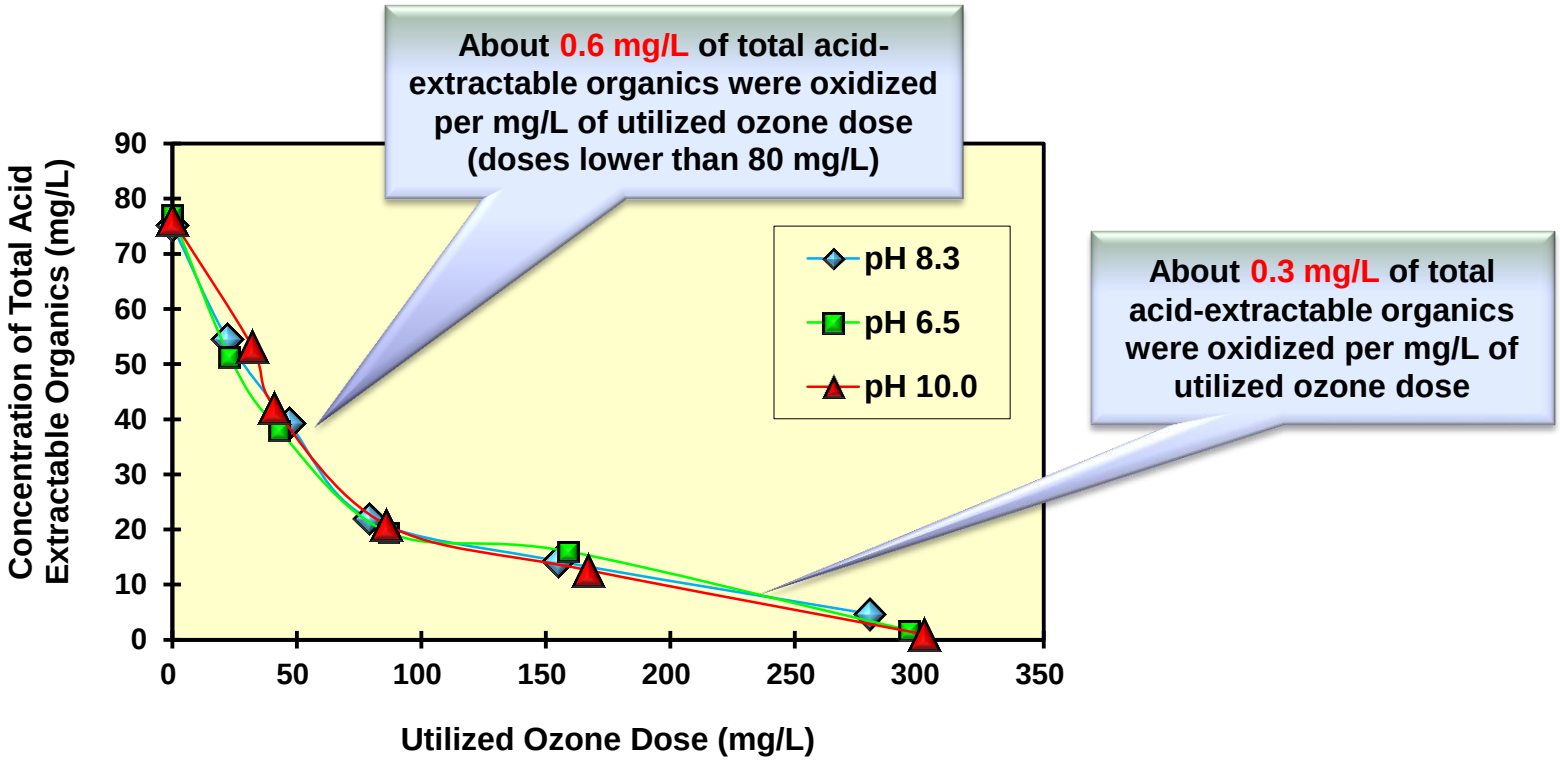
## Utilized Ozone Dose

$$\Delta O_3 = \int_0^t \frac{(Q_{G,in} C_{G,in} - Q_{G,out} C_{G,out})}{V_L} dt - C_L$$

- $\Delta O_3$: Amount (mg/L) of the utilized $O_3$
- $C_{G,in}$: $O_3$ concentration (mg/L) in the feed gas
- $C_{G,out}$: $O_3$ concentration (mg/L) in the off-gas
- $C_L$: Residue $O_3$ concentration (mg/L) in the liquid phase
- $V_L$ : Effective reactor volume (L)
- $Q_{G,in}$: Feed gas flow rate (L/min)
- $Q_{G,out}$: Off-gas flow rate (L/min)
- **t**: $O_3$ contact time (min)

