2019 Water Mining Research Report

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PUBLISHED JULY 2020

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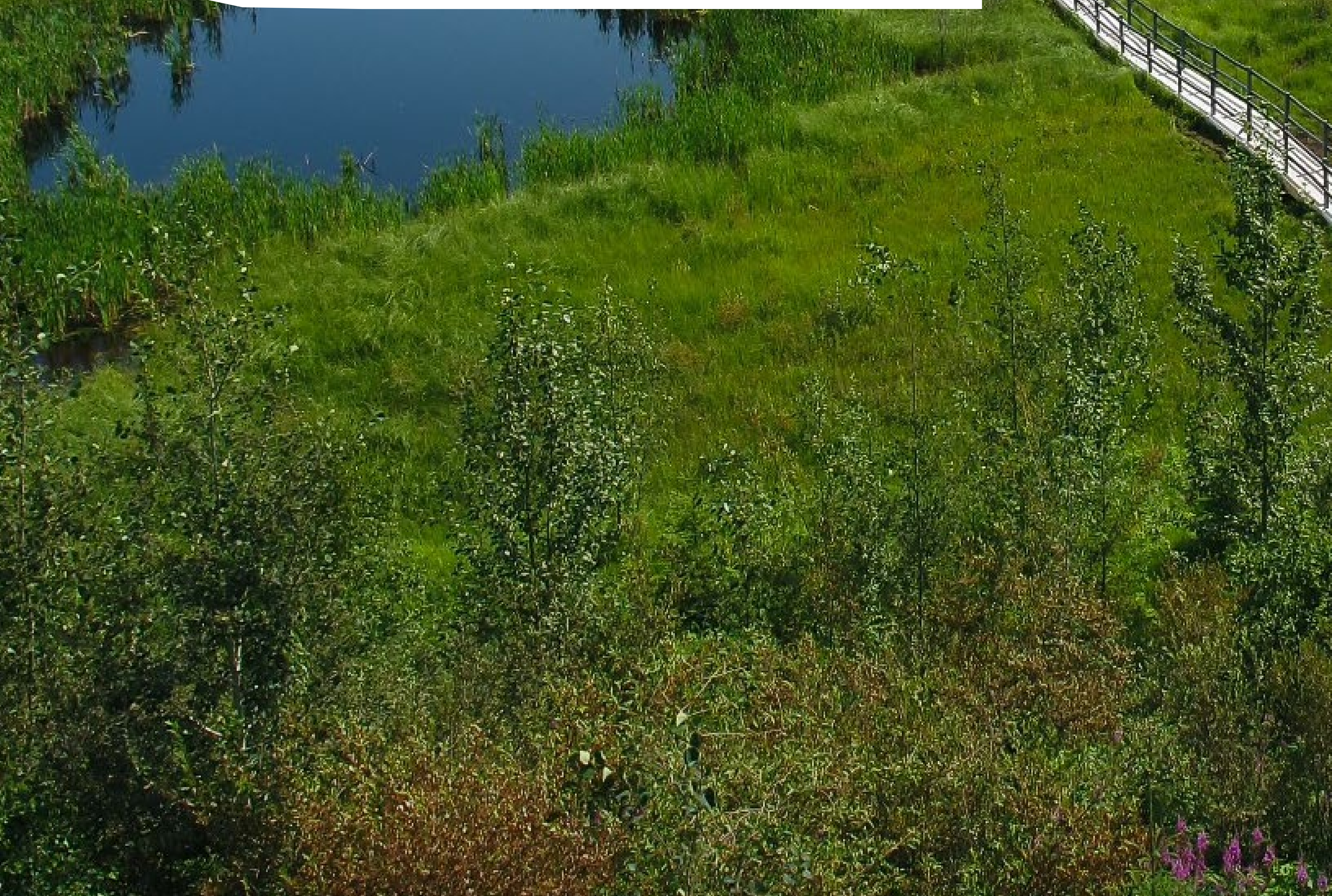

INTRODUCTION

This report summarizes progress for research projects related to improving the use and management of water by the Mining Subcommittee Group of Canada's Oil Sands Innovation Alliance (COSIA) Water Environmental Priority Area (EPA). Projects included cover the period from 2012 to 2019.

Please contact the Industry Champion identified for each research project if any additional information is needed.

The COSIA Water EPA Mining Subcommittee Group participants during the period of this report were: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Shell Canada Energy, Suncor Energy, Syncrude Canada Ltd., Teck Resources Limited and Total E&P Canada Ltd.

In 2019, Canadian Natural Resources Limited purchased Devon Canada and in 2017 Canadian Natural Resources Limited purchased Shell Canada Energy's Albian Sands operations. All COSIA Water EPA projects previously supported by Devon Canada and Shell Canada were transferred to Canadian Natural Resources Limited.

This report is funded by:

- Canadian Natural Resources Limited
- Cenovus Energy Inc.
- ConocoPhillips Canada Resources Corp.
- Husky Energy
- Imperial Oil Limited
- Suncor Energy
- Syncrude Canada Ltd.
- Teck Resources Limited

June 2020

The cover photo is of Syncrude's Base Mine Lake (2019).

MINE DEPRESSURIZATION WATER

Mine Depressurization Water Management Study

COSIA Project Number: WE0008

Research Provider: Four Elements Consulting Ltd. And Others

Industry Champion: Canadian Natural

Industry Collaborators: Imperial, Shell, Suncor, Syncrude, Teck, Total

Status: Complete

PROJECT SUMMARY

The Mine Depressurization Water Management Study was undertaken to address knowledge gaps to help oil sands mining operations determine cost effective, energy efficient and environmentally protective water management approaches for high salinity depressurization water. The study objectives were as follows:

- Summarize water management options for highly saline depressurization streams. The summarized options include reduce, re-use, return, reinjection or return followed by freeze-thaw treatment.
- Summarize studies and models to date on the impact of mining operations on attenuation of natural groundwater flows to the Athabasca watershed and outline potential quantitative adjustments to determine net production of depressurization water and identify potential further studies.
- Summarize existing regulatory requirements affecting direct discharge to river and protection of aquatic life.
- Assess near-field mixing constraints and propose outflow configuration options, including controls to manage release to the Athabasca River and assess potential for acute toxicity to passing organisms.
- Characterize the toxicity of high salinity groundwater to aquatic organisms, particularly rainbow trout.

<u>Background</u>

Open pit mines usually intersect the ground water table, and if left untouched, will cause slope stability and mine excavation flooding. As part of the oil sands mining process, the local water table up gradient of the mine face is pumped down in a process called “depressurization” and is necessary to maintaining a safe working environment at mine sites located in the oil sands region. Oil sands mine depressurization waters are highly variable in salinity, typically ranging in total dissolved solids (TDS) concentrations from 1,200 mg/L to 30,000 mg/L, with some wells reaching concentrations up to 80,000 mg/L.

To date, commercially deployed management methods for depressurization water on active mining leases depend on the salinity of the water. For highly saline streams, existing methods include reinjection further away from the mine face and onsite storage. When the salinity is relatively low, existing methods include mixing with tailings water recycle streams and/or release to the Athabasca River. There are limitations and disadvantages to the existing methods. Using high salinity water from depressurization in the extraction process can result in reduced extraction efficiency, corrosion of equipment and adverse effects on the reclamation landscape due to elevated chloride concentration.

Other recent studies on alternatives such as advanced treatment and re-use or release to the Athabasca River have been completed prior to this study and identified additional knowledge gaps. As with all integrated water management assessments, the principles of reduce-reuse-return apply. When applying these principles, it is critical to assess the Environmental Net Effects (ENE) as well as the cost implications of any water management scheme. Release of depressurization waters including highly saline waters to the Athabasca River watershed in a manner that is protective of the river may present operators with a highly favorable ENE and cost option. While work completed by COSIA members previously, such as Regional Salt Management, Substance Load allocation, Technology and Sector-Based Effluent Quality Objectives addressed some of the knowledge gaps, there were still unanswered questions that needed to be addressed to facilitate better management of highly saline depressurization water

PROGRESS AND ACHIEVEMENTS

Analysis and research were completed to address each of the objectives of the project and summary reports were completed.

Options Analysis

An options analysis was completed to evaluate ENE for a range of water management options under five management strategies (reduction, reuse, release, disposal, and storage). The evaluation of net environmental effects included evaluation of using depressurization water as a water source for other applications following guidance provided in the Conservation and Allocation Guideline for Oilfield Injection. Management options were evaluated using a Kepner-Tregoe analysis. Management objectives were identified, ranked in order of importance, and given a weight representing their importance relative to the other management objectives. Next, performance scores were created to characterize the performance for the water management options relative to the key management objectives. Performance was scored between one and five, with five representing favourable performance and one representing poor performance. Weighted performance scores, according to each objective and overall for each water management option, were calculated by multiplying performance scores by the relevant management objective weight.

Based on this decision analysis, direct release to the Athabasca River was identified as the most favourable management option. Release to the Athabasca River would help mitigate changes in the Athabasca River flow associated with depressurization and would require minimal infrastructure and energy requirements. Release of depressurization water would be managed such that changes in water quality in the Athabasca River would be minimal and no effects to aquatic life would be expected.

Re-injection is also a favourable management option, based on the decision analysis. Re-injection requires minimal infrastructure and energy requirements and does not generate waste. Re-injection volumes are limited by aquifer capacity.

Reuse options involving desalination and all desalination technologies are considered less favorable based on the decision analysis. Desalination technologies separate waste streams into freshwater and a highly-concentrated brine or solid waste. Desalination has high capital and lifecycle costs as well as high energy requirements and greenhouse gas production. Using high salinity depressurization water in the extraction process could result in unacceptable loss of extraction efficiency and corrosion of equipment. These options also result in highly concentrated tailings, brine or solid waste that create significant challenges for storage as well as for successful reclamation and closure.

Athabasca River Evaluation of Depressurization Water Release and Attenuation of Seepages

This component included evaluation of potential effects of mining operations on attenuation of natural groundwater flows and release of high salinity depressurization water on the Athabasca River. Depressurization activities could change the seepage flow of natural high salinity groundwater to the Athabasca River. There has been a concern that regional depressurization activities could reduce the seepage and affect water quality and quantity in the Athabasca River.

Natural saline water is ubiquitous in the region and includes several documented point sources as distributed surface release or seepages into the river-bed. Some of the streams such as the Hangingstone River, Horse River, and Saline Creek have chloride concentrations approaching or exceeding the chronic guideline for the protection of aquatic life. Point source releases from fens and springs to the Athabasca River have been described in several studies (Wells and Price 2015; Gue 2012; Gue et al. 2015, 2017; Roy 2016; Grasby 2006) and seepage directly into the Athabasca River has also been extensively studied.

Several studies have been completed to quantify natural groundwater seepage flow and water quality to the Athabasca River. Jasechko et al. (2012) estimated natural high salinity groundwater seepage to surface waters along the Athabasca River at four monitoring stations located at Hinton, the Town of Athabasca, Fort McMurray and Old Fort. They estimated an average natural high salinity groundwater input of 1.08 m3/s to the Athabasca River between Fort McMurray and Old Fort, and 20th and 80th percentile flows of 0.5 m3/s and 3.4 m3/s respectively. Gue et al. (2018) measured flow and concentration from point sources and used mass balance of stable isotopes to estimate loads from point sources and seepages within the river bed. Loads from high salinity groundwater seepage within the reach between Fort McMurray and Old Fort were estimated to be approximately 20% to 30% of the chloride and negligible for metals and organic constituents. A 2018 study by Warren B. Kindzierski of the School of Public Heath at the University of Alberta estimates natural chloride discharges from springs and ground water to the Athabasca River watershed of up to 1100 tonnes/day.

There is uncertainty about how local depressurization activities due to mining could influence natural high salinity groundwater seepage; therefore, potential effects of depressurization were evaluated by considering a range of reductions in natural high salinity groundwater seepage flows.

Modelling was completed for a regional depressurization scenario using the Athabasca River Model. The reduced groundwater seepage would have a negligible affect on flow in the Athabasca River. Reduced seepages from depressurization activities could result in a measurable decrease in chloride concentration in the Athabasca River, but the magnitude would not result in effects to aquatic life. No change in the concentration of other major ions was predicted.

Substance concentrations in the Athabasca River were predicted for a hypothetical scenario with regional releases of depressurization and oil sands process water corresponding the substance load allocations derived for the Regional Substance Load Allocation (RSLA) study. Even for the worst-case conditions assumed for the modelling, substance concentrations were predicted to be elevated only in a small area downstream of the outfall and were predicted to be below the guidelines at the regulatory mixing zone boundary. For representative conditions only a small change in substance concentrations in the Athabasca River was predicted, even directly downstream of the outfall.

Existing Regulatory Requirements for Release

A comprehensive summary of all existing regulatory requirements related to the release of depressurization water to the Athabasca River was completed. Potential high salinity groundwater release was evaluated relative to the Industrial Release limits Policy (AENV 2000) and the Water Quality-Based Effluent Limits Procedures Manual (AEP 1995). The existing policy states that more stringent of technology and water quality-based limits be applied. The options analysis concluded that there are no applicable technology standards for chloride, and therefore water quality-based limits for chloride would be applied to any depressurization water release. The key regulatory restriction for release of high salinity depressurization water would be to prevent acute effects to passing organisms. This requirement was evaluated further under the last two components of the study, as described in the next two sections.

Near-Field Mixing Analysis

Near-field modelling of a hypothetical release of high salinity depressurization water to the Athabasca River was undertaken using the Cornell Mixing Zone Expert System (CORMIX). The release rate was based on the current depressurization rate of 100 m^3/h and major ions concentration were based on a recently collected sample. Modelling was conservatively based on the lowest one-day flow in 10 years in the Athabasca River and considered five different locations on the Athabasca River with different velocity and depth profiles.

The modelling was used to demonstrate that acute toxicity (lethality to passing organisms) would not occur downstream of the hypothetical release and that concentrations in the effluent would be substantially reduced within a very short distance downstream of the outfall.

Regulatory guidance from the United States Environmental Protection Agency (USEPA) provides alternative criteria to prevent acute lethality to passing organism. Based on the criteria provided, meeting acute guidelines at the edge of the acute mixing zone should be sufficient to prevent lethality to passing organisms as long as the travel time through the mixing zone is less than 1 hour. Travel times through the acute mixing zone for the hypothetical release were estimated to be less than 2 minutes. Acute lethality can be prevented by having a release velocity higher than 3 m/s. Meeting the rainbow trout LC50 within 1 m of the diffuser would provide an added level of certainty that acute lethality would not occur.

Acute guidelines for chloride, bicarbonate, and whole-effluent acute toxicity would be met at the acute regulatory mixing zone of 30 m downstream of the outfall. The level of dilution that would be required to attain the rainbow trout LC50 values that could be applied at 1 m downstream of the outfall would be an 80% reduction, corresponding to the literature-derived LC50 values and LC50 values estimated from high salinity ground water samples.

Near-field mixing is affected by water depth and velocity at the outfall site as well as the density of the release water and the outfall configuration. The outfall configurations considered include submerged diffusers with single-port and multi-port configurations. Multi-port diffusers release water from a number of ports over a larger area compared to a single-port diffuser, and result in more mixing in the near field. CORMIX model predictions show that the high-density water would have a tendency to sink, increasing interactions with the bottom of the channel. Optimal configurations have greater upward momentum resulting in delayed interaction with the channel bottom. The level of dilution required to meet the acute guidelines at 30 m and the rainbow trout LC50 immediately downstream of the outfall could be achieved for a range of outfall configurations even for worst-case low-flow conditions in the Athabasca River. Results were similar for a range of outfall locations along the Athabasca River with different depth and velocity profiles.

Toxicity Characterization

A review of available information was undertaken to characterize the toxicity of high salinity groundwater to aquatic organisms, in particular rainbow trout. The investigation included review of applicable literature as well as analysis of the results of historical toxicity testing completed on high salinity groundwater. The analysis evaluated the potential sources of toxicity for depressurization water after removal of sulphide, ammonia, and naphthenic acids and characterized the role of the bicarbonate system and major ion composition on the toxicity of chloride.

LESSONS LEARNED

The study addressed information gaps related to high salinity depressurization water management. Release of water to the Athabasca River was found to be the most favourable option based on net environmental effects. Based on modelling and review of toxicity information, there is a high degree of confidence that high salinity depressurization water could be released, without acute effects to passing organisms or to benthic invertebrates.

PRESENTATIONS AND PUBLICATIONS

Conference Presentations/Posters

Mine Depressurization Water Management Study - COSIA - AI-EES Water Conference

Reports & Other Publications

- Mine Depressurization Water Management – Near-Field Mixing Analysis
- Mine Depressurization Water Management – Athabasca River Evaluation of Release, Reuse, and Reinjection Options
- Mine Depressurization Water Management – Draft Information Review

RESEARCH TEAM AND COLLABORATORS

Institution: Four Elements Consulting Ltd.

Principal Investigator: Tammy Rosner, Ecologist

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Theo Paradis	Canadian Natural	Engineer		
Scott Morton	Canadian Natural	Geologist		
Nicole Northcott	Canadian Natural	Geologist		
John Brogly	Canada's Oil Sands Innovation Alliance	Engineer		
Anita Selinger	Suncor	Engineer		
Warren Zubot	Syncrude	Engineer		
Andrew Clow	Four Elements Consulting Ltd.	Engineer in Training		

Mine Depressurization Water Management – Phase II and III

COSIA Project Number: WJ0063

Research Provider: None

Industry Champion: Canadian Natural

Industry Collaborators: Stoakes Consulting Group, Golder

Status: Complete

PROJECT SUMMARY

Canadian Natural currently depressurizes Basal McMurray Aquifer (BW) from mine operations in order to mine the hydrocarbon resource at Horizon Oil Sands in a safe and efficient manner. Once depressurized, Canadian Natural needs to manage BW. Basal water is currently stored on surface in a containment pond and this type of surface storage exposes Canadian Natural to long-term risk if not managed properly.To reduce the liability risk, the AER has requested Canadian Natural provide a Basal Water Management Plan. The Basal Water Management Update was submitted to the AER for review in December 2019. The Mine Depressurization Water Management Project was to help inform the AER requested Basal Water Management Plan.

PROGRESS AND ACHIEVEMENTS

Results of geological investigation show a formation with the potential for injection. In July 2018, an injection test into the Lower Prairie Evaporites was completed and reached steady state indicating injection into the Lower Prairie Evaporites was possible. The results from the injection test also informed a conceptual hydrogeological model of the Lower Prairie Evaporite Formation. Commercial injection rates will be determined in 2020.

LESSONS LEARNED

Injection into the Lower Prairie Evaporites allows Canadian Natural to manage BW that supports safe mining practices. The geological data collected during this project allowed for a re-interpretation of the geologic setting of the Waterways Formation from structural setting to an erosional environment at Horizon. This new interpretation can be used by others to support investigations and understanding of Devonian strata underlying the surface minable area. The hydrogeological data collected lead to further understanding of complex carbonate formation flow in the Lower Prairie Evaporites.

PRESENTATIONS AND PUBLICATIONS

There are no presentations or publications that are available in the public sphere.

RESEARCH TEAM AND COLLABORATORS

Institution: Canadian Natural

Principal Investigator: Scott Morton

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
John Wozniewicz	Golder	Principal Hydrogeologist		
Frank Stoakes	Stoakes Consulting Group	Owner/Geologist		

Mine Basal Water Disposal Project

COSIA Project Number: WJ0145

Research Provider: None

Industry Champion: Canadian Natural

Industry Collaborators: Suncor

Status: Complete

PROJECT SUMMARY

Canadian Natural currently depressurizes Basal McMurray Aquifer (BW) from its mine operations in order to mine the hydrocarbon resource at Horizon Oil Sands in a safe and efficient manner. Once depressurized, Canadian Natural needs to manage BW. Basal water is currently stored on surface in a containment pond and this type of surface storage exposes Canadian Natural to long-term risk if not managed properly. To reduce the liability risk, the AER has requested Canadian Natural provide a Basal Water Management Plan. The Basal Water Management Update was submitted to the AER for review in December 2019. The Mine Depressurization Water Management Project was to help inform the AER requested Basal Water Management Plan.

The objective is to understand the thresholds of Basal water on a range of local species, collect field data to compare with site data, and establish baseline data to confirm model predictions before submitting a full-scale application to release Basal water into the Athabasca River.

PROGRESS AND ACHIEVEMENTS

The field program was conducted spring 2019 in order to collect baseline data to compare with model predictions made in 2016/2017. The field data that was collected was from a natural saline seep located along the Athabasca River and included water quality, sediment collection and analysis, and plume characterization.

LESSONS LEARNED

By running the 2019 field pilot, CNRL was allowed to gather natural seepage rates, flow, and volumes and compare to model predictions. Preliminary results show concentrations of TDS can vary over time in natural seepages. Concentrations from the natural seepage collected in 2019 has 50% less TDS than concentrations in BWSP2. Even with the differences in TDS values, modelling shows that chloride concentrations from the natural seepages and water from Basal Water Storage Pond 2 both reach acute guidelines within 2.0 m from the outfall compared to current AER policy which allows 30 m distance to reach acute guidelines.

PRESENTATIONS AND PUBLICATIONS

Application for Pilot Release

RESEARCH TEAM AND COLLABORATORS

Institution: Canadian Natural

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Tammy Rosner	Four Elements Consulting	Owner/ Water Specialist		

NATURAL AND ANTHROPOGENIC INPUTS TO THE ATHABASCA WATERSHED

Metals vs Minerals in the Lower Athabasca River

COSIA Project Number: WE0057

Research Provider: University of Alberta

Industry Champion: Canadian Natural

Industry Collaborators: Imperial, Syncrude, Suncor, Teck

Status: Year 2 of 3

PROJECT SUMMARY

Open pit bitumen mining in northern Alberta generates considerable volumes of dust. The dusts are derived not only from the mines, but from wind erosion of dry tailings and gravel roads, construction activities, and quarries, in addition to natural sources such as riverbanks and sand bars. The dusts themselves consist mainly of mineral particles, some of which are chemically reactive (e.g., calcite, a calcium carbonate) whereas others are effectively insoluble (such as quartz, a silicate). Most environmental impact studies to date have not clearly distinguished between heavy metals (such as cadmium and lead) from the combustion of fossil fuels needed for bitumen upgrading and heavy metals that are hosted within the crystal lattice of the mineral particles themselves. Heavy metals that are emitted to the air during combustion at high temperatures tend to be very small (< 1 micron) and in soluble form (such as oxides), whereas mechanically-generated mineral dusts tend to be rather large (10 to 100 microns) and much less soluble (e.g., silicate minerals such as quartz and feldspar). Very small, soluble, metal-containing particles may represent a threat to biota, depending on the pH of soil and water, and other factors, but large, insoluble particles most likely do not.

The main goal of this study is to clearly distinguish between these two sources of heavy metals to the air, using size-resolved analyses of snow and *Sphagnum* moss from bogs. The secondary objective is to understand what impact, if any, the two sources of heavy metals may have on the chemical composition of meltwater and peatland surface waters from bogs, fens and swamps that drain into the Athabasca River.

PROGRESS AND ACHIEVEMENTS

Snow

Scanning electron micrographs show that particulate matter is predominantly in the form of large particles (ca. 10 to 100 µm), primarily aluminosilicate minerals. The snow from McM (near the airport at Fort McMurray) is exceptional in that there appears to be small, spheroidal (fly ash) particles, approximately 3 µm in diameter. These deserve further attention, given the proximity of the site to a major population centre. Potentially toxic "heavy metals" (Cd, Pb, Sb, Tl) are mainly (88-99 %) in the particulate fraction. This is even more so for elements enriched in bitumen (V, Ni, Mo: 96 - 99 %), and especially true of conservative, lithophile elements (Al, La, Th: > 99.5 %)

Peat bog surface water

We have undertaken the first study to use peat bog surface waters to examine the chemical reactivity of atmospheric dusts. In general, most trace elements in the dissolved fraction (< 0.45 µm) increase in concentration toward industry. This finding suggests that there is some dissolution of atmospheric dusts in the acidic bog waters. In general, the greatest differences in trace metal concentrations are seen in respect to mobile lithophile elements such as the alkali (Li, Rb, Cs) and alkaline earth metals (Be, Sr, Ba), as well as those more soluble under anoxic conditions (Mn, Fe). Lithium in particular seems to be a sensitive indicator of dust particle dissolution, with values near industry up to 10 x greater than the control site (UTK). Smaller differences are seen in conservative, lithophile elements e.g. Al, Th, REE e.g. up to 7 x. Arsenic and Cr increase in concentration toward industry, but Cd, Pb and Tl show inconsistent patterns; the concentrations of these elements, however, tend to be very low.

The surface waters at JPH4 (12 km from the mid-point between two central upgraders) is much less acidic (pH 5.5) than the other bogs (all pH 3.5). However, where we have sampled, JPH4 is a very shallow peatland. Thus, the elevated surface water pH may be a reflection of the proximity of underlying sediment (ie minerotrophic, fen-like conditions, with alkaline groundwaters), and the upward migration of metal cations from mineral dissolution in the layers below the peatland. Alternatively, the pH may be high because of the proximity of the site to open pit mines, and the dissolution of alkaline dust particles e.g. carbonates. Additional work on the peat depth, stratigraphy, surface and groundwater chemistry is needed, in order to be able to distinguish one from the other; this will be the subject of a Ph.D. thesis. At McK (25 km), bog surface water exhibits anomalous EC values, as well as clearly elevated concentrations of Li, Be, Rb and Cs. These results suggest that there may be unique dust inputs to this site; this needs to be assessed and confirmed using snow analyses. In contrast to these sites, very little change in water chemistry is seen in the bog water from ANZ which is close to an upgrader. Thus, changes in the chemistry of bog surface water is mainly a reflection of proximity to open pit bitumen mines (and quarries, and gravel roads ie sources of dust), and not to bitumen upgraders. In the water samples collected in October, the greatest Cu concentrations by far, were from the control site (UTK) which illustrates the importance of having high quality data from peat bogs far removed from industry.

Higher plants

In the berries of higher plants (cranberry, lingonberry, and others) and the leaves of Labrador Tea, most trace elements, and in particular those that have no biological function (e.g. Ba, Co, Cs, Fe, Li, Pb, Th, U, V, and the REE) are associated with dust particles. In contrast, micronutrients such as Cu, Zn, Ni and Mo are unaffected by dust; these elements are dominated by plant uptake from the substrate. The leaching behaviour of trace elements from plant leaves is very different: Mn, Ni, Cu and Zn are readily extracted by hot water, suggesting that they are predominantly in biological forms within the plant tissues. In contrast, the lithophile elements are inefficiently extracted, consistent with the view that they are in the form of insoluble minerals on the surface of the plant leaves. Metals showed differential leaching behaviour: high purity RO/DI water is better at leaching some metals (e.g. Al, La, Th) whereas pristine groundwater from a carbonate terrain is better at leaching others (e.g. Ni, Cu, Pb). Apparently, the chemical reactivity of these dusts varies with water composition.

LESSONS LEARNED

Our findings to date are consistent with previous research done by the University of Alberta, laboratory using moss and snowpack sampling. Specifically, that most of the trace element inventory of these media can be attributed to comparatively large (ca. 10 to 100 µm), aluminosilicate minerals which are relatively insoluble. Particulate matter collected at McM, near the airport at Fort McMurray, contains abundant fly ash particles; the source and significance of these should be investigated further.

There is a chemically reactive fraction of dusts which is revealed by the elevated concentrations of alkali and alkaline earth metal cations in acidic bog waters closest to the mines. Dissolution of these dusts has modest and inconsistent effects on chalcophile trace elements; the concentrations of these tend to be very low. Arsenic is clearly more abundant in bog waters near industry, but the concentrations are at or below the values found in the Athabasca River which represent background values. The lack of change in trace element concentrations in acidic bog waters near the bitumen upgrader at Anzac, suggests that upgrading is not a significant source of reactive dusts.

The abundance of essential trace elements (Cu, Mn, Ni, Zn) in these plants is independent of dust inputs and governed by root uptake. Thus, the biogeochemical cycles of plant micronutrients appear to be unaffected by dust inputs. Although Cd has no biological role in plants, this potentially toxic "heavy metal" in plants is also governed by plant uptake. However, the dusts generated from mining activities appear to be an unimportant source of Cd

PRESENTATIONS AND PUBLICATIONS

Publications

Javed, M.B., Zheng, J. and Shotyk, W. Trace elements in snow from ombrotrophic bogs in the Athabasca Bituminous Sands Region, Alberta: implications for Athabasca River water quality

Shotyk, W., Noernberg, T. and Javed, M.B. Trace elements in Labrador Tea (Rhododendron groenlandicum): how the predominant sources of trace elements to the plants affect the chemical composition of hot water extracts. *Environmental Research* 183, 2020, 109272.

Shotyk, W. (2020) Trace elements in wild berries from reclaimed lands: biomonitors of contamination by atmospheric dust. *Ecological Indicators* March 2020, 105960.

Shotyk et al. Trace elements in surface waters of ombrotrophic bogs: evidence of dissolution of atmospheric dusts from open pit bitumen mining. Environmental Science and Technology (manuscript in preparation)

Shotyk et al. Trace elements in pore water expressed from Sphagnum moss in ombrotrophic bogs: a new tool for understanding the chemical reactivity of atmospheric dusts from natural and industrial sources Environmental International (manuscript in preparation)

Stachiw, S., Bicalho, B., Grant-Weaver, I., Noernberg, T. and Shotyk, W. (2019) Trace elements in berries collected near upgraders and open pit mines in the Athabasca Bituminous Sands Region (ABSR): distinguishing atmospheric dust deposition from plant uptake. *Science of the Total Environment* 670: 849-864.

Conference Presentations/Posters

Javed M.B.; Cuss C.W.; Noernberg T.; Zheng J.; Shotyk W. Snow and Sphagnum moss in the Athabasca Bituminous Sands region: indicators of contemporary wintertime and summertime atmospheric deposition of trace elements. COSIA, Oil Sands Innovation Summit (OSIS), 3 – 4, June 2019, Calgary, Alberta, Canada.

Javed M.B.; Donner M. Shotyk W. Resolving natural and anthropogenic influences to groundwater and surface water environments in the Lower Athabasca region. Alberta Innovates Water Innovation Program (WIP) Forum, 22 – 23, May 2019, Edmonton, Alberta, Canada.

Javed M.B.; Cuss C.W. Donner M. Noernberg T, Shotyk W. Natural and anthropogenic inputs of trace elements to the surface- and ground-waters in the Athabasca Bituminous Sands region, Alberta, Canada. European Geosciences Union (EGU) General Assembly, 7–12 April 2019, Vienna, Austria.

Shotyk, W. Metals versus Minerals in the Mining Environment: Misconceptions and Misunderstandings. Mining and the Environment Conference, Sudbury, Ontario, Canada, June 23 to 28, 2019 (invited keynote presentation, 60 minute presentation, 200 attendees).

Shotyk, W. Trace elements in country foods, from berries to beavers: a geochemical perspective on micronutrients and heavy metals. Canadian Society of Chemistry Annual Conference, Session on Environmental Impacts of Unconventional Energy Resources. Québec City, Canada, June 3 to 7, 2019 (invited keynote presentation, 40 minute presentation, 80 attendees).

Shotyk, W. Natural versus anthropogenic sources of trace elements to the Lower Athabasca River watershed: a geochemical perspective from the SWAMP laboratory. Alberta Institute of Agrologists, Annual General Meeting, Banff, AB, March 27-29, 2019 (invited Plenary Speaker, 30 minute presentation, 320 attendees).

Reports & Other Publications

Shotyk, W. Natural versus anthropogenic sources of trace elements to the Lower Athabasca River watershed: a geochemical perspective from the SWAMP laboratory. Alberta Institute of Agrologists, Annual General Meeting, Banff, AB, March 27-29, 2019, 12 pp.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator(s): William Shotyk

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Na Chen	University of Alberta	M.Sc. Student	September 2019	August 2021
Juan Alarcon	University of Alberta	Field and Lab Technician		
Tracy Gartner	University of Alberta	Project Management		
Iain Grant-Weaver	University of Alberta	Lab Technician		
Sonia Hammami	University of Alberta	Lab Technician		
Muhammad Babar Javed	University of Alberta	Postdoctoral Fellow		
Nikola Petojevic	University of Alberta	Lab Technician		
Kimberly Than	University of Alberta	Summer Student		

Impact of Climate Change on Surface Water and Groundwater Resources

COSIA Project Number: WE0063

Research Provider: Aquanty Inc.

Industry Champion: Suncor

Industry Collaborators: Canadian Natural, Imperial, Syncrude, Teck

Status: Year 1 of 2

PROJECT SUMMARY

The impact of anthropogenic climate change on water resources is of considerable interest to water resource managers, industry and the public. Understanding, and adequately representing, the multi-physical processes is key to quantify climate change impacts on water resources systems and to develop policies for sustaining healthy ecosystems and water supply. The primary tasks of this project are:

- To condition the weather and hydrologic models to the observed historic period.
- Perform an integrated surface-subsurface flow model simulation driven by Weather Research and Forecast (WRF) datasets for mid- and end-century.
- Analyze climate change impact on the surface water and groundwater system of the Athabasca River Basin (ARB).
- Conduct extreme event and drought analysis based on the future simulation results.

The primary objective of this project is to gain insight on potential climate change impacts in the ARB by using state of the art dynamically downscaled climate projections based on the WRF model to drive a tightly coupled fully integrated hydrologic model of the ARB based on the HydroGeoSphere (HGS) simulator.

PROGRESS AND ACHIEVEMENTS

In this project, coupled climate-integrated hydrologic simulations in the ARB are used to assess the potential impact of climate change on water resources within the ARB and to predict long-term surface water and groundwater flows within the basin. The following provides a summary of project progress and major achievements to date:

- The ARB, covering approximately 165,600 km^2, was discretized at a resolution of 0.5 to 3 km. The conceptual geologic model consists of 13 layers; a soil layer was assigned on top of the model and the bottom of the model is bounded by the Devonian Elk Point Group.
- The ARB model was calibrated based on monthly normal transient flow conditions with observed groundwater depths and surface flow rates, which were set as calibration targets. The climate forcing data applied to this study are the Climate Research Unit (CRU) and WRF T and G configurations. There is high agreement between the simulated and observed flow rates with the maximum flow difference less than 100 m^3/s in the downstream area.

- A total of 103 parameter sets obtained from a previous study related to a steady-state ARB model were applied to examine model parameter uncertainty. The uncertainty of the ARB model is acceptable, and the ARB model is robust under various hydrologic and hydrogeological conditions.
- The validation of the ARB model was performed with historic monthly average flows for 15 years from 1979 to 1994. For the results of the model validation with the CRU datasets, there is also reasonably close agreement between the simulated and observed hydrographs at the four stations across the ARB.
- Although the simulated stream flow with the eight WRF datasets is slightly overestimated, the seasonal cycle is reproduced well. Additionally, snowmelt and stream peak timings match well with the observations in the upstream areas.

LESSONS LEARNED

As described in the project summary section, there is a need to assess the potential impact of climate change on water resources in the ARB. Therefore, it is important to understand and quantify the potential changes in hydrologic and climatic variability of the ARB using multi-physical processes such as integrated surface and groundwater interactions and dynamically downscaled regional climate projections. The main lessons from this project are:

- The integrated HGS model combined with WRF forcing data is able to capture and reproduce seasonal variability for historic hydrologic/hydrogeologic conditions based on the model calibration and validation results.
- The variation of the stream flow responses in the ARB with respect to various hydrologic/hydrogeologic parameter sets, falls within the observed streamflow variation. Therefore, the uncertainty associated with the ARB model is acceptable.
- However, there are relatively large differences between the simulated and observed stream flow near the Rocky Mountains. The results suggest that the freeze-thaw cycles during the winter period in the area may be required for improving the hydrologic and hydrogeological responses such as temporal and physical flow conditions.

PRESENTATIONS AND PUBLICATIONS

Conference Presentations/Posters

Berg, S. J., H-T. Hwang, A. Erler, O. Khader, S. Frey, E. Sudicky, N. Barnes, D. Heisler, T. White, S. Tuttle and J.P. Jones (2019). Impact of Climate Change on Surface Water and Groundwater Resources in the Athabasca River Basin. 2019 Oil Sands Innovation Summit, Calgary, Alberta. June 3-4, 2019

Erler, A. R., H-T. Hwang, O. Khader, S. J. Berg, E. A. Sudicky, J. P. Jones (2020). Projected Changes in Hydro-climatic Extremes in the Athabasca River Basin, the 54 th Canadian Meteorological and Oceanographic Society (CMOS) Congress, Ottawa, Ontario. May 24-28, 2020

RESEARCH TEAM AND COLLABORATORS

Institution: Aquanty Inc.

Principal Investigator: Hyoun-Tae Hwang

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Hyoun-Tae Hwang	Aquanty Inc.	Senior Scientist/Developer (Ph.D.)		
Andre Erler	Aquanty Inc.	Senior Climate Scientist (Ph.D.)		
Omar Khader	Aquanty Inc.	Senior Applications Engineer (Ph.D.)		
Steven Berg	Aquanty Inc.	Senior Hydrogeologist/ President (Ph.D.)		
Edward Sudicky	Aquanty Inc.	Scientific Lead (Ph.D.)		

Natural vs Anthropogenic Inputs: Water Quality in the Lower Athabasca River

COSIA Project Number: WJ0017

Research Provider: University of Alberta

Industry Champion: Syncrude

Industry Collaborators: Canadian Natural, Shell, Imperial, Suncor, Teck

Status: Completed

PROJECT SUMMARY

The Athabasca bituminous sands have received global attention due to the highly visible impact of industrial operations on the surrounding landscape. These striking images have provoked increased scrutiny related to other potential impacts, such as the unintentional release of trace elements (TEs) into the Lower Athabasca River (LAR). Comprehensive and scientifically sound testing is therefore required to assess the possibility and extent of such releases. However, prior efforts to test and analyze LAR waters have suffered from several shortcomings, including:

- Sampling and analysis have not been conducted using adequate metal-free techniques and equipment, potentially leading to contamination and an inability to measure concentrations at low background levels.
- Likely sources of spatiotemporal variation, such as the channelization of the LAR and seasonality of inputs, have not been assessed.
- Changes in the geochemical behaviour of TEs caused by the input of considerable dissolved organic matter (DOM) and iron oxyhydroxide (FeOOH) by tributaries have not been quantified.
- The extent to which filtration method and water quality conditions may impact the measured concentration and speciation of dissolved trace elements has not been systematically evaluated.
- The chemical form and speciation of the TEs has not been measured, so the implications for source attribution and impact on aquatic organisms remain unclear.

This project is addressing these concerns, while developing new technologies and knowledge, including:

- Apparatus and methods for collecting samples across transects of the LAR, at several depths, under metal-free conditions.
- An analytical method for measuring the speciation of TEs over a size continuum from ca. 1 nm to 5 µm without the need for filtration.
- Measuring the impacts of seasonal differences and high-DOM, high-Fe inputs on the geochemical behaviour of TEs in the LAR.
- Understanding the impacts of DOM, turbidity, and filtration method on the concentration and speciation of TEs in the dissolved (< 0.45 µm) fraction.

PROGRESS AND ACHIEVEMENTS

In the autumns of 2017, 2018, and 2019, the concentrations of several TEs increased from the region of the LAR that is upstream of industrial operations, through to the area that is downstream. However, the concentration and speciation of some TEs are quite variable from the east to west sides of the LAR, over the region from the Clearwater River, north through the area of industrial operations, past Fort MacKay. This spatial variation is connected to the delayed mixing of inputs from tributaries which dominate the east side of the river, particularly the Horse, Clearwater, and Steepbank Rivers. These inputs mix slowly from the east to the west side of the LAR from upstream to downstream, taking as far as 70 - 100 km for complete mixing for the Clearwater River. As a result, water samples that are collected only in the middle of the river may give the impression that TE concentrations increase from upstream to downstream of industrial activities. However, these trends may be the consequence of (1) tributary inputs upstream being isolated on the east side of the river, and (2) tributary inputs downstream having mixed across the entire river.

In the spring of 2018 and 2019, the mixing of tributaries was not delayed for as far of a distance downstream. However, the concentrations of most TEs were higher due to increased inputs of particles derived from sediment and soil, likely from the increased runoff during freshet/snowmelt upstream.

Concentrations of dissolved and total trace elements increased significantly from upstream to downstream in the fall of 2017; however, concentrations decreased significantly from upstream to downstream in the spring of 2018.

Progress to date includes:

- The metal-free sampling apparatus (the SWAMP lab "FISH") for collecting water samples as a function of depth in the river has been constructed and successfully deployed during three sampling tours (fall 2017, spring 2018 and fall 2018).
- The analytical method is currently capable of measuring the distribution of TEs amongst major colloidal species in the range from 1 nm to 0.45 μm. Progress on the second size range has been limited by the lack of suitable students; however, a prospective PhD student was recruited in Sept. 2019 and method development is underway.
- Samples have been collected for five seasons, and they have been fully analyzed for four of these seasons. Minor laboratory analysis remains for a subset of the samples and is currently underway.
- Preliminary assessment of filtration and storage artefacts has been conducted using a small sample set. The PhD student will work on filtration artefacts in earnest over the coming months.
- To improve the spatial resolution and provide a more fine-grained assessment of potential inputs, an additional sample collection period beyond the proposed work was added to the study at no extra cost (Fall, 2019).

Data analyses are complete for the initial sampling campaigns, and manuscripts are currently being prepared for submission to scientific journals. Additional manuscripts will be written using the remaining data.

LESSONS LEARNED

The apparent increase in TE concentrations from upstream to downstream in the LAR is assumed to be due to industrial activities, but previous studies have not accounted for spatial variation in the background concentrations caused by tributary inputs; therefore, any such attributions require re-assessment. Future sampling programs in the Athabasca River should account for this variation. Any planned discharges to the LAR should also account for the different concentrations and reactivity of material on different sides of the river, which could impact transport and bioavailability (e.g., organic and inorganic colloids). Similarly, previous work has not accounted for the increased background concentrations of TEs in the spring that are caused by soil and sediment inputs during freshet. The size and speciation of these spring inputs also make them less bioaccessible, and therefore they pose lower risk to aquatic organisms.

PRESENTATIONS AND PUBLICATIONS

Presentations

Cuss CW et al., (2019) *Impacts of tributaries on the concentrations of dissolved trace elements in the Athabasca River*. Presentation at the Oil Sands Innovation Summit, Calgary.

Cuss CW et al., (2019) *Spatial variation in the concentration and colloidal distribution of trace elements in a large boreal river—implications for representative sampling*. Poster presented at the European Geosciences Union, Vienna, Austria.

Ghotbizadeh, M et al., (2019) *Spatial variation of dissolved trace element concentrations and colloidal distribution of trace elements along the Athabasca River.* Presentation at the Faculty of Engineering Graduate Research Symposium, Edmonton.

Ghotbizadeh, M et al., (2019) *Spatial variation of trace elements along and across the Lower Athabasca River.* Presentation at the Faculty of Agriculture, Life and Environmental Sciences Graduate Student Conference, Edmonton.

Ghotbizadeh, M et al., (2019) *Application of AF4-ICP-MS to identify natural versus industrial sources of trace elements to the Athabasca River in Alberta, Canada*. Poster presented at the 11th Western Canadian Symposium on Water Quality Research, Edmonton.

Ghotbizadeh, M et al., (2019) *Application of AF4-ICP-MS to identify natural versus industrial sources of trace elements to the Athabasca River in Alberta, Canada*. Poster presented at the European Geosciences Union, Vienna, Austria.

Ghotbizadeh, M et al., (2019) *Spatial variation of total and dissolved trace element concentrations along the Athabasca River*. Poster presented at the Oil Sands Innovation Summit, Calgary.

Ghotbizadeh, M et al., (2019) *Spatial variation in the speciation, composition, and morphology of trace element-bearing colloids in the Athabasca River.* Poster presented at the Faculty of Agriculture, Life and Environmental Sciences Research Symposium, Edmonton.

Xue, J et al., (2019). *Size-fractionated dissolved organic matter and associated trace element distributions in the lower Athabasca River by EEM-PARAFAC and AF4-ICPMS*. Presentation at the Faculty of Agriculture, Life and Environmental Sciences Graduate Student Conference, Edmonton.

Cuss, CW et al., (2018). *Separation of nanominerals and colloids into bioaccessibility-based fractions using FFF-ICPMS.* Presentation at Nanolytica Conference, Simon Fraser University, British Columbia.

Cuss, CW et al., (2018). *Spatial variation in the speciation profile of dissolved trace elements in mixing zones, transects, and depth profiles of the Lower Athabasca River and its tributaries in Alberta, Canada.* Presentation at the International Conference on Field- and Flow-based Separations, South Carolina, USA.

Cuss, CW et al., (2018). *Dynamics of dissolved (< 0.45 µm) trace elements and organic matter in tributary mixing zones of the lower Athabasca River, Alberta*. Presentation at the Canadian Chemical Society Annual Meeting and Conference, Edmonton.

Cuss, CW et al., (2018). *Measuring the distribution of metals and metalloids amongst dissolved colloidal species using AF4-UV-ICPMS*. Presentation at the Canadian Chemical Society Annual Meeting and Conference, Edmonton.

Ghotbizadeh et al., (2018). *Spatial variation in the composition, size and morphology of dissolved colloids along the Athabasca River.* Poster presented at the Canadian Chemical Society Annual Meeting and Conference, Edmonton.

Ghotbizadeh et al., (2018). *Measuring spatial variation in the speciation, composition, and morphology of trace element-bearing colloids in the lower Athabasca River and its tributaries.* Poster presented at the Oil Sands Innovation Summit, Calgary.

Cuss, CW et al., (2018). *Routine analysis of trace element distributions among major dissolved colloidal species using AF4-UV-ICPMS (with applications).* Presentation at the International Conference on Heavy Metals in the Environment, Georgia, USA.

Ranville, J et al. (2018). *Characterization of single nanoparticles, nanomineralogy, geochemistry, and mining contaminant sites.* Excerpt from ICHMET presentation at Goldschmidt Conference, Boston, USA.

Cuss, CW et al. (2018). *AF4-ICPMS in the SWAMP: Challenges, strategies, and applications for routine analysis with the 300-Dalton membrane*. Presented at Postnova User's Meeting Utah, USA.

Cuss, CW et al. (2018). *AF4-ICPMS to assess spatiotemporal variation in the distribution of trace elements amongst major colloidal species: method, quality control, applications*. Presented at Postnova User's Meeting Utah, USA.

Montaño, M et al. (2018). *Analysis of selected LAR and tributary samples using single-particle ICP-TOF-MS.* Presented via collaboration with Dr. Jim Ranville, Dr. Manuel Montaño and Dr. Frank Von Der Kammer): Advancing Engineered and Natural Nanoparticle Detection and Characterization in the Environment Using spICP-TOF-MS. Presented at the International Conference on the Environmental Effects of Nanoparticles and Nanomaterials, North Carolina, USA.

Theses

Ghotbizadeh, M. *Spatiotemporal variation in trace element speciation along the Lower Athabasca River: distinguishing natural from industrial inputs.* M.Sc. thesis (in progress).

Xue, J. *Geochemistry and speciation of bitumen-derived trace elements along the Lower Athabasca River, and implications for assessing environmental impacts.* M.Sc. thesis (in progress).

Wang, Y. *Colloid-facilitated transport mechanisms of trace elements in Athabasca River mixing zone.* PhD thesis (in progress)

Journal Publications

Cuss, C.W. et al. *Delayed mixing of iron-laden tributaries in large boreal rivers: implications for iron transport and water quality sampling* (in preparation).

Ghotbizadeh, M. et al. *Spatial variation, speciation and source apportionment of trace elements along the Lower Athabasca River* (in preparation).

Ghotbizadeh, M. et al. *Temporal variation, speciation and source apportionment of trace elements along the Lower Athabasca River* (in preparation).

Noernberg, T. et al. *The SWAMP FISH: A metal-free water sampling device for use in large rivers* (in preparation).

Wang, Y. *Quantitative analysis of sample loss mechanisms during the fractionation of dissolved trace elements in natural water* (in preparation).

Reports & Other Publications

Shotyk, W (2019). *Natural versus anthropogenic sources of trace elements to the Lower Athabasca River watershed: a geochemical perspective from the SWAMP laboratory.* Presentation at the Alberta Institute of Agrologists, Annual General Meeting, Banff, AB, (plus 13-page paper for the published proceedings).

RESEARCH TEAM AND COLLABORATORS

Institution: SWAMP Lab Facility, Department of Renewable Resources, University of Alberta

Principal Investigator: Dr. William Shotyk

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Tommy Noernberg	University of Alberta	Mechanical Engineer and Field Specialist		
Tracy Gartner	University of Alberta	Project Manager		
Beatriz Bicalho	University of Alberta	Research Associate		
Chad Cuss	University of Alberta	Research Associate		
Marjan Ghotbizadeh	University of Alberta	BSc (MSc candidate)	2018	2020
Jinping Xue	University of Alberta	BSc (MSc candidate)	2018	2020
Yu Wang	University of Alberta	MSc (PhD candidate)	2019	2023
Karen Lund	University of Alberta	Lab technician		
Iain Grant-Weaver	University of Alberta	Lab technician		
Acacia Markov	Guelph University	Summer student		

Research Collaborators: This program is 50% funded by the National Science and Engineering Research Council of Canada (NSERC).

OP-FTIR Optical Remote Sensing Field Measurement of VOC & GHG Emissions on Suncor's Tailings Pond and EF Model Development

COSIA Project Number: WJ0064

Research Provider: Suncor

Industry Champion: Suncor

Industry Collaborators: None

Status: Completed

PROJECT SUMMARY

Suncor undertook a 2-month long Volatile Organic Compounds (VOCs) and GHG emissions testing and monitoring program to better understand air emissions from the tailings pond 2/3. The program included measurement of VOC and GHG emissions from the tailings pond using the Vertical Radial Plume Mapping (VRPM) method as described within U.S. EPA Other Test Method 10, Optical Remote Sensing for Emission Characterization from Non-Point Sources. The VRPM study involved use of a scanning Open-Path Fourier Transform Infrared (OP-FTIR) instrument and four retro-reflector mirror assemblies to measure downwind concentrations of many target compounds. On-site meteorological data were also collected and used in the analysis.

PROGRESS AND ACHIEVEMENTS

An Optics trailer equipped with OP-FTIR, auto-positioner, and wind monitor was installed on the south bank of the tailings pond. The trailer was connected to the internet via air card and all raw spectral and wind data was transferred in real time to a dedicated server for further analysis and system real-time monitoring. Three horizontal retro-reflecting mirrors were installed on poles constructed on soil pads. The fourth retro-reflecting mirror was elevated on a man lift.

A quantification algorithm was run on VOC and GHG compounds, which identified that only six compounds were suitable for VRPM analysis, as they originated from the surface area of the tailings pond and were sufficiently above their minimum quantification levels (MQLs), and included total Alkaline Mixture (AM), carbon dioxide, methane, o-xylene, ammonia, and nitrous oxide. Several more compounds were detected, but not in a high enough frequency for calculating their emission rate using the ratio method.

It was observed for most compounds that there was a significant difference in average emission rates in the three wind direction sectors: 280º – 329 º, 330º – 350º, and 36º – 80º. In general the results demonstrate that emission rates from the east pool are lower compared to the emission rates from the middle and west pools. For CO_2 and N_2O at the middle and west pools the emission rates for the higher wind speeds was much greater than the emission rates at the lower wind speeds which indicates that emissions in these two pools are originated from surface areas further upwind.

This phenomenon was not observed for methane which could be explained by the fact that methane is much lighter than air and vertical plume capture from further upwind sources is poor.

For south-southeast wind directions (and wind speed > 3 m/s) a much lower CO_2 to CH_4 mass emission ratio of 40 was measured, indicating that methane plumes originated from the north middle were not fully captured by the south bank VRPM configuration. Analysis for northwest wind directions (and wind speed > 3 m/s) representing emissions originated from the northwest surface area, measured a CO_2 to CH_4 mass emission ratio of 34 vs. approximately 200 at the south bank).

LESSONS LEARNED

The success of this type of emission study is strongly dependent on the location, dimensions, and orientation of the VRPM beam configuration with respect to the interrogated upwind source and the prevailing wind direction during the study period.

OP-FTIR was found to be a very useful tool for measuring VOCs emissions (primarily as total AM for this type of source), GHGs (CO_2, CH_4, and N_2O), inorganics (such as NH_3 and SO_2), aromatics (toluene, xylenes, benzene, and 1,2,4 tri-methylbenzene), and the light end of PAHs such as naphthalene. For several compounds that were significantly above the OP-FTIR MQL, the VRPM algorithm was used for calculating the emission rates. The rest of the relevant compounds that were emitted from the surface source, the ratio method was used (compared to total Alkane Mixture (AM) concentrations and emission rates) for calculating the average emission rate for the whole study.

It was demonstrated that this technology is capable of accurately estimating the lower bound of total emission rates from large diffused area source with the constrained pond's emissions apportionment model. In addition, this project has measured N_2O emissions for the first time for this type of source due to a very sensitive MQLs algorithm.

PRESENTATIONS AND PUBLICATIONS

OP-FTIR Optical Remote Sensing Field Measurement of VOC & GHG Emissions on Suncor's OS Tailings Pond & EF Model Development – COSIA-AMEARA workshop, June 2-3 2015.

RESEARCH TEAM AND COLLABORATORS

None

Surveying Conductive Anomalies within the Athabasca River

COSIA Project Number: WJ0146

Research Provider: DMT Geosciences

Industry Champion: Canadian Natural

Industry Collaborators: Suncor

Status: Year 3 of 4

PROJECT SUMMARY

Canadian Natural contracted WorelyParsons in 2008 to run a Waterborne Geophysical Investigation and was made aware of naturally occurring saline spring water flowing into the Athabasca River near Horizon Oil Sands. Canadian Natural decided to monitor annual fluctuations in the naturally occurring saline springs that seep into the bottom of the Athabasca River by use of Marine Resistivity Surveys beginning in 2015. DMT Geosciences was contracted to acquire the survey data and process the data for interpretation. Minor annual changes have been identified in the data but the locations of these natural saline springs have remained consistent.

PROGRESS AND ACHIEVEMENTS

Since 2008, Canadian Natural has completed six Marine Resistivity Surveys and plans to continue running surveys in tandem with Suncor - Fort Hills to enhance our understanding of the changes in resistivity seen as operations continue. By continuing to monitor the fluctuations, Canadian Natural has been able to establish a baseline resistivity created by the natural flow of saline groundwater into the Athabasca River. The data collected will be integrated into future monitoring.

LESSONS LEARNED

Technical lessons learned are that resistivity responses are relatively consistent year over year.

Demonstrated differences are likely due to operational challenges acquiring survey data such as annual changes in river bathymetry and acquisition noise. River bathymetry forces survey lines to vary annually due to changes in sand bar location. Every effort is made to mimic previous survey lines when possible. Acquisition noise has been minimized by only collecting data in a downstream direction as travelling upstream applies boat turbulence to the receivers.

Future uses of the data could include adding this dataset to a model estimating volumes of natural saline water discharging into the Athabasca River.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications

RESEARCH TEAM AND COLLABORATORS

Principal Investigator: Canadian Natural Resources Ltd.

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Jane Dawson	DMT Geosciences	Geophysicist		
Doug McConnell	DMT Geosciences	Geophysicist		
Ross Penner	DMT Geosciences	Geophysicist		
Rob Perrin	DMT Geosciences	Geophysicist		

OIL SANDS PROCESS-AFFECTED WATER CHEMISTRY AND TOXICITY

Development of a Passive Sampler-Based Framework for Derivation of Water Quality Benchmarks for Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WJ0045, WJ0109, WJ0147

Research Provider: ExxonMobil Biomedical Sciences, Inc.

Industry Champion: Imperial

Industry Collaborators: CNRL, Teck, Suncor, Syncrude

Status: Year 5 of Ongoing

PROJECT SUMMARY

Acid extractable organics (AEOs), also referred to as naphthenic acids, are a principal class of compounds in oil sands process-affected water (OSPW) that can pose aquatic toxicity concerns if the OSPW is untreated. AEOs represent a complex mixture that varies in composition in different OSPWs, altering aquatic toxicity and complicating the development of water quality criteria. Defendable numerical water quality criteria for AEOs are lacking, which limits the ability to consistently evaluate the effectiveness of OSPW treatment options and the potential suitability of treated OSPW for eventual discharge to the environment. A commonly accepted approach for determining toxicity of complex mixtures is Whole Effluent Toxicity (WET) testing using standard species such as the rainbow trout. However, these kinds of toxicity tests often take close to a week from sampling to results which is simply too long as a routine toxicity test. In order to ensure long-term, responsible management of OSPW, industry needs to develop water quality criteria for AEOs, ideally using a test that is near real-time.

The first objective of this research was to use the Target Lipid Model (TLM), a surrogate measurement of bioavailable AEOs, to characterize the relative sensitivity and general modes of toxic action of organic acids. The resulting species sensitivity distribution (SSD) was then compared to the SSD observed for aquatic organisms exposed to other polar and nonpolar organic chemicals. The second objective was to validate the Biomimetic Extraction (BE) method for application to organic acids commonly found in OSPW. BE measurements were used to evaluate concentration responses of aquatic species to a variety of test substances, including single chemicals and extracts of OSPW (and fractions thereof). This data was used to develop an SSD based on BE, which was then compared to SSDs developed for BE derived previously using petroleum substances, and to critical target lipid body burdens (CTLBBs) predicted by the TLM. The third objective was to identify recommendations for developing BE-based water quality benchmarks for OSPW. Presently, ExxonMobil Biomedical Sciences, Inc. (EMBSI) is the principle practitioner of the BE-SPME (Solid-Phase-MicroExtraction) method (Parkerton et al. 2000, Redman et al. 2018a; 2018b). The final objective of the research program was to establish BE-SPME analytical capability across a range of commercial, academic and government laboratories currently performing testing and research in support of Canadian oil sands operations via a laboratory round robin testing.

PROGRESS AND ACHIEVEMENTS

One outcome of this research was the development of passive sampler methods to support the derivation of water quality benchmarks for organic constituents in OSPW. Preliminary thresholds based on BE were developed for several invertebrates and fishes exposed to organics extracted from OSPW (Redman et al., 2018). The data in Redman et al. (2018b) and additional data collected since form the basis of a SSD (Fig. 1) that could potentially support the derivation of water quality benchmarks by characterizing the range of acute and chronic thresholds of organic substances related to OSPW. Nine laboratories are presently participating in a round robin to establish BE-SPME analytical capability. Results reported for the analysis of a single OSPW in the preliminary, capability transfer phase of the program are presented in Figure 2. The participating laboratories are currently analyzing a more extensive set of OSPW samples as part of the second phase of the program.

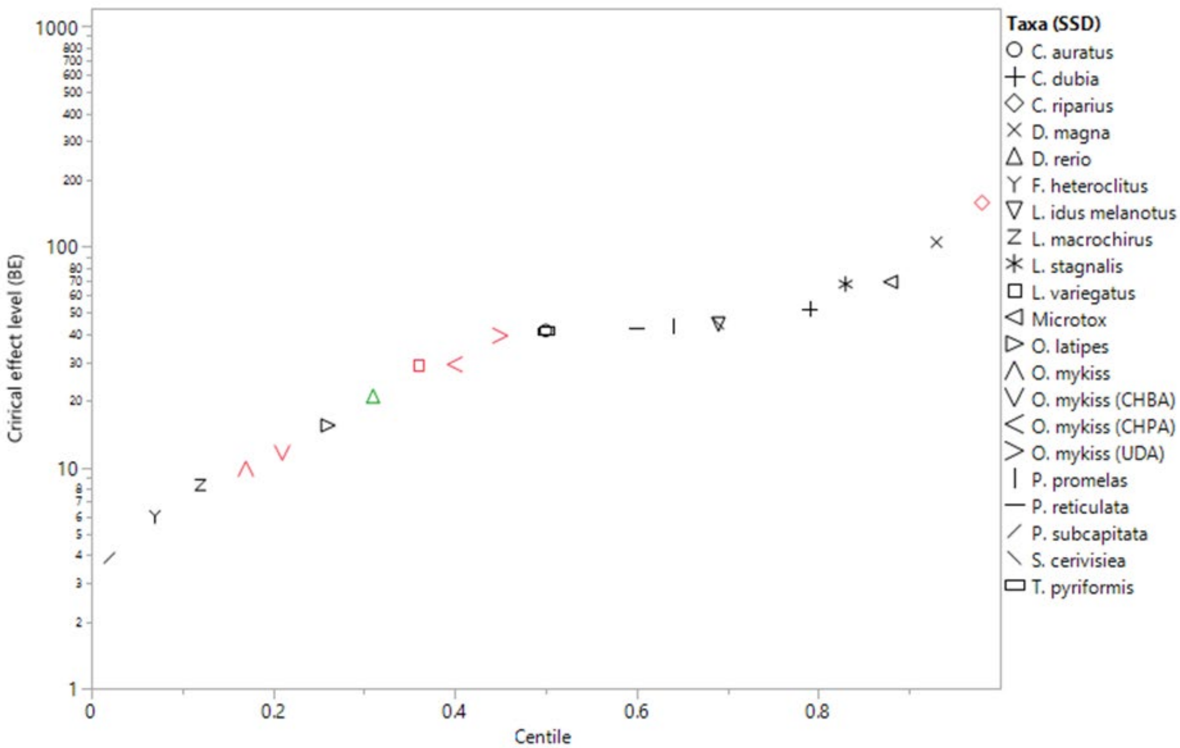

Fig. 1. Species sensitivity distribution of median effect level endpoints (combination of data from Redman et al. (2018b) and new data collected since). Redman data in black, new data in red, updated data in green.