***Sources:*** *- Gamal El-Din, M., Smith, D.W. 2002. J. Environ. Eng. Sci., 1(1), 45-57.*
*- Gamal El-Din et al. 2011. Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. Sci. Total Environ., 409(23), 5119-5125.*

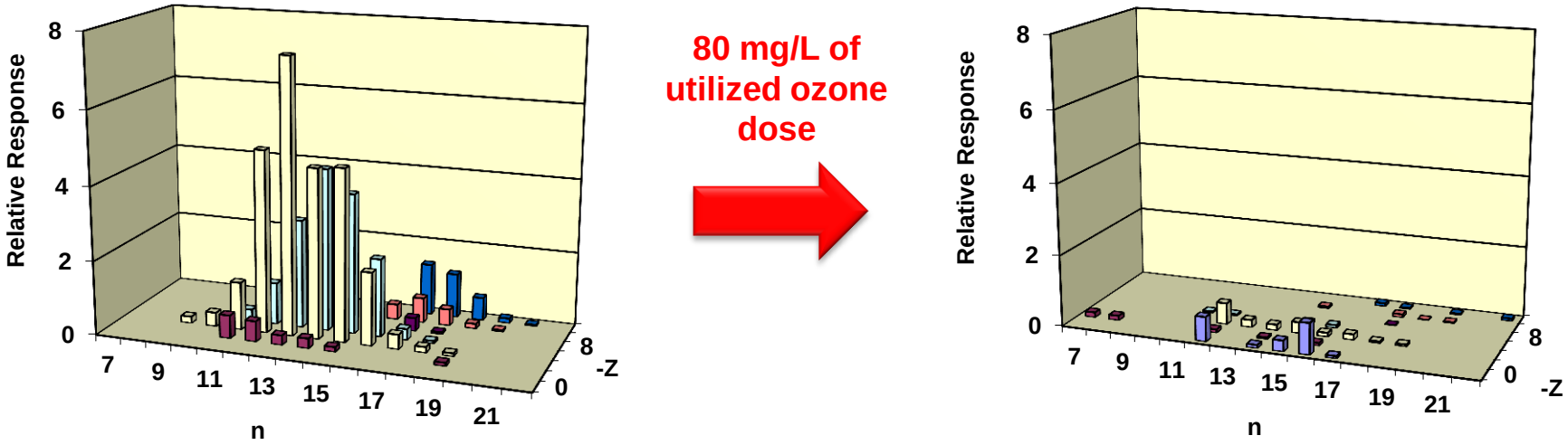
# Effect of Ozonation on the Levels of Total Acid Extractable Organics




**Degradation levels of total acid-extractable organics were independent of the OSPW pH**

*Source: Gamal El-Din et al. 2011. Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. Sci. Total Environ., 409(23), 5119-5125.*

# Effect of Ozonation on NAs Speciation




**Total NA concentrations decreased by 90% after ozonation with a utilized ozone dose of 80 mg/L**

**Ozone preferentially reacts with NAs with higher *Z* number (i.e., higher number of rings)**

***Source*: Gamal El-Din et al. 2011. Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. Sci. Total Environ., 409(23), 5119-5125.**

# Effect of Ozonation on NAs Speciation

**Ozone degraded NAs with high number of rings more effectively than NAs with small Z numbers**

**NAs with high carbon numbers were degraded more effectively than NAs with less carbon numbers**

***Source**: Wang et al. 2012. Impact of an integrated ozonation-biodegradation process on naphthenic acids reactivity and oil sands process-affected water toxicity. Environ. Sci. Technol. (in preparation).*

# Treatment of OSPW using $O_3/H_2O_2$

29% of extractable acid fraction of OSPW was degraded using 30 mg/L $O_3$ alone

By adding $H_2O_2$ with a ratio of 2:1 to ozone, the organic acid fraction removal increased to 39%

Increasing the $O_3$ concentration to 85 mg/L resulted in an increase of the organic acids removal to 62%