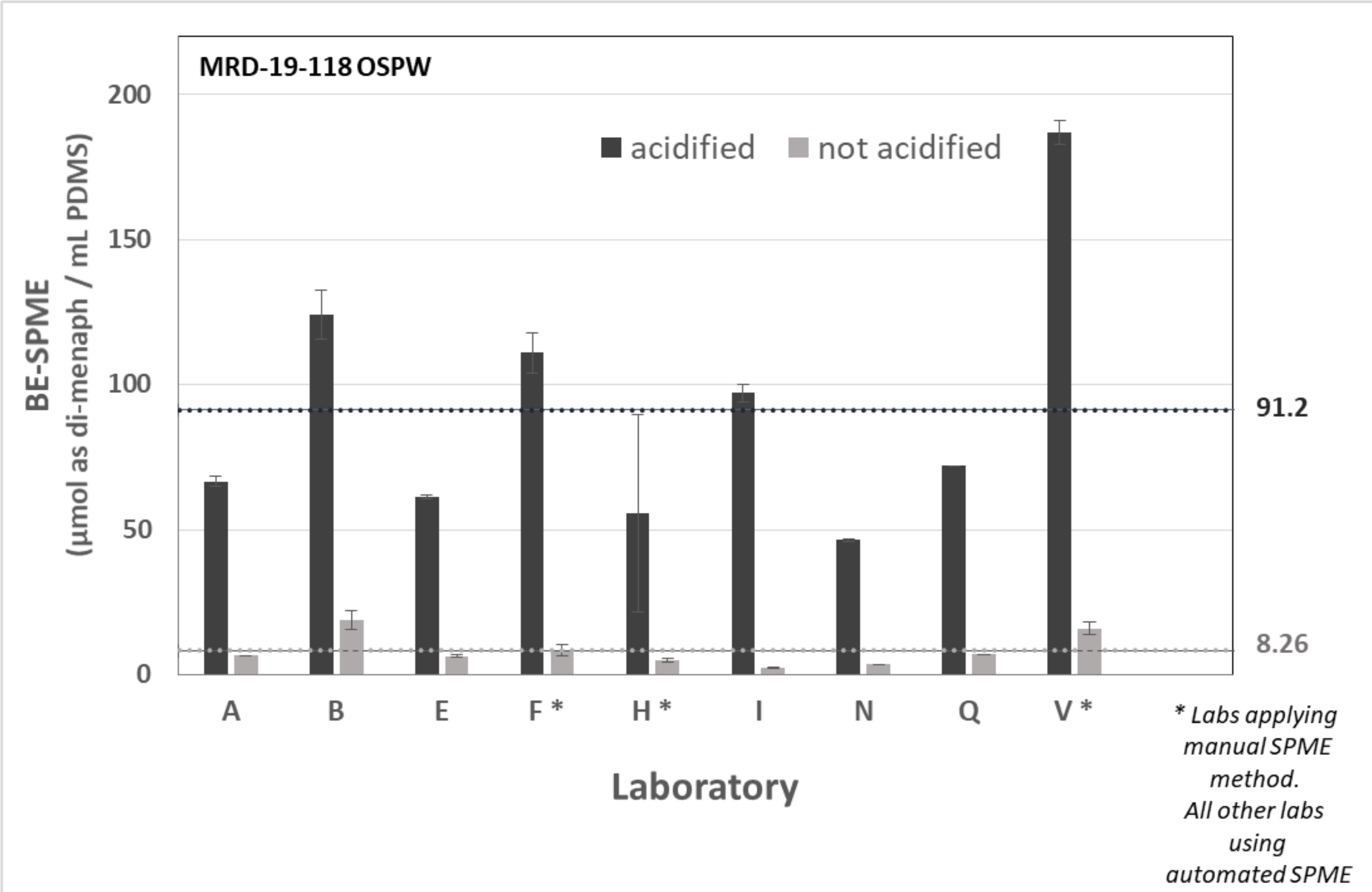

Fig. 2. BE-SPME results of analysis of a single OSPW sample across participating labs in the preliminary phase of the round robin

LESSONS LEARNED

Data collected during multiple phases of this research project supports BE-SPME as a valuable tool when working with complex petroleum mixtures, such as OSPWs. BE-SPME-derived species sensitivity distributions demonstrate the ability to use BE-SPME as an exposure metric with the ability to predict toxicity. The BE method could serve as a rapid, cost effective and convenient analytical screening tool for estimating the toxicity of raw and treated OSPW, relative to performing whole effluent testing with various species which can require several days or weeks to complete. Furthermore, the BE method can be applied to treated OSPW at ambient pH, and under acidified conditions, to characterize relative contributions from hydrocarbons (e.g., bitumen, Polycyclic aromatic hydrocarbons (PAH), and residual solvent) and organic acids. The successful technology transfer of the BE-SPME methodology to laboratories supporting Canadian oil sands operations will encourage the adoption of the method and allow collection of high-quality data to inform the management of water.

PRESENTATIONS AND PUBLICATIONS

Presentations

Smith, A.J., B.M. Hedgpeth, D.J. Letinski, H. Bailey, L. Clothier, A. Bekele, T.F. Parkerton, A.D. Redman. BE-SPME as an analytical tool for predicting toxicity in OSPW. SETAC North America 40th Annual Meeting, Toronto, Ontario, November 3-7, 2019.

Letinski, D.J., A.J. Smith, C.W. Davis, A. Bekele, A.D. Redman, B. Hedgpeth. 2019. Development and Application of a Passive Sampling Method to support OSPW Research. COSIA Mine Water Release Workshop, Edmonton, Alberta, Oct 22-23, 2019.

Smith, A.J., B.M. Hedgpeth, D.J. Letinski, H. Bailey, L. Clothier, A. Bekele, T.F. Parkerton, A.D. Redman. BE-SPME as an analytical tool for predicting toxicity in OSPW and appropriate levels for discharge. COSIA Innovation Summit 2019, Calgary, Alberta, June 3-4, 2019.

Publications

Redman AD, Parkerton TF, Butler JD, Letinski DJ, Frank RA, Hewitt LM, Bartlett AJ, Gillis PL, Marentette JR, Parrott JL, Hughes SA, Guest R, Bekele A, Zhang K, Morandi G, Wiseman S, Giesy JP. 2018b. Application of the Target Lipid Model and Passive Samplers to Characterize the Toxicity of Bioavailable Organics in Oil Sands Process-Affected Water. Environmental Science & Technology 52 (14):8039-8049. doi:10.1021/acs.est.8b00614

RESEARCH TEAM AND COLLABORATORS

Institution: ExxonMobil Biomedical Sciences, Inc.

Principal Investigators: Daniel Letinski; Dr. Abraham Smith; Dr. Aaron Redman

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Daniel Letinski	ExxonMobil Biomedical Sciences, Inc.	Distinguished Scientific Associate		
Dr. Abraham Smith	ExxonMobil Biomedical Sciences, Inc.	Ecotoxicology Laboratory Coordinator		
Dr. Aaron Redman	ExxonMobil Biomedical Sciences, Inc.	Sr. Environmental Scientist		

Development of Microbial Fuel Cell Biosensor for Detection of Naphthenic Acids

COSIA Project Number: WJ0116

Research Provider: University of Alberta

Industry Champion: Imperial

Industry Collaborators: None

Status: Year 3 of 4

PROJECT SUMMARY

In processed water that is generated from oil sands operations, naphthenic acids (NAs) are identified as one of the primary sources of acute toxicity. Therefore, the monitoring of NAs in aqueous environmental matrices is crucial for oil sands and crude oil production industries. Commonly used analytical methods for NAs include Fourier transform infrared spectroscopy, gas chromatography-mass spectrometry, and high-performance liquid chromatography. However, these methods are off-line; meaning that these samples must be sent to an analytical lab. In addition, these methods are time-consuming, resource-intensive, and require skilled operations due to the involvement of sophisticated analytical instruments. To help address these challenges, a fast, low-cost analytical method for on-site quantification of NAs is being developed.

The objective of this research is to develop a microbial electrochemical biosensor for in field detection and quantification of NAs in the oil sands process affected water (OSPW) samples. In recent years, microbial electrochemical biosensors have been extensively studied for monitoring microbial activities, organics, and other contaminants in various wastewater treatment systems. Briefly, these sensors use electroactive biofilms to produce an electrical signal in response to the presence of a target contaminant; the electrical signal can be correlated to the concentration of the contaminant. We envision that the development of a microbial electrochemical biosensor can provide a cost-effective way for on-site and rapid measurement of NAs in OSPW. Furthermore, biosensors can be deployed in engineered remediation systems (e.g., constructed treatment wetlands, end pit lakes) for in field monitoring of NAs. The specific objectives of this project include:

- Understanding interactions among various NAs and environmental parameters.
- Examine the long-term performance of the biosensor with a real OSPW sample.
- Development of miniaturized biosensor design for field application.

PROGRESS AND ACHIEVEMENTS

In Year-1, we demonstrated the proof-of-concept of microbial electrochemical biosensor for the detection of model NA compound (cyclohexane carboxylic acid, CHA) in the water sample. We also characterized the bacterial communities in order to gain insights into the biosensing mechanism. Proof-of-concept tests were performed with a bench-scale biosensor consisting of an anode, a cathode, and a reference electrode (Fig. 1a). In Year-2 and 3, we optimized a charging-discharging based calibration method to further improve analytical performance in terms of precision, time-efficiency, sensitivity, and reproducibility (Fig. 1b). Then, we explored the effects of salinity levels and water temperature on the sensitivity of the biosensor.

Our proof-of-concept test results demonstrated an increase in CHA concentration in water samples and linearly increased the electrical signal from the biosensor. Initially, the calibration of the biosensor was performed based on the current generation at different CHA concentrations under continuous closed-circuit operation. However, measurements of steady-state electrical signals require a longer time (usually 8 hours for CHA). For a practical field-scale application, a biosensor should be able to provide a quick estimation of NA concentrations. Moreover, the current generation from the continuous closed-circuit operation was very low (microampere range), while larger output currents are required for better sensitivity and higher precision of analysis. Due to the capacitive nature of anode biofilms, microbial electrochemical cells can produce substantially higher output currents under consecutive open and closed-circuit alternation (i.e., charging-discharging mode). During an open-circuit operation, the electroactive microbes oxidize organic matters and accumulate captured electrons in the anode biofilms. When the system switched to a closed-circuit mode, the accumulated electrons from the anode biofilms are rapidly discharged, and transient peak currents are produced. Hence, we further investigated whether such an approach could be used to enhance the sensitivity of biosensor for CHA concentrations detection. For demonstration tests, selected charging (open-circuit) and discharging (close-circuit) times were 5 minutes and 1 minute, respectively. Then, a calibration curve was established between the transient peak currents and CHA concentrations, which demonstrated perfect linearity between CHA concentrations and the peak currents (R^2=0.96). Moreover, electrical signals were much higher than that typically observed during continuous monitoring of electrical signals (microampere vs. milliampere range), which ultimately led to the high precision calibration of biosensor compared to the calibration performed with the steady-state electrical signal data. Then, we investigated the effects of different salinity levels and temperatures on the sensitivity of biosensor during CHA measurement. Our results indicated that the biosensor would be sensitive to salinity levels and temperature changes; however, once calibrated, it can be used for measurement of NA concentrations.

LESSONS LEARNED

Our results demonstrated that the utilization of a charging-discharging operation could enable fast and precise calibration methods for the measurement of NA concentrations with the microbial electrochemical biosensor. Moreover, the results highlighted that changes in salinity levels and water temperature could potentially interfere with the biosensor response. For further development, understanding the interference of other parameters (e.g., polycyclic aromatic hydrocarbons), detection of NAs in real OSPW, and long-term stability of biosensor will be explored in future research.

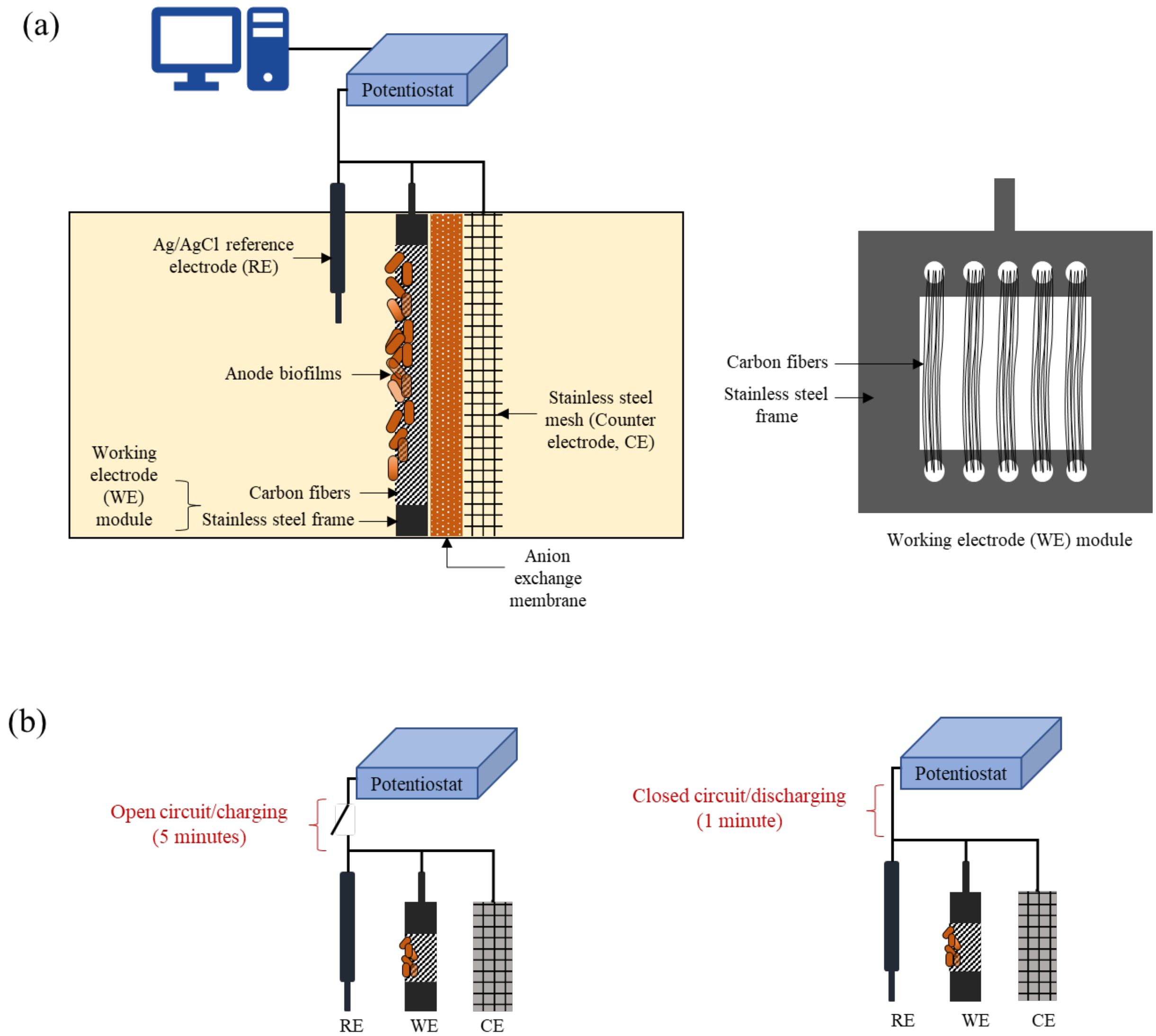

Fig. 1. Schematic diagram showing (a) configuration of microbial electrochemical biosensor, and (b) charging-discharging operation for calibration of microbial electrochemical biosensor.

PRESENTATIONS AND PUBLICATIONS

Presentations

Chung, T.; Zakaria, B.S.; Dhar, B.R. (2019). Development of microbial electrochemical cell as a rapid biosensor for the detection of naphthenic acids,11th Western Canadian Symposium on Water Quality Research, May 10, Edmonton, AB, Canada.

Chung, T.; Zakaria, B.S.; Dhar, B.R. (2019). Calibration of bio-electrochemical naphthenic acids sensor using electrical response from charging-discharging cycles, Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit, June 7-8, Calgary, Alberta.

Publications

Chung, T.H.; Meshref, M.; Dhar, B.R. (2020). Microbial electrochemical biosensor for rapid detection of a naphthenic acid model compound in water samples, manuscript submitted (under review).

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Dr. Bipro Dhar

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Dr. Mohamed Meshref	University of Alberta	Postdoc		
Tae Chung	University of Alberta	M.Sc. Student	2018	2020
Basem Zakaria	University of Alberta	Ph.D. Student	2017	2021

Research Collaborators:

Dr. Alberto dos Santos Pereira, InnoTech Alberta Inc.

Dr. Karen Budwill, InnoTech Alberta Inc.

PIT LAKES

Mesocosm Research in Support of Pit Lakes

COSIA Project Number: WJ0013

Research Provider: InnoTech Alberta

Industry Champion: Suncor

Industry Collaborators: CNRL, Imperial, Syncrude, Teck

Status: Year 7 of 8

PROJECT SUMMARY

In the spring of 2017, a study was undertaken to investigate the chemical, biological and physical effects of oil sands process water (OSPW) and densified fluid fine tails (dFFT) on aquatic ecosystems to support the development of pit lake (PL) technology.

This research was the first of a series of mesocosm-based studies investigating the design and performance of PL scenarios. Mesocosms are simplified aquatic ecosystems and as research tools, they afford more realism than bench-scale experimentation, while providing more control and replication than large field pilots. This series of studies is an important progression between laboratory testing and full-scale implementation to de-risk factors unforeseeable at the laboratory scale.

This study utilized thirty 15,000 L mesocosms, simplified and replicated aquatic ecosystems, which had been designed and constructed by InnoTech Alberta in 2016. The study design was a partial factorial with controls and treatment groups as shown in Table 1.

Table 1: 2017/18 experimental groups

Experimental Group	OSPW content	Sediment	Plants	Number of mesocosms
CTRL1	0%	Unconditioned soil	Present	6
CTRL2	0%	None	Present	6
CTRL3	0%	None	Absent	3
TRMT1	0%	dFFT	Present	3
TRMT2	25%	dFFT	Present	3
TRMT3	50%	dFFT	Present	3
TRMT4	100%	dFFT	Present	3
TRMT5	50%	None	Present	3

The purpose of the study was to examine the effects of the materials on the simplified ecosystems through time, with no additions after the initial material installation. A broad range of chemical, physical and ecological parameters were measured. Hypothesis for the study were:

- Dilution of OSPW is not required to decrease the toxicity of OSPW to less than chronic levels through natural processes
- The concentration of dissolved organics, the main toxic constituents of OSPW, will decrease over time through natural processes
- The dFTT substrate would not impede the establishment of biota

The mesocosms were prepared in accordance with Table 1 in late May of 2017, followed by four months of data and sample collection. The project was overwintered in place and monitoring/sampling continued in 2018 following the 2017 program design, with some additional parameters (chlorophyll, phytoplankton coverage and acute *Daphnia* toxicity) and slight modifications to the sampling schedule. The mesocosms were decommissioned in October 2018 so a new study could be undertaken in 2019/2020.

PROGRESS AND ACHIEVEMENTS

In 2017, the presence of OSPW in the mesocosms was associated with increases in conductivity, turbidity, and various elements and compounds while concurrent decreases were observed in dissolved oxygen, water temperature at depth, and calcium. For the most part, the physicochemical effects of OSPW decreased over time. The presence of OSPW reduced the richness of the macroinvertebrate community while reducing the diversity (Shannon-Wiener) of the zooplankton community. Submerged vegetation was also negatively impacted by OSPW; *C. demersum* did not survive in mesocosms containing 50% or 100% OSPW by volume. Colonization of the bottom of the mesocosms with adventitious vegetation, while common in the control mesocosms, did not occur in mesocosms containing OSPW or dFFT. Conversely, the presence of OSPW and dFFT had a small stimulatory effect on the growth of emergent vegetation (*T. latifolia* and *C. aquatilis*). The acute toxicity of mesocosm water, which contained various dilutions of OSPW according to the experimental group, was assessed using rainbow trout 96-hour LC50 and Microtox® assays. While both assays indicated fairly low levels of toxicity at the beginning of the study, trout mortality decreased over time while Microtox® toxicity remained unchanged. The effects of dFFT were similar to those attributed to OSPW, but often of a lesser magnitude. Many of these effects were mediated by the slow efflux of solutes from the dFFT layer into the overlying water. In contrast, polycyclic aromatic hydrocarbons (PAHs) were strongly associated with the presence of dFFT but not OSPW despite both materials originating from the same source. The surface-water concentration of these compounds decreased over time.

In 2018 a chemocline formed in concert with thaw, however, this dissipated through the season, with the severity of the chemocline and time to dissipate proportionate to the salinity of the water in the mesocosm. In 2018, effects of OSPW were similar to those in 2017, with some notable exceptions. Field measurements indicated that turbidity associated with OSPW had decreased to levels that were not significantly different from controls, and dissolved oxygen and temperature differences observed in 2017 to be associated with OSPW were no longer present. Hydrocarbons (BTEX, PAHs) associated with OSPW in 2018 were at or below detection limits (not significantly different from controls). Naphthenic acid concentrations remained elevated in the presence of OSPW, however, the total concentrations were significantly lower in 2018 than in 2017. The stimulant effect on emergent plant (*A. americanus, C. aquatilis, C. atherodes* and *T. latifolia*) growth was no longer evident in 2018, and while *C. demersum* growth was slowed, OSPW was not associated with mortality. Effects of OSPW on macroinvertebrate and zooplankton communities observed in 2017 were no longer present in 2018. OSPW did not register with any of the acute toxicity tests (Rainbow Trout, *Daphnia* and Microtox®) in 2018. Lastly, floating metaphyton (algal mats) that were observed in controls were less expansive in the presence of OSPW, though not inhibited.

The effects of dFFT were similar between years, with the same attenuation of effects observed with OSPW observed in the presence of dFFT. The only notable difference is that dFFT appeared to inhibit metaphyton floating mat (algae coverage) from developing, wherever present, regardless of OSPW concentration. Also, while naphthenic acid concentrations decreased in OSPW, the concentrations observed in the presence of dFFT, while comparatively low, did not significantly change.

The results from the 2017/18 Aquatic Mesocosm Study demonstrated beyond the laboratory scale *a posteriori* that some of the ecological effects and chemical constituents associated with OSPW and dFFT attenuate with time. Acute toxicity values of LC50 and EC20 (in Rainbow trout, *Daphnia* and MicroTox) associated with raw materials registered below detection limits over the course of the study. Macroinvertebrate and zooplankton ecological community indices that were negatively affected by OSPW and dFFT presence recovered to comparable levels observed in controls within one year. Naphthenic acid concentrations were elevated in the presence of OSPW, however, decreases of up to 50% were observed without any intervention.

All materials were removed from the mesocosms in the Fall of 2018 and cleaned. A new study incorporating lessons of the 2017/18 study was commissioned in the spring of 2019.

LESSONS LEARNED

This work demonstrates beyond the laboratory scale what ecological effects are short term (attenuate in a short period of time) and which are long-term (may need to be addressed before full scale implementation). The pairing of the ecological monitoring with chemical analysis allows research to be focused on the chemical constituents that remain in solution and may be associated with ecological effects; focused research enables more efficient use of time and resources.

PRESENTATIONS AND PUBLICATIONS

Conference Presentations/Posters

Melnichuk, R. Using aquatic mesocosms to investigate biological, chemical and ecological community responses to oil sands process-affected water and tailings to inform pit-lake design. COSIA Mine Water Release Workshop. Edmonton, AB.

Melnichuk, R., J. Davies, M. Hiltz, B. Eaton and C. Aumann. Using aquatic mesocosms to investigate biological, chemical and ecological community responses to oil sands process-affected water and tailings to inform pit-lake design: a 2-year study. Oil Sands Innovation Summit (OSIS). Calgary, AB.

Melnichuk, R. Using aquatic mesocosms to inform pit lake design: Toxicology study. BML Research and Monitoring Technical Update. Edmonton, AB.

Melnichuk, R. Using aquatic mesocosms to inform pit lake design: Chemical responses to oil sands by-products. BML Research and Monitoring Technical Update. Edmonton, AB.

Melnichuk, R., J. Davies, M. Hiltz, B. Eaton and C. Aumann. Using aquatic mesocosms to inform pit lake design: Ecological responses to oil-sands by-products. COSIA Pit Lake Workshop. Edmonton, AB.

Melnichuk, R., J. Davies, C. Aumann, M. Hiltz and B. Eaton. Using aquatic mesocosms to examine potential ecological responses to oil sands water and tailings to inform pit lake adaptation in Alberta's oil sands. Oil Sands Innovation Summit (OSIS). Calgary, AB.

RESEARCH TEAM AND COLLABORATORS

Institution: InnoTech Alberta

Principal Investigator: Ryan Melnichuk

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Ryan Melnichuk	InnoTech Alberta	PhD- Research Scientist		
Jim Davies	InnoTech Alberta	MSc, DVM-Researcher		
Zhongzhi Chen	InnoTech Alberta	PhD- Researcher		
Craig Aumann	InnoTech Alberta	PhD, MSc-Senior Researcher		

Lake Miwasin – Demonstration Pit Lake

COSIA Project Number: WJ0091

Research Provider: Hatfield Consultants, AECOM, University of Alberta, University of Saskatchewan, Athabasca University and University of Waterloo

Industry Champion: Suncor

Industry Collaborators: Canadian Natural, Syncrude, Alberta Innovates

Status: Year 2 of 6

PROJECT SUMMARY

Lake Miwasin is a scaled down pilot demonstration of Suncor's commercial scale pit lake at Dedicated Disposal Area 3 (DDA3, the future Upper Pit Lake (UPL)), which uses the Permanent Aquatic Storage Structure (PASS) process, an inline tailings treatment process consisting of coagulant addition followed by flocculant addition. The PASS process enables:

- more rapid reclamation of the treated fluid tailings (FT) into a freshwater lake environment;
- integration of the lake into the surrounding watershed; and
- mitigation of potential adverse environmental effects.

The goal of the Lake Miwasin pilot study is to monitor and evaluate if the PASS process, when combined with the watershed design for the pilot pit lake, will accelerate the reclamation of a DDA to a self-sustaining boreal lake ecosystem. Specific objectives of the Research & Monitoring (R&M) Plan are to: (1) test assumptions in the pit lake design and; (2) address critical gaps in the pit lake design.

The Lake Miwasin pilot project is expected to have four operational and reclamation phases:

- Phase 1: Dewatering and treatment of FT (Q3 2017 to Q3 2018)
- Phase 2: Placement of the aquatic cover (Q3 2018)
- Phase 3: Controlled water flow through and return to closed-circuit water system on site (~2019 to ~2021)
- Phase 4: Water release under natural flow (location and timing to be determined)

The Lake Miwasin project completed Phases 1 and 2 operations at the end of 2018 and is currently in Phase 3. Research and monitoring activities are planned to take place over a 15-year period (2018-2033) in order to meet the goal and objectives.

Lake Miwasin R&M Program

The Lake Miwasin R&M Plan adopts an Effectiveness Monitoring (EM) design within an adaptive management framework (CEMA 2013). EM is the process of identifying and monitoring key indicators of ecosystem response to evaluate the success of a reclamation initiative or goal. The EM framework is structured on a Goal – Objective – Assumption – Question – Indicator hierarchy. Following the EM design, measurable and obtainable assumptions were selected on the basis that they are fundamental to achieving the Lake Miwasin Project goal. Key test questions, hypotheses, and indicators were also identified.

The R&M plan identifies three priority monitoring areas to monitor and assess the performance of the Lake Miwasin project:

- treated tailings deposit;
- aquatic cover and watershed; and
- biodiversity.

In addition, research questions specific to the Lake Miwasin project are also being investigated to close knowledge gaps in the design. These research questions are grouped into five research priority areas:

- deposit characteristics;
- water quality;
- closure modelling;
- landform design; and
- performance trajectories.

PROGRESS AND ACHIEVEMENTS

The first 5-year Lake Miwasin research and monitoring program was initiated in 2019 with the field monitoring activities commencing in March 2019. The aerial deposition monitoring started in October 2019 as part of the air monitoring program, which also includes air emission monitoring.

Detailed data analyses are currently ongoing and will be available in the next progress report. Preliminary results of the 2019 Lake Miwasin monitoring program are presented below for each discipline-specific component.

- Treated tailings deposit:
  - The PASS treated tailings deposited at Lake Miwasin has settled ~3m from October 2017 to October 2019 which has resulted in a reduction of tailings volume by approximately 50%.
  - The average clay water ratio (CWR) of the deposit is approximately 0.5.
- Water Budget
  - Precipitation is the major water balance input, while evapotranspiration (ET) is likely the largest water balance output. Ongoing monitoring will close the water budget for Lake Miwasin and provide quantitative estimates of water flows through the Lake Miwasin landscape.
- Physical Limnology
  - The lake exhibited chemical and thermal stratification from the beginning of monitoring in May 2019 until a wind-induced mixing event in mid-August 2019, after which stratification partially redeveloped until the end of September, when the water column mixed and remained mixed until freeze-up.
- Groundwater
  - No groundwater seepage to the underlying Wood Channel Sand Aquifer has been measured.
- Water Quality
  - Low total suspended solids (< 13 mg/L, with a median of 2.1 mg/L) has been observed throughout the year, indicating high light penetration which is fundamental to lake development.
  - The majority of water quality indicators were below environmental quality guidelines for the protection of aquatic life.
  - Some petroleum-associated compounds were measurable in Lake Miwasin, although most were below analytical detection limits. No visible oil sheen has been observed at Lake Miwasin.
  - Trophic status based on concentrations of major nutrients and chlorophyll indicated an "oligo-mesotrophic" level of aquatic productivity.
  - Dissolved oxygen remained high in the upper water column (up to 3 m deep) during the open water season. While the lake was stratified in spring/summer, dissolved oxygen was near zero in bottom waters (< 0.5m above the mudline).

- No acute or sublethal toxicity to phytoplankton, invertebrates, or fish was identified in water samples collected from Lake Miwasin.
- Biodiversity
    - Lake Miwasin has been colonized by a mix of phytoplankton and zooplankton species common to regional lakes, with the phytoplankton community including several taxa while the zooplankton community was dominated by cladocerans.
    - The colonization of the sediments by invertebrates is still in the early stages, with very few invertebrates observed in sediment samples. Sediment toxicity assays indicated sediment toxicity to benthic invertebrates.
    - Amphibian surveys observed wood frogs, boreal chorus frogs, and Canadian toads using the Lake Miwasin littoral environment during breeding season.

LESSONS LEARNED

Key lessons learned based on the baseline testing and Year 1 monitoring program include:

- Lake Miwasin has been performing as expected both prior to and after the aquatic cover placement (completed in Oct 2018).
- Tailings and water quality conditions generally met performance expectations.
- Lake Miwasin has been colonized with native boreal aquatic organisms, including insects, plankton, and amphibians. Natural processes such as primary production, nutrient and carbon cycling, and community succession are established in the lake, and are supporting the establishment of the aquatic ecosystem.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Martin Davies	Hatfield Consultants	Sr. Vice-President		
Dr. Benjamin Beall	Hatfield Consultants	Aquatics Manager		
Dr. Ted Lewis	Hatfield Consultants	Sr. Hydrologist		
Dr. Ekram Azim	Hatfield Consultants	Sr. Environmental Scientist		
Mike McBride	Hatfield Consultants	Hydrogeologist		
Dr. Raïssa Philibert	Hatfield Consultants	Environmental Information Systems Specialist		
Hannah Koslowsky	Hatfield Consultants	Environmental Specialist		
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Mark Modrak	AECOM	Senior Scientist		
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Dr. James Stafford	University of Alberta	Professor		
Dr. Bill Shotyk	University of Alberta	Professor		
Dr. Chad Cuss	University of Alberta	Research Associate		
Dr. Karsten Liber	University of Saskatchewan	Professor		
Dr. Scott Ketcheson	Athabasca University	Professor		
Dr. Rich Petrone	University of Waterloo	Professor		

Base Mine Lake Monitoring and Research Program

COSIA Project Number: WJ0121

Research Provider: Multiple Researchers and Institutions

Industry Champion: Syncrude

Industry Collaborators: Canadian Natural, Imperial, Suncor

Status: Multi-year project, ongoing

PROJECT SUMMARY

BML is the first, and currently the only full-scale commercial demonstration of the end pit lake technology in the oil sands industry. An oil sands end pit lake (EPL) is an area where overburden and oil sand has been removed and is then filled with fluids prior to closure. An EPL contains water (from the process of oil sands extraction or freshwater or both) and may or may not contain treated or untreated fluid tailings (FT), or other solids (for example, coarse tailings sand, or overburden).

BML is located in the former West In-Pit (WIP) of the Syncrude Mildred Lake (Base Lease) operation. It consists of a mined-out oil sands pit filled with untreated fluid fine tailings (FFT). Fluid fine tailings are comprised of silt, clay, process-affected water and residual bitumen. The FFT is physically sequestered below a combination of oil sands process-affected water (OSPW) and fresh water. This pit lake configuration is often referred to as Water Capped Tailings Technology (WCTT). Based on previous research and modelling, the prediction for WCTT is that with time, EPL water quality improves and the fluid tailings (or other tailings) will remain sequestered below the water cap.

Freshwater is pumped into Base Mine Lake from the Beaver Creek Reservoir (BCR) and as required; water is pumped out of BML to the tailings recycle water system (RCW) where it is utilized in the bitumen extraction process. This flow through process dilutes the BML water cap over time and will be in place until a more substantial upstream surface watershed is reclaimed and connected to BML, and outflow is established into the Athabasca River. As the tailings continue to dewater over time, the lake water will get deeper.

Placement of fluid tailings began in 1995, was completed in late 2012, and BML was commissioned as of 31 December 2012. No tailings solids were added after this time. During 2013, fresh water and OSPW was added to the existing OSPW upper layer to attain the final water elevation.

A key purpose of the BML Monitoring and Research Program (MRP) is to support an adaptive management framework. The BML MRP is designed to assess lake performance against key performance indicators and evaluate the need for management interventions. The initial focus of the research program is to support the demonstration of water-capped tailings technology, and to provide a body of scientific evidence that demonstrates that BML is on a trajectory to become integrated into the reclaimed landscape. The outcomes from the BML MRP can be used to inform the design and management of future pit lakes, including those that may contain tailings materials, such as treated or untreated fluid tailings. At the same time, the program establishes a baseline of biophysical data to assess the changes in BML through time, and the state of the lake at certification, including water quality and other lake processes. The monitoring program is designed to track trends in the lake both seasonally and annually and measure these trends against some key performance metrics as outlined above. The research program focuses on key scientific questions designed to elucidate the mechanisms and processes that govern the current state of BML, and explain changes detected by the monitoring program. In other words, the monitoring program tracks the trends in the lake through time, and the research program investigates why those changes are occurring.

The specific objective of the BML Monitoring Program is to provide information to support the validation of WCTT as a viable tailing's management and reclamation option. In the early stages, the BML Monitoring Program will demonstrate that fluid fine tailing are sequestered and that the water quality in the lake is improving. The monitoring program is designed to do this by tracking the physical, chemical and biological changes in BML. The program captures these changes both temporally and spatially, and eventually in the context of regional climate cycles. The monitoring program supports regulatory compliance, but also informs adaptive management of BML.
The BML Research Program uses a multi-university, multi- and inter- disciplinary approach that focuses on the analysis and interpretation of monitoring data, hypothesis driven research activities, and integration and collaboration among and between research programs. Research results are integrated with monitoring results on an ongoing basis, with the ultimate goal of identification and quantification of the processes and properties in BML that are responsible for the trends observed in the Monitoring Program. The various components comprising the BML Monitoring and Research Program are closely linked.

The current focus of the Research Program is to support the demonstration of the Water Capped Tailings Technology (WCTT). The program also provides supporting information about key processes fundamental to the progression of BML towards a functional component of the closure landscape. The current research programs were focused on key parameters influencing early BML development.
The program has two overarching themes. The first theme is validating the WCTT. Several research programs will determine the potential fluxes from the FFT to the water column, including chemical, geochemical, mineral, gases and heat. Physical, biological and chemical mechanisms are being investigated.

The second key (and related) theme relates to the oxygen dynamics in the lake. The programs focus on understanding the oxygen balance and process of oxygen consumption (e.g. methanotrophy) and oxygen production (photosynthesis). The Research Program is summarized in the below table:

	Objectives	**Summary of key findings so far**
Physical limnology	To understand the circulation of BML and its potential for meromixis.	• The lake thermally stratifies during summer and turns over in the fall. • Turbidity decreases during summer stratification and increases at fall turnover. • Water becomes nearly anoxic under ice during the winter. • The surface hydrocarbon sheen may impact waves. • Meromixis is unlikely and not expected
Mass loading from FT into the water column	To identify how heat and chemicals are transferred between the tailings and water, how these change over time, and how the movement of these chemicals affect the cap water chemistry.	• Salts move from the FT porewater to the BML water cap through porewater release during FT settling. • Microbial processes like sulfate reduction can change the porewater chemistry.
Chemical flux across tailings-cap water interface	To understand how microbial activity and gas production affect movement of chemicals from the FT to cap water, to quantify the rate of chemical fluxes, and use these values to model pit lake development.	• In the laboratory, microbially-produced methane bubbles move out of the FT into the water cap, causing dissolved salts to move from the FT porewater into the cap water.

		• Microbial activity also changes the porewater chemistry, and causes faster FT settling and more porewater released to the cap water.
Cause and treatment of turbidity	To use laboratory columns to study the effect of gas production on water cap turbidity, and test various additives to reduce turbidity.	• Bubbling can resuspend the fine particles in FT and increase turbidity in laboratory settings. • Alum is more effective than $CaCl_2$ in reducing turbidity.
Oxygen consumption rates in the water cap	To determine the changes in oxygen concentrations in the BML water cap, the rate of oxygen consumption, and the primary biogeochemical processes which consume oxygen, and to identify long-term trends in the dissolved oxygen concentrations in BML.	• The BML water cap is thermally stratified and remains oxic down to the FT-water interface, which means oxygen is being replenished from the top of the water column. • FT is the main source of oxygen-consuming reactions, which cause lower oxygen concentrations near the FT-water interface. Oxidation of dissolved methane and ammonia coming out of the FT is the largest contributor to oxygen demand.
Microbial communities and methane oxidation	To study Biological Oxygen Demand (BOD) in the lake, especially methane oxidation and nitrification, and the role of methanotrophs in NA degradation.	• Methane oxidation makes up most of the BOD, and methane-oxidizing bacteria help to reduce the toxicity of OSPW. The exact mechanism is still being studied. • Microbial communities are highly variable over time, and do not show any clear trends.
Air-Water exchanges and water balance	To measure the water balance in BML, physical mechanisms controlling evaporation, and CH_4 and CO_2 release from BML.	• Runoff does not currently contribute significantly to the water balance. • Evaporation was suppressed after BML commissioning; this may have been due to a hydrocarbon sheen. • Evaporation has increased through time and is now comparable to what is expected from a boreal lake.

PROGRESS AND ACHIEVEMENTS

The two key desired outcomes for BML that are important for the validation of the technology are the physical sequestration of the fine tailings below the water cap and water quality improvements over time. Key results demonstrating these two key outcomes are discussed below.

Results so far indicate that the FFT is settling as expected by model predictions, the mudline is declining in elevation year over year, the water cap is increasing in depth, and although the turbidity in the water cap fluctuates seasonally, there is generally a decrease in the suspended solids concentration over time, especially in the upper layers of water. The rate and magnitude of settlement of the FFT within BML is an important driver for the rate and magnitude of advective transport of pore-water constituents from the FFT into the overlying water cap. In turn, this flux has direct implications for the chemistry and ecological evolution of the water column. Hence, a forward projection of this rate and magnitude is an important component of operating and adaptively managing BML to ensure successful stewardship to the desired closure outcomes.

A range of physical parameters of the FFT have been assessed in BML over time. In situ geotechnical testing performed in BML shows the FFT peak undrained shear strength (S_u) approximately ranges from 0.5 to 1 kPa in most testing locations within the lake. Physical sampling of the FFT indicates a distinctive mudline, there is a sharp contrast of the fluid samples collected above and below the mudline. A statistical analysis of Oil Water Solids (OWS) data demonstrated that overall, the solids contents (SC) of the FFT is higher in 2017 than in previous years. This pattern of S_u and SC is consistent with both the prediction and measurement of the FFT settling with time.

The surface of the FFT continues to settle annually, and the overall water depth in BML increases at a corresponding rate, taking into account lake surface elevation changes. Overall settlement of the FFT surface is continuing as expected. The magnitude of cumulative settlement in BML since 2012 has been up to 6 m. The volume of FFT in BML decreased from 174.86 Mm^3 in October 2017 to 172.91 Mm^3 in October 2018 due to settlement.

Total Suspended Solids (TSS) concentrations in BML remained relatively high from 2013 through 2015, before decreasing and becoming more stable from 2016 through 2018. Seasonal variations in TSS concentrations were apparent in BML in 2018, with median concentrations measuring 1.1 mg/L in winter, 5 mg/L in spring, 4 mg/L in summer, and 6.9 mg/L in fall. This seasonal trend was consistent with previous years, with the exception of 2016 when the alum treatment caused TSS concentrations to decrease between the summer and fall sampling events.

There is no evidence of an increase in TSS since commissioning, which indicates that the fines are physically isolated beneath the water cap. In contrast to previous years, there were no unusually high near-bottom TSS concentrations recorded in 2018 (an individual max of 190 mg/L TSS in 2018 vs 5,600 mg/L TSS in 2017). The more consistent TSS measurements in recent years may be due to a more distinct FFT-water interface, allowing for better delineation of the water-FFT interface in advance of near-bottom water sampling. This aligns with the empirical evidence that the FFT is settling and strengthening as expected over time.

Surface water quality has been improving with time in Base Mine Lake, as expected to demonstrate Water Capped Tailings Technology. The lake water is not acutely toxic. Except for F2 hydrocarbons (where the guideline value is interim and derived from soil guidelines) all parameters measured are below Alberta Surface Water Quality short term guidelines for the Protection of Aquatic Life.

Water toxicity testing assesses lethal or inhibitory effects that BML water may have on representative aquatic organisms. These tests are laboratory assays that use standardized methods to assess the relative toxicity of a water sample on cultured bacteria, algae, aquatic vascular plants (i.e. macrophytes), benthic invertebrates, zooplankton, and fish. Survival endpoints report the proportion of test organisms that survive over a fixed duration. The measurement endpoints (e.g. LC50) are estimates of the concentration of exposure medium (i.e. BML water) that results in a lethal or sub-lethal effect on test organisms, with increasing concentrations representative of decreasing effects on test organisms. Water toxicity results for 2018 and a description of trends since commissioning are summarized in Table 3-1.

Type and Duration of Tests	Endpoint	Short-term trends (2018)	Long-term trends (2013-2018)
Acute Toxicity			
Rainbow Trout 96 hour Static Acute	LC50	No trend; no acute toxicity effects observed	No trend; no acute toxicity effects observed since July 2014
Daphnia 48 hour Static Acute	LC50	No trend; no acute toxicity effects observed	No trend; no acute toxicity effects observed
Daphnia 48 hour Static Acute	EC50	No trend; no acute toxicity effects observed	No trend; no acute toxicity effects observed
Chronic Toxicity			
Fathead Minnow 7-day Survival	LC50	No trend; no chronic toxicity effects observed	No trend; no chronic toxicity effects observed since July 2013
Fathead Minnow 7-day Growth	IC25	No trend; moderate monthly variation, moderate spatial variation	No trend; infrequent chronic toxicity effect since July 2013
Algal Growth 72-hour Inhibition	IC25	No trend; moderate monthly variation, moderate spatial variation	No trend; high monthly and inter-annual variation
Lemna minor 7-day Growth (Dry Weight)	IC25	No trend; moderate monthly variation, high spatial variation	No trend; high monthly and inter-annual variation
Lemna minor 7-day Growth (Frond Number)	IC25	No trend; high monthly variation, high spatial variation	No trend; high monthly and inter-annual variation
Ceriodaphnia 7-day Survival Test	LC50	No trend; low monthly variation, moderate spatial variation	No trend; moderate monthly and inter-annual variation
Ceriodaphnia 7-day Reproduction	IC25	No trend; moderate monthly variation, moderate spatial variation	No trend; high monthly and inter-annual variation
Bacterial Luminescence (15 min)	IC20	No trend; low monthly variation, high spatial variation	No trend; high monthly and inter-annual variation
Bacterial Luminescence (15 min)	IC50	No trend; low monthly variation, low spatial variation	No trend; moderate monthly and inter-annual variation

Since monitoring was initiated in 2013, chronic toxicity effects have been observed for some test organisms, while acute toxicity has not been observed in BML since the summer of 2014. The lake is not acutely toxic. No clear seasonal trends in chronic toxicity have been evident since the onset of monitoring in 2013, with standard deviations between years and months overlapping across most test organisms. In 2018, toxicity effects of BML water were within the range of results from previous years.

Chloride has remained the dominant anion in BML since monitoring was initiated in 2013 and is useful as a conservative tracer for tracking water quality improvements. Median chloride concentrations from 2016 to 2018 measured 400 mg/L, representing a modest decline from the first three years of monitoring (440 mg/L median). Chloride concentrations are below the Government of Alberta (GoA) short-term surface water quality guideline (640 mg/L), but have remained greater than the GoA long-term surface water quality guideline for the protection of aquatic life (120 mg/L) since the lake was commissioned. Consistent with previous years, there were no vertical concentration gradients of chloride in BML in 2018.

The parameters that are currently exceeding long-term guidelines are expected to improve with time. As the lake continues to develop, freshwater import dilutes the water cap, and the contribution of chemistry from FFT pore-water advection as a result of settlement declines. As the tailings continue to consolidate and dewater, there is less advective contribution of FFT pore-water to the water cap. The FFT pore-water is the source of elevated chemical concentrations in the water cap and as consolidation begins to slow over time, so too does the influence of pore-water on the water cap. Syncrude will continue to monitor water quality and FFT settlement and will use this information in combination with the water balance to determine mass balance in the water cap and assess how this will change over time. This will in turn inform adaptive management of the lake, specifically decisions about water import and export.

LESSONS LEARNED

Results from research and monitoring indicate that the fines are physically isolated beneath the water cap. The FFT is settling as predicted by the numerical model, the mudline is declining in elevation year over year, and the water cap is increasing in depth. Profiles of shear strength indicate about 0.5 to 1 kPa over almost the entire depth of the FFT in most locations within the lake. The profiles of solids content of the FFT is also increasing over time. Although the turbidity in the water cap fluctuates seasonally, there is generally a decrease in the suspended solids concentration over time, especially in the upper layers of water. Alum addition was an effective method to mitigate mineral turbidity in the lake.

Surface water quality has been improving with time in Base Mine Lake, as expected. This is a crucial component for the successful demonstration of Water Capped Tailings Technology. The lake water is not acutely toxic. Except for the F2 hydrocarbon fraction in the water, all parameters measured are below Alberta Surface Water Quality short term guidelines for the Protection of Aquatic Life. The F2 guideline value is interim and derived from soil guidelines, which makes it challenging to interpret for surface water quality performance. Monitoring of the lake water quality as hydrocarbon mitigation actions are taken will help Syncrude understand the long term changes that can be expected for this parameter. A large proportion of the lake chemical parameters are already below long-term Surface Water Protection of Aquatic Life guidelines, which are important for closure outcomes. Many of these parameters are naturally elevated in the region or are expected to improve as the lake continues to develop.

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RESEARCH TEAM AND COLLABORATORS

Institution: Multiple Research Institutions Managed by Syncrude Canada

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
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Dr. Greg Lawrence	University of British Columbia	Professor		
Dr. Ted Tedford	University of British Columbia	Research Associate		

Dr. Roger Pieters	University of British Columbia	Research Associate		
Dr. Jason Olsthoorn	University of British Columbia	Post-doctoral		
Dr. Marjan Zare (50% time)	University of British Columbia	Post-doctoral		
David Hurley	University of British Columbia	Masters student	2015	2017
Tomy Doda	EPFL	Masters student	2016	2017

WATER TREATMENT

Industrial Research Chair in Oil Sands Tailings Water Treatment – First Term

COSIA Project Number: WJ0035

Research Provider: University of Alberta

Industry Champion: Syncrude

Industry Collaborators: Canadian Natural, Suncor, Shell, Total

Status: Complete

PROJECT SUMMARY

Rationale

Water management is vital not only for the continuous development of the oil sands industry, but also for managing current and future water allocations and preserving healthy ecosystems and human well-being. Currently, the majority of water used for surface mining operations is recycled from settling basins, while the remainder of the required water is withdrawn from the Athabasca River. To effectively manage water during operations, support progressive reclamation, and allow for final closure, there is a need to discharge treated oil sands process water (OSPW) into the environment. As part of the oil sands industry's reclamation plan, tailings ponds will eventually be developed into terrestrial or aquatic habitat that can sustain functions similar to natural habitats in the region. Therefore, water treatment/reclamation approaches are required to ensure that the OSPW quality is safe for release into the environment.

Project Scope and Objectives

In 2011, the NSERC Industrial Research Chair (IRC) Program in Oil Sands Tailings Water Treatment First Term was established to conduct fundamental and applied research in the field of oil sands tailings water treatment. The vision of the NSERC IRC Program was to "*contribute broadly to the research base, fundamental engineering and scientific knowledge, and foundational data that would lead to the environmentally responsible development of the oil sands operations*". The NSERC IRC Program aimed to achieve this vision by developing and assessing innovative water treatment technologies and strategies and their applicability to oil sands operations for the potential safe release of treated process waters to the receiving environment that would help promote and protect both the environment and public health. To achieve the vision and main goal of the NSERC IRC Program First Term, the following short-term objectives were established:

1) Detailed characterization of the water matrices in terms of physical, chemical and biological characteristics along with the toxicological effects, before and after treatment;
2) Understanding of the fundamentals of various active treatment processes for treating selected oil sands source waters;
3) Development of new treatment processes and approaches by utilizing new concepts and materials;
4) Optimization of selected treatment processes and minimization of operational and maintenance problems; and
5) Identification and characterization of by-products generated by different treatment regimens as well as assessment of the toxicity caused by untreated and treated oil sands process water using fish and mammals.

The long-term objectives of the NSERC IRC Program First Term included:

1) Providing training to highly qualified personnel with the skills necessary to promote and protect the environmental and public health;
2) Integrating the achieved knowledge into actual water management options by the oil sands industry; and
3) Providing a scientific foundation for the sustainable and integrated management of oil sands tailings waters which will lead to the sustainability of the economic development of the Athabasca oil sands.

Methodology

To achieve the objectives of the NSERC IRC Program First Term, twenty projects were established, focusing on active treatment approaches. Table 1 summarizes the different projects and the personnel per project for the period 2011-2016.

Table 1: Projects Conducted during NSERC IRC Program – First Term

#	Project	Personnel
1	Evaluation and Comparison of the Performance of Ozone Treatment Process Using a Statistical Approach.	This project was conducted by two postdoctoral fellows sequentially appointed (Dr. Leonidas Pérez-Estrada and Dr. Mohamed Changalov).
2	Application of Multivariate Analysis for the Data Mining of High-Resolution Mass Spectrometry Datasets.	This project started in September 2011, when a M.Sc. student (Mr. Yuan Chen) was recruited. Mr. Chen finalized his M.Sc. project in May 2014.
3	Development of Nanocomposite Membranes with Enhanced Properties for the Treatment of OSPW.	This work was conducted by a Ph.D. student (Ms. Chelsea Benally). The project started in September 2012. Ms. Benally had her Ph.D. defense in June 2018.
4	a) Conventional and Novel Coagulants for OSPW Treatment. b) Enhanced Coagulation/Flocculation with Polyaluminum Chloride (PACl) and Ferrate (VI) for the Remediation of OSPW.	a) This project started before 2011 and was transferred to the NSERC IRC Program in July 2011. The project was completed in October 2012. Ms. Parastoo Pourrezaei had her Ph.D. defense in October 2012 b) This project started in November 2012. In order to continue the work of Project #4, a new Ph.D. student (Mr. Chengjin Wang) was recruited in November 2012. Mr. Wang had his Ph.D. defense in May 2016.
5	a) Investigation of the Thermodynamics of Adsorption of Ionized Naphthenic Acids on Expanded Graphite. b) Evaluation of A Low Cost Tailored Mesoporous Activated Xerogel Carbon for OSPW Remediation.	a) A Ph.D. student started this work in September 2009 and was transferred to the NSERC IRC Program in July 2011. Mr. Ahmed Moustafa had his Ph.D. defense in March 2015. b) This project started in September 2012. In order to continue the work of Project #5, a new Ph.D. student (Mr. Mohamed Ibrahim) was recruited in September 2012. Mr. Ibrahim had his Ph.D. defense in December 2017.
6	Reactivity of Model and Commercial Mixtures of Naphthenic Acids (NAs) in Advanced Oxidation Processes (AOPs) and the Effects of Water Matrix on the Reaction Mechanisms.	This project started in 2008 and was transferred to the NSERC IRC Program in July 2011. The Ph.D. student (Ms. Atefeh Afzal) conducting this research project successfully passed the Ph.D. defense in March 2013.
7	Reactivity of Naphthenic Acids from OSPW in Advanced Oxidation Processes (AOPs) and Effect of	This project started in September 2012 (Mr. Mohamed Meshref). The Ph.D. student conducting

	Treatment Conditions and Water Matrix Characteristics on Their Degradation.	this research project successfully passed the Ph.D. defense in May 2017.
8	Persulfate and Solar Advanced Oxidation Processes (AOPs) for OSPW Treatment.	The postdoctoral fellow working on this project (Dr. Przemysław Drzewicz) finished his appointment in June 2012. The postdoctoral fellow that continued the project on AOP (Dr. Kambiz Khosravi) finished his appointment in October 2013.
9	a) Granular Activated Carbon (GAC) Biofilm Microbial Community Analysis Using 454-Pyrosequencing and Impact of Microbial Communities on OSPW Quality. b) Simultaneous Adsorption and Biodegradation Treatment of OSPW c) Biotransformation of Aromatic Compounds in Oil Sands Process Affected Water by *Pseudomonas*. d) The Impact of Sand and Granular Activated Carbon Biofiltration of Raw and Ozonated OSPW on the Treatment Naphthenic Acids, Fluorophore Organics and Overall OSPW Toxicity.	a) This project was conducted by a Ph.D. student and started in January 2011. The Ph.D. student was transferred to the NSERC IRC Program in July 2011. b) The Ph.D. student (Mr. Md. Shahinoor Islam) had his Ph.D. defense in August 2014. c) A postdoctoral fellow (Dr. Yanyan Zhang) worked on this project. d) A postdoctoral fellow (Dr. Yanyan Zhang after Dr. Kerry McPhedran's departure) worked on this project.
10	The Application of Anoxic-Aerobic Membrane Bioreactors for OSPW Treatment.	This project started in September 2012 (Mr. Jinkai Xue). The Ph.D. student successfully passed the Ph.D. defense in May 2016.
11	Deionization of OSPW by Reverse Osmosis and Nanofiltration.	This project was conducted by a postdoctoral fellow (Dr. Eun-Sik Kim).
12	Composite PVDF Membrane Filled with nanoFe_2O_3 and Carbon Nanotubes for Catalytic Degradation of Organic Contaminants in Oil Sands Process Water.	This project was carried by a postdoctoral fellow (Dr. Alla Alpatova).
13	Feasibility Study on the Treatment of OSPW by Ceramic Membrane Filtration.	The MSc student (Ms. Shimiao Dong) had the M.Sc. defense in March 2014.
14	The Impact of Various Ozone Pretreatment Doses on the Performance of Endogenous Microbial Communities for the Remediation of OSPW.	This project was conducted by one M.Sc. student (Mr. Tao Dong). Mr. Tao Dong had the M.Sc. defense in August 2014.
15	a) Operation and Optimization of the Performance of Membrane Bioreactors. b) Submerged MF System Followed by a High-Pressure Reverse Osmosis System.	a) The project was conducted by one postdoctoral fellow (Dr. Yanyan Zhang) and one Ph.D. student (Mr. Jinkai Xue). This project started in September 2012. b) This project was conducted by one M.Sc. student (Ms. Shimiao Dong).
16	Assessment of the OSPW Toxicity Using Several Comprehensive Toxicity Assays.	The project was conducted by two postdoctoral fellows (Dr. Arvinder Singh and Dr. Li Fu). A Ph.D. Student (Ms. Chao Li) was also recruited in September 2012. The Ph.D. student successfully passed the Ph.D. defense in October 2017.
17	Typology Study of Oil Sands Process Waters.	This activity started in 2011 and was conducted by all personnel working on OSPW treatment.
18	a) Fractionation of Oil Sands Process Water using pH-Dependent Extractions: A Study on Dissociation Constants for Naphthenic Acids Species. b) Atmospheric Pressure Ionization (APPI) Characterization of Oil Sands Process Water with Solid Phase Extraction Pre-Treatment.	a) This project started in April 2013. The Project was conducted by a postdoctoral fellow (Dr. Rongfu Huang). b) This project started in April 2013. The project conducted by a postdoctoral fellow (Dr. Rongfu Huang).

19	a) Prediction of NAs Degradation by Kinetic and Surrogate Models During the Ozonation of OSPW. b) Identification and Characterization of Treatment Byproducts.	a) One PhD student, one postdoctoral fellow, and one Research Associate (Mr. S. Islam; Dr. J. Moreira; and Dr. Chelme-Ayala) conducted this project. b) This project started in 2011. All personnel conducting advanced oxidation processes (AOPs) investigated the byproduct formation.
20	Forward Osmosis as an Energy-Efficient Approach to Simultaneously Treat OSPW and On-Site Basal Depressurized Water	This project was conducted by a Ph.D. student (Ms. Shu Zhu). The Ph.D. student successfully passed the Ph.D. defense in April 2017.

Significance of the Research to Industry

In 2011, Dr. Mohamed Gamal El-Din became the NSERC Industrial Research Chair (IRC) in Oil Sands Tailings Water Treatment – First Term. This Program has impacted: (i) academia as indicated by a number of publications in high quality journals and presentations at national and international conferences; (ii) industry by providing an understanding of water treatment process fundamentals that can be applied in full-scale applications; and (iii) training of highly-qualified personnel (HQP) by their contributions to the Canadian workforce in terms of competitiveness and productivity.

From a technical point of view, the most significant impacts of the NSERC IRC Program First Term on the industry are: (1) understanding of the fundamentals of different treatment processes such as coagulation/flocculation and sedimentation, adsorption, biological degradation, membrane filtration and advanced oxidation; (2) understanding of the impacts of the OSPW chemistry (i.e., physico-chemical, chemical and biological characteristics) on the treatment performance; and (3) understanding of the impacts of different pretreatment steps on the process performance in terms of target pollutant removal and toxicity reduction. This knowledge will help to design the most suitable multi-barrier treatment approaches for OSPW reclamation.

In terms of treatment processes, the NSERC IRC Program First Term has provided the fundamental knowledge of novel treatment processes and strategies that are being assessed specifically for the oil sands industry. Another benefit to the supporting organizations as a result of the NSERC IRC Program Frist Term includes advances in high-resolution analytical methods that have allowed the characterization of OSPW. The complete characterization of the OSPW matrices and the toxicity assessment have helped to achieve a better understanding of the potential impacts of treated OSPW on the environment and have assisted the industry to prepare the future water management plans for the possible release of treated OSPW into the environment.

The impact of the NSERC IRC Program First Term can also be measured by the number of publications and presentations (more than 70 peer-reviewed journal publications and more than 140 oral and poster presentations in national and international conferences and workshops). The results of this program have been published in journals of high impact factor within the environmental engineering field such as Water Research; Environmental Science & Technology; Journal of Membrane Science; and Bioresource Technology; among others.

The NSERC IRC Program First Term has trained more than 40 trainees, including Ph.D. and Master students, postdoctoral fellows, research associates, technicians, research assistants, and summer students. The industrial and non-industrial partners have had access to highly talented and trained personnel who can help to meet the demands of the industry and can implement these novel treatment solutions at full-scale level. The trainees have achieved remarkable levels of success and have gained hands-on experience to develop skills through their research in cooperation with the supporting organizations. The NSERC IRC Program First Term has also provided a value-added experience to the trainees by helping them to develop the important and relevant skills for the workplace through interaction with the industry and government sectors. The trainees have had direct contact with industrial representatives and technology advisors through regular research meetings. This interaction is critical because it grounds the work, ensuring that it is industrially relevant.

PROGRESS AND ACHIEVEMENTS

The NSERC IRC Program First Term achieved many organizational and research goals, including: training of highly qualified personnel with multidisciplinary expertise; researching technical issues of strategic importance to Canada; and promoting cooperation and knowledge exchange between academia, industry and government.

The characterization of raw (i.e., untreated), and treated OSPWs in terms of physical, chemical and biological properties was conducted for different process waters (i.e., different OSPWs from three different oil sands producers). The OSPW characterization was conducted in each project, before and after treatment, to evaluate the treatment performance. Because OSPW contains thousands of organic compounds that have not been identified so far and the complexity of the OSPW mixture as well as the variety of different structures of naphthenic acids (NAs), among other organics, present in OSPW, advanced analytical methods such as ultra-performance liquid chromatography time-of-flight mass spectrometry (UPLC-TOF-MS) and ion mobility spectroscopy were used to characterize OSPW.

Significant progress was achieved in terms of process fundamentals. As illustration, the mechanisms of destabilization during coagulation/flocculation process (Pourrezaie et al., 2011) and the mechanism of adsorption during petroleum coke treatment (Pourrezaie et al., 2014a) were reported. The mechanisms of oxidation of model naphthenic acids (NAs) compounds by hydroxyl radicals, molecular ozone, and chlorine radicals (Afzal et al., 2014; Shu et al., 2014) as well as the microbial community structure and operational performance of fluidized bed biofilm reactors treating OSPW (Islam et al., 2014) were also investigated. Moreover, the mechanisms of adsorption and biodegradation of NAs during simultaneous adsorption and biodegradation treatment during biofilm-based treatment were elucidated (Islam et al., 2015). The key roles of *Pseudomonas fluorescens* and *Pseudomonas putida* to biodegrade aromatic compounds in OSPW were also demonstrated (Zhang et al., 2015). The thermodynamics of adsorption and competitive interactions of weak acids on a graphite surface was also examined, showing that multilayer adsorption may occur via hydrophobic bonding with the CH_3 ends of the self-assembled layer. The impacts of pK_a, K_{ow}, molecular structure and competition of weak acids on their adsorption on charged carboxyl/phenolic groups found on carbon surfaces were also demonstrated (Moustafa et al., 2014). In terms of physical treatment, the mechanisms of fouling of ceramic membranes during OSPW treatment were investigated (Alpatova et al., 2014), showing that pore blocking and cake layer formation were the dominant fouling mechanisms at the beginning of filtration, whereas cake layer formation was the primary fouling mechanism at later stages.