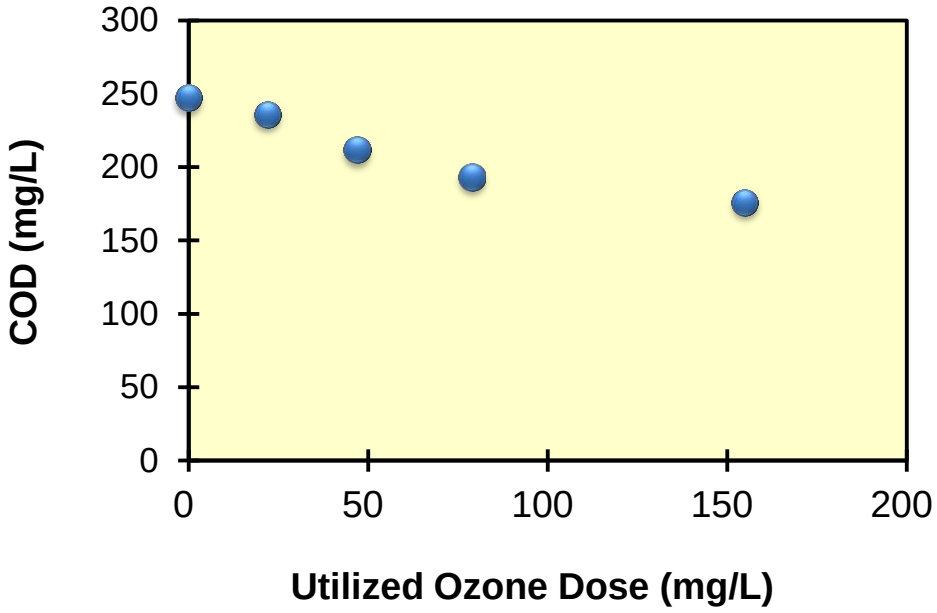
85 mg/L $O_3$ combined with $H_2O_2$ (ratio of 1:3) removed 90% of the total extractable acids from OSPW

*Source: Afzal et al. 2012. Treatment of a model naphthenic acid, cyclohexanoic acid, using $O_3/H_2O_2$ advanced oxidation process. Environ. Sci. Technol. (in preparation).*

# Effects of Ozonation on OSPW Biodegradability

# Effect of Ozonation on COD Levels

**A COD reduction of 22% was achieved at utilized ozone dose of 150 mg/L**




**Low COD reductions may be due to the degradation of organic compounds with higher molecular weight (i.e., NAs) into simpler organic compounds, which still contributed to the COD of the OSPW samples**

***Source**: Gamal El-Din et al. 2011. Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. Sci. Total Environ., 409(23), 5119-5125.*

# Effect of Ozonation on OSPW Biodegradability

**Ozonation makes molecules smaller, more oxidizable and more biodegradable**

**$BOD_5$/COD measures biodegradability**

**$BOD_5$/COD >0.3 better biodegradability**

**$BOD_5$/COD Fresh OSPW = 0.02**

**$BOD_5$/COD Aged OSPW = 0.11**

*Source: Dong et al. 2012. Impact of ozonation on the removal of naphthenic acids from oil sands process-affected water. Environ. Sci. Technol. (in preparation)*

# Effect of Ozonation on OSPW Toxicity

# Toxic Effects of Ozonated OSPW

**The toxicity of OSPW towards *V. fischeri* decreases after ozonation**

**100% raw OSPW significantly decreased the mean weight of *C. dilutus* larvae, from 0.015 g to 0.005 g**

**Ozonation (30 mg/L) of OSPW effectively removed the inhibitory effect of raw OSPW on the growth of *C. dilutus***

*Data from Dr. John P. Giesy's Research Group (University of Saskatchewan)*

***Source**: Wang et al. 2012. Impact of an integrated ozonation-biodegradation process on naphthenic acids reactivity and oil sands process-affected water toxicity. Environ. Sci. Technol. (in preparation).*

# Immunotoxic Effects of Ozonated OSPW (*in vitro* and *in vivo Bioassays*)

**Mice that were exposed to the organic fraction of OSPW had reduced expression of the pro-inflammatory cytokines TNF-α and IFNγ in the liver**