Several materials/processes were developed, including synthetic coagulants (i.e., synthetic polyaluminum chloride), adsorbents chemically functionalized, and nanocomposite membranes. As instance, nanosilver and multi-walled carbon nanotubes thin-film nanocomposite membranes with enhanced permeability and anti-biofouling properties were developed (Kim et al., 2013). Composite porous polyvinylidene fluoride (PVDF) membranes filled with nanoFe_2O_3 and carbon nanotubes were fabricated and tested for the catalytic degradation of organic contaminants in OSPW (Alpatova et al., 2015). Zero valent iron combined with peroxydisulfate and zero valent iron in presence of petroleum coke were used as environmentally friendly alternatives for the removal of NAs, extractable organic fraction, and fluorophore organics from OSPW (Drzewicz et al., 2012; Pourrezazei et al., 2014b). Ferrate(IV) for coagulation/flocculation and oxidation processes was also synthetized and purified in our laboratories (Wang et al., 2016).

The optimization of selected treatment processes was also investigated. As illustration, different coagulants and coagulant doses were assessed. The impact of various ozone pre-treatment doses on the performance of endogenous microbial communities for the remediation of OSPW was assessed. The optimization of ozonation combined with integrated fixed film activated sludge (IFAS) or membrane bioreactor (MBR) was also investigated.

The identification and characterization of by-products generated during ozonation and UV/hydrogen peroxide treatments of model NAs compounds were reported (Afzal et al. 2014, Drzewicz et al. 2010). The identification of the by-products generated after OSPW treatment is a paramount challenge that cannot be trivialized as the regular by-product analysis. Significant progress was achieved in term of assessment of the toxicity caused by untreated and treated OSPWs using fish and mammals (Garcia-Garcia et al. 2012, Hagen et al. 2012, Hagen et al. 2014). The toxicology studies reported and demonstrated for the first time the immunotoxic effects of the organic fraction of OSPW on fish and mammalian immune responses.

LESSONS LEARNED

The following are the key outcomes achieved during the NSERC IRC Program First Term:

- A comprehensive study designed to characterize different process waters streams from different oil sands companies was conducted for the first time. This study has helped to determine similarities and major differences between water matrices as well as to identify the types of the water treatment strategies (i.e., approaches) suitable for each stream.
- Studies conducted under the NSERC IRC Program First Term have shown that coagulation/flocculation process as a pre-treatment step can improve the desalination of OSPW for both nanofiltration and reverse osmosis membranes.
- Ferrate(IV) has been found to have a dual capacity to remove organic matter in OSPW through oxidation and coagulation. However, the results show that the removal of organics mainly occurs through oxidation process. In addition, ferrate(VI) oxidation has proven to be an effective process in degrading naphthenic acids (NAs) and the aromatic compounds, and reducing the acute toxicity of OSPW toward *Vibrio fischeri*.
- It has also been reported for the first time the mechanism of adsorption (physisorption) of NAs onto petroleum coke. The application of petroleum coke combined with zero valent iron has been found to remove organic compounds, including NAs, extractable organic fractions, and fluorophore organic compounds from OSPW through a simultaneous adsorption and oxidation mechanisms. The use of electro-adsorption technique developed by combining petroleum coke with electricity has resulted in a substantial removal of NAs and chemical oxygen demand (COD) from the OSPW.
- In terms of chemical treatment, the mechanism of degradation of cyclohexanoic acid, a model compound of NAs, during ozonation and UV/hydrogen peroxide (H_2O_2) treatment in pristine water has been reported for the first time. Some of the by-products generated after UV/H_2O_2 treatment using cyclohexanoic acid have also been identified and characterized. In addition, ozone combined with hydrogen peroxide (O_3/H_2O_2) treatments has proven to be effective in degrading the persistent organic fraction in OSPW.
- By using biological treatments, Dr. Gamal El-Din's group has proved that ozone pre-treatment decreases the toxicity of OSPW and provides extra biodegradable carbon sources to accelerate the growth of microbial populations. Moreover, the increasing bacterial number and the appearance of emergent microorganisms could further mitigate the toxicity of OSPW and the degradation of the recalcitrant organic compounds including NAs. Therefore, combining ozone and biodegradation seems to be a promising technology for OSPW treatment.

- The results obtained using biofilm reactors are promising and show that endogenous population of microorganisms in OSPW can readily form biofilms; these endogenous biofilms are able to degrade and remove NAs and other organic contaminants. Moreover, the combination of ozonation and biological treatment (i.e., ozone treatment followed by biofilm reactors) has been found to be a promising approach for OSPW treatment.
- A prefiltration integrated system equipped with low and high pressure-driven membranes to remove the extractable organic fraction and ionic species from OSPW has been developed. Such integrated membrane systems could have promising applications of OSPW treatment without physico-chemical pre-treatment, which implies huge benefits to the oil sands industry. Considering the effectiveness of membrane bioreactors (MBRs) in treating toxic and refractory petrochemical wastewaters, MBRs treating OSPW have never been evaluated. Studies conducted under the NSERC IRC Program First Term have showed that MBR is a promising approach for removing recalcitrant organics in raw and mild ozonated OSPWs.
- Nano-silver and multi-walled carbon nanotubes thin-film nanocomposite membranes with enhanced permeability and anti-biofouling properties have been developed. The findings of this study are promising, allowing the design of fit-to-purpose membranes with improved characteristics to meet different OSPW treatment requirements.
- Ceramic ultrafiltration membrane is an effective treatment to remove inorganic and organic compounds from OSPW. The results have also demonstrated that due to their low turbidity and silt density index, permeates produced by ceramic ultrafiltration membrane are suitable for further treatment by high pressure membrane processes such as nanofiltration and reverse osmosis in order to enhance the removal of low molecular weight compounds and dissolved ions. Electrodialysis has been found to be an effective alternative for the treatments of OSPW and basal depressurization water, showing high removal efficiencies of all measured components.
- The *in vitro* cellular and molecular assays developed and tested under the NSERC IRC Program First Term are valuable tools for the assessment of OSPW toxicity. Moreover, the *in vitro* and *in situ* models of OSPW exposures that have been developed can easily be adapted by the oil sands industry to screen the effects of multiple treatment technologies and approaches and their applicability for OSPW remediation. Comprehensive toxicity assays have been developed to assess the impacts of OSPW on mammalian cells and mouse model (for development and reproduction). These functional assays allow us to screen the toxicity of fractionized OSPW and even other toxicants effects in cells and animals, which may be directly linked to potential risk associated with OSPW exposures to humans.

Providing innovative multi-barrier treatment approaches and water reuse/release scenarios will help promote and protect environmental and public health, enhance water quality, and support the ongoing efforts that assist the economical and sustainable development of Alberta oil sands resources. Currently, the NSERC IRC Program – Second Term is focusing on developing and assessing innovative water treatment/reclamation technologies and strategies through a combination of passive and semi-passive treatment strategies that will help promote and protect both the environment and public health.

PRESENTATIONS AND PUBLICATIONS

NSERC IRC Program First Term resulted in more than 70 peer-reviewed journal publications and more than 140 oral and poster presentations in national and international conferences and workshops, which is unfortunately too long to list in this document. For a complete list of publications, contact the Principle Investigator, Dr. Gamal El-Din at the University of Alberta or COSIA.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Mohamed Gamal El-Din

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Dr. Leonidas Perez-Estrada	University of Alberta	Postdoctoral Fellow	2011	2012 (completed)
Dr. Mohamed Changalov	University of Alberta	Postdoctoral Fellow/ Lab Technician	2012	2013 (completed)
Dr. Rongfu Huang	University of Alberta	Postdoctoral Fellow	2013	2019 (completed)
Dr. Przemysław Drzewicz	University of Alberta	Postdoctoral Fellow	2008	2012 (completed)
Dr. Kambiz Khosravi	University of Alberta	Postdoctoral Fellow	2012	2013 (completed)
Dr. Eun-Sik Kim	University of Alberta	Postdoctoral Fellow	2010	2013 (completed)
Dr. Alla Alpatova	University of Alberta	Postdoctoral Fellow	2011	2014 (completed)
Dr. Nikolaus Klamerth	University of Alberta	Postdoctoral Fellow	2013	2016 (completed)
Dr. Jesus Moreira	University of Alberta	Postdoctoral Fellow	2013	2014 (completed)
Dr. Kerry McPhedran	University of Alberta	Postdoctoral Fellow	2014	2015 (completed)
Dr. Yanyan Zhang	University of Alberta	Postdoctoral Fellow	2013	2016 (completed)
Dr. Arvinder Singh	University of Alberta	Postdoctoral Fellow	2012	2016 (completed)
Dr. Li Fu	University of Alberta	Postdoctoral Fellow	2014	2017 (completed)
Dr. Mingyu Li	University of Alberta	Postdoctoral Fellow	2015	2020 (completed)
Dr. Selamawit Ashagre Messele	University of Alberta	Postdoctoral Fellow	2015	
Dr. Pamela Chelme-Ayala	University of Alberta	Program Manager	2012	
Dr. Vanessa Incani	University of Alberta	Program Manager	2015	2015 (completed)
Ms. Parastoo Pourrezaei	University of Alberta	Ph.D. Student	2007	2012 (completed)
Mr. Chengjin Wang	University of Alberta	Ph.D. Student	2012	2016 (completed)
Mr. Ahmed Moustafa	University of Alberta	Ph.D. Student	2009	2015 (completed)
Mr. Mohamed Ibrahim	University of Alberta	Ph.D. Student	2012	2017 (completed)
Ms. Atefeh Afzal	University of Alberta	Ph.D. Student	2008	2013 (completed)
Mr. Mohamed Meshref	University of Alberta	Ph.D. Student	2012	2017 (completed)
Mr. Shahinoor Islam	University of Alberta	Ph.D. Student	2009	2014 (completed)
Ms. Chelsea Benally	University of Alberta	Ph.D. Student	2012	2018 (completed)
Ms. Shu Zhu	University of Alberta	Ph.D. Student	2013	2017 (completed)
Mr. Jinkai Xue	University of Alberta	Ph.D. Student	2012	2016 (completed)
Mr. Lei Zhang	University of Alberta	Ph.D. Student	2014	2018 (completed)
Mr. Abdallatif Abdalrhman	University of Alberta	Ph.D. Student	2014	2019 (completed)
Ms. Chao Li	University of Alberta	Ph.D. Student	2012	2017 (completed)
Mr. Tao Dong	University of Alberta	M.Sc. Student	2012	2014 (completed)
Mr. Yuan Chen	University of Alberta	M.Sc. Student / Research Assistant	2011	2014 (completed)
Ms. Shimiao Dong	University of Alberta	M.Sc. Student / Research Assistant	2011	2014 (completed)
Mr. Zengquan Shu	University of Alberta	Research Assistant	2012	2015 (completed)
Ms. Nian Sun	University of Alberta	Technician	2011	2014 (completed)
Ms. Maria Demeter	University of Alberta	Laboratory Manager	2011	2014 (completed)
Dr. Brandon Weber	University of Alberta	Laboratory Manager	2015	2015 (completed)
Ms. Nicole Loewen	University of Alberta	Undergraduate Student	2014	2014 (completed)
Mr. Tae Chung	University of Alberta	Undergraduate Student	2016	2016 (completed)

Research Collaborators:

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- Dr. Hongbo Zeng, Professor, Department of Chemical and Materials Engineering, University of Alberta.
- Dr. Jonathan W. Martin, Adjunct Professor, Department of Laboratory Medicine and Pathology, University of Alberta.
- Dr. John P. Giesy, Professor, Toxicology Centre, University of Saskatchewan.
- Dr. Seoktae Kang, Professor, Department of Civil Engineering, Kyung Hee University, South Korea.
- Dr. Keith Tierney, Professor, Department of Biological Sciences, University of Alberta.
- Dr. Greg Goss, Professor, Department of Biological Sciences, University of Alberta.
- Dr. Jonathan Veinot, Professor, Department of Chemistry, University of Alberta.
- Dr. Lukas Y. Wick, Department of Environmental Microbiology, Helmholtz Centre for Environmental Research (UFZ), Leipzig, Germany.

Non-COSIA Collaborators:

- EPCOR Water Services
- Alberta Innovates
- Alberta Environment and Parks
- IOWC Technologies Inc. (BioLargo Inc.)

Industrial Research Chair in Oil Sands Tailings Water Treatment – Second Term

COSIA Project Number: WE0025

Research Provider: University of Alberta

Industry Champion: Syncrude

Industry Collaborators: Canadian Natural, Imperial, Suncor, Teck

Status: Year 3 of 5

PROJECT SUMMARY

Rationale

As one of COSIA's identified priority areas, water management is vital not only in the continuous development of the oil sands industry but also in managing current and future water allocations and preserving healthy ecosystems and human well-being. Currently, the majority of water used for surface mining operations is recycled from settling basins, while the remainder of the required water is withdrawn from the Athabasca River.

Oil sands process water (OSPW) is generated during the extraction process. OSPW will need to be treated and released to the environment. Therefore, water treatment/reclamation approaches are required to ensure OSPW quality is safe for release.

Project Scope and Objectives

Second Term (2017-2022) is focused on developing and assessing innovative water treatment/reclamation technologies and strategies through a combination of passive (low-energy) and semi-passive treatment approaches that will help promote and protect both the environment and public health.

The short-term objectives of the NSERC IRC Program - Second Term are:

- Understand the fundamentals of low-energy and engineered passive treatment processes.
- Conduct life-cycle assessments and cost analyses of different treatment approaches.
- Assess the performance of selected treatment processes at the pilot-scale level.
- Assess the performance of four large field pilots on active mine sites.
- Develop a "toolbox" with the best available technologies for different water stream scenarios.

The long-term objectives, including those beyond the 5-year period covered by this program, are:

- Train highly qualified personnel with the skills necessary to promote and protect environmental and public health.
- Support current research programs focused on the treatment/reclamation of OSPW by facilitating the transfer of knowledge and new discoveries.
- Integrate the knowledge gained into actual water management options by the oil sands industry.

Methodology

To achieve the objectives of the NSERC IRC Program – Second Term, 15 projects were established. The projects were grouped into six research areas: water and tailings quality, advanced oxidation processes, biological treatments, material development, piloting tests and cost assessment (see Table 1).

Table 1: NSERC IRC Program – Second Term Projects

Project ID #	Research Area	Title
1	Water and Tailings Quality	Long-Term Assessment of Oil Sands Process Water Quality Due to Self-Attenuation
2a	Advanced Oxidation Processes	Selection of Photocatalysts for the Treatment of OSPW
2b	Advanced Oxidation Processes	Assessing the Catalytic Potential of the OSPW Inorganic Matrix on Advanced Oxidation Process
2c	Advanced Oxidation Processes	Application of Catalytic Advanced Oxidation Processes on OSPW Treatment
3	Advanced Oxidation Processes	In Situ Generation of Hydrogen Peroxide Using Sewage Sludge Biochar as a Catalyst
4	Biological Treatments	Biological-Based Active Treatment Processes with Innovative Biofilm Carriers – Bench and Scale-up Studies
5	Advanced Oxidation Processes	Electro-Assisted Biodegradation for OSPW Remediation
6	Biological Treatments	Remediation of OSPW Using Deep Biofilters – Bench and Scale-up Tests
7	Advanced Oxidation Processes	In-Pipe Treatment to Assist in OSPW Remediation
8a	Material Development	Adsorption Using Carbon Xerogel
8b	Material Development	Applications of Cellulose Nanofibers for Process Water Remediation
8c	Material Development	Sludge-Based Materials for Catalytic Oxidation
9	Piloting Tests	Coke-Treatment Piloting
10	Piloting Tests	Wetland Piloting
11	Piloting Tests	Mesocosm Piloting
12	Piloting Tests	Suncor Demonstration Pit Lake (DPL) Piloting
13	Cost Assessment	Life Cycle Assessment and Cost Analysis
14	Water and Tailings Quality	Application of biomimetic solid phase micro-extraction (BE-SPME) Method as a Screening Tool

15	Water and Tailings Quality	Assessing the Effects of Polymers and Polymer Degradation on Water Chemistry and the Quality of the Tailings
16	Water and Tailings Quality	Development of Mass Spectrometry Based Analytical Methods for the Detection of Multiple Naphthenic Acids Model Compounds and Identification of Byproducts

Significance of the Research to Industry

The NSERC IRC Program - Second Term aligns with ongoing efforts for the economic development of Alberta oil sands resources. Assessment of the various types of low energy OSPW treatment processes (i.e., semi-passive and engineered passive approaches) will contribute to a better understanding of how treated/reclaimed OSPW could be safely discharged into the environment. The comprehensive characterization of OSPW before and after treatment, the dose-response analysis of toxic effects induced by different OSPW fractions, and the use of different treatment processes for OSPW will allow for the development of reclamation strategies for the safe release of OSPW into the environment and, ultimately, protection of public health.

PROGRESS AND ACHIEVEMENTS

The NSERC IRC Program - Second Term is achieving many short and long term objectives, including: training of highly qualified personnel with multidisciplinary expertise; researching technical issues of strategic importance to Canada; and promoting cooperation and knowledge exchange between academia, industry and government.

Extensive research on developing treatment processes for the reclamation of OSPW continues to be conducted and significant progress has been achieved on process fundamentals. For example, the degradation mechanisms of NA model compounds during catalytic oxidation and electro-oxidation have been investigated. Considering the nature and structure of NAs and the characteristics of OSPW (with its high electrical conductivity), electro-oxidation seems to be a potentially effective and cost-efficient option for OSPW treatment and NA degradation. Applying anodic oxidation by using inexpensive electrodes materials (such as graphite) under low voltage conditions can preferentially degrade NAs of higher cyclicity and carbon number and decrease the number of rings and molecular weight without resulting in complete mineralization. Therefore, the application of electro-oxidation should enhance OSPW biodegradability and reduce toxicity. The lower voltages required for treatment will result in a sustainable and environmentally friendly process that can operate by solar energy. As well, the exclusion of added chemicals will prevent the production of any additional hazardous sludges.

In terms of material development, studies conducted under the NSERC IRC Program have, for the first time, reported the mechanism of adsorption of NAs onto carbon xerogels. The results have demonstrated that mesoporous carbonaceous materials such as carbon xerogels can successfully be used to adsorb persistent organic contaminants from OSPW. Mesoporous carbonaceous material may have the potential to be utilized in a fixed bed adsorption column for continuous treatment of OSPW or as a semi-passive treatment method in pit lakes for the removal of organic constituents from OSPW. Sewage sludge is also being used as a raw material for the production of carbon material since sewage sludge is a carbon-rich, renewable and vast resource which can be obtained at low cost. Increasing the content of mesopores in the generated carbon material would be an efficient way to shorten the equilibrium time since the mass transportation could be accelerated. The carbon materials can be used as adsorbents or as catalysts for advanced oxidation.

In terms of biological treatment, biofiltration and mild ozonation show complementary advantages on the degradation of NAs. The biofiltration-ozonation-biofiltration process shows higher NA removal than the biofiltration of raw OSPW. The biofiltration pre-treatment can benefit the ozonation of NAs while the post biofiltration process shows its contribution to the improved removal of the oxidized NAs from OSPW.

In terms of analysis, the biomimetic solid phase micro-extraction (BE-SPME) method can be used in hazard assessment of acute lethality to aquatic organisms. The BE-SPME method could be utilized as a new criterion to be added to the water quality regulations for the oil sands industry. Moreover, the atmospheric pressure gas chromatography-time-of-flight-mass spectrometry (APGC-TOF-MS) method developed in this project could be utilized to characterize PAHs, in addition to NAs, in OSPW.

LESSONS LEARNED

The following are the key outcomes achieved so far:

- The characterization and treatment of OSPW pose many challenges, including the presence of dissolved organic compounds such as NAs, other organic acids, total suspended solids, bitumen, salinity, trace metals, and other dissolved organic and inorganic compounds.
- The BE-SPME method presented in the NSERC IRC program could serve as a rapid and convenient analytical screening tool for estimating the toxicity of raw and treated OSPWs. The BE-SPME technique could serve as a benchmark technology to monitor the transformation of bioavailable NAs in treatment processes (e.g., wetland biodegradation), as well as to monitor the natural transfer and transformation of bioavailable NAs in the natural environment.
- Using sewage sludge as a precursor for the production of sewage sludge-based material (sludge-based biochar) has many advantages. First, the amount of waste materials is partially reduced. Second, the low-cost adsorbent/catalyst, if developed, can reduce the contaminants in OSPW at a reasonable cost.
- Low-current electro-oxidation is a promising pre-treatment option for OSPW while being routed to pit lakes and/or wetlands as it can lead to improved biodegradability and reduced toxicity of OSPW organics. The lower voltages required and low-cost graphite electrodes will result in a sustainable and environmentally-friendly process that can be operated by solar energy or can be used for in-pipe treatment.
- In situ catalytic oxidation may play a critical role in enhancing the remediation of OSPW when applied as a pre-treatment step to accelerate the degradation of NAs, among other organics, in OSPW.
- Biofiltration possesses remarkable advantages, such as low energy costs and low capital demand. The fixed-bed biofilm reactor shows high potential to be applied and scaled-up for the in situ treatment of OSPW.

Providing innovative multi-barrier treatment approaches and water reuse/release scenarios will help promote and protect environmental and public health, enhance water quality, and support the ongoing efforts that assist the economical and sustainable development of Alberta oil sands resources.

PRESENTATIONS AND PUBLICATIONS

To date there have been 35 presentations and 36 publications. Several Key publications are listed below.

Abdalrhman, A.S., and M. Gamal El-Din. 2020. *Degradation of Organics in Real Oil Sands Process Water by Electro-Oxidation Using Graphite and Dimensionally Stable Anodes*. Chem. Eng. J., 389, 124406.

Abdalrhman, A.S., S.O. Ganiyu, and M. Gamal El-Din. 2019. *Degradation Kinetics and Structure-Reactivity Relation of Naphthenic Acids During Anodic Oxidation on Graphite Electrodes*. Chem. Eng. J., 370, 997-1007.

Benally, C., S.A. Messele, and M. Gamal El-Din. 2019. *Adsorption of organic matter in oil sands process water (ospw) by carbon xerogel*. Water Res., 154, 402-411.

Fang, Z., R. Huang, P. Chelme-Ayala, Q. Shi, C. Xu, and M. Gamal El-Din. 2019. *Comparison of UV/Persulfate and UV/H_2O_2 for the Removal of Naphthenic Acids and Acute Toxicity towards Vibrio fischeri from Petroleum Production Process Water*. Sci. Total Environ., 694, 133686.

Fang, Z., P. Chelme-Ayala, Q. Shi, C. Xu, and M. Gamal El-Din. 2018. *Degradation of naphthenic acids model compounds in aqueous solution by UV activated persulfate: influencing factors, kinetics and reaction mechanisms*. Chemosphere, 211, 271-277.

Li, M., S.A. Messele, Y. Boluk, and M. Gamal El-Din. 2019. *Isolated Cellulose Nanofibers for Cu (II) and Zn (II) Removal: Performance and Mechanisms*. Carbohydr. Polym., 221, 231-241.

Messele, S.A., P. Chelme-Ayala, and M. Gamal El-Din. 2020. *Catalytic Ozonation of Naphthenic Acids in the Presence of Carbon-Based Metal-Free Catalysts: Performance and Kinetic Study*. Catalysis Today. https://doi.org/10.1016/j.cattod.2020.01.042.

Qin, R., Z.T. How, and M. Gamal El-Din. 2019. *Photodegradation of Naphthenic Acids Induced by Natural Photosensitizer in Oil Sands Process Water*. Water Res., 164, 114913.

Zhang, L., Y. Zhang, J. Patterson, M. Arslan, Y. Zhang, and M. Gamal El-Din. 2020. *Biofiltration of Oil Sands Process Water in Fixed-Bed Biofilm Reactors Shapes Microbial Community Structure for Enhanced Degradation of Naphthenic Acids*. Sci. Total Environ., 718, 13728.

Zhang, L., Y. Zhang, and M. Gamal El-Din. 2018. *Degradation of recalcitrant naphthenic acids from raw and ozonated oil sands process-affected waters by a semi-passive biofiltration process*. Water Res., 133, 310-318.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Mohamed Gamal El-Din

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Rongfu Huang	University of Alberta	Research Associate		2019 (completed)
Pamela Chelme-Ayala	University of Alberta	Research Associate		
Selamawit Messele	University of Alberta	Postdoctoral Fellow		
Mingyu Li	University of Alberta	Postdoctoral Fellow		2020 (completed)
Lingling Yang	University of Alberta	Research Associate		
Soliu Ganiyu	University of Alberta	Postdoctoral Fellow		
Zou Tong How	University of Alberta	Postdoctoral Fellow		
Shailesh Sable	University of Alberta	Postdoctoral Fellow		
Muhammad Arslan	University of Alberta	Postdoctoral Fellow		
Abdallatif Abdalrhman	University of Alberta	Ph.D. Student	2014	2019 (completed)
Rui Qin	University of Alberta	Ph.D. Student	2014	2019 (completed)
Lei Zhang	University of Alberta	Ph.D. Student	2014	2018 (completed)
Lingjun Meng	University of Alberta	Ph.D. Student	2017	2021
Chelsea Benally	University of Alberta	Ph.D. Student	2012	2018 (completed)
Jia Li	University of Alberta	Ph.D. Student	2019	2023
Monsuru Suara	University of Alberta	Ph.D. Student	2019	2023
Zhexuan An	University of Alberta	Ph.D. Student	2019	2023
Akeen Bello	University of Alberta	Ph.D. Student	2019	2023
Foroogh Mehravaran	University of Alberta	Ph.D. Student	2019	2023
Deborah Crominski da Silva	University of Alberta	Ph.D. Student	2019	2023
Jia Li	University of Alberta	Master Student	2017	2018 (completed)
Alice Da Silva	University of Alberta	Research Assistant		2018 (completed)
Shimiao Dong	University of Alberta	Research Assistant		2018 (completed)
Yanlin Chen	University of Alberta	Research Assistant		2019 (completed)

Research Collaborators:

- Dr. Miodrag Belosevic, Distinguished University Professor, Department of Biological Sciences and School of Public Health, University of Alberta.
- Dr. James Stafford, Associate Professor, Department of Biological Sciences, University of Alberta.
- Dr. Yaman Boluk, Professor, Nanofibre Chair in Forest Products Engineering, Department of Civil and Environmental Engineering, University of Alberta.
- Dr. Dev Jennings, T.A. Graham Professor of Strategy and Organization and the Director of the Canadian Center for Corporate Social Responsibility (CCCSR), Alberta School of Business.
- Dr. M. Anne Naeth, Professor of Land Reclamation and Restoration Ecolog
- y, Department of Renewable Resources, Associate Dean Research and Graduate Studies in the Faculty of Agricultural, Life and Environmental Sciences, Director of the Land Reclamation International Graduate School (LRIGS) and Director of the Future Energy Systems (FES), University of Alberta.
- Dr. Xuehua Zhang, Professor, Department of Chemical & Materials Engineering, University of Alberta.
- Dr. John Headley, Senior Research Scientist, Environment Canada.
- Dr. Sandra Contreras Iglesias, professor, and Dr. Francisco Medina Cabello, professor, department of Chemical Engineering, Universitat Rovira, Spain.

- Dr. Quan Shi, professor, and Dr. Chunming Xu, professor, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing.

Non-COSIA Collaborators:

- EPCOR Water Services
- Alberta Innovates
- Alberta Environment and Parks

Cultivating the Uncultivables in the Canadian Oil Sands

COSIA Project Number: WE0041 (Phase 0), WE0055 (Phase 1a)

Research Provider: OPE Group B.V.

Industry Champion: Suncor

Industry Collaborators: Canadian Natural, Cenovus, ConocoPhillips Canada, Husky, Imperial, Syncrude, Teck

Status: Year 1 of 2

PROJECT SUMMARY

The desired result of this project is to demonstrate, at a laboratory scale, that specifically trained, naturally occurring, oil sands microbial communities are a low energy solution to degrade organics in Oil Sands Produced Water, particularly naphthenic acids (NAs).

OPE Group has developed a specialty culture enrichment technology (SCE-Tech) to generate, train and optimize microbial communities to perform desired biological processes by dynamically controlling their cultivation environment in bioreactors. By rewarding desired behavior, microbial communities are enriched and keep improving over time, while also maintaining a large resilience to additional environmental factors.

This is a multi phase project, which is currently partially through Phase 1 – Laboratory Downscaling

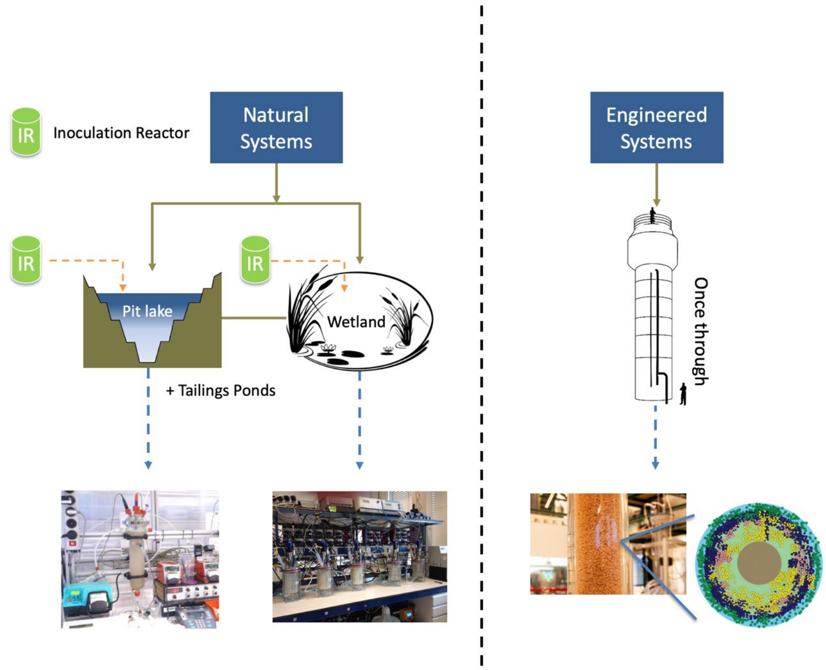
Active/Complete Phases:

Phase 0 –- Literature Review and Design Bioprocess Specification (2017-2018)

- Developed the design for Phase 1 including required degradation rates, the downscaled bioreactor designs, selection of the research strategies, and defining the boundary conditions for a successful go/no-go decision.