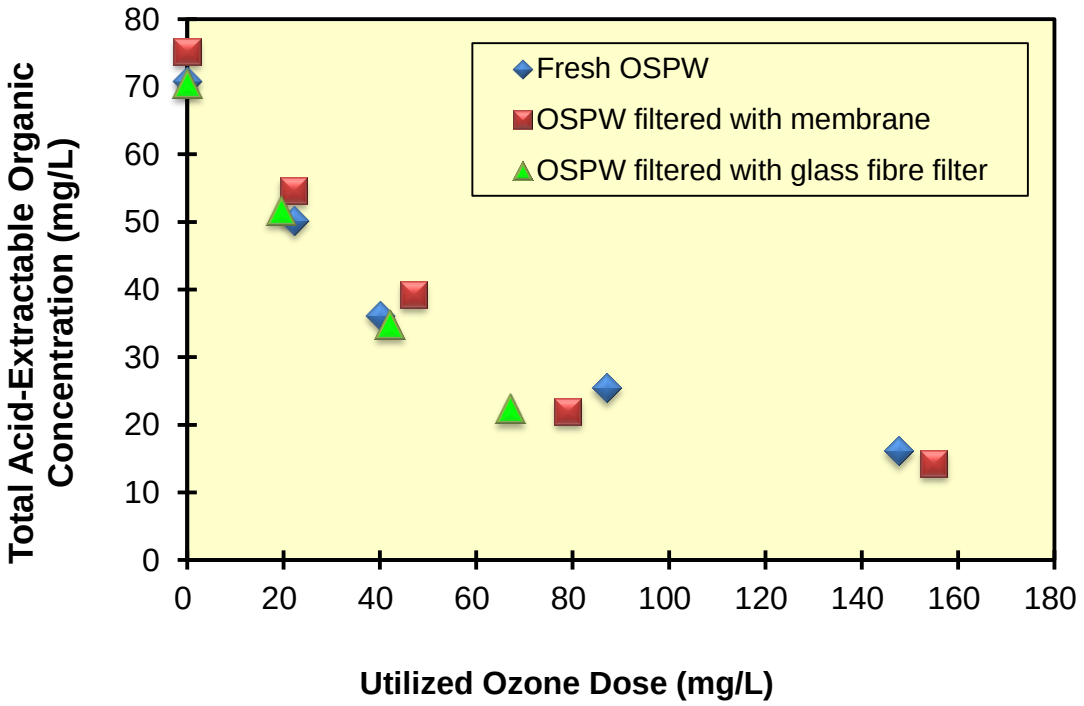
**Ozonation seems to be an adequate technique to reduce the mice immunotoxicity caused by OSPW**

*Data from Dr. M. Belosevic's Research Group (University of Alberta)*

*Source: Wang et al. 2012. Impact of an integrated ozonation-biodegradation process on naphthenic acids reactivity and oil sands process-affected water toxicity. Environ. Sci. Technol. (in preparation).*

# Impacts of Pretreatment Steps on Ozonation Performance

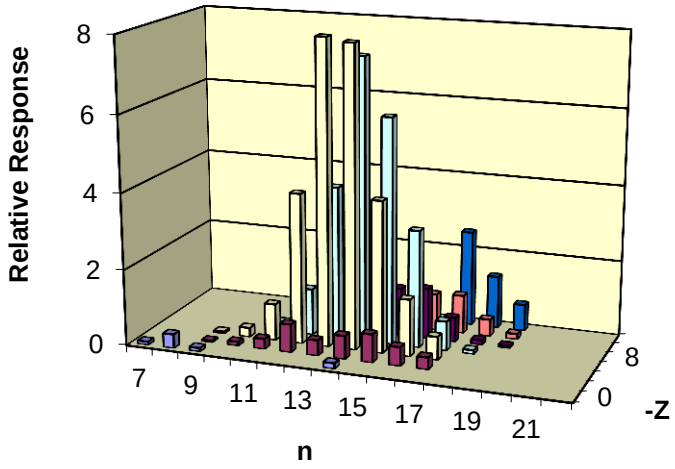
# Effect of Filtration on the Ozonation Performance



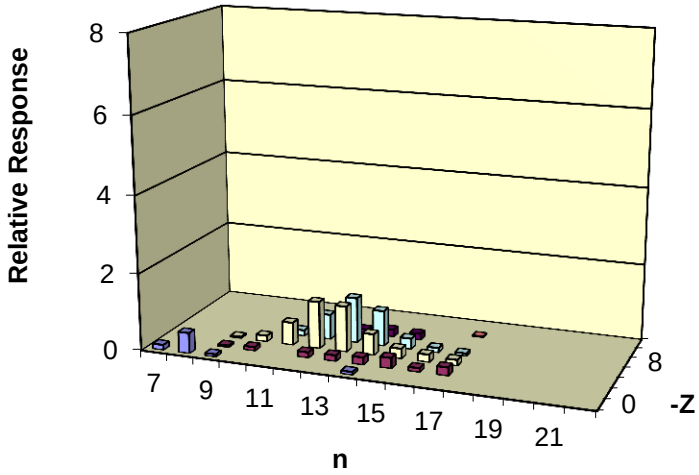

**The type of filter did not play an important role in the oxidation of total acid-extractable organics**

*Source: Gamal El-Din et al. 2011. Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. Sci. Total Environ., 409(23), 5119-5125.*