Phase 1- Laboratory Downscaling

- Laboratory based experiments to cultivate microbial biodiversity that could be exposed further to ever more stringent and diverse selective reward strategies and has been split into two phases 1a and 1b. Phase 1a is wrapping up. In Phase 1a, a large set of different environmental conditions was created in highly controlled bioreactors, which were inoculated with a microbial library collected from various oil sands regional representative natural sources. The most promising environmental conditions tested, displaying microbial growth and NA degradation, were further propagated on Oil Sands Process Water (OSPW) to characterize and generate sufficient biomass. The metabolic conversion rates achieved in these cultures was determined as rate-0 and is the starting point for the second part of the work; (Phase 1b). Phase 1b will cover the training and evolution of the microbial communities in downscaled laboratory bioreactor systems for both natural ecosystems (i.e. wetlands, pit lakes and tailings ponds) and engineered ecosystems (i.e. once through) (see figure below).



These initial laboratory steps are crucial to determine the commercial viability of a full-scale implementation of this low energy organics treatment technology.

PROGRESS AND ACHIEVEMENTS

Phase 0- (2017-2018) - Literature Review and Design Bioprocess Specification. As a precursor to the laboratory phase of the current 2019 project, a design phase was conducted in 2018. In this design phase, which did not include laboratory work, two workshops with COSIA member experts were organized to align the most promising research lines applying SCE-Tech with the highest priority needs of the COSIA members. The purpose of this phase was to collect process information and incorporate detailed information from the COSIA members to finalize the designs of our microbial enrichment systems to be applied in the laboratory stage. The final deliverable of this design phase was the report "Biotechnology Solutions for Passive Organics Treatment", which describes a detailed research plan and contains the designs of the proposed bench scale bioreactor systems (i.e. wetlands, pit lakes, tailings ponds and once through).

Phase 1 (2019-2020) – Laboratory Downscaling. The first part, Phase 1a, evaluated the viability of biotechnological treatment solutions for OSPW. The principle goal of the work was to produce the initial biomass that will be used for the dynamic enrichment cultivations in the downscaled laboratory bioreactor systems, which is planned for Phase 1b. The research focused on an application level, where the aim was to gain a clearer insight in the current biological NAs degradation capabilities and it resulted in the first generation of trained microbial communities, with new insights in biological bottlenecks and their potential solutions at full-scale. Throughout phase 1a several aspects of the microbial world in the presence of OSPW were studied to elucidate three factors: inhibition, limitation, and rate-0. These new insights will be applied to test environmental conditions and operating parameters to effectively reward and/or punish specific biological activities with a strong focus on NAs degradation. The research made use of many insights from published literature on microbial cultivation in OSPW, in which specific microbial cultivation expertise were added in more advanced bioreactors than are conventionally used, allowing for more control and real time characterization.

By operating multiple bioreactors in parallel on OSPW for a wide range of environmental conditions (some that are not directly applicable to the Oil Sands natural ecosystem), it enabled to screen and diversify the richness of microbial communities that can grow on OSPW. This wealth of microbial diversity serves as an important cornerstone in the future phases, where these diverse microbial strategies can collaborate, compete, and co-evolve to optimally fit any of the three proposed downscaled ecosystems (see figure above). As a result of this work, we now have a good understanding on inhibitory and limiting conditions for biological activity, and has reasons to believe that a complex carbon cycling ecosystem arises in natural OSPW ecosystems that diminishes the rate, or eliminates its capacity to degrade NA.

LESSONS LEARNED

Phase 1a tested environments that most closely resemble the natural ecosystems and would mimic the Oil Sands environment. This factor could be highly relevant with respect to for example the seasonal cycles and could warrant specific cultivation strategies that include freeze/thawing as a prerequisite of the microbial communities.

A wealth of microbial species was observed over a wide range of environments, with significantly different metabolic properties. This diversity is key to (i) easily removing recalcitrant NAs, (ii) allow application in varying OSPW reservoirs and habitats, (iii) allow more engineered environments that reward more complex combination of characteristics.

During the investigation of inhibiting and limiting compounds in OSPW reservoirs, OPE encountered a significant effect where limiting nutrients were cycled between microbial communities that did not participate in the NA degradation, due to the presence of easier cyclable organic material. The natural presence of decaying organic material seems to affect the microbial community composition, eliciting competition for growth factors other than carbon, and therefore other than NAs. Transient degradation improvements could be achieved with nutrient supplication, but its effectiveness was highly dependent on the timing with respect to the microbial community members that were dominant. This principle could be a key factor in the naturally observed degradation rates and be a contributing insight for the eventual solution for the Passive Organics Treatment.

PRESENTATIONS AND PUBLICATIONS

Conference Presentations/Posters

- OSIS 2019 presentation (04-Jun-2019): Microbial Community Engineering in the Oil Sands

Reports & Other Publications

- COSIA blog (06-Feb-2020) “Training Microbes to do a Better Job”: https://www.cosia.ca/blog/training-microbes-do-better-job

- COSIA Oil Sands Innovation Summit - (03-Apr-2018) Biotechnology Solutions for Passive Organics Treatment

- Nexen / COSIA (11-Mar-2014) Biotechnology Opportunities in the Oil Sands

RESEARCH TEAM AND COLLABORATORS

Institution: OPE Group B.V., Leiden, The Netherlands

Principal Investigator: M. Martens

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Mathijs Martens	OPE Group	MSc, Managing Director		
Paul Spelt	OPE Group	MSc, Business Director		
Gerben Stouten	OPE Group	PhD, Scientific Director		

Application of Ceramic Nanofiltration Membranes for Water Treatment in Oil Sands Mines

COSIA Project Number: WJ0014

Research Provider: Canadian Natural

Industry Champion: Canadian Natural

Industry Collaborators: Canadian Natural, Alberta Innovates Technology Futures ("AITF"), Fraunhofer IKTS, Andreas Junghans

Status: Complete

PROJECT SUMMARY

The ability to reuse mine process water as feed to the utilities plant is often restricted by contaminants. Typical water treatment technologies such as reverse osmosis are very susceptible to bitumen and fine solids fouling. In addition, conventional polymeric nanofiltration membranes cannot withstand the harsh conditions encountered when treating the oil sands process water. These drawbacks on water treatment require the use of river make up water for utilities plants. One of the environmental goals of the oil sands industry is to minimize its use of fresh water. A more robust water treatment technology would minimize fresh water make up intake for mining utility operations, which could be extended to in-situ operations. Ceramic nanofiltration membrane technology is considered a promising technology for the treatment of oil sands process water. A membrane technology that can operate effectively on a wide range of water quality conditions (temperature, pressure, organics, clay and sand) will allow operators to recycle more water.

This project focuses on the application of ceramic nanofiltration membranes on produced water treatment in oil sands mines for commercial application. The project started on June 1, 2015 with the testing of a small scale (5 m^2) Titania (TiO_2) nanofiltration membrane system with financial support from AITF. The initial results were very encouraging and lead to the upscaling of the ceramic membrane unit. A Titania (TiO_2) Membrane De-risking Unit (TDU) was built to test the boundary conditions and limitations of a semi-commercial scale. The TDU consists of two 40 ft. sea-containers, 4 ceramic nanofiltration membrane units in series, with a 20 m^3/h feed capacity and fully automated. The Titania membrane has a 0.9 nanometer (nm) average pore size. With the acquisition of Albian assets by CNRL, the semi-commercial unit was transferred to the latter company (not the 5 m^2 unit). The TDU project started in the field early 2017 with closing activities in 2019.

Uncertainties of testing the TDU include the performance of the membranes under an ample range of process water qualities, and its effect on the membrane permeability. Another set of uncertainties involve the performance of the system and membranes at high recovery rates, and high operating pressures, as well as the rate of fouling that increases the frequency of membrane clean up and replacement.

The main objective of the project is to determine the performance of the TDU to treat process water in an oil sands mine. Performance is measured as produced water flow and quality (ion and solids rejection) under undisturbed mining processing conditions. Feed water to the unit has the same quality used in current oil sands processing. It is expected that after the project enough information will be collected and analyze to determine the use of TDU commercially and showcase its advantages over current water treatment methods. Titania membranes are more resistant to fouling, allowing for easier maintenance and a longer lifespan. To date no field tests have been performed with ceramic nanomembranes to treat water of mineable oil sands.

PROGRESS AND ACHIEVEMENTS

The construction of TDU was completed in 2015 in Germany, shipped to a Canadian oil sands mine site and connected to the recycle water supply at the utilities plant. Site construction, tie-ins and hookups of the skid were completed in late 2016. The TDU started to be tested in January 2017 with recycled oil sands process water under different process conditions. The TDU was down from late August 2017 until middle of January 2018 due to a failure of a electro - mechanical part of the system that could not be quickly replaced due to a global shortage of this part from the vendor.

The key performance indicators used for the different tests have been ion and component rejection (defined as the ratio of ions in permeates vs. feed) and quality improvement or membrane efficiency (defined as the ratio of water quality in permeates vs. feed). Other performance indicators are fouling rate and effectiveness of self-cleaning protocol, stability of operation, ion selectivity (ratio of divalent ion rejection vs. monovalent ion rejection), and data and sampling collection.

The TDU was tested for almost two years under actual oil sands recycled process water characteristics. No chemical or physical pre-treatment of the recycled process water was used during any of the tests. The tests evaluated in this work where done at stage cuts (ratio of permeate over feed) of 50% or higher. A dramatic difference in clarity was observed between the recycle process water fed to the TDU and the produced permeate streams in all cases. Results to date show a strong correlation between trans-membrane pressure (TMP) and ion and component rejection. Total Suspended Solids (TSS) were rejected almost 100%, which was expected considering that the pore size of the used membranes is 0.9 nm. Total Organic Carbon (TOC) rejection was above 75% at all conditions. This is a very encouraging result in terms of water usage in the oil sands mining process, since most of the organic components are coming from residual bitumen. Divalent ions, such as calcium and magnesium, have been rejected up to 60%. Monovalent ions like sodium and potassium have shown rejection values of up to 50%.

Overall, the results indicate that it is possible to implement ceramic nanofiltration membranes in the oil sands mines and obtain significant water quality improvements, with no pre-treatment, which could reduce river water intake due to a higher level of water quality. The experimental program for the TDU project has been fully and successfully executed to date.

LESSONS LEARNED

The use of ceramic nanofiltration membranes is novel for the oil sands mining industry. The ability of these membranes to resist fouling, remove the ultrafine solids and bitumen, and partial removal of ions has been demonstrated in proof of concept experiments and further demonstrated in a field semi-commercial setting at Albian Sands.

The main learnings from the TDU testing program so far are:

- High ion concentration reduction is observed for multi-ionic systems with high solids content and dispersed organic material, such as oil sands processing water streams. A higher reduction is generally achieved at higher trans-membrane pressure and with a low stage cut.

- Divalent and monovalent ions are rejected differently, and total organic carbon (TOC) and total suspended solids (TSS) are almost completely rejected with the TDU. The differences in ions rejection could be due to a combination of phenomena such as sieving, electrostatic phenomenon, and differences in ions diffusion coefficients.

- In terms of equipment, the rotating components of the unit have worked well considering the relatively high fine solids content found in the process water. The robustness of the electrical components could be improved in future semi-commercial prototypes, or in a large scale of the system.

The current results show that ceramic nanofiltration membranes have the potential to be used as a single step water treatment process prior to a reverse osmosis system (RO). Some of the current water treatment systems in oil sands involve a combination of two water treatment processes, such as microfiltration (MF) and ultrafiltration (UF), prior to a reverse osmosis system. With these results in mind, the TDU and similar technologies could be applicable in diverse areas of the oil sands (and oil and gas) industry, such as:

- Treatment of recycled water in Utilities areas of oil sands i.e. boilers, cooling towers.

- Thermal assets, water conditioning for produced water recycling and steam production – reduction of injection well scaling

The amount of membrane modules required for a specific application should consider the main process criteria (ion rejection, TOC rejection, water quantity/stage cut) since a compromise may be necessary. For example, the unit could be used for high stage cuts (> 80%) and high TOC rejection but with a compromise on water quality (low to medium ion rejection). Determining the optimal operating envelope of the TDU should be part of future de-risking processes.

PRESENTATIONS AND PUBLICATIONS

No public presentations and publications available.

RESEARCH TEAM AND COLLABORATORS

Institution: Canadian Natural

Principal Investigator(s): Sandra Motta Cabrera, Tailings Engineering Supervisor; Gavin Freeman, Lead Process Innovation

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Eric Saulnier	Canadian Natural	Field Operator	N/A	N/A
Rick Nelson	AITF	Project Evaluator	N/A	N/A

Calcite Treatment Technology Review

COSIA Project Number: WJ0029

Research Provider: Teck

Industry Champion: Teck

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

The project reviewed test work and studies conducted by Teck for the treatment of calcite saturated water and conducted a technology scan to identify other calcite treatment technologies capable of meeting the discharge permit objectives for non-oil sands mining assets. It emphasized assessing alternative calcite treatment technologies to anti-scalants, as anti-scalants are not proven calcite removal, and may pose an environmental risk if used in streams with high constituents of potential concern (COPC). For Teck's non-oil sands mining assets, these COPC include; cadmium, nickel, and selenium, to name a few. The treatment of calcite-saturated water may have an adverse effect on COPC as the co-precipitation with calcite reduces their concentrations in the water. The report does not select a technology for implementation, rather identifies technologies to evaluate further.

PROGRESS AND ACHIEVEMENTS

Water softening or hardness removal is well understood, especially in the context of scale prevention and removal in heat exchangers and cooling towers. However, the application of calcite treatment technologies in the mining industry for calcite removal and prevention in freshwater streams is relatively new.

The project ranked treatment technologies in the table below considering; key process data, treatment effectiveness, capital and operations cost, and liquid/solid waste generation was completed, and the findings were summarized in a report.

The table below shows the different technologies and their ranking based on the treatment objective.

Treatment Objective				
Rank	Calcite prevention in high COPC environments	Calcite removal in high COPC environments Score	Calcite Prevention Score	Calcite Removal Score
Highest Ranked	*Fluidized Bed Reactor/Crystalactor*	*Creek Excavation*	*Acid addition*	*Creek Excavation*
	IDE's MaxH2O DESALTER	*IDE's MaxH2O DESALTER*	*Fluidized Bed Reactor/ Crystalactor*	*Acid addition*
	ZVI	Fluidized Bed Reactor/Crystalactor	IDE's MaxH2O DESALTER	IDE's MaxH2O DESALTER
	MICP via urea hydrolysis	ZVI	Spray Chamber	Fluidized Bed Reactor/ Crystalactor
	EICP via Carbonic Anhydrase	MICP via urea hydrolysis*	MICP via urea hydrolysis	MICP via urea hydrolysis*
	Pond treatment with PCC	EICP via Carbonic Anhydrase*	EICP via Carbonic Anhydrase	EICP via Carbonic Anhydrase*
	Trickling Filter	Pond treatment with PCC*	ZVI	Pond treatment with PCC*
	Media Bed	Trickling Filter*	Pond treatment with PCC	Trickling Filter*
	CAPS	Media Bed*	Media Bed	Media Bed*
	Cascade	CAPS*	Creek Excavation*	CAPS*
	Acid addition*	Cascade*	Trickling Filter*	Cascade*
Lowest Ranked	Spray Chamber*	Acid addition*	CAPS*	Acid addition*
	Creek Excavation*	Spray Chamber*	Cascade*	Spray Chamber*

LESSONS LEARNED

Based on the technology evaluation analysis, fluidized bed reactors (FBRs) and IDE's MaxH2O DESALTER scored the highest and second highest, respectively for calcite prevention in high-COPC environments. For calcite removal, creek excavation and acid addition ranked first and second, respectively. In water where there are high-COPC, creek excavation and IDE's MAxH2O DESALTER scored first and second, respectively. Acid addition and FBRs scored the highest and second highest for calcite prevention in environments where COPC is not a concern.

Technologies are at different stage of development hence, depending on the circumstances, additional bench scale or pilot work is required to implement on the field.

PRESENTATIONS AND PUBLICATIONS

Internal Technical Services Report 2019RR03

RESEARCH TEAM AND COLLABORATORS

No external research teams or collaborators.

Demonstration of Biochar and Ash to Sequester Zinc and Cadmium

COSIA Project Number: WJ0042.1

Research Provider: University of British Columbia

Industry Champion: Teck

Industry Collaborators: None

Status: Ongoing

PROJECT SUMMARY

A research project between UBC and Teck Resources Ltd. was initiated to test the effectiveness of using Biochar and or pulp mill ash as adsorbents for metal ions zinc (Zn+2) and cadmium (Cd+2) in order to reduce the concentrations of these in water. Five commercially available biochars and five pulp mill boiler ashes were tested.

PROGRESS AND ACHIEVEMENTS

Only the steam-activated Biochar from one vendor removed appreciable amounts of Zn from a 500mg/L solution: 99% removal and a capacity of 10.3mg Zn/g biochar. All five of the pulp mill boiler ashes removed close to 100% Zn: 9.8 –10.4mg-Zn/g Biochar.

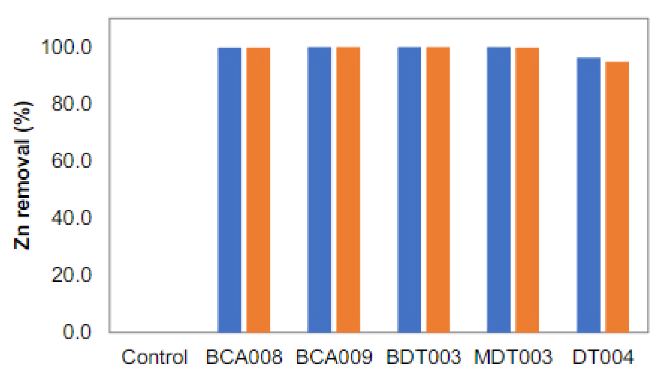


Figure 2 – Zn removal using biochar-rich, mineral-rich and as-received ash: absence of sulfate (■) and in the presence of sulfate ([SO_4^{2-}]=730mg·L^{-1}) (■). Control: sacrificial testing tube with no adsorbent. [Zn(II)]$_{t=0}$=500mg·L^{-1}; t=24h; adsorbent load=50g·L^{-1}; T=25°C; 250rpm

LESSONS LEARNED

- Fly ash is a better option for zinc removal than biochar in synthetic solutions.
- The mechanism of removal will be investigated in order to determine the stability of zinc on the surface of the adsorbent material.
- The work demonstrated that pulp mill ash residues and Biochar can be a cost-effective alternative for the recovery of zinc from MIW. Both fractions of the ashes, biochar and mineral-rich, were able to remove zinc.
- Further work is required to determine:
  - Recovery of Zn over a range of concentrations typically found in mine-impacted water on many non-oil sands mine sites.
  - The effect of competing anions and cations in mine-impacted water (other than sulfate) on the recovery Zn.
  - The kinetics of Zn adsorption.
  - The mechanisms involved.
  - Leaching of other elements from the ashes when used for Zn recovery.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: University of British Columbia

Principal Investigator: Dr Susan Baldwin

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Suellen Satyro	University of British Columbia	PhD		

Microbiology Program – MiniPilots for Nitrate and Selenium Removal Report

COSIA Project Number: WJ0042.2

Research Provider: None

Industry Champion: Teck

Industry Collaborators: None

Status: Completed

PROJECT SUMMARY

Three MiniPilot designs were evaluated for their ability to mimic Fluidized Bed Reactor (FBBR1) nitrate and selenium treatment at a water treatment facility: upflow reactor (UFR), continuously stirred tank reactor (CSTR), and a continuously stirred tank reactor with a basket stirrer (CSTRB). The three minipilot designs were subjected to two stages of testing. The first stage of testing evaluated responses to modified hydraulic retention times. After the UFR was determined to be the more effective design, an optimized version of the UFR (Biowheel UFR) was used during the second stage of testing in order to evaluate chemical oxygen demand (COD) to nitroigen ratios. The UFR treated nitrate and selenium most similarly to the full scale FBR1, achieving near complete removal of nitrate with a simultaneous conversion of Se(VI) to Se(IV). Results from the MiniPilot evaluation have confirmed that similar results to the full-scale FBR1 system can be achieved with the UFR design. It is recommended that future MiniPilot work utilize the UFR design as it mimics FBR1

PROGRESS AND ACHIEVEMENTS

The best design, in terms of operations, was the optimized biowheels UFR. This setup achieved reducing conditions faster and more consistently than the other mini reactors. Some of the challenges with the other units include air intrusions, plugging and inconsistent nitrate treatment. In comparison, the UFR designs consistently achieved below 0.5 mg/L nitrate as N at the 5:1 COD:N ratio at a 0.5 hr hydraulic retention time (HRT). During COD:N ratio testing with the Biowheel UFR design in Stage 2, nitrate and nitrite concentrations responded as expected with greatest removal at the highest ratio tested (7.5:1 ratio on average having 0.38 mg/L nitrate and 0.25 nitrite as N in outflow) and least removal at the lowest ratio testing (3:1 ratio on average having 5.11mg/L nitrate and 2.16 mg/L nitrite as N in outflow). In comparison, at the 5:1 COD:N ratio the Biowheel UFR had on average 0.67 mg/L nitrate and 0.52 –1.37 mg/L nitrite as N in the outflow. The UFRs required a 0.5 hr HRT in order to achieve near complete removal of nitrate, and to convert Se(VI) to Se(IV) with minimal removal of selenium (i.e., formation of elemental Se). The nitrate and dissolved selenium outflow concentrations responded as expected to COD:N ratio modifications, with more nitrate and dissolved selenium removal occurring at higher COD:N ratios.

LESSONS LEARNED

Results from the MiniPilot evaluation have confirmed that similar results to the full-scale FBR1 system can be achieved with the UFR design. It is recommended that future MiniPilot work utilize the Biowheel UFR design as it closely mimics FBR1 without the operational challenges associated with the CSTRs and CSTRBs. A loose packing material (such as biowheels) should to be used as minimal blockage issues occurred without compromising treatment. The Biowheel UFR design could be also resized to decrease water volumes needed.

Based on results from these trials, aspects that could be tested at MiniPilot scale include:

- Comparing different carbon sources and mixed sources (e.g., acetic acid and methanol),
- Switching carbon sources,
- COD dosing,
- Other levers such as temperature, pH, addition of nutrients.

PRESENTATIONS AND PUBLICATIONS

Teck WLC Microbiology Program – 2019 MiniPilot Treatment Stages Report. Document #034_1019_67B; November 2019

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Vanessa Friesen	Contango Strategies	PhD		
Clemente Miranda	Teck	PhD		

Statistical Evaluation of Microbiology Ecology Data to Operational Data in Selenium Treatment Reactors

COSIA Project Number: WJ0042.3

Research Provider: Barr Engineering

Industry Champion: Teck

Industry Collaborators: None

Status: Completed

PROJECT SUMMARY

The goal of the project was to assess correlations between microbial ecology data and operational data to inform development of potential operational tools. There is limited precedent in wastewater or academic literature of facilities using microbial ecology data to directly inform operations. Microbial ecology data collected included 16S ribosomal RNA (rRNA) community profiles, adenosine triphosphate (ATP) measurements, and microscopy data. The work focused on data collected from the selenium treatment facility over the last four years. The statistical correlation evaluations primarily focused on data collected since system restart in October 2018.

PROGRESS AND ACHIEVEMENTS

Several dominant microbial groups were correlated to production of reduced selenium species. When these species were further evaluated to determine operational conditions that support or inhibit them, the operational parameters identified as likely to limit reduced selenium in the effluent were typically the same parameters identified through direct pairwise correlation of operational parameters and effluent reduced selenium. As such, the direct application of microbial ecology data to inform plant operation supported the operational findings but did not explicitly define unique opportunities to guide operations. The table below shows the drivers for selenium reduction and the microbial community composition.

Reactor	Drivers of Selenium Speciation(2)	Drivers of Microbial Community Composition(2)
FBR1	Methanol feed rate, total flow, ORP, nitrate, temperature, flow sources	Total flow, ORP, temperature, flow sources
FBR2	Total flow, pH, ORP, temperature, flow sources	Total flow, temperature, flow sources
MBBR	Influent COD, temperature, flow sources	Temperature, flow sources, plant flow through

FBR- Fluidized Bed Reactor, MBBR – Moving Bed Biofilm Reactor

LESSONS LEARNED

- Microbial community composition is not useful for day-to-day operations of water treatment facilities for several reason. The main reason is the long turn-around time for results.
- Microbiology data provides several benefits:
  - Microbial community composition can provide an operational baseline to understand what “good” performance looks like and to help understand potential causes of system upsets by identifying likely metabolic activity of dominant microbial groups.
  - Specific growth preferences of microbial groups that have been well-characterized in other applications can be used to select or inhibit abundant microbial groups identified as beneficial or problematic in the targeted application.
  - Microbial diversity measurements can serve as an indicator of reactor stability.
  - ATP data correlated strongly to some reduced selenium species and may be a useful real-time measurement of microbial activity and reactor performance.
  - Microscopy data, especially related to abundance of filaments, may be a good real-time indicator of poor reactor health in the MBBR.
- Databases completeness and available genera information was limited in some cases, especially for Selenium reducing bacteria. Additional fundamental work will be required in the area.

PRESENTATIONS AND PUBLICATIONS

Internal Report Teck Technical Services 2019RR07

Barr Engineering Report Statistical Evaluation of Microbiology in Selenium Treatment Reactors, Jan 2020

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Ali Ling	Barr Engineering	PhD, PEng		

Quenching of AOP Ozone and Peroxide Residual using Sodium Sulfite

COSIA Project Number: WJ0042.4

Research Provider: None

Industry Champion: Teck

Industry Collaborators: None

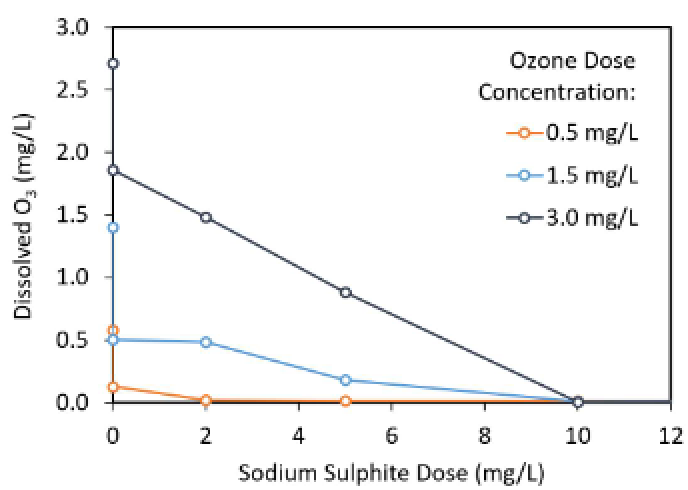
Status: Complete

PROJECT SUMMARY

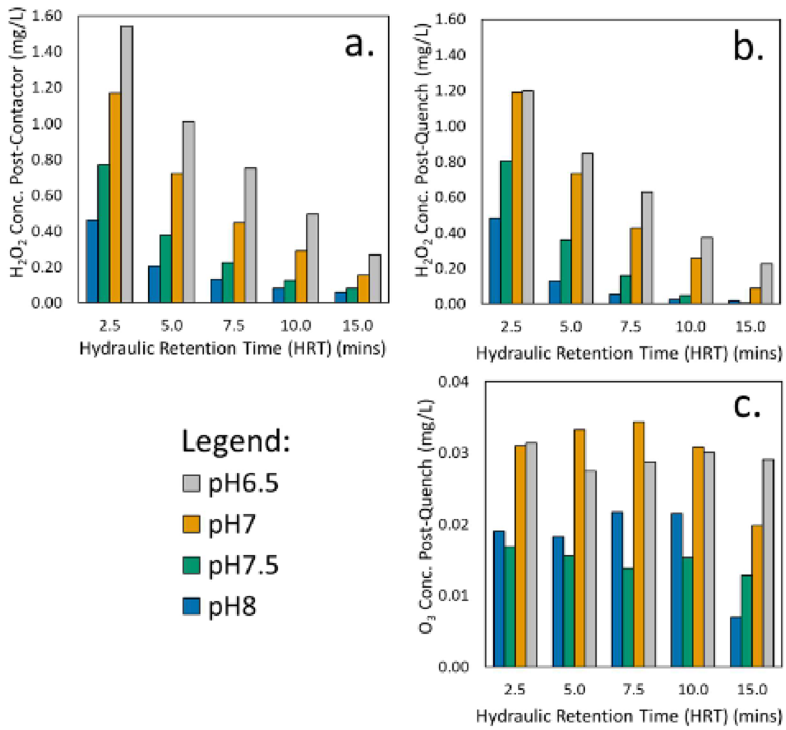
As residual O_3 and H_2O_2 in the AOP-treated water could contribute to toxicity of the final effluent, these compounds must be removed to concentrations below 0.01 mg/L and 0.4 mg/L, respectively. This is achieved after the AOP contactor, in a subsequent process step called quenching using sodium sulphite (Na_2SO_3). Based on experimental data generated from this work, a Na_2SO_3 concentration of 10 mg/L in the quench tank was necessary to achieve concentrations of residual O_3 below 10 µg/L when the residual O_3 concentration in the contact tank effluent was 1.5-3.0 mg/L. Overall, Na_2SO_3 was not effective in removing residual H2O2 at the tested HRTs.

PROGRESS AND ACHIEVEMENTS

At all concentrations of initial dissolved O_3 (0.5-3.0 mg/L) after the contactor, the reduction in the O_3 concentration followed a linear trend with the concentration of sodium sulfite.



Overall, higher hydraulic retention time (HRT) resulted in lower H_2O_2 concentrations post-contactor at all pH values tested. The significant decrease in the concentration of H_2O_2 (>95%) from an initial concentration of 3.0 mg/L, is largely attributed to its reaction with O_3 in the contactor as little H_2O_2 removal is seen in the quench tank. Higher pH values also led to higher removal of H_2O_2 in the contactor.



LESSONS LEARNED

- At a residence time (HRT) of 5 min in the quench tank, a concentration of 10 mg/L sodium sulfite (Na_2SO_3) was required to quench dissolved O_3 at concentrations ranging between 1.5 and 3.0 mg/L exiting the contactor.
- Addition of Na_2SO_3 insignificantly reduced the H_2O_2 concentration in the quench tank. Removal of H_2O_2 is mainly due to reaction with O_3.
- Increasing HRT in the contactor decreased residual H_2O_2. At HRT's longer than 10 min very low H_2O_2 concentrations (< 0.2 mg/L) were observed leaving the contactor.
- Granular activated carbon (GAC) is a promising alternative technique for both H_2O_2 and O_3 removal. An empty bed contact time (EBCT) of 4 minutes provided effective removal of H_2O_2 (to below 15 µg/L) and O_3 (to below 5 µg/L).
- Further work on analytical techniques for H_2O_2 assays and alternative quench process options is highly recommended.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Andrew Holmes	Geosyntec Consultants	PhD		

Wetland Treatment of Oil Sands Process-Affected Water

COSIA Project Number: WJ0046

Research Provider: Simon Fraser University

Industry Champion: Imperial

Industry Collaborators: None

Status: Year 5 and On-going

PROJECT SUMMARY

Large volumes of oil sands process-affected water (OSPW) has been generated through mining operations and bitumen extraction in the Canadian oil sands. The Canadian oil and gas industry have successfully reduced water requirements during bitumen extraction; but to date industry has adhered to a zero-release practice. Treatment technologies are being evaluated to reduce the ecological footprint and mitigate the risks of OSPW. To date, industry has sought to find feasible treatment solutions that have the potential to improve water quality of OSPW. Treatment wetlands have emerged as viable solutions to various wastewater challenges including municipal and domestic wastewater, mine water, agricultural runoff, leachate, and industrial wastewaters. Despite their success in various applications around the world, industrial application of treatment wetlands for treating OSPW in Canada is in its early stages. To investigate the application of treatment wetlands in the Canadian oil and gas industry, a 1-ha surface-flow wetland was constructed on Imperial's Kearl Oil Sands site.

The overall goal of the study is to improve the science of treatment wetland technology in Canada's oil sands. Passive sampling using polyethylene (PE) and polar organic chemical integrated samplers (POCIS) provided a cost-effective method to measure freely dissolved polycyclic aromatic hydrocarbons (PAHs) and naphthenic acids (NAs), respectively in the OSPW entering and leaving the wetland. With this data, wetland treatment efficiency was evaluated, and a contaminant-fate model has been applied and tested for neutral organic contaminants. A contaminant-fate model will be used to assess the feasibility of treatment wetlands for mitigating various wastewater challenges. The model will help to identify which contaminants can be removed via wetland treatment. Further, to effectively communicate treatment efficiency of the wetland for OSPW contaminants, the change to OSPW toxicity will be quantified and integrated into these modelling efforts. The specific objectives of this project are to:

(i) investigate the ability of the Kearl Treatment Wetland to treat OSPW from Kearl Oil Sands site (Imperial Oil Resources Ltd.) in northern Alberta,

(ii) apply, test, and calibrate a contaminant-fate model of the Kearl treatment wetland,

(iii) measure toxicity of wetland influent (OSPW) and effluent (treated OSPW), and

(iv) correlate this toxicity data with the profile of OSPW contaminants.

PROGRESS AND ACHIEVEMENTS

Industrial wastewater was introduced into the wetland in 2017, 2018, and 2019 to investigate the removal of contaminants by passive wetland treatment. Polyethylene (passive) samplers (PES) and Polar Organic Chemical Integrative Samplers (POCIS) were deployed in the KTW to measure freely dissolved concentrations of PAHs and NAs, respectively. Table 1 shows the deployments of the passive samplers in the wetland through the course of the project.

Table 1: Deployments of passive samplers in the wetland.

Year	Start	Sampler deployed

2017	July 21 August 28	PES PES
2018	August 25	PES + POCIS
2019	May 12 June 9	POCIS POCIS

Polycyclic Aromatic Hydrocarbons (PAHs)

Average concentration-reduction was measured at 72 (SD 18)%, 32 (SD 31)%, and 50 (SD 26)% for each of the three deployments, respectively. Large variability in E_C was observed for individual PAHs which ranged from 0% (i.e. no statistical differences in concentration through the wetland) to 92% for fluoranthene during the first deployment. This treatment produced reductions in the concentrations of total PAHs in OSPW from 56% to 82%. In some cases, the concentrations of certain PAHs in the effluent fell below the regulatory criteria values as a result of the wetland treatment.

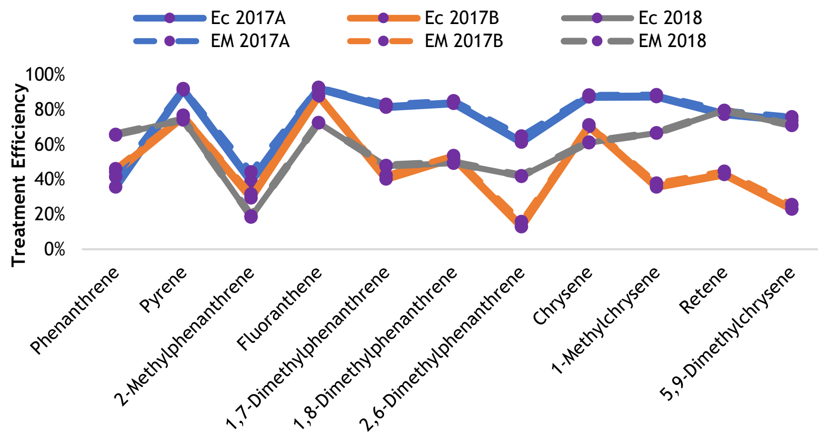


Fig. 1: Concentration-reduction (E_C) and mass-removal (E_M) efficiency for polycyclic aromatic hydrocarbons measured with PES in the Kearl Treatment Wetland. Purple data points represent statistically significant change in concentration ($p < 0.05$).

NAs ($C_nH_{2n-z}O_2$)

The relative abundance of the NAs is greatest for O_2-NAs with carbon numbers (n) of 13 to 15 and Double Bond Equivalents (DBE) = 3 or 4 (z = -4 or -6), for all three POCIS deployments.

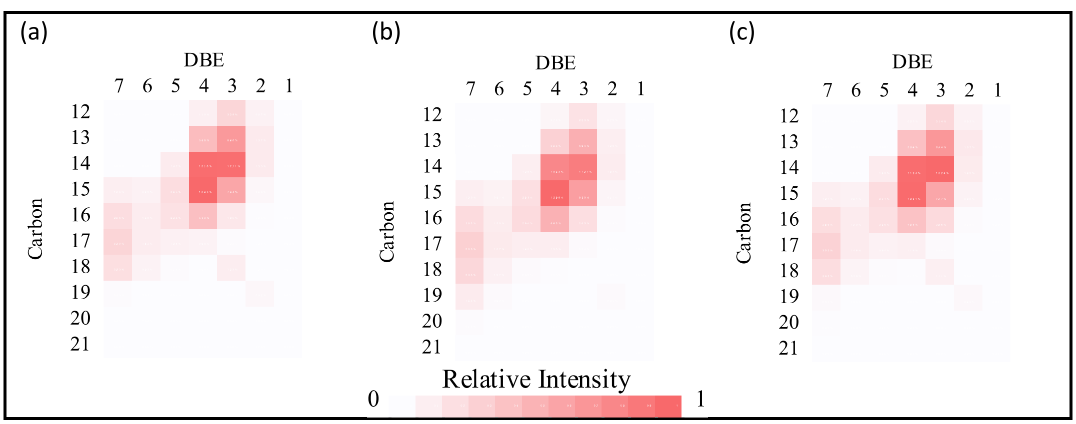


Fig. 2: Relative distribution of NA concentration in OSPW on day 0 for all three POCIS deployments at the KTW.

Total O_2-NA concentration in OSPW entering the wetland for each deployment was measured at 19.7, 20.7, and 13.3 mg/L, respectively. The concentration of individual O_2-NAs in OSPW entering the wetland ranged from 2 224 ng/L to 2680 ng/L . The average E_C for each deployment was 13.2, 62.0, and 3.2%, respectively over all NAs detected in the POCIS samples. Statistical analysis indicates that both carbon number and DBE are strong predictors of E_C ($p < 0.01$).

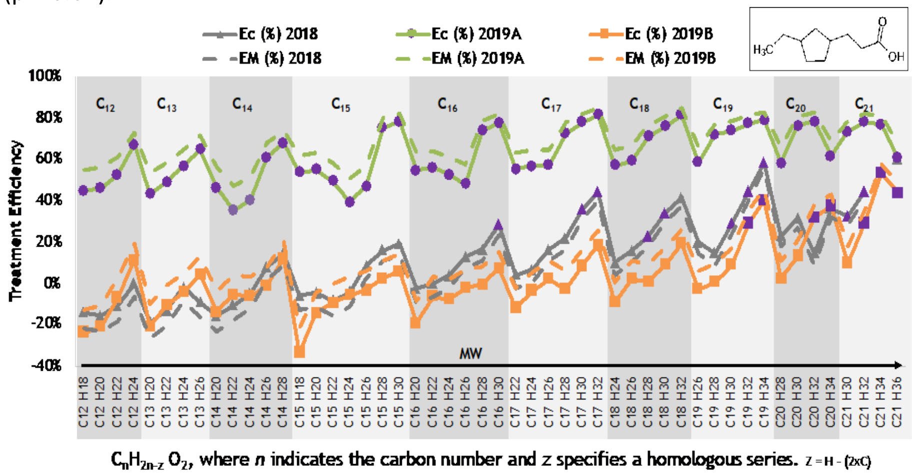


Fig. 3: Concentration-reduction (E_C) and mass-removal (E_M) efficiency for naphthenic acids measured with POCIS in the Kearl Treatment Wetland. Purple data points represent statistically significant change in concentration ($p < 0.05$).

Model Development

Model parameterization to the KTW was completed to set up model application and testing. Fig. 1 illustrates the model performance by showing the model estimated and empirically derived effluent concentrations for all PAHs measured in the KTW. Overall model bias shows low systematic bias of the model estimations for PAHs of 0.98 (0.73 – 1.31) and for NAs of 1.02 (0.94 – 1.12) for the steady-state version of the model. The model estimates the contributions of various biogeochemical removal mechanisms. Further testing and model applications will help to understand wetland treatment dynamics for various chemicals.

The data collected from the 2017-2019 campaign for the Kearl Treatment Wetland allows us to investigate the treatment efficiency for PAHs and NAs (objective 1). The contaminant-fate model has been developed for neutral organic contaminants (i.e. PAHs) and for ionisable organic contaminants (i.e. NAs; objective 2). Efforts to investigate OSPW toxicity entering and leaving the KTW have begun and will be incorporated into the model to help better understand changes to OSPW toxicity through wetland treatment.

LESSONS LEARNED

The results from the 2017-19 investigations demonstrate the capacity for the Kearl Treatment Wetland to reduce concentrations of PAHs and NAs in OSPW. Our results show specific congeners of NAs are more susceptible to wetland degradation. Higher concentration reductions are shown for NAs with lower DBE compared to other NAs within the same carbon group.

Our data suggest treatment wetlands may be an effective tool to help treat OSPW. The calibrated model can be used to evaluate the fate of hydrophobic organic contaminants in oil sands process wastewaters and allows companies such as Imperial to estimate treatment efficiency and feasibility of these systems for specific wastewater challenges. It also demonstrates the roles of different biogeochemical removal mechanisms, showing that biodegradation is a critical mechanism for contaminant removal. At the resolve of the 2017-19 study, we have established a successful sampling plan to measure contaminants of concern in OSPW using polyethylene samplers and POCIS. We will continue with our investigative approach to quantify chemical removal and OSPW treatment in the KTW, and we will expand our modelling framework to incorporate measure of toxicity into our contaminant-fate modelling.

PRESENTATIONS AND PUBLICATIONS

Conference Presentations/Posters

Cancelli, A. M., Gobas, F. A.P.C., Bekele, A. (2019). *The removal of organic contaminants from OSPW in the Kearl Treatment Wetland.* Society of Environmental Toxicology and Chemistry, 40th North American Annual Meeting, Toronto, ON.

Cancelli, A. M., Gobas, F. A.P.C., Bekele, A. (2019). *The removal of organic contaminants from OSPW in the Kearl Treatment Wetland.* Canadian Oil Sands Innovation Alliance, Oil Sands Innovation Summit, Calgary, AB.

RESEARCH TEAM AND COLLABORATORS

Institution: Simon Fraser University

Principal Investigator: Frank A.P.C. Gobas

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Prof. Frank A.P.C. Gobas	Simon Fraser University	Professor		
Alexander M. Cancelli	Simon Fraser University	Ph.D. Student	2014	2020

Tailings Water Treatment Plant Engineering Design Specifications

COSIA Project Number: WJ0051

Research Provider: None

Industry Champion: Suncor

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

Suncor contracted an EPC company in 2012 to complete the Engineering Design Specification (EDS) for the Tailings Water Treatment Plant (TWTP) in Fort McMurray, Alberta, Canada.

The scope associated with the EDS phase of the Project includes preliminary, FEED-level design of the facilities required to treat tailings water from pond 7. The treated effluent from this plant will be of sufficient quality for reuse as boiler feed water and/or discharge to the Athabasca River. The TWTP is one component of an integrated site-wide water management plan, which itself is an environmentally driven project with significant stakeholder and reputation drivers.

PROGRESS AND ACHIEVEMENTS

Several options were evaluated that have the opportunity to reduce overall assembly/fabrication schedule or construction schedule in the field.

- Option 1 – Self-contained, weather-proof, prefabricated pods including process equipment/HVAC/fire protection, etc. with interconnections on slab – no building structure.
- Option 2 – Process equipment and building structure shipped from the assembly location and installed on-site by stacking prefabricated pods with process equipment or building components, to create one structure with shared utilities.
- Option 3 – Process equipment pre-installed and shipped on skids from the assembly site for final installation inside pre-engineered building on site.
- Option 4 – Process equipment pre-installed and shipped on skids for final installation inside pre-engineered fabric tent on site.

The TWTP design was developed over time, with the primary basis for it being membrane-based technology. Ultrafiltration followed by Reverse Osmosis (RO) was initially the selected design basis, then in the Design Basis Memorandum (DBM) engineering stage a dissolved gas flotation (DGF) - Polymeric Immersed Hollow Fibre Ultrafiltration - RO flow sheet was used. Later on, work was progressed to change to Ceramic Ultrafiltration-RO flow sheet due to improvements in reliability and operations as well as a neutral to positive LCVA comparison between the options.

The EDS report contains the details of the system design which was designed for a nominal capacity of 5,000 USgpm or 27 ML/d.

LESSONS LEARNED

No lessons learned to be shared at this point.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

None

Spray Evaporators for Water Management

COSIA Project Number: WJ0055, WL0088

Research Provider: None

Industry Champion: Suncor

Industry Collaborators: None

Status: Completed

PROJECT SUMMARY

Spray evaporators were examined as a potential tailings water volume management technique at Suncor's Base Plant Pond 7. The objective of the study was to quantify air emissions from a spray evaporator and to determine if the operation of spray evaporators resulted in an unacceptable change in ambient air quality when compared against standard limits.

The project involved measuring the air quality changes related to eight compounds from the spray evaporator. Continuous monitoring instruments located at the pond measured the concentration of the compounds in question and Airdar technology was used to measure the emission rates and variability of these compounds from the sprayer. Daily manual air samples (close to the evaporator) were taken by Suncor personnel and tested by laboratory, to confirm Airdar results and determine air quality within 20 ft of the evaporator.

PROGRESS AND ACHIEVEMENTS

While detectable emission rates from the pond spray evaporator were observed for benzene and toluene, the concentrations measured were below Alberta Ambient Air Quality Objectives (AAAQOs). The spray trial plume concentrations of benzene were not markedly higher than other major sources in the area. Toluene showed higher emissions concentrations from the sprayer than from other sources.

LESSONS LEARNED

The monitoring showed variability in the emission rates for benzene and toluene. The toluene emission rates shows three dominant sporadic emission events. The pump operator's report shows that these sporadic higher level emissions events occurred coincident with periods when the evaporator pump entrained hydrocarbon-rich water. The emission rate of toluene from the sprayer observed outside the three sporadic events was low. The timing of the observations of higher benzene emissions from the sprayer indicated that the intermittently elevated benzene emissions were affected by hydrocarbon-rich tailings water being inadvertently entrained by the pump.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

None

Treatment Threshold Validation for Passive Solar Photocatalytic Treatment of Oil Sands Process Water (OSPW)

COSIA Project Number: WJ0096

Research Provider: University of Toronto, H2nanO

Industry Champion: Canadian Natural

Industry Collaborators: Imperial, Shell, Suncor, Syncrude, Teck

Status: Complete

PROJECT SUMMARY

The COSIA Water Environmental Priority Area Steering Committee has identified a need for technologies to passively treat dissolved organic compounds present in Oil Sands Process Water ('OSPW'). A consortium of COSIA members, the Frank Gu Lab at the University of Toronto, and H2nanO Inc. conducted a series of studies from 2016 to 2018 demonstrating photocatalysis as effective treatment tool to transform dissolved organics, including naphthenic acids, in OSPW and eliminate Rainbow Trout ('RBT') and Fathead Minnow ('FHM') toxicity. The project has utilized a sunlight-powered photocatalytic treatment system developed by H2nanO called SolarPass™. In 2018, a series of treatment studies were performed with SolarPass on a cross-section of OSPW samples from surface mining operators. This project demonstrated the process was capable of treating a variety of OSPW chemistries. The combined treatment data elucidated a general rate model and threshold solar UV-light dose for elimination of RBT and FHM toxicity using photocatalytic oxidation.

The project aims to improve understanding of the solar photocatalytic treatment mechanism in OSPW through the application of advanced analytical chemistry techniques and algorithmic iterative analysis of the detailed chemistry datasets. The study examined the relationship of toxicity reduction in RBT and FHM bioassays and key chemical constituents, including selected naphthenic organics compounds, that may be correlated with toxicity across the various water chemistries of OSPW tested.

For this project, the research team:

1. Performed photocatalytic treatment on a series of OSPW samples from COSIA members;
2. Compared the treatment dose threshold and treatment extent with prior demonstration studies;
3. Appled high-resolution petroleomics chemistry datasets from partially and fully treated OSPW;
4. Evaluated chemical constituents' correlations with biological assays across varied OSPW chemistries.

With improved understanding of the specific chemical classes and constituents affecting the treatment dose threshold, photocatalytic oxidation treatment may be more effectively optimized for varied OSPW chemistries and develop improved chemical metrics to assess the extent and efficacy of treatment along with standard whole effluent toxicity analysis.

PROGRESS AND ACHIEVEMENTS

The initial analysis of as-received water quality demonstrated similar initial RBT and FHM mortality and growth inhibition to prior studies on the same OSPW sources.

The team conducted initial photocatalytic treatment tests on the OSPW samples received with preliminary characterization data indicated similar rate of treatment as observed in prior studies. Sample generation through addition treatment tests and processing for high-resolution mass spectrometry was completed towards receiving new datasets to add to the petroleomics analysis.

LESSONS LEARNED

Key findings for this study are forthcoming, however initial analysis of the OSPW samples as received indicated a consistency in the speciated water chemistry and degree of inhibition and mortality with RBT and FHM species. Results from the current study provided a strong basis for comparison in the photocatalytically treated OSPW samples forthcoming.

PRESENTATIONS AND PUBLICATIONS

Published Theses

Leshuk, T. Recyclable photocatalysts for oil sands process-affected water treatment. Doctoral Thesis, University of Waterloo, Waterloo, Ontario, Canada. 2018. https://uwspace.uwaterloo.ca/handle/10012/13262.

Journal Publications

Leshuk, T., Peru, K.M., de Oliveira Livera, D., Tripp, A., Bardo, P., Headley, J.V., Gu, F. *Petroleomic analysis of the treatment of naphthenic organics in oil sands process-affected water with buoyant photocatalysts*. Water Res., September 2018, 141, 297–306. https://doi.org/10.1016/j.watres.2018.05.011.

Leshuk, T., Krishnakumar, H., de Oliveira Livera, D., and Gu, F. *Floating photocatalysts for passive solar degradation of naphthenic acids in oil sands process-affected water*. Water, February 2018, 10 (2), 202. https://doi.org/10.3390/w10020202.

Leshuk, T., de Oliveira Livera, D., Peru, K.M., Headley, J.V., Vijayaraghavan, S., Wong, T., and Gu, F. *Photocatalytic degradation kinetics of naphthenic acids in oil sands process-affected water: multifactorial determination of significant factors*. Chemosphere, December 2016, 165, 10–17. https://doi.org/10.1016/j.chemosphere.2016.08.115.

Leshuk, T., Wong, T., Linley, S., Peru, K.M., Headley, J.V. and Gu, F. *Solar photocatalytic degradation of naphthenic acids in oil sands process-affected water*. Chemosphere, February 2016, 144, 1854–1861. https://doi.org/10.1016/j.chemosphere.2015.10.073.

Conference Presentations/Posters

Leshuk, T., Wilson, B., Young, Z., Gu, F. *SolarPass Water Treatment: Accelerated Passive Organics Treatment in OSPW.* Oil Sands Innovation Summit 2019. Calgary, AB, Canada, June 3-4, 2019.

Leshuk, T., Wilson, B., Young, Z., Gu, F. *SolarPass Water Treatment: Accelerated Passive Organics Treatment in OSPW.* COSIA 2019 Mine Water Release Science Workshop. Calgary, AB, Canada, October 22-23, 2019.

Gu, F., Leshuk, T., Paradis, T., Guest, R., Zubot, W., Bekele, A., and White, T. *Passive water treatment: remediation with solar catalysts.* Oil Sands Innovation Summit 2018. Calgary, AB, Canada, June 7-8, 2018.

Paradis, T., Gu, F., Leshuk, T., Guest, R., Zubot, W., Bekele, A., and White, T. *Passive water treatment: remediation with solar catalysts.* COSIA AM Annual Meeting. Calgary, AB, Canada, Nov 14-15, 2018.

RESEARCH TEAM AND COLLABORATORS

Institution: H2nanO Inc., and the University of Toronto

Principal Investigator: Dr. Frank Gu

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Dr. Tim Leshuk	H2nanO Inc. University of Toronto	Co-Founder Post-Doctoral Fellow, Chemical Engineering	-	-
Zac Young	H2nanO Inc.	Co-Founder	-	-

Research Collaborators:

InnoTech Alberta. Collaboration and services for petroleomic chemical analysis for OSPW treatment to identify and elucidate the benefits of the photocatalytic treatment process.

Clean Water Return Demonstration Pilot – Phase I

COSIA Project Number: WJ0132

Research Providers: Hatfield Consultants Inc, Limnotek Research and Development, Nautilus Environmental, Environment Canada and Climate Change (ECCC), University of Alberta

Industry Champion: Syncrude

Industry Collaborators: Suncor, Canadian Natural, Imperial, Teck, University of Alberta, Alberta Innovates.

Status: In-Progress

PROJECT SUMMARY

Since 1967, operators have subscribed to a "zero-release" practice for oil sands process water (OSPW), which is water that has been used for extraction of bitumen from ore. Water and fluid materials have been and continue to be stored in "out-of-pit" and "in-pit" tailings facilities. To reduce long-term containment requirements, minimize landscape disturbances, expedite terrestrial and aquatic reclamation activities, mitigate OSPW salinization, and achieve mine closure outcomes, appropriately treated water will have to be released to the environment.

Consequently, the oil sands industry has been conducting Research and Development activities to assess water treatment technologies and practices to treat OSPW for safe release to the environment. A key objective is to reduce concentrations of certain constituents present in OSPW to ensure the treated water can be released to the Athabasca River at a rate that is protective of human and ecological health. Previous studies have shown that contact between OSPW and petroleum coke, a by-product of Syncrude's Fluid Coking process, will reduce concentrations of dissolved organic compounds based on an adsorption process (Zubot et al 2012). Syncrude's Fluid Coking operation requires coke to be constantly withdrawn from the fluid coker. It is mixed with OSPW to form a slurry that is hydraulically transported by pipeline to a designated storage area. Presently, this is the Mildred Lake Settling Basin (MLSB). Following deposition of the slurry, the water runs off the beach and reports to the operational inventory of OSPW. However, a unique water treatment opportunity is possible if the slurry transport water is suitably isolated and collected. Operationally, this may be achievable by discharging the slurry into a dedicated containment structure with engineered underdrainage to allow collection of the porewater.

This is the basis of Syncrude's Water Return Demonstration Project (WRDP), which was partially commissioned in 2019. A simplified process flow diagram is provided in Figure 1 and shows the three treatment components (i.e., reactors) that comprise the process. Firstly, the petroleum coke (i.e., activated carbon) which is produced from the fluid cokers is mixed with OSPW (i.e., untreated water) that has been sourced from tailings ponds. The water/coke is then transported in a pipeline (Part 1) as a slurry and deposited into a large containment cell that is equipped with engineered under-drainage (Part 2). The hydraulically placed coke deposit contained within the earthen cell is subsequently under-drained to perform as a filter bed. The purpose of Parts 1 and 2 is to reduce concentrations of total suspended solids (e.g., clay particles), free phase hydrocarbons (e.g. bitumen) and dissolved organic constituents (e.g. naphthenic acids). Part 3 is the final stage of treatment. It is an aerated pond with an eight-day residence time to permit biological degradation of ammonia and to serve as a holding facility to allow for final water quality testing.

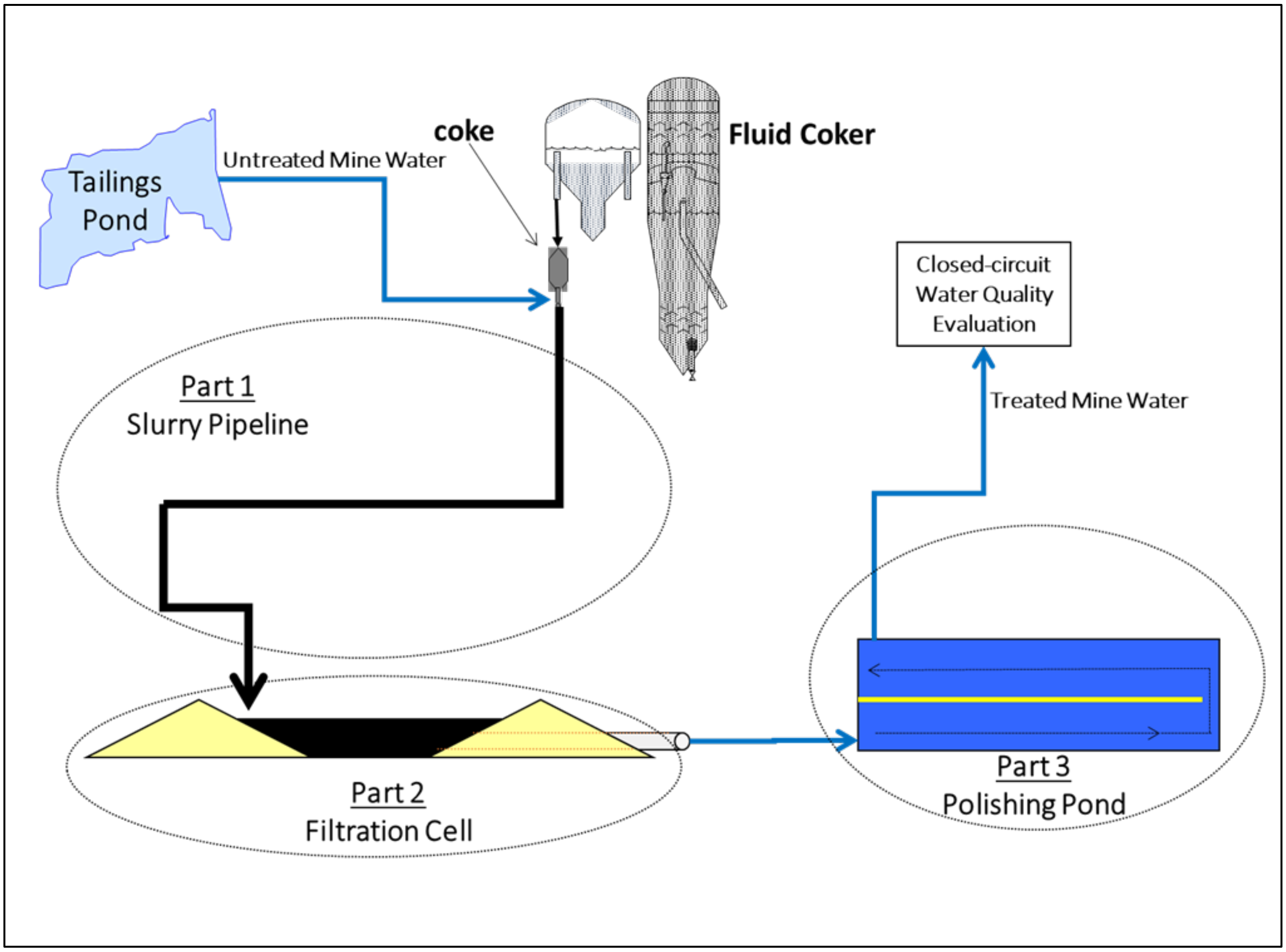


Figure 1: Three Reactor OSPW Treatment Process (WRDP)

The 2019 WRDP has been informed by a smaller pilot program that was completed at the Syncrude site in 2012. The 2012 pilot program involved the hydraulic deposition of freshly produced OSPW/coke slurry from an operating coke slurry line (Part 1) into two earthen containment cells (600 m^3 each) and two steel tanks (60 m^3). This enabled the water treatment performance of the contained coke deposits (Parts 2) to be assessed in quadruplicate. An aerial view of the commissioned pilot facility is shown in Figure 2. The Coker 8-1 coke slurry line is indicated in red and identified as Reactor 1. The coke deposits contained in the two cells and two tanks are identified as Reactors 2. As shown, a culvert housed the common pipe that was used to drain treated OSPW from the coke deposit and permit sample collection for laboratory analyses. The photograph on the right portion of Figure 2 shows one of the two earthen cells during commissioning. The underdrain pipe network was wrapped in geotextile fabric to facilitate drainage and manifolded to a common header which extended through the base of the dyke to form a single drain point. The rate of release of treated OSPW (i.e., water contained in the voids) was controlled via gravity drainage of the deposit. The 2012 program did not include a “Reactor 3 polishing pond” in the design and operation. The facility was operated as a closed-circuit process and the treated OSPW was directed to the operational OSPW inventory.