# Effect of Adsorption on the Ozonation Performance




**Petroleum Coke Adsorption (20 %wt)**




**Petroleum coke adsorption can be a suitable pretreatment step not only by removing dissolved organics from OSPW, but also by reducing the levels of applied and utilized ozone doses**

***Source**: Gamal El-Din et al. 2011. Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. Sci. Total Environ., 409(23), 5119-5125.*

# Ozonation Combined with Biological Treatment (Suspended Growth Systems)

# Effects of Ozone Dose on Bioreactor Performance

**Ozone can improve the biodegradation of total acid extractable organics**

***Source*: Dong et al. 2012. Impact of ozonation on the removal of naphthenic acids from oil sands process-affected water. Environ. Sci. Technol. (in preparation)**

# Effects of Ozone Doses on COD Removal

**With ozonation, COD removal slows down after 60 days incubation**

**Ozone contributed to the decomposition of the recalcitrant organic compounds which could be easily degraded by the endogenous microorganisms**

***Source**: Dong et al. 2012. Impact of ozonation on the removal of naphthenic acids from oil sands process-affected water. Environ. Sci. Technol. (in preparation)*

# Effects of Ozone Doses on Communities of Endogenous Microorganisms

**Changes in the communities of endogenous microorganisms were found after 73 days of treatment**

**Some strains disappeared while other strains became the dominant species in the community**

***Source**: Dong et al. 2012. Impact of ozonation on the removal of naphthenic acids from oil sands process-affected water. Environ. Sci. Technol. (in preparation)*

# Effects of Ozone Doses on Bacteria Population

**Ozone accelerated the growth of microorganisms**

**The increase of bacteria population contributed to the acceleration of the removals of total acid extractable organics and COD**

***Source*: Dong et al. 2012. Impact of ozonation on the removal of naphthenic acids from oil sands process-affected water. Environ. Sci. Technol. (in preparation)**

# How to Improve the Biodegradation?

## Inorganic nutrient requirements

**The major compounds for microbial nutrition in bioremediation are**

- **nitrogen as ammonia**
- **phosphorus as orthophosphate**

## Organic nutrient requirements

**Organic material addition may help to promote the degradation of individual NAs by co-metabolism**

# Ozonation Combined with Biological Treatment (Attached Growth Systems)

# Biofilm Density and Thickness (Confocal Laser Scanning Microscopy)

**Endogenous populations in OSPW can readily form biofilms**

**Thicker biofilms were observed on PVC surfaces and with ozonated OSPW**

***Source*: Hwang et al. 2012. Environ. Sci. Technol. (submitted for publication).**

# Biofilm Density and Thickness

**Higher biofilm density and thickness were observed in ozonated bioreactors**

**Biofilm growth varied depending on the biofilm carrier materials**

**PVC supported better biofilm adhesion and growth than PE**

***Source*: Hwang et al. 2012. Environ. Sci. Technol. (submitted for publication).**

# Microbial Community - Denaturing Gradient Gel Electrophoresis (DGGE) Results

**Ozonation caused a noticeable change in the microbial community in OSPW**

**PVC supported a greater microbial community diversity compared to PE**

***Source*: Hwang et al. 2012. Environ. Sci. Technol. (submitted for publication).**

# Characterization of OSPW Before and After Biological Treatment in Continuous Flow Biofilm Reactors

**Ammonium ion was not detected after biological treatment for both fresh and ozonated OSPW**

**Ozonation at 80 mg/L as utilized ozone dose**

**Ammonia was one of the limiting nutrient components for microbial growth in OSPW**

***Source*: Hwang et al. 2012. Environ. Sci. Technol. (submitted for publication).**

# Concluding Remarks

- **Treatment of oil sands process-affected water is intended for:**
  - **Water Reuse (utility, process and operation water)**
  - **Safely Released into the receiving environment**

- **Innovative multi-barrier treatment approaches and water reuse/release scenarios are required to promote and protect the environmental and public health**

# Thank you!

**For Additional Information:**

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