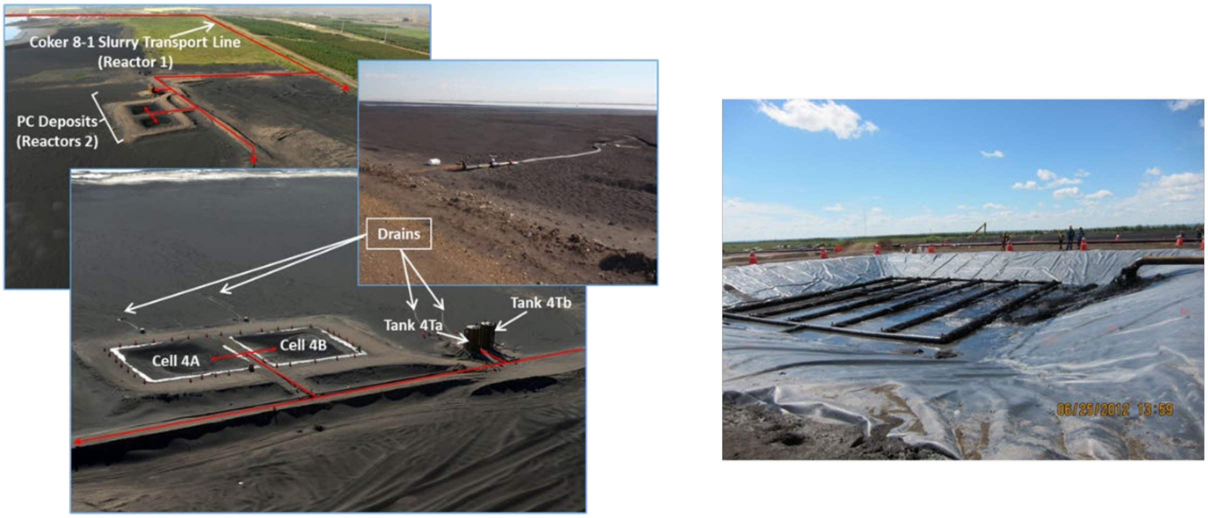


Figure 2: Commissioned 2012 Field Pilot

The 2012 pilot program examined the quality (i.e., physical, chemical and toxicological) of treated OSPW as a function of time within the coke deposit under natural climatic conditions. The treatment effectiveness was assessed by comparing the quality of untreated water (i.e., fresh OSPW contained in tailings structures) to the water produced from Reactors 2. The program indicates petroleum coke has significant potential to be utilized in a commercial scale water treatment process to permit treatment of OSPW for return to the environment. Key program findings are summarized as follows:

- Although the adsorptive capacity of petroleum coke is significantly less than commercially available activated carbons, Syncrude's Fluid Coking operation results in the production of coke in quantities that can potentially treat between about 8 and 12 Mm^3 of treated OSPW per year;
- The program has provided additional evidence and confirmed laboratory experiments that showed the adsorption of organic constituents (i.e., naphthenic acids (NAs), chemical oxygen demand, dissolved organic carbon, and colour) is a biphasic process. Initially the removal rate is fast and is followed by a slower diffusion-controlled process. The 2-reactor treatment process utilizes the kinetics to maximize removal of organic compounds. The kinetically fast reactions occur within the slurry transport pipeline (Reactor 1); the kinetically slow reactions occur within the coke deposit (Reactor 2). These attributes can be exploited in a commercial scale treatment process to optimize the quality of the treated OSPW;
- Based on the analytical method of Fourier Transform Infrared Spectroscopy (FTIR), NAs are typically present at concentrations between 50 and 80 mg/L in fresh OSPW. The field pilot program indicates porewater residence times in Reactor 2 of between 4 and 8 weeks will remove NAs to concentrations less than 10 mg/L corresponding to treatment efficiencies exceeding 80%;
- Laboratory results indicate the coke water treatment performed better in the field under natural climatic conditions compared to laboratory results. Scale-up appears to improve treatment performance;
- With the exception of vanadium, most trace elements did not significantly leach or mobilize from the petroleum coke matrix into OSPW. Two constituents which did increase in concentrations were cadmium and molybdenum. Cadmium levels, however, did not exceed the current Canadian Council of Ministers of the Environment (CCME) freshwater aquatic life guideline of 1 µg/L. Molybdenum concentrations did exceed the CCME guideline value of 73 µg/L in both untreated (~100 µg/L) and treated OSPW (~1000 µg/L). The CCME does note that molybdenum is an essential trace element for aquatic organisms and is a growth promoter for phytoplankton, periphyton and macrophytes;
- Vanadium concentrations were elevated (approximately 2-10 mg/L) after initial Coke/OSPW contact (i.e., Reactor 1). With extended retention of OSPW in a coke deposit (Reactor 2), geochemical interactions result in significant reductions of vanadium in the treated OSPW. The field data indicates that porewater

retention times of 8 weeks or more will result in vanadium concentrations of less than 1 mg/L. The use of steel tanks in the pilot program has provided additional evidence that metal oxides (e.g., rust) can be used to increase removal of vanadium;

- The treatment process reduced OSPW concentrations of barium, selenium, and strontium;
- Parent and alkylated polycyclic aromatic hydrocarbon (PAHs) in untreated OSPW were measured at concentrations up to 8.5 µg/L. The treated OSPW contained PAH concentrations that were significantly reduced, and most individual PAH constituents were present at concentrations less than analytical detection limits;
- Whole effluent toxicity testing using bacteria, zooplankton and fish indicated the treated water was not acutely toxic;
- Ceriodaphnia bioassays indicated some non-lethal chronic effects. However, this is a salt intolerant species and the response may be affected by OSPW salinity;
- Filtration of OSPW through a coke deposit significantly reduced concentrations of total suspended solids (TSS). TSS concentrations were generally less than laboratory detection limits. Concentration differences between dissolved metals and total metals in the treated OSPW were generally less than 10% demonstrating the effectiveness of the coke deposit to act as a filter bed to reduce levels of fine solids; and
- Aesthetic properties of treated OSPW are significantly improved relative to untreated OSPW. The treated water did not exhibit any visual or olfactory evidence of turbidity, color, or hydrocarbons.

In 2017, Syncrude received approval from the Alberta Energy Regulator (AER) to operate the WRDP as a closed-circuit process (Phase 2) which was initially commissioned in 2019. A photograph of the un-commissioned treatment facility is provided in Figure 3. The size of the filtration cell (Reactor 2) is approximately 500 m long x 150 m wide by 5 m deep and has an ultimate capacity to produce about one million cubic meters of treated OSPW. It is located on the south-east corner on the dyke of the MLSB tailings structure.

A key program purpose of the WRDP pilot program is to execute a comprehensive chemical, biological, and toxicological evaluation program of the treated water exiting the polishing pond to produce a body of relevant scientifically defendable data to enable evaluation for potential future release to the Athabasca River.

Figure 3: Treatment facility for the 2019 Water Return Demonstration Project.

The assessment of treated OSPW using the technology comprising the WRDP will be evaluated using a "triad approach" to ensure the treated water presents negligible risk if released to the Athabasca River. Specifically, the study incorporates the following components:

- Chemical characterization of untreated and treated OSPW;
- Toxicological testing of treated OSPW; and
- Mesocosm assessment of aquatic invertebrate community responses to treated OSPW.

A detailed aquatic toxicity study has been designed to test the effectiveness of the treatment process over an approximately six-week period using a large-scale field trial, and a broad suite of toxicity tests. This phase incorporates both laboratory and on-site testing of the treated OSPW. The on-site component includes on-lease chronic toxicity testing using a mobile testing facility and the use of mesocosms (i.e., artificial streams) inoculated with periphyton and benthic macroinvertebrate assemblages from the Athabasca River watershed. This approach combines precise evaluation of toxicity using standard test organisms and recognized protocols, with the evaluation of community responses of river biota to chronic exposure to treated OSPW.

Mesocosms are regularly used to test hypotheses of change among benthic assemblages exposed to contaminants or other substances and allow separation and replication of treatments with physical and chemical diagnostics. Tight control of potential confounding variables that are typical in field studies (e.g., flow, depth, habitat and substrate characteristics, water temperature and chemistry, etc.) is a key rationale for undertaking mesocosm studies.

Supporting the WRDP pilot will be off-lease standard and non-standard acute and sub-lethal toxicity testing at external laboratories. Water quality analyses conducted at each step of the treatment process and during the on-lease testing ensure causal inference conclusions will be robust. Results from all three tests components will contribute technical information to support decisions regarding potential release of treated OSPW directly to the Athabasca River.

A primary objective of the 2019 program is to demonstrate that treated OSPW will be protective of ecological and human health. Figure 4 provides a summary of the specific elements of the study proposed for 2021, and the related decision points. The study will be conducted in two phases: (1) preliminary screening of treated OSPW; and (2) a detailed aquatic toxicity study incorporating chronic assessments of treated OSPW at environmentally relevant concentrations.

The first phase begins following commissioning of Reactor 3, when the fully treated OSPW will be subjected to the Rainbow Trout and *Daphnia magna* acute toxicity tests. If these tests indicate that the treated OSPW is acutely toxic, subsequent investigations will be completed to assess cause.

Subject to the treatment process producing water that is non-acutely toxic, the second phase consists of a detailed aquatic toxicity study designed to test the effectiveness of the Syncrude OSPW treatment process over an approximately six-week period using a large-scale field trial, and a broad suite of toxicity tests. This phase incorporates both laboratory and on-site testing of the treated OSPW. The on-site component includes on-lease chronic toxicity testing using a mobile testing facility and the use of mesocosms (i.e., artificial streams) inoculated with periphyton and benthic macroinvertebrate assemblages from the Athabasca River watershed.

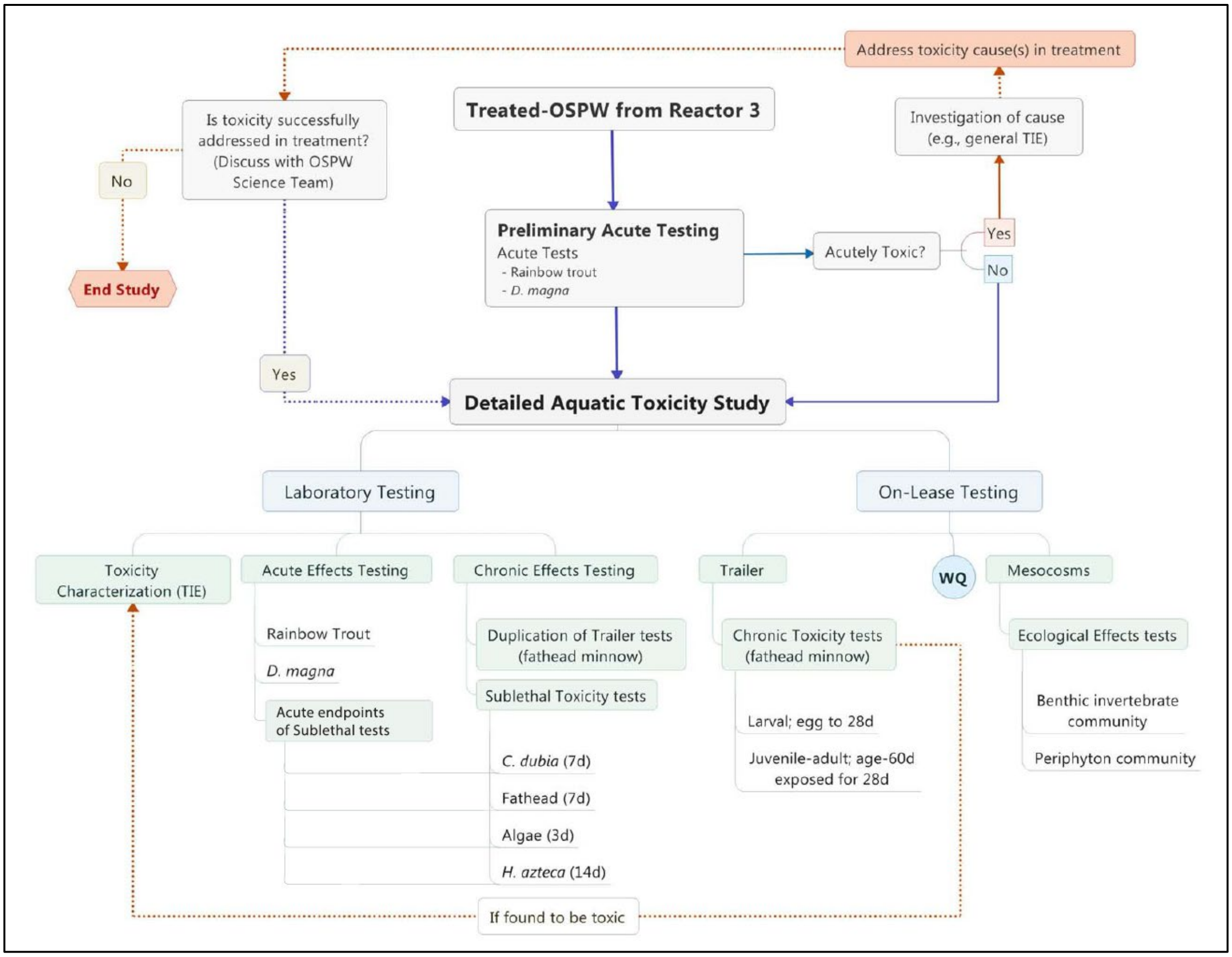


Figure 4: Summary the 2019 aquatic toxicity study

PROGRESS AND ACHIEVEMENTS

Initially project commissioning began in 2019. Final commissioning and testing as per Figure 4 will continue in 2021.

LESSONS LEARNED

Lessons learned will be shared after the WRDP pilot is complete in 2021.

PRESENTATIONS AND PUBLICATIONS

Zubot, W., MacKinnon, M.D., Chelme-Ayala, P., Smith, D.W., Gamal El-Din, M., 2012. Petroleum coke adsorption as a water management option for oil sands process-affected water. Sci. Total Environ. 427-428, 364-372.

RESEARCH TEAM AND COLLABORATORS

A project team of highly experienced individuals have been assembled to advance the closed-circuit phase of the WRDP and collect a defendable body of scientific information to support potential release of treated water to the Athabasca River. Because Reactor 1 of the WRDP is an operating coke sluicing line that is an integral component of

Syncrude's crude oil production process, the entire treatment facility will be operated and maintained by Syncrude staff. To support the toxicological and biological evaluation of the treated water, Syncrude has retained the expertise of Hatfield Consultants Inc. Hatfield is a leading provider of aquatic environmental monitoring in western Canada with clients in various sectors including pulp and paper, mining, oil and gas, and government.

In addition, Hatfield has retained the professional services of Limnotek Research and Development, Nautilus Environmental, and Environment Canada and Climate Change (ECCC) to provide additional scientific expertise to support the closed-circuit evaluation. Limnotek has been providing research and consulting services since 1984 and has extensive experience in the design, field implementation and interpretation of mesocosm studies. They have worked on numerous jointly implemented studies with ECCC and have a history of innovative custom equipment design for field-based studies. Nautilus Environmental operates toxicity testing laboratories in Calgary and Vancouver that are accredited by the Canadian Association of Laboratory Analyses (CALA). They have extensive experience operating mobile testing laboratories and conducting long-term tests with species such as fathead minnows and other organisms. Modern approaches to the use of mesocosms to evaluate water quality were pioneered by ECCC in the 1980s. ECCC scientists have been supporting the mesocosm experiments with respect to design and construction. They will continue to provide a key role by informing data analyses and interpretation. Additionally, ECCC will lead development of scientific publications with support from the project team.

Project partners consists of participating COSIA companies, members of Alberta's OSPW Science Team, and the IRC chair holder in tailings water treatment at the University of Alberta, Dr. Gamal El Din. The OSPW Science Team was formed by Dr. Fred Wrona, Chief Scientist, Alberta Environment and Parks as recommended to him by the Alberta Environment and Parks Science Advisory Group (AEPSAG) on 17 January 2018. Its key purpose is to provide credible scientific information to inform appropriate government regulatory bodies (the Alberta Energy Regulatory, Alberta Environment and Parks (AEP), Environment and Climate Change Canada) regarding the ability for the potential release of treated oil sands process water (OSPW) by Syncrude Canada using a carbon-based filtration process.

Carbonix Activated Carbon Project

COSIA Project Number: WJ0139

Research Provider: Trent University, SGS-Lakefield Research

Industry Champion: Carbonix, Suncor

Industry Collaborators: None

Status: Year 3 of 4

PROJECT SUMMARY

This collaborative project between Suncor and Carbonix, an Indigenous technology start up, seeks to leverage the activated carbon(s) manufacturing process technology previously developed by Carbonix to Suncor specific applications. Specifically, this project investigates the conversion of Suncor manufactured by-product petcoke to functionalized activated carbons and assesses and closes knowledge gaps to technology scale up – both production and applications.

This technology could provide an economic means for mine closure operations, as it requires no additional energy input to achieve the intended reclamation/remediation tasks.

This project is currently at phase two. Phase one of this project was bench scale proof of concept started September 2017. It was jointly supported by Ontario Center of Excellence (OCE), Alberta Innovates, and Suncor. After phase one success, Carbonix applied to NRCAN (Natural Resources Canada) Clean Growth Program (CGP), with support from Suncor, and was rewarded $3.2M in July 2019 for technology pilot prototyping (phase two of this project).

The objectives of phase one included:

- The investigation of effective and efficient protocols to convert Suncor petcoke into activated carbons, which possess the necessary controllable surface area and pore size and distribution required to be effective and economical for the intended applications.
- The development of protocols that enable the tailoring and/or postproduction functionalization of activated carbons to effectively adsorb specific adsorbates.

The objectives of the current phase – phase two – includes:

- Demonstrate reproducibility of functionalized activated carbons at pilot scale.
- Demonstrate efficacy of functionalized activated carbons through pilot scale column tests and infield tests.
- Develop product deployment protocols and estimate annual product requirements.
- Execute pre-FEED to develop bank grade engineering drawings, capital equipment costs, operating costs and pro forma model for valuation purposes.

Hypothesis to be tested includes:

- the conversion of Suncor petcoke into functionalized activated carbon is sustainable.
- the efficacy of functionalized activated carbons by Carbonix technology meets Suncor closure needs.
- the application of functionalized activated carbon in Suncor closure is sustainable.

PROGRESS AND ACHIEVEMENTS

During phase one of each investigation (petcoke conversion and application functionalization), independent protocols were established, then iteratively modified, executed and analyzed by standard lab methods. Product functionalization included; modifying pore wall chemistry or depositing nano-materials within pores for the purposes of enhancing target adsorbate interactions. Key metrics captured included; product attributes such as surface area, pore size and distribution and pore volume, correlated with respective temperatures, durations, re-agent ratios and washing procedures applied.

The results from phase one demonstrated consistent high yield (60%), surface area being controlled between 500 to 2,000 m^2/g, and nitrogen content being controlled between 1.5% to 4% (for functionalization). And the level of process control illustrated enabled products to be tailored for a variety of applications in different environments.

Based on phase one results, the process and unit operations required both to manufacture and tailor the products for different applications were modeled in Aspen, a process simulation software package widely used in industry. The model was run iteratively using various protocols to gain insight on the cost-effectiveness of the technology at commercial scale. An operations model (pro-forma model) was then built to incorporate all capital and operating costs together with relevant business assumptions including production rates, revenue projections (based on Suncor cost plus model), management and overhead costs. As a result, the estimated cost of production ranged from C$1,390/tonne to C$1,500/tonne. As a comparison, the 2019 Q1 import average pricing for commodity grade activated carbon is C$2,910/tonne, and C$4,470/tonne for specialty grade.

To date, Carbonix has reported positive results:

1) Improved conversion protocols to eliminate petcoke agglomeration occurred during production scale up.
2) Simplified the flowsheet to reduce capital and operating costs and related technology risk, while maintaining product quality, with significant reduction in energy requirement, cost of production, and capital equipment compared to the previous flowsheet.

LESSONS LEARNED

1) The hardness of petcoke based products is significantly higher than that of biomass-based products. The additional hardness helps eliminate or reduce particle attrition and thus avoid pressure drop across beds in both liquid and air phase applications. This has a significant impact on product efficacy and operations.
2) Using X-ray photoelectron spectroscopy (XPS), it was demonstrated that the impurities such as vanadium and cadmium, often present in petcoke, were leached out during the conversion process.
3) Combining process modeling with business and financial modeling enabled the use of multiple valuation methodologies, which significantly helped the evaluation of the commercial potential of this technology.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Trent University / SGS-Lakefield Research

Principal Investigator: Andrew Vreugdenhil / Kevin Bradley

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Oliver Strong	Trent University	Research Associate		
Elmira Nazari	Trent University	Ph.D. Candidate	Sept 2018	August 2022
Kyle Fisher	Trent University	Ph.D. Candidate	Sept 2019	August 2023
Tyler Roy	Trent University	Ph.D. Candidate	January 2020	December 2024
Kelly Wright	Trent University	Ph.D. Candidate	Sept 2018	August 2022

Research Collaborators: NRCan (Natural Resources Canada), Alberta Innovates, Ontario Center of Excellence

Naphthenic Acid Degradation by Gamma Irradiation

COSIA Project Number: WJ0150

Research Provider: University of Windsor

Industry Champion: Suncor

Industry Collaborators: Canadian Natural, Imperial, Syncrude, Shell

Status: Completed

PROJECT SUMMARY

This goal of this research program was to investigate the effects of high-energy gamma irradiation to remove and reduce the toxicity of Naphthenic Acid (NA) mixtures in oil sands mine Fluid Fine Tailings (FFT) and Oil Sand Process Water (OSPW). Preliminary bench scale trials documented 95% reduction of NA concentration in OSPW and 50% reduction in the FFT. This research program confirmed the efficacy of Gamma Irradiation (GI) in breaking down NA mixtures in OSPW and FFT, assessed biological responses to the irradiated materials in the laboratory, and use field cells to monitor the longer-term characteristics of the gamma treatments in a natural environment.

The objective of this research was to assess the immediate and longer-term toxicity and quantify changes in concentrations of parent and daughter NA compounds of fresh and aging GI-treated Oil Sand Process Materials (OSPM) relative to untreated materials. It demonstrated the utility of GI as a putative remediation method by;

- Confirming the efficacy of GI in degrading NAs in OSPW and OSPM and inherent toxicological risk; and
- Documenting the biological development and the associated by-products generated by microbes in the irradiated OSPW and OSPM materials in the laboratory and in a pilot scale field trial.
- Assessing the composition, biomass, abundance and persistence of aquatic plants, zooplankton and benthic invertebrates colonizing mesocosms constructed with irradiated vs. unirradiated OSPM and reference materials over two years.

PROGRESS AND ACHIEVEMENTS

The study indicated that the NA concentrations in the OSPW and FFT gamma irradiated microcosms were only 5% of the concentrations in unsterilized microcosms, showing a 94.8% reduction in the group of organic compounds considered to comprise NAs. It is believed that the ionizing radiation likely disrupted the cyclic chemical structure of various NA congeners making the compounds more readily susceptible to microbial degradation. This suggests that gamma irradiation may have significant potential as means of NA and complex hydrocarbon removal from mine tailings materials prior to their release into the environment.

The greatest biological differences observed between tailings mesocosms and reference mesocosms was evident from the quantities of vegetation. Tailings microcosms accrued minimal submerged aquatic vegetation whereas reference mesocosms supported almost complete cover by *Chara*, and various emergent plant species. Mesocosms supporting aquatic plants had much more abundant zooplankton than irradiated tailings mesocosms (3-6 times greater numbers and 2-3 times more biomass). Nevertheless, mesocosms created with gamma irradiated tailings materials had 28 times more individuals and 6 times more biomass than those created with unirradiated tailings. The benthic invertebrate community was depauperate by comparison with the fauna typically found in surrounding wetlands, likely due to high summer temperatures and complete freezing during winter. Ostracod crustaceans occurred in thousands in irradiated mesocosms containing tailings from two sources but were virtually absent from their unirradiated counterparts. Ostracods were equally abundant in treated and untreated mesocosms containing tailings from a different source. Beetles were consistently more abundant in irradiated than unirradiated mesocosms. The reverse pattern was observed for midge larvae.

Overall, mesocosms filled with GI-treated FFT and OSPW contained slightly more plant cover and more species and much greater abundances of zooplankton and benthic invertebrates, clearly indicating that irradiation effectively reduced toxicity. However, the treated mesocosms remained relatively turbid, which (together physical properties of the tailings sediments) impeded plant establishment relative to reference mesocosms and limited the abundance and diversity of invertebrates that depend on submergent plant communities.

LESSONS LEARNED

The combined laboratory and field studies demonstrated that gamma irradiation of OSPW effectively degraded and increased bioavailability potential of NAs and reduced toxicity to aquatic biota. The long-term persistence of the refractory degradation products that may be generated by the irradiation process remains unknown. Currently no further testing is planned, as treated OSPW release technology development efforts are focused on low energy solutions.

PRESENTATIONS AND PUBLICATIONS

Boudens R., Reid T., Van Mensal D., Prakasan S., Ciborowski J., Weisener C.G. (2016) Biophysicochemical effects of gamma irradiation treatment for Naphthenic acids in oil sands fluid fine tailings. *Science of the Total Environment*. 539, 114-124.

Dings-Avery, C., Ciborowski, J. Weisener, C.G. 2015. Constraints on biodiversity and ecosystem functioning in the Athabasca oil sands - Using gamma irradiation to detoxify fine fluid tailings waste. *Proceedings of the 42nd Annual Canadian Ecotoxicity Workshop. Oct. 4-7, 2015, Saskatoon, SK.. 87*

Dings-Avery, C., Weisener, C.G. Ciborowski, J.J.H. 2016. Assessing the detoxification of oil sands process material through gamma irradiation- a community based approach. *2016 Annual Meeting of the North American Lake Management Society, Banff, AB. Nov 1-4 2016.*

Dings-Avery, C. 2019. Effects of gamma irradiation treatment of oil sands process material on zooplankton accrual and early community development in field based mesocosms. M.Sc. Thesis, University of Windsor, Windsor, ON.

VanMensal D, Chaganti S, Boudens R, Reid T,, Ravendrtan S, *Weisener C.G. (2017) Proteobacteria response and genomic features of gamma irradiated oil sands fluid fine tailings: A community structure perspective. *Environmental Microbiology,* 74:362-372.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Windsor

Principal Investigator: Christopher Weisener and Jan Ciborowski

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Ryan Boudens	University of Windsor	M. Sc.	2013	2015
Danielle Van Mensel	University of Windsor	M. Sc.	2014	2016
Chantal Dings-Avery	University of Windsor	M.Sc.	2014	2019
Amalia Despenic	University of Windsor	B.Sc	2012	2016
Kellie Menard	University of WIndsor	M.Sc.	2014	2016

SolarPass Demonstration for Treatment of Dissolved Organics Water

COSIA Project Number: WJ0164

Research Provider: H2nanO Inc., University of Toronto

Industry Champion: Suncor

Industry Collaborators: None

Status: In Progress

PROJECT SUMMARY

Oil sands process-affected water (OSPW) is a by-product generated through bitumen extraction in Canada's oil sands. Due to OSPW toxicity associated with dissolved organics, OSPW may require treatment before it is discharged to the environment. Towards this, COSIA issued a challenge for "Passive Organics Treatment Technology" that will deliver scalable and low-energy/input OSPW treatment. H2nanO Inc., (a water treatment technology company), in partnership with the University of Toronto, has developed a sunlight-activated, reusable treatment process for passive organics treatment.

The treatment technology, called SolarPass™, uses a proprietary buoyant photocatalyst that, when mixed with water, continuously treats and eliminates organics in water with exposure to sunlight. The purpose of this project is to evaluate photocatalysis treatment using SolarPass™ as the approach to passively treat dissolved organics in OSPW to water return quality.

This project had three objectives:

- Validate H2nanO SolarPass™ treatment of OSPW in a Northern Alberta environment.
- Demonstrate a SolarPass™ pilot prototype with mobility and an increasing treatment capacity while maintaining treatment efficacy.
- Confirm the elimination of Rainbow Trout and Fathead Minnow toxicity in the treated water.

The pilot project included the design and deployment of a new mobile treatment concept, called the Mobile Reactor (MR-01). The MR-01 system incorporated the H2nanO's SolarPass™ technology into a mobile, containerized treatment system for simple transport, set-up, and operation to demonstrate OSPW treatment. The MR-01 design utilized H2nanO's proprietary process and represented a significant advancement to the H2nanO's previously funded projects under COSIA from 2016 to 2018.

The SolarPass™ MR-01 system was deployed at a testing facility of InnoTech Alberta in Edmonton during the pilot study. The project evaluated both chemical and toxicological indicators to characterize and assess the treatment process compared to prior demonstration results, along with rigorous capture of solar intensity and environmental conditions data.

PROGRESS AND ACHIEVEMENTS

The SolarPass™ MR-01 demonstration helped answer some of the key questions on the scalability and transferability of the SolarPass™ technology for OSPW treatment in a natural operation environment.

In terms of the treatment metrics, water treated within MR-01 showed elimination of acute toxicity to Rainbow Trout and Fathead Minnow with two days or less of average summer sunlight energy, validating the capability to meet a key quality requirement of the COSIA challenge without compromising treatment output. Demonstration in the Alberta climate and solar conditions validated the solar dose as an objective metric between operating locations and evaluated scaling factors for total volume and water depth to inform the potential for use in larger-scale operations. The deployment of the MR-01 system also demonstrated the first continuous treatment system designed to mirror operational scale processes for the first time, providing several key insights into operational designs and control strategies.

LESSONS LEARNED

The main learnings to date:

- The pilot prototype MR-01 can be scaled and fitted onto a platform for future projects that require mobility and transport.
- The sunlight-powered photocatalytic reactions using SolarPass™ has established a track record with proven treatment efficacy in multiple water sampled from across a number of ponds.

PRESENTATIONS AND PUBLICATIONS

SolarPass™ water treatment accelerated passive organics treatment in OSPW. The COSIA 2019 Mine Water Release Science Workshop. Edmonton, AB. Oct 22-23, 2019.

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Job Title
Frank Gu	H2nanO	CEO
Zac Young	H2nanO	COO

Appendix

Project Number	Summary Report Title	Topic	Year Summary Published	Page #
WE0027	Standardize Measurement and Quantification Techniques	Best Practices	2018 Mining Research Summary	2
WJ0099	Overburden Dewatering Effectiveness Study	Best Practices	2018 Mining Research Summary	4
WJ0061	Mining Best Practices Report for Alternate Water Sourcing and Salinity Management	Best Practices	2018 Mining Research Summary	7
WE0010	Salt Load Model	Mine Water Return	2018 Mining Research Summary	10
WE0013	River Ecosystem Health Assessment Using Pilot Facility	Mine Water Return	2018 Mining Research Summary	13
WE0009	Regional Substance Loading Allocation Study	Mine Water Return	2018 Mining Research Summary	16
WE0018	Impacts of Atmospheric Dust Deposition on the Speciation of Trace Elements in Snowmelt and Peatland Surface Waters	Natural and Anthropogenic Inputs to the Athabasca Watershed	2018 Mining Research Summary	20
WE0057	Water Quality in the Lower Athabasca River	Natural and Anthropogenic Inputs to the Athabasca Watershed	2018 Mining Research Summary	24
WE0059	Current Knowledge of Oil Sands Process-Affected Water Seepage from Tailings Ponds and its Environmental Influence in Northeastern Alberta	Natural and Anthropogenic Inputs to the Athabasca Watershed	2018 Mining Research Summary	28
WJ0017	Natural vs Anthropogenic Inputs: Water Quality in the Lower Athabasca River	Natural and Anthropogenic Inputs to the Athabasca Watershed	2018 Mining Research Summary	32
WE0011	Oil Sands Process-Affected Water (OSPW) Typology	OSPW Chemistry and Toxicity	2018 Mining Research Summary	37
WE0016	Toxicity of Ozone -Treated and Untreated OSPW	OSPW Chemistry and Toxicity	2018 Mining Research Summary	39
WE0037	Literature Review and Evaluation of Dissolved Chloride for Treated Oil Sands Process Affected Water (OSPW) Return	OSPW Chemistry and Toxicity	2018 Mining Research Summary	43
WE0049	Investigations of the Bioaccumulation Potential of Dissolved Organics in Oil Sands Process-Affected Water: A Review	OSPW Chemistry and Toxicity	2018 Mining Research Summary	46
WJ0024	Vanadium Toxicity to Aquatic Organisms Representative of the Athabasca Oil Sands Region	OSPW Chemistry and Toxicity	2018 Mining Research Summary	48
WJ0025	The Base Mine Lake Toxicity Identification and Evaluation Study	OSPW Chemistry and Toxicity	2018 Mining Research Summary	50
WJ0045	Development of a Passive Sampler-Based Framework for Derivation of Water Quality Benchmarks for Oil Sands Process-Affected Water	OSPW Chemistry and Toxicity	2018 Mining Research Summary	53
WJ0113	Analytical and Toxicological Evaluation of Bioavailable Naphthenic Acids from Oil Sands Process-Affected Water and Groundwater Using Biomimetic Extraction - Solid Phase Microextraction	OSPW Chemistry and Toxicity	2018 Mining Research Summary	56

WJ0116	Development of Microbial Fuel Cell Biosensor for Detection of Naphthenic Acids	OSPW Chemistry and Toxicity	2018 Mining Research Summary	60
